BNWL-1185
UC-70

5-
1-70

WASTE SOLIDIFICATION PROGRAM
VOLUME 5
PHOSPHATE GLASS SOLIDIFICATION PERFORMANCE DURING FIRST RADIOACTIVE TESTS IN WASTE SOLIDIFICATION ENGINEERING PROTOTYPES

January 1970

AEC RESEARCH & DEVELOPMENT REPORT

ROUTE TO		
W. F. Brehm	33070 324T1	APR 10 1970

BNWL-1185

BATTELLE NORTHWEST
BATTELLE MEMORIAL INSTITUTE   PACIFIC NORTHWEST LABORATORIES
BATTELLE BOULEVARD, P. O. BOX 999, RICHLAND, WASHINGTON 99352

PACIFIC NORTHWEST LABORATORY
RICHLAND, WASHINGTON
operated by
BATTELLE MEMORIAL INSTITUTE
for the
UNITED STATES ATOMIC ENERGY COMMISSION UNDER CONTRACT AT(45-1)-1830

BNWL-1185

UC-70,
Waste Disposal
and Processing

WASTE SOLIDIFICATION PROGRAM
VOLUME 5
PHOSPHATE GLASS SOLIDIFICATION PERFORMANCE DURING FIRST RADIOACTIVE TESTS IN WASTE SOLIDIFICATION ENGINEERING PROTOTYPES

By

BNW

J. L. McElroy
J. N. Hartley
K. J. Schneider

Chemical Technology Department
Chemistry and Metallurgy Division

BNL

R. F. Drager

Engineering Division
Brookhaven National Laboratory

January 1970

BATTELLE MEMORIAL INSTITUTE
PACIFIC NORTHWEST LABORATORIES
RICHLAND, WASHINGTON 99352

Printed in the United States of America
Available from
Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U.S. Department of Commerce
Springfield, Virginia 22151
Price: Printed Copy $3.00; Microfiche $0.65

WASTE SOLIDIFICATION PROGRAM, VOLUME 5
PHOSPHATE GLASS SOLIDIFICATION PERFORMANCE DURING FIRST RADIOACTIVE TESTS IN WASTE SOLIDIFICATION ENGINEERING PROTOTYPES

J. L. McElroy, J. N. Hartley, K. J. Schneider (BNW)
R. F. Drager (BNL)

ABSTRACT

Solidification of high level radioactive waste by the Brookhaven National Laboratory phosphate glass process has been successfully demonstrated by Battelle-Northwest. More than 7 million curies of radionuclides were processed and collected in 8 and 12-inch diameter containers during six engineering-scale demonstration runs in WSEP at the Pacific Northwest Laboratory. Radioactivity processed was increased from 350,000 curies in the first run to 2,400,000 curies in the sixth run. The self-generating heat rate within each receiver pot full of solidified waste was increased from 1.6 to 9.6 kilowatts (155 W/liter of solid), respectively. The solidified waste within a full 8-inch diameter pot represented 1.3 tonnes of power reactor fuel (irradiated at 20,000 MWd/tonne at a power level of 15 MW/tonne) for sulfate-containing PW-2 waste and 0.64 tonnes for sulfate-free PW-1 waste. High level aqueous radioactive waste was processed at overall rates of 9.4 to 18 liters/hr. The equivalent processing rates ranged from 0.20 to 0.61 tonnes/day of original fuel. From 2 to 10% of the total ruthenium fed to the solidifier was volatilized and/or entrained from the solidifier; entrainment of nonvolatiles varied from 0.2 to 0.3%. 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 equipment consisting of an evaporator, an acid fractionator, filters, and a caustic scurbber reduced radionuclides in the stack gas to well below 10CFR20 release limits. The radionuclide content in the final liquid effluent was decontaminated by a factor of 10^8 for nonvolatiles and 10^6 for radioruthenium to concentrations acceptable for low-level treatment processes. The phosphate glass solid caused no significant 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.

TABLE OF CONTENTS

ABSTRACT iii
LIST OF FIGURES. ix
LIST OF TABLES xi
1.0 INTRODUCTION 1.1
2.0 SUMMARY. 2.1
  2.1 Phosphate Glass Solidifier Performance. . . . 2.1
  2.2 Auxiliary Process Performance. 2.4
  2.3 Filled Pot Performance 2.6
  2.4 Status of Phosphate Glass Solidification . . 2.8
3.0 BACKGROUND. PROCESS DESCRIPTION. AND PROCESS TECHNOLOGY. 3.1
  3.1 Background 3.1
  3.2 Process Description 3.1
  3.3 Process Technology 3.5
4.0 PHOSPHATE GLASS SOLIDIFICATION PERFORMANCE . . . 4.1
  4.1 Overall Processing Rates 4.2
  4.2 Radionuclide Heating Effects 4.6
  4.3 Waste Volume Reduction 4.8
  4.4 Performance of Denitrator– Evaporator . . . 4.12
  4.5 Performance of Melter 4.25
  4.6 General Performance and Operating History. . 4.34
5.0 AUXILIARY EQUIPMENT PERFORMANCE. 5.1
  5.1 Operating Modes 5.2
  5.2 Ruthenium Control. 5.7
  5.3 Control of Other Radionuclides 5.14
  5.4 Auxiliary Handling of Acid Purex Waste. . . 5.17
  5.5 General Performance of Auxiliaries 5.18
6.0 FILLED RECEIVER POT PERFORMANCE. 6.1
  6.1 Evaluations. 6.1
  6.2 Pot Handling, Contamination Control and Welding 6.18
7.0 PROJECTED FLOWSHEETS FOR PW-1 AND PW-2 . . . . 7.1

8.0 FUTURE WORK 8.1
8.1 Waste Types 8.1
8.2 Equipment and Process Requirements 8.1
8.3 Auxiliaries 8.2
8.4 Filled Pot Performance 8.3
9.0 APPENDIX 9.1
9.1 Run Description 9.1
9.2 Startup Procedure for Phosphate Glass Solidification Process 9.26
9.3 Normal Operating Procedure 9.28
9.4 Shutdown Procedures 9.29
10.0 ACKNOWLEDGMENTS 10.1
REFERENCES Ref-1

LIST OF FIGURES

3.1 Phosphate Glass Solidification Process 3.3

4.1 Typical WSEP Phosphate Glass Solidification Processing Rates 4.5

4.2 Phosphate Glass Receiver Pot Thermocouple Arrangement 4.9

4.3 Run PG-5 Receiver Pot and Furnace Temperatures for Zones 4, 5, and 6 4.10

4.4 Radionuclide Accumulation in Denitrator-Evaporator Condensate 4.17

4.5 Original Airlift Pot with Fixed Orifice 4.21

4.6 Airlift Pot with Variable Orifice Control 4.23

4.7 Typical WSEP Melter Temperature Profile 4.27

4.8 Ruthenium Accumulation in Melter Condensate 4.30

5.1 WSEP Process Options 5.3

5.2 Operating Mode Applications 5.5

5.3 Ruthenium Volatility from the WSEP Auxiliary Evaporator 5.11

5.4 Radionuclide Accumulation in the WSEP Auxiliary Evaporator Condensate (Fractionator bottoms) 5.13

5.5 Radionuclide Accumulation in Acid Fractionator Condensate 5.15

6.1 Temperature Drop (Centerline to outside wall) in Receiver Pots Containing Solidified Waste 6.4

6.2 Pot Wall Temperature in Air and in Air-Cooled Receiver Pot Furnace 6.5

6.3 Heat Required in a Cylindrical Pot to Attain a 900 °C Centerline Temperature 6.8

6.4 Effective Thermal Conductivity of Radioactive Phosphate Glass 6.9

6.5 Product Frozen Wall Thickness for 8-Inch Thermal Maximum Pots 6.11

6.6 Radiation and Temperature Profiles of Receiver Pots Filled with Phosphate Glass 6.13

6.7 Leach Rates of Radioactive PW-2 Phosphate Glass 6.16

7.1 Fission Product Heat Generation Rate with Time for One Tonne of Reactor Fuel Irradiated to 20,000 MWd/tonne at 15 MW/tonne 7.4

7.2	Heat-Age Environment Relationships for High-Level Radioactive Phosphate Glass Showing Fission Product Heat Rate Density Limits	7.5
7.3	Typical Flowsheet for Processing One Tonne of PW-1 Waste with Mode A Operation	7.7
7.4	Typical Flowsheet for Processing One Tonne of PW-2 Waste with Mode A Operation	7.8
9.1a	Equipment Arrangement for Phosphate Glass Runs	9.32
9.1b	Equipment Arrangement for Phosphate Glass Runs	9.33
9.2	Denitrator-Evaporator (TK-121) Solution Parameters During Run PG-1	9.34
9.3	Denitrator-Evaporator (TK-121) Solution Parameters During Run PG-2	9.35
9.4a	Denitrator-Evaporator (TK-121) Solution Parameters During Run PG-3	9.36
9.4b	Denitrator-Evaporator (TK-121) Solution Parameters During Part of Run PG-3	9.37
9.5	Denitrator-Evaporator (TK-121) Solution Parameters During Run PG-4	9.38
9.6a	Denitrator-Evaporator (TK-121) Solution Parameters During Run PG-5, Part 1	9.39
9.6b	Denitrator-Evaporator (TK-121) Solution Parameters During Run PG-5, Part 2	9.40
9.7	Denitrator-Evaporator (TK-121) Solution Parameters During Run PG-6	9.41
9.8	Run PG-3: Pot Radiation Profile at 6-Inches from Wall	9.42
9.9	WSEP Auxiliary Equipment Flow Diagram	9.43
9.10	WSEP Solidification Equipment Flow Diagram	9.44
9.11	Laboratory Foam Test Apparatus Used with Nonradioactive Feed	9.45
9.12	Laboratory Foam Test Apparatus Used with Radioactive Feed	9.46

LIST OF TABLES

2.1 Phosphate Glass Solidification Runs in WSEP 2.3

3.1 Effect of Rare Earth Content on Melt Formation in PW-2 Waste 3.7

3.2 Effect of Uranium on PW-1 Waste 3.8

3.3 Results of Preliminary Radioactive Incell Laboratory Tests with Adjusted Phosphate Glass Feeds 3.10

4.1 Major Run Variables 4.2

4.2 WSEP Phosphate Glass Solidification Processing Rates 4.4

4.3 Pot Receiver Temperatures Caused by Internal Heat Generation 4.7

4.4 Volume Reductions 4.11

4.5 Capacity of a Receiver Pot 4.12

4.6 Denitrator-Evaporator General Operating Parameters 4.13

4.7 Volatilization and Entrainment from Denitrator-Evaporator 4.15

4.8 Denitrator-Evaporator Internal Heat Generation Effects 4.20

4.9 Airlift Pot Operating Parameters 4.25

4.10 Volatilization and Entrainment from Melter 4.29

4.11 Performance of Melter Condenser 4.32

4.12 General Waste Composition Ranges 4.36

4.13 Phosphate Glass Equipment Operating History 4.37

5.1 Typical Effluents During Operation with Modes A and B (First Six Phosphate Glass Runs) 5.6

5.2 Radioruthenium and Radiocerium Decontamination Factors 5.9

5.3 WSEP Auxiliary Operating Summary 5.20

5.4 Overall Material Balances for Phosphate Glass Runs 5.24

6.1 Receiver Pot Pressure Data 6.17

6.2 Remote Pot Welding Experience 6.20

7.1 Compositions of PW-1 and PW-2 7.2

7.2 Fission Products from a Power Reactor Fuel Exposed to 20,000 MWd/tonne at 15 MW/tonne 7.3

7.3 Calculated Curies in Fractionator Acid per Tonne of Fuel Irradiated to 20,000 MWd/tonne at 15 MW/tonne and Aged 0.5 Years 7.12

7.4 Projected Radionuclides in Condensate from the Acid Fractionator per Tonne of Feed Processed 7.13

9.1 Nominal and Actual Feed Compositions Used in Phosphate Glass Runs PG-1 Through PG-6 9.47

9.2 Operating Parameters and Results of Phosphate Glass Solidification Demonstration in Runs PG-1 Through PG-6 in WSEP 9.48

9.3 Material Balances for Phosphate Glass Runs PG-1 Through PG-6 in WSEP 9.54

9.4 Distribution of Radioactivity for Phosphate Glass Runs PG-1 Through PG-6 9.57

9.5 Feed Pump Experience During WSEP Phosphate Glass Runs 9.59

WASTE SOLIDIFICATION PROGRAM, VOLUME 5
PHOSPHATE GLASS SOLIDIFICATION PERFORMANCE DURING FIRST RADIOACTIVE TESTS IN WASTE SOLIDIFICATION ENGINEERING PROTOTYPES

J. L. McElroy, J. N. Hartley, K. J. Schneider (BNW)
R. F. Drager (BNL)

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 14 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

---

* 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 first six radioactive demonstration runs with the phosphate glass solidification system in WSEP. Similar results for the first six radioactive demonstrations with the pot calcination system in WSEP were reported in Volume 4 of this series.(3) 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 non-radioactive data. Detailed descriptions of each demonstration run are presented in the Appendix (Section 9.0).

2.0 SUMMARY

Solidification of high-level, aqueous, radioactive wastes containing more than 7 million curies was successfully completed in six demonstration runs using the phosphate glass solidification process in the Waste Solidification Engineering Prototypes (WSEP). Major accomplishments in the demonstrations were as follows:

- Heat generation from fission products produced temperatures in the glassy product at near the maximum contemplated for the process as prescribed in WSEP. Adequate heating and cooling control of the pots was demonstrated during filling to promote uniform filling and prevent excessive temperatures.
- Radioactive 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 easily met government regulations and were directly released to the atmosphere.
- The aqueous effluent directly from solidification was low enough in radioactivity to permit recycling to a fuel reprocessing plant. The aqueous effluent after acid fractionation was low enough in radioactivity to permit treatment as low level wastes for disposal.

2.1 PHOSPHATE GLASS SOLIDIFIER PERFORMANCE

The principal variables investigated in the first six runs were heat generation rate in the solidified waste, and two waste chemical compositions.

Radioactivity levels were increased from about 350,000 curies (which represents 1600 watts of decay heat) in the receiver pot in the first run to 2,400,000 curies (9600 watts) in the sixth run. The escalation of radioactivity in the waste did not appear to significantly affect the process in any way.

High level aqueous radioactive wastes simulating sulfate-free PW-1[a] and sulfate-containing PW-2[a] compositions were processed at overall rates of 9.4 to 18 liters/hr. The equivalent processing rates for PW-1 waste ranged from 0.20 to 0.28 tonnes/day of power-reactor fuel exposed to 20,000 MWd/tonne[b] at a power level of 15 MW/tonne, while for PW-2 waste it ranged from 0.18 to 0.21 tonnes/day. In general, the lower equivalent processing rates for PW-1 waste were caused by the larger quantity of additives required to process PW-1 waste. Factors influencing the overall rates were feed compositions and erratic feeding to the melter. Sparging of the melter with 0.5 scfm of nitrogen to increase melt circulation and heat transfer to the melt had no apparent effect on melting capacity.

The radioactive waste used for these demonstration runs did not always permit preparation of feeds having exact PW-1 and PW-2 compositions. Because of the modest variations in chemical compositions of the feeds, the overall volume reduction factors varied from 3.5 to 4.0 for PW-1 and 6.4 to 9.1 for PW-2 wastes, based on aqueous waste at 378 liters/tonne. Expected volume reduction factors for nominal PW-1 and PW-2 wastes are calculated to be 4.4 and 8.6, respectively. The lower volume reduction of PW-1 waste is due to a larger quantity of additives that are required to process the waste.

General conditions for each run are summarized in Table 2.1.

---

a. For detailed chemical composition, 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.

TABLE 2.1. Phosphate Glass Solidification Runs in WSEP

	PG-1	PG-2	PG-3	PG-4	PG-5	PG-6
Feed Type	PW-2	PW-2	PW-2	PW-2	PW-1	PW-1
Pot Diameter, in.	12	8	8	8	12	8
Pot Material	MS$^{(a)}$	304L SS	MS	MS	MS	304L SS
MCi in Feed to Denitrator	0.43	0.67	1.5	1.2	2.8	2.6
MCi in Feed to Receiver Pot	0.35	0.40	0.60	1.1	2.2	2.4
Heat Generation Rate in Receiver Pot, kW	1.6	1.7	3.3	4.2	8.8	9.6
Heat Rate Density in Receiver Pot, W/liter	17	49	95	57	78	155
Equivalent tonnes in Receiver Pot, actual	2.16	0.89	0.69	1.24	1.06	0.64
For full pot	(2.5)	(1.5)	(1.2)	(1.1)	(1.2)	(0.64)
Equivalent Age to Reduce Watts to Run Value, yr$^{(b)}$	7.5	2.5	1.0	1.45	0.53	0.22

(a) Mild steel
(b) Based on fuel irradiated to 20,000 MWd/tonne at 15 MW/tonne

The denitrator-evaporator successfully concentrated and denitrated the incoming feed. The boiling temperature was held at 132 and 137 °C for PW-1 and PW-2, respectively.

Excessive foamover losses of concentrated waste from the denitrator-evaporator occurred during the first three demonstration runs with PW-2 waste. The foaming was caused primarily by small amounts of dibutyl phosphate (a foaming agent) in the Purex waste used for feed makeup. Satisfactory control of foaming was achieved in subsequent runs by the addition of a silicone antifoam agent into the denitrator.

Plugging of the airlift air line, airlift recirculation line, melter feed line and specific gravity and liquid level tubes in the denitrator with solids were major problems during the processing of PW-1 waste. The remotable features of the new airlift pot used during PW-1 demonstrations permitted on-stream removal of the solids buildup in the airlift pot and allowed successful completion of the runs. Several methods of keeping the dip tubes clear of solids were tested; the only successful method was hourly blowdowns of the dip tubes with steam.

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. Pot wall temperatures of 600 °C were satisfactory to slump the continuous discharge of melt in the receiver to give uniform filling. Stalagmites formed during run PG-3 when the pot wall temperature was 300 °C. Batch dumping of melt through the drain freeze-valve was done at the end of each run to completely empty the melter. This action minimized the possibility of the platinum melter stretching due to the different thermal expansion coefficients of the glass and the platinum.

The amount of ruthenium that volatilized from the solidifier including that from the melter varied from 2 to 10% of the total amount fed to the solidifier; entrainment of nonvolatile~varied from 0.2 to 0.3%. Volatilized and entrained material from the denitrator was further processed in the WSEP auxiliary process equipment, while the volatilized and entrained material from the melter was collected in a separate condensate receiver.

2.2 AUXILIARY PROCESS PERFORMANCE

The auxiliary equipment (i.e., condensers, evaporator, acid fractionator, scrubber, and filters) decontaminate and separate nitric acid, water, and noncondensable effluents from the process. The WSEP auxiliary effluent treatment system is typical of many schemes used in fuel reprocessing plants for treating effluents from concentration of high level aqueous wastes.

Ruthenium cumulative decontamination factors (DF_c) across the auxiliaries (ratio of ruthenium in the original denitrator-evaporator feed to that accumulated in the condensate from the acid fractionator) were typically about 10^6, while comparable. DF_c's for nonvolatiles were about 10^8. Off-gases to the stack were consistently well below the discharge limits for both ruthenium and gross beta activity. Decontamination factors from feed to stack gas were consistently greater than 1×10^{10} and 1×10^{12} for ruthenium and gross beta (less ruthenium) respectively.

The DF_c across the auxiliary evaporator for ruthenium in the evaporator (the ratio of ruthenium in the evaporator at end of a run to ruthenium evolved from the evaporator during the run) were typically nearly constant at 20 to 40, and varied from 11 to 420. Inleakage of 5 to 10 scfm of air into the phosphate glass system is believed to have caused some of the off-gas leaving the process condenser to bypass contact with liquid in the evaporator bottoms and could explain these somewhat low DF's. Instantaneous ruthenium decontamination factors (DF_i is the ratio of the concentration in the boiling liquid to the concentration in the condensed vapor measured at the same time) increased as the nitric acid concentration in the overheads was decreased. When the acidity in the overheads was less than approximately 0.4M, ruthenium DF_i's exceeded 1000. The DF's were not appreciably affected by the addition of sugar to the bottoms as a reductant. Evaporator DF's with high level waste (versus reconcentrated condensate) in the evaporator bottoms were consistently as good as the higher values obtained for all runs. The DF_i's for nonvolatiles across the evaporator and its high efficiency glass fiber mist eliminator varied from 10^4 to 10^6.

Ruthenium DF_c's in the fractionator (ratio of ruthenium in the fractionator at end of a run to ruthenium evolved from the fractionator during the run) varied from 55 to 6000. Values of 200 to 1000 were typical of the average data.

Handling of the PW-1 and PW-2 phosphate glass feeds in the feed tanks and auxiliary evaporator caused no unexpected operating difficulties. The primary solid in these wastes is a zirconium phosphomolybdate compound which is a hydrous amorphous precipitate that has never been observed to cake in the laboratory even after standing several months.

Although some minor malfunctions of auxiliary equipment occurred, no serious problems arose. The minor equipment problems which did occur can be eliminated by suitable design modifications. The malfunctions were:

- two types of feed pumps failed,
- insulation on electrical and instrument wiring deteriorated from radioactive exposure, and
- high efficiency filters in the feed tank vent system failed repeatedly because the filter preheater was too small to evaporate moisture in the gas stream.

The process filter which serves effluents from the phosphate glass process downstream of the evaporator and acid fractionator gave good performance.

2.3 FILLED POT PERFORMANCE

Although it is too early to evaluate the near-term (approximately 5 years) performance of pots filled with phosphate glass, current observations are encouraging. No pressurization has occurred during the 0.9 to 1.6 years of storage in any of the six pots, and the pressure in at least four of the pots is remaining less than atmospheric. No gas generation within the phosphate glass is indicated. Leak checks made on three receivers indicate good welds. A leak check made on a fourth receiver revealed a leaking mechanical joint. (Leak checks were not made on the remaining two receivers.) No significant changes were detected in the external receiver dimensions of any of the six receivers within the accuracy (±1/4 inch) of the remote in-cell measurements.

Heat generation rates in filled receiver pots were satisfactorily measured in a calorimeter. The maximum centerline temperature at the end of a run measured 780 °C for the pot of run PG-6. The maximum wall temperature measured was 400 °C for the PG-6 receiver. Thermal conductivities of the phosphate glass products in the six receivers ranged from 0.94 to 1.13 W/(m)(°C) (or 0.54 to 0.64 Btu/hr x ft^2 x °F/ft). The leach rates obtained on samples from four of the runs agreed with those obtained on simulated nonradioactive samples and are grouped around 10^{-6} g/(cm^2)(day). Leach rates for ^{137}Cs were 3 to 4 times higher than for ^{144}Ce. The melts with PW-1 wastes leached at rates about 5 times and 4 times those with PW-2 wastes for ^{137}Cs and ^{144}Ce, respectively.

Gross radiation profiles indicate that the fission products are probably uniformly distributed. The measurements, however, cannot be interpreted quantitatively. Bulk densities of the product compared closely with measured densities in runs PG-1 and PG-5, thereby indicating the absence of voids. The bulk densities of the products for the other receivers were not available for comparison.

Although wall thickness measurements have not yet been made on the pots, no visible external corrosion is indicated to stainless steel receivers stored in air or in water or to mild steel pots stored in water containing corrosion inhibitors or in air.

Automatic tungsten inert gas (TIG) welding of the receiver pot sealcap produced good fusion welds in all six pots. The welding head was positioned remotely over a step-type weld joint. Visual observation through a spotting scope outside the cell window was satisfactory to control the welding torch.

2.4 STATUS OF PHOSPHATE GLASS SOLIDIFICATION

Although the phosphate glass solidification demonstration runs are not all complete, the six runs made to date permit a projection of expected performance of the process. Wastes from fuels irradiated to 20,000 MWd/tonne at a power level of 15 MW/tonne can be solidified within 0.2 years out of the reactors. At this level, a fission product heat generation rate of 195 W/liter (11,700 watts) in the product will be the maximum capable of being handled in an 8-inch diameter receiver pot (with natural convection cooling in air) when the WSEP restriction of limiting the molten core radius to not more than 1/2 the receiver radius is considered. With this restriction applied to the approximately 700 °C product remelt temperature, receiver pot centerline and wall temperatures of 900 and 427 °C, respectively, are not attained (assuming Ke does not change considerably at higher temperatures).

Some individual nuclides (e.g., ruthenium) were not at the levels expected for a 20,000 MWd/tonne exposure at a 15 MW/tonne power level. However, data from these radioactive runs can be used to project results for full levels of all nuclides. By applying the overall decontamination factors experienced to date, several general statements can be made about the expected levels during operation of the solidifier, the auxiliary evaporator, and the acid fractionator with radioactive wastes.

- From 2.0 to 10% of the ruthenium will be volatilized out of the solidifier. In the processing of PW-1 waste, most of this can be recycled to the fuel reprocessing plant high level waste system. In the case of PW-2 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 high level waste system as previously discussed. Less than 2% of the total ruthenium fed to the solidifier will reach the acid fractionator. The ruthenium concentration in the condensate from the fractionator when solidifying waste aged 0.5 years will have been decontaminated by a factor of 10^6, which is 37,000 to 800,000 times higher than the discharge limits quoted in 10CFR20.* Ruthenium-106 is the nuclide in the final aqueous effluent with the highest concentration ratio to the limits in 10CFR20, followed by ^{90}Sr and ^{144}Ce-Pr. In general, an additional decontamination of 10^3 to 10^4 is needed to reduce all nuclides, except ruthenium, in the fractionator condensate to below 10CFR20 values. However, since approximately 300 to 400 liters of total condensate is generated per tonne of fuel processed (from 378 liters/tonne waste), the fractionator condensate could be used in a fuel reprocessing plant such as an acid dilutant and/or dissolver wash during dissolution steps, first cycle scrub stream, etc. Alternatively, the radioactivity level is acceptable for additional low level treatment such as by distillation to 10CFR20 concentration limits for discharge of the water to the environment.

- The concentrated nitric acid produced in the acid fractionator (approximately 200 to 300 liters/tonne of 8 to 14M acid) will contain 300 to 1500 μCi/mℓ of total β radioactivity. Radioruthenium will be the principal contaminant. The acid would be acceptable for reuse for fuel dissolution

---

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

in fuel reprocessing. (Fuel dissolution requires at least 1000 liters of 10M nitric acid per equivalent tonne, or three to five times that available from solidification of the wastes.)

- Solidifier product from acidic wastes will have a volume of 42 to 108 liters per tonne of spent fuel for the two types of Purex wastes. The smaller volumes will be representative of PW-2 wastes. These volumes represent 6.4 to 16.1 liters/1000 MWd_e.*

Demonstration runs in WSEP showed the phosphate glass solidification process, at capacities in the range of 0.2 to 0.6 tonnes of fuel per day is 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. Redesign of the denitrator-evaporator liquid transfer unit and liquid level and specific gravity monitoring devices, and possibly, development of methods for reducing the reliance on visual access for monitoring melter operation, are needed. In addition, modifications to the design of the denitrator-evaporator and melter may be beneficial. Remaining investigations suggested in WSEP include:

- Demonstration runs at higher radioactivity content to determine the true maximum acceptable heat generation rate (i.e., the maximum exposure level of the fuel and the minimum age of the wastes).
- Solidification of two other waste types likely to be encountered in the future nuclear power economy. One waste should be typical of a low salt, high fission product waste from thermal reactor fuel (exposed to 45,000 MWd/tonne at 15 MW/tonne) produced by "clean" Purex reprocessing (i.e., low iron, low sodium, and no sulfate). The other

---

* Assuming 33.3% thermal efficiency.

waste should be representative of spent core fuels from Liquid Metal Fast Breeder Reactors. Demonstration of these wastes should reasonably well complete the bracketing of the majority of wastes that can be predicted at this time.

- Demonstration of potential for automatic control.

After the above tests are completed and reported, further reports will relate phosphate glass solidifier performance to the other two solidification processes under demonstration in WSEP from technical, operational, and economic viewpoints.

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 on simulated waste solutions using laboratory scale, bench scale, and engineering scale pilot plant equipment.(4,29) Supplemental development work was performed by Battelle-Northwest(5) including some radioactive laboratory studies.(6)

Nonradioactive laboratory studies were made to determine the most satisfactory glass compositions and to test materials of construction for the evaporator and melter.(4,7) 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 testinq of a platinum melter(7) and to confirm design features of WSEP equipment,(8,9) both prior to and during the radioactive WSEP runs. A total of seven nonradioactive design verification tests(10) was made by BNW with the WSEP equipment(1) for final confirmation of the WSEP equipment design and process operating parameters before radioactive operation.

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.(9)

3.2 PROCESS DESCRIPTION

The phosphate glass process is carried out in two continuous steps: a low temperature (130 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 volatilization 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 sulfate is not present in the waste. If sulfate is in the waste, it is volatilized from the melter, and these effluents must be treated separately. The phosphate glass process is shown schematically in Figure 3.1.

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 nonradioactive studies, (except briefly at startup) severe foaming did occur during the first three radioactive demonstration runs. In subsequent runs, however, after addition of an antifoam agent, severe foaming did not occur.

Transfer of the concentrated waste from the denitrator-evaporator to the melter feed system is initiated in **WSEP** 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.

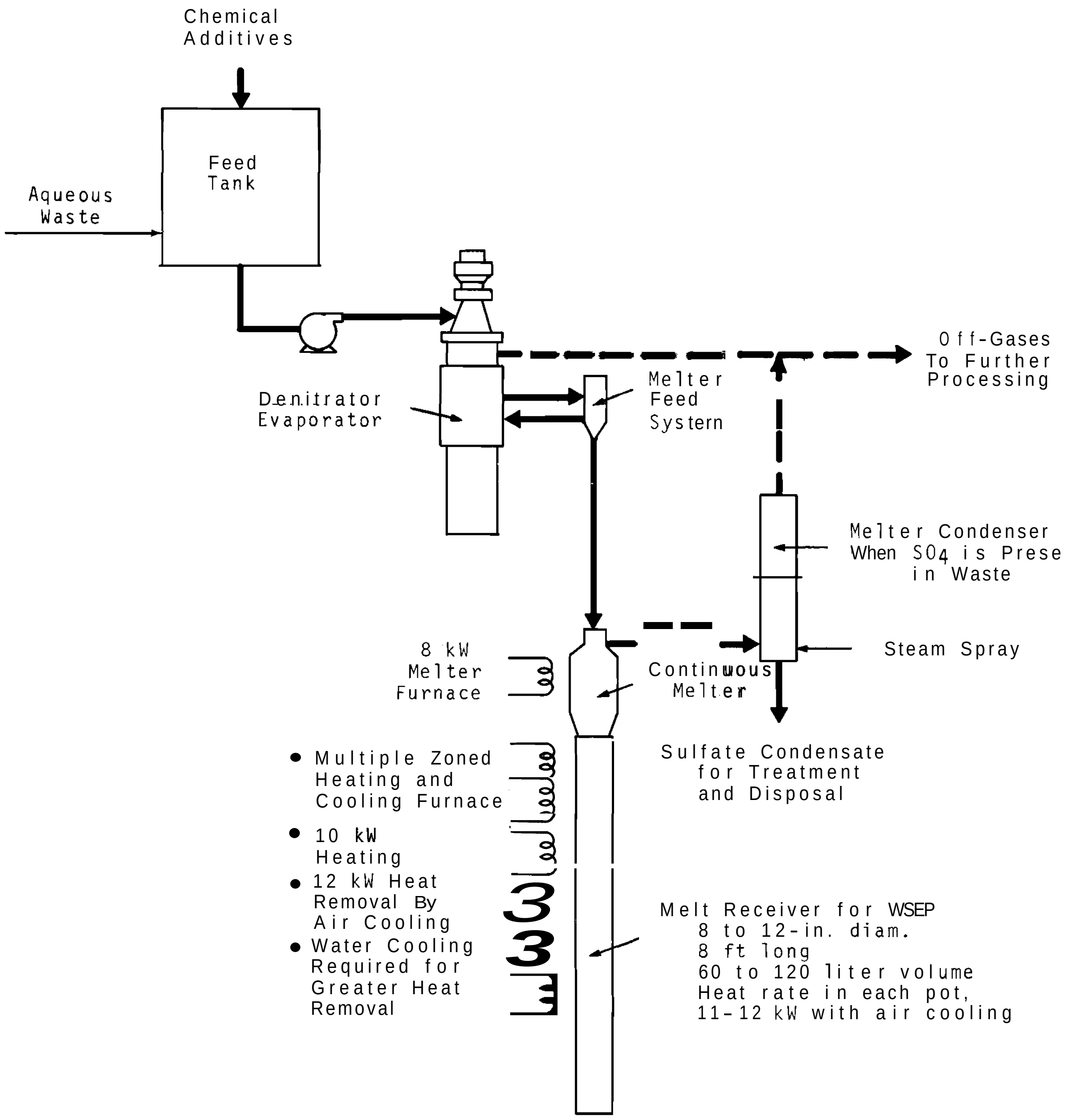


FIGURE 3.1. *Phosphate Glass Solidification Process*

The air-lifted concentrated feed is introduced to the melter through a solution feeder which is cooled by means of a boiling water jacket. The solution feeder is needed to conduct the concentrated solution near the surface of the molten glass pool to minimize spattering and entrainment while maintaining the solution at a warm temperature without concentration.

Once in the melter the concentrate is continuously dried through a calcine stage and to a molten glass at temperatures up to 1200 °C. Essentially all of the nitrate, water, and sulfate (when present in the waste), and a small amount of phosphate distill in this step. In WSEP, the melt is discharged continuously through an overflow weir or may be batch discharged through a drain freeze valve.

When the molten glass is discharged continuously at low rates from the melter, such as 1 liter/hr, the receiver pot wall must be maintained at approximately 600 °C to assure uniform void-free filling of the receiver and to prevent stalagmite formation. Continuous discharge of molten glass at rapid rates into an insulated receiver pot was satisfactorily accomplished at BNL without heating the receiver. Also, batch discharge of melt through the drain freeze valve at rapid rates can be satisfactorily accomplished without heating the receiver pot.

The melter off-gases are routed through a platinum-iridium pipe which must be maintained at temperatures above the condensation point of the vapors to avoid corrosion in the off-gas line. Condensation and scrubbing of the vapors is done in a melter off-gas condenser. Dilution of the corrosive sulfate containing melter condensate is accomplished by the addition of a steam spray which also serves to cool and wet the lower wall of the condenser. Dilution is not necessary for sulfate-free condensate.

The effluents from the melter and the denitrator-evaporator contain 1 to 10% of the radionuclide contents in the original waste. Consequently they are intermediate level wastes which still contain toxic levels of radioactivity. These secondary effluent streams must be further treated or recycled to the fuel reprocessing plant and before ultimate discharge to the environs. In WSEP, the auxiliaries for treatment of these effluents consist of a condenser and an evaporator, a condenser and an acid fractionator and another condenser, and a scrubber and a high efficiency filtration system.(1)

3.3 PROCESS TECHNOLOGY

The addition of approximately one mole of phosphoric acid per equivalent of nonvolatile cation is required to make a good phosphate glass product for PW-1* and PW-2* wastes. A short digestion period (about 8 hours with simulated waste at room temperature) following the addition of phosphoric acid permits the bulk of the cations in the waste to be complexed. Precipitation of fission product zirconium phosphate, barium and strontium sulfates, and phosphomolybdate complexes occurs to the extent that the solution will contain approximately 10% settled solids. The solids content of the feed prepared for use in the six phosphate glass radioactive demonstration runs ranged from 10 vol% in run PG-4 to 50 vol% in run PG-3, and averaged about 21 vol%.

Substitutions of some of the more costly chemical elements in PW-1 and PW-2 wastes with less expensive, chemically similar elements were made in development studies. Development studies indicated that the selected substitutions could be made with no noticeable effects on process or product characteristics. Iron, cobalt and nickel were substituted for ruthenium, rhodium, and palladium, respectively, and in WSEP copper was substituted for silver and cadmium. Other substitutions were made as indicated in Table 9.1 in the appendix. The use of manganese

---

* See Table 9.1 in the appendix for nominal composition of these wastes.

as a substitute for ruthenium was discontinued during early nonradioactive tests because manganese formed heavy solids in the denitrator-evaporator at operating temperatures.

Specific nonradioactive experiments were conducted to determine the effects of aluminum, rare earths, and uranium, which were present in excess amounts in some of the batches of radioactive waste stocks used in the WSEP demonstrations. The tests showed that substitution of aluminum for iron produced no marked effects other than to change the glass to a somewhat lighter color. Aluminum can be substituted for any part or all of the iron in PW-1 waste on a mole-for-mole basis without changing the melting characteristics of the phosphate glass process product.(10)

The tests also showed that substitution of aluminum for half the iron in PW-2 on a mole-for-mole basis would not significantly change the characteristics of denitrator-evaporator concentrate or the final melt. No tests were made to determine the effects of substituting aluminum for more than half the iron in PW-2 waste.

Since 4-year-old concentrated radiocerium solution was used to provide most of the radioactive decay heat for the waste used in run PG-4, the rare earth (RE) content in the feed was approximately six times the nominal 0.12M. Nonradioactive test melts were prepared from simulated feed solutions containing 0.237, 0.335, and 0.67M total rare earths. The other PW-2 constituents were held at the nominal 378 liters/tonne levels, and phosphoric acid was added to maintain the metal equivalents/phosphate ratio (M/P) at 1.0. The only apparent effect of the increased rare earth content was an increase in melt formation point of about 50 °C to 975 °C with 0.67M rare earths. The addition of 0.5 to 1.0M sodium completely counteracted the increase in the melt formation point. Results are shown in Table 3.1.(11)

TABLE 3.1. *Effect of Rare Earth Content on Melt Formation in PW-2 Waste*

Concentration in Waste at 378.5 liters/tonne, M					
Total RE	Additive Na	Al	Fe	P	Melting Point, °C
0.113	0.0	0.001	0.445	3.134	925
0.237	0.0	0.001	0.445	3.489	950
0.237	0.3	0.001	0.445	3.789	900
0.237	0.6	0.001	0.445	4.089	850
0.237	0.9	0.001	0.445	4.389	850
0.335	0.0	0.001	0.445	3.783	950
0.335	1.0	0.001	0.445	4.783	825
0.67	0.0	0.001	0.445	4.790	975
0.67	1.0	0.001	0.445	5.790	850
0.67	2.0	0.001	0.445	6.790	775

The radioactive waste used for demonstration run PG-5 contained excess uranium so that the final feed had about six times the nominal concentration of 0.01M in PW-1 waste. Results of a nonradioactive investigation(11) showed (Table 3.2) that when phosphate was added to maintain an M/P ratio of 1.0, the effect of the uranium in the feed was negligible (see Table 3.2). The effect of the additional amounts of uranium plus the added phosphoric acid was to increase the viscosity and melting point of the melt, but the increases were very slight at 0.10M uranium. All three melts formed products which were visually less glassy than typical PW-2 phosphate glass products.

Although the uranium cation equivalence was selected arbitrarily as six times the molarity, the true answer appears to be closer to four times the molarity. The point can be shown by assuming that the weight loss shown in Table 3.2 was

P_2O_5 which volatilized because it was in excess of that required to coordinate with uranium. From the weight losses, the phosphorus/uranium ratios in the last 2 melts in Table 3.2 were calculated to be 4.28 and 4.34.(5)

TABLE 3.2. Effect of Uranium on PW-1 Waste

Concentration in Waste at 378 liters/tonne,[a] M						Melt Weight	
Total Na[b]	Total P	Total U	M/P Ratio[c]	Melt Point, °C	Slump Point, °C	Measured, g	Theoretical,[d] g
2.648	6.44	0.01	0.973	775	600	663	668
2.648	6.8	0.01	1.00	800	650	708	719
2.648	8.00	0.30	1.00	850	650	826	860

---

a. The PW-1 flowsheet for run PG-5 was expected to contain 2.6M total sodium and 6.44M phosphate (in 378 liters/tonne solution).

b. Inadvertently slightly higher than the desired 2.60M, but conclusions are not affected.

c. U metal ion equivalence = 6X uranium molarity.

d. Based on 1 liter of PW-1.

Laboratory investigations(11) with nonradioactive feed and with actual radioactive feed for run PG-3 were made to determine the cause of and methods for prevention of foaming. Nonradioactive laboratory studies established dibutyl phosphate (DBP) was the foaming agent in the evaporator concentrate in the radioactive runs. A silicone antifoam agent (Dow Corning Antifoam B) was found to counteract the DBP-induced foaming in the laboratory test apparatus (see Figure 9.11) during short-term tests, but was less successful in tests lasting several hours. Radioactive tests were conducted on the feed for PG-3 to investigate foaming in a glass, scaled-down test apparatus similar in geometrical shape to that of the denitrator (see Figure 9.12 in Appendix). Foaming was found to be time-dependent with some foam-making material accumulating in the denitrator. Subsequently, the antifoam agent was again found to successfully subdue foam and prevent its recurrence if the antifoam was added continuously to the system. In the full-scale denitrator, a continuous addition of approximately 100 ppm/hr* was required for adequate control.

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 process. 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 3.3.

---

* Parts per million of the normal holdup in the denitrator of about 50 liters of concentrate.

TABLE 3.3. *Results of Preliminary Radioactive Incell Laboratory Tests with Adjusted Phosphate Glass Feeds*

WSEP Run	PG-1	PG-2	PG-3	PG-4	PG-5	PG-6
Feed Type	PW-2	PW-2	PW-2	PW-2	PW-1	PW-1
Heat generation rate in feed, W/liter	1.3	3.9	10[a]	7	Batch 1 Batch 2 12 8	16.8
Boiling point of Feed, °C	∿105	∿100	At 70 °C bubbles appeared. At a87 °C white fumes appeared. Loose foam at a103 °C.	110	Not Available	100
Suspended solids content in adjusted feed, vol%[b]	∿75	a50	Not Available	∿20	Not Available	Not Available
Foaming tendency in denitrator-evaporator	Foaming appeared at 126 °C. Heaviest at 128 °C. Persisted until it boiled down to thick sludge at 146 °C.	No severe foaming to 146 ’C.	Jelly-like at 140 °C. Slight foaming at a167 °C.	Spattering and light foam during boildown. ∿10% foam in heating to 150 °C.	Fuming at 90 °C. White fumes at 110 "C. Some foaming at 140 °C but no fumes.	Medium size viscous bubbles at 140 °C. Big viscous bubbles between 170 and 200 °C. One large bubble between 210-220 °C. Bubble subsided at 230 °C.
Foaming tendency in melter		Melt climbed up sides of crucible between 600-800 °C. White fumes noted in this interval.	No foaming observed up to 400 °C.	Swelling of calcine at 450 °C. Sulfate evolution at 550 °C.	Some fumes at 300 °C. Slumping of calcine at 700 °C.	Putty-like at 500 °C. No fumes or foaming observed up to 900 °C.
Volatilization	None visible after holding at 1000 °C for 30 min.	No visible volatilization noted after 30 min at 900 °C.		No visible volatilization after 30 min at 950 °C.		No visible volatilization at 900 °C.
Corrosiveness of melt to pot material	Oxidized after 8 hr at 650 °C. Mild steel coupon used.	Oxidized after 8 hr at 650 °C, but no visual penetration 304L SS coupon used.	No visible corrosion of mild steel coupon after 8 hr at 650 °C.	Oxidized but no visual penetration of mild steel coupon after 4 hr at 650 °C.	Mild steel coupon oxidized by air after 8 hr at 750 °C but no apparent penetration by melt.	No visible corrosion of mild steel coupon after 24 hr at 650 °C.
Product appearance	Glassy		Gray and unmelted at 800 °C.			
Initial Melting point, °C	825	750-800	850	850	800	800

---

a. By heat rise test assuming Cp = 0.9 kcal/kg-°C for concentrated wastes.

b. Estimated volume.

4.0 PHOSPHATE GLASS SOLIDIFICATION PERFORMANCE

Six radioactive demonstration runs have been completed in the WSEP to demonstrate the phosphate glass solidification process. A major objective was to increase the concentrations of radionuclides in the waste in each successive run to permit prediction of the maximum allowable heat generation rate in a receiver pot. Other objectives included determination of the performance of the phosphate glass process coupled with the auxiliary equipment. Collection of several 200 liter portions of actual PW-2 sulfate condensate for hot laboratory and hot pilot plant demonstration tests was done as the runs progressed. Major variables of the runs are shown in Table 4.1.

TABLE 4.1. Major Run Variables

PG Run	Mode	Pot Diam, in.	Waste Type	Curies to Pot	Tonnes[(a)] to Pot	W/tonne in Waste[(a)]	Equivalent[(b)] Age, yr
1	A,B	12	PW-2	349,000	2.16	740	7.5
2	A	8	PW-2	419,000	0.89	1,900	2.5
3	A	8	PW-2	604,000	0.69	4,800	1.0
4	A	8	PW-2	1,110,000	1.24	3,500	1.45
5	A,B	12	PW-1	2,180,000	1.04	8,500	0.53
6	A	8	PW-1	2,430,000	0.66	14,500	0.22

---

a. Tonne is a metric ton of original fuel
b. Rased on 20,000 MWd/tonne at 15 MW/tonne

Engineering scale performance of the phosphate glass solidification process with highly radioactive feed generally confirmed earlier development work.(9) 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 except for excessive losses of feed from the denitrator due to foaming of the denitrator concentrate. The foaming in the denitrator was caused primarily by small amounts of foam-making material (dibutyl phosphate in the Purex waste used for feed makeup). Satisfactory control of foaming was achieved by the addition of a silicone antifoam agent into the denitrator. Data presented in Section 4.0 are from References 5 and 11 through 15.

Plugging of the specific gravity and liquid level dip tubes, the airlift air line, the airlift pot recirculation line, and the melter feed line with granular solids was a major problem during processing of PW-1 waste. The remotable features of the new airlift pot used during the PW-1 demonstrations did help in overcoming solids building up in the airlift pot. Several methods were tried to keep the dip tubes clear of solids; the only successful method was hourly steam blowdowns. Relatively few processing problems were encountered while solidifying PW-2 wastes. However, as with the PW-1 wastes, the inability to maintain a continuous feed flow to the melter resulted with the use of the airlift pots. Solidification of wastes during the first six radioactive demonstrations produced a phosphate glass with a heat generation rate as high as 9600 watts in an 8-inch diameter pot. Reasonable levels of radioactivity in the acid and water effluent streams were obtained so that the streams were suitable for reuse or treatment as low level streams. The final gaseous effluent leaving the stack was well below 10CFR20 relesse limits.

4.1 OVERALL PROCESSING RATES

Overall processing rates (based on melter feed time before denitrator dilution) ranged from 0.20 to 0.61 tonne/day for PW-2 wastes and from 0.20 to 0.34 tonne/day for PW-1 wastes. These rates represent production of glass products at 20.6 to 28.8 liters/day for PW-1 and from 10.5 to 29.1 liters/day for PW-2. The internal heat generation rate within the phosphate glass melt was a high as 1 kilowatt. The total power requirements are 2 to 6 kilowatts for the melter. No apparent increase in processing rates was observed as the internal heat rate increased. Even with the internal heat and resulting decrease in melter power requirement, the melter still limits the capacity of the process.

Table 4.2 summarizes the data on processing rates. Results were fairly consistent except during run PG-3. The uncontrolled foaming of concentrate in the denitrator-evaporator which occurred during most of run PG-3 resulted in only about 16 hours of steady state operation. Continuous flow of concentrate to the melter was difficult to maintain because of the variations of operating conditions tested in attempts to control the excessive foaming. These two conditions resulted in an intentionally low processing rate for PG-3.

Figure 4.1 shows the feed rates and feed consumption curves for typical demonstration runs with PW-1 and PW-2 wastes. The feed rates were maximum during the initial concentration period when the concentrate in the denitrator-evaporator was being concentrated to the normal operating boiling point and specific gravity. The overall feed rate to the denitrator averaged 12.1 liters/hr during PW-1 runs and ranged from 9.4 to 18 liters/hr during PW-2 runs based on adjusted feed at 378 liters/tonne.

The general factors affecting rates were only qualitatively investigated. The limiting factor affecting the processing rate is the transmission of power required to form a good melt (2 to 4 kilowatts of power). Other factors influencing the rates are feed composition and erratic feed rates to the melter. The processing rates are not limited by the denitrator-evaporator since it can evaporate greater than 35 liters/hr of distillate. Nitrogen sparge tests of the melter were conducted at an average sparge rate of about 0.5 scfh to determine if sparging through the melt would increase melter processing rates.

TABLE 4.2. WSEP Phosphate Glass Solidification Processing Rates

PG Run No.	Mode	Feed Type	Feed Conc., liters/tonne fuel	Pot Diameter 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 Steadystate, liter/hr
1	A	PW-2	480	12	1600	964	61.4	52	21.6	14.6
	B	PW-2	580			431	31.0	26	19.0	13.0
2	A	PW-2	586	8	1700	873	48.5	32	22.0	14.0
3	A	PW-2	458	8	3300	697	57.0	16	11.0	16.0
4	A	PW-2	540	8	4200	725	77.0	65	20.0	7.5
5	A	PW-1	666	12	8800	420	38.0	32	25.0	10.0
	B	PW-1	1143			842	66.0	60	25.8	11.5
6	A	PW-1	889	3	9600	616	50.0	43	23.6	10.5

PG Run No.	Average Overall Feed Rate liter/hr	Total Run Time, h[d]	Total Equivalent Feed to Melter Liters[b]	Total Equivalent Feed to Melter Tonnes of Fuel	Steady-State Processing Rate to Receiver Pot	
					Equivalent tonnes/day	liters melt/day[c]
1	15.7	73	709	1.48	0.61	29.1
	13.9	46	394	0.68	0.44	21.0
2	18.0	63	520	0.89	0.38	14.9
3	11.0	71	318	0.69	0.21	10.5
4	9.4	90	669	1.24	0.34	19.0
5	11.1	40	271	0.41	0.28	28.8
	12.8	76	728	0.64	0.20	20.6
6	12.3	64	584	0.66	0.28	26

---

a. Total in pot at end of run.
b. Amount of material fed to the melter in terms of the volume fed to the denitrator-evaporator.
c. Based on melter feed time up to denitrator-evaporator dilution and tonne equivalents to pot up to denitrator-evaporator dilution.
d. Total WSEP systems (solidifier and auxiliary systems) operating time.

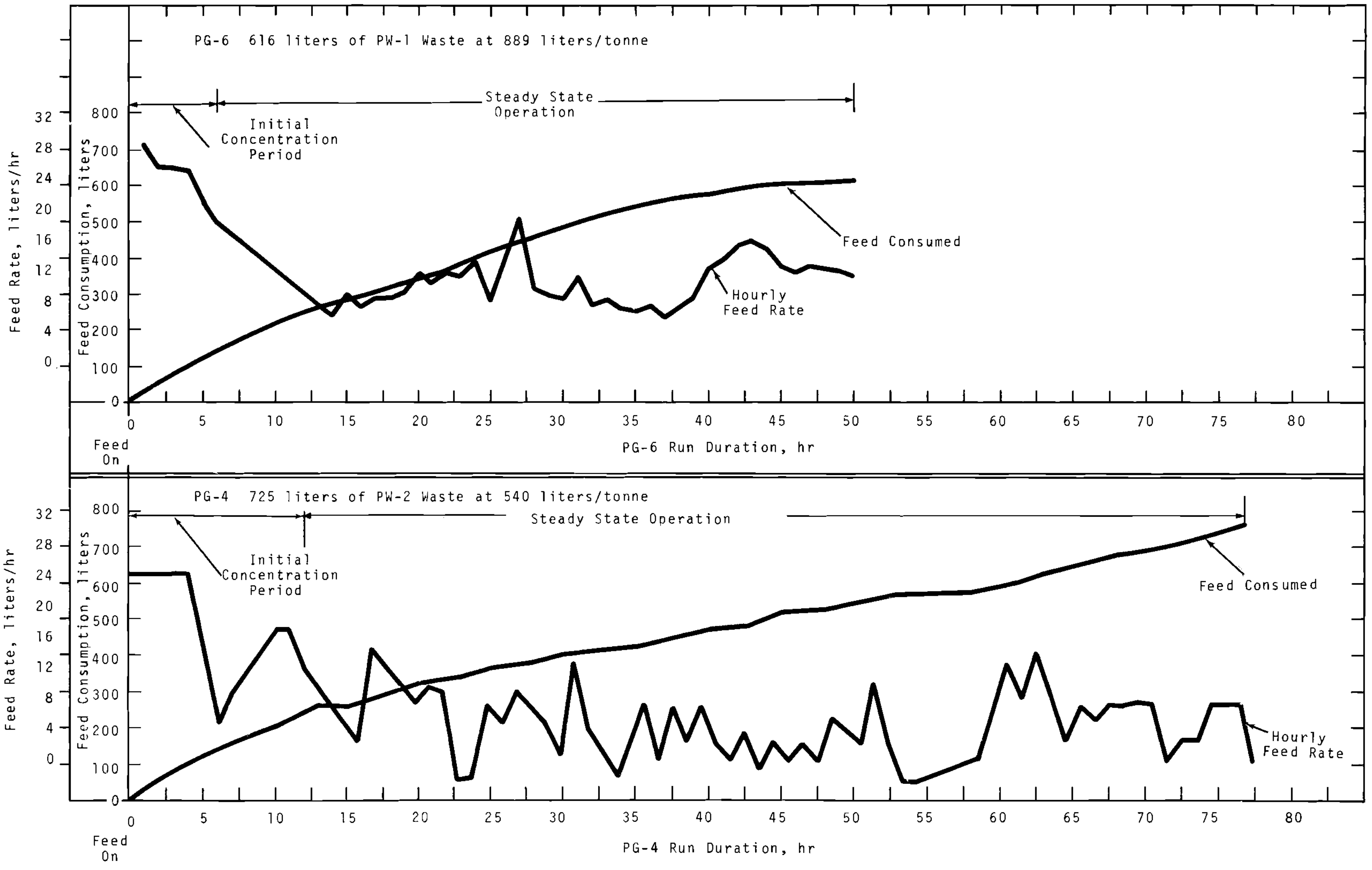


FIGURE 4.1. *Typical WSEP Phosphate Glass Solidification Processing Rates*

Although erratic feeding of the melter occurred during the tests and 1 to 2 of the 4 available sparge tubes were plugged, sparging had no apparent effect on processing rates.

4.2 RADIONUCLIDE HEATING EFFECTS

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 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 temperatures established for WSEP are to limit the product temperature to 900 °C and to limit the receiver pot wall temperature to 427 °C. Also, if a molten core exists in the receiver pot, the thickness of the frozen wall of the solidified waste is not to be less than one-half the pot radius. The 900 °C limit reduces corrosion to the stainless steel thermowells used to house the internal thermocouples. (The wells will probably not be used in production model receiver pots.) The 427 °C wall temperature prevents 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 6 pots are listed in Table 4.3. During the first radioactive demonstrations of the phosphate glass process in WSEP, the internal heat rate density was increased in each successive pot to 155 W/liter with an internal centerline temperature of 780 °C in run PG-6. Because the phosphate glass product has a 700 °C remelt temperature, the maximum heat rate density is limited by the frozen wall thickness restriction and will be approximately 180 to 200 W/liter for an 8 inch diameter receiver pot stored in air.

TABLE 4.3. Pot Receiver Temperatures Caused by Internal Heat Generation

PG Run	Pot Diam, in.	Pot Material	Total Heat Rate, W	Total Heat Rate Density, W/liter	Centerline Temp,[a] °C	Centerline to Wall Temp Difference,[a] °C
1	12	Mild Steel	1600	17	316[b]	89[b]
2	8	304L SS	1700	49	355	135[b]
3	8	Mild Steel	3300	95	655[b]	255
4	8	Mild Steel	4200	57	510[b]	175[b]
5	12	Mild Steel	8800	78	712	352
6	8	304L SS	9600	155	780	380

---

a. Receiver pot in furnace with forced air cooling outside the susceptor except where otherwise designated.
b. Receiver pot in furnace without forced air cooling of the susceptor.

During runs PG-1 and PG-2 the receiver pot furnace was held at 590 and 580 °C, respectively. These furnace temperatures were used to assure that the pot wall temperature remained sufficiently high so that the steady drip of melt entering the receiver pot at rates as low as 0.62 liters/hr would cause no stalagmites. During run PG-3, the receiver pot furnace temperature was tested at 300 °C and glass stalagmites formed in the product receiver. Pot wall temperatures of 300 °C allowed the entering melt to cool too rapidly to permit the melt to slump, thereby causing a buildup of melt on the pot thennowells. Batch dumping of the melt at rates of 1 to 2 liters/min through the drain freeze-valve produced no stalagmites at a pot temperature of 300 °C. Stalagmites also formed during run PG-4 after the fill level extended into the unheated zone of the receiver pot where the wall temperature was 300 °C. Pot wall temperatures were maintained at 575 °C during runs PG-5 and 6 without any stalagmite formation. Pot wall temperatures of about 600 °C are recommended when melt is to be continuously discharged via the melter weir.

Figure 4.2 is a schematic of a receiver pot which shows the location of the pot thermocouples. Using one receiver pot cooling air blower rated at 275 scfm was sufficient to control the centerline temperature of the pot contents below 900 °C, and the pot wall below 427 °C during run PG-6 which contained the highest heat-rate density tested to date of 155 W/liter. The cooling air blows onto the outside of the furnace susceptor.* A typical receiver pot temperature profile using data from run PG-5 is shown in Figure 4.3.

4.3 WASTE VOLUME REDUCTION

Because of the variations in chemical compositions of the waste processed during solidification, the overall volume reduction factors varied from 3.5 to 9.1 (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 estimates of the volume reduction to be expected in the solidification of PW-1 and PW-2 feeds used in each run. Estimated values of volume reduction differed from observed values by 4.3% in run PG-1 to 14.3% in run PG-5. The average difference for the six runs was less than 10%. Difficulties in analyzing the feed for some of the oxide forming metallic cations such as Fe and Al in the presence of phosphates were mainly responsible for the differences. During the first three demonstration runs with PW-2 waste, the volume reduction averaged 8.5,

---

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

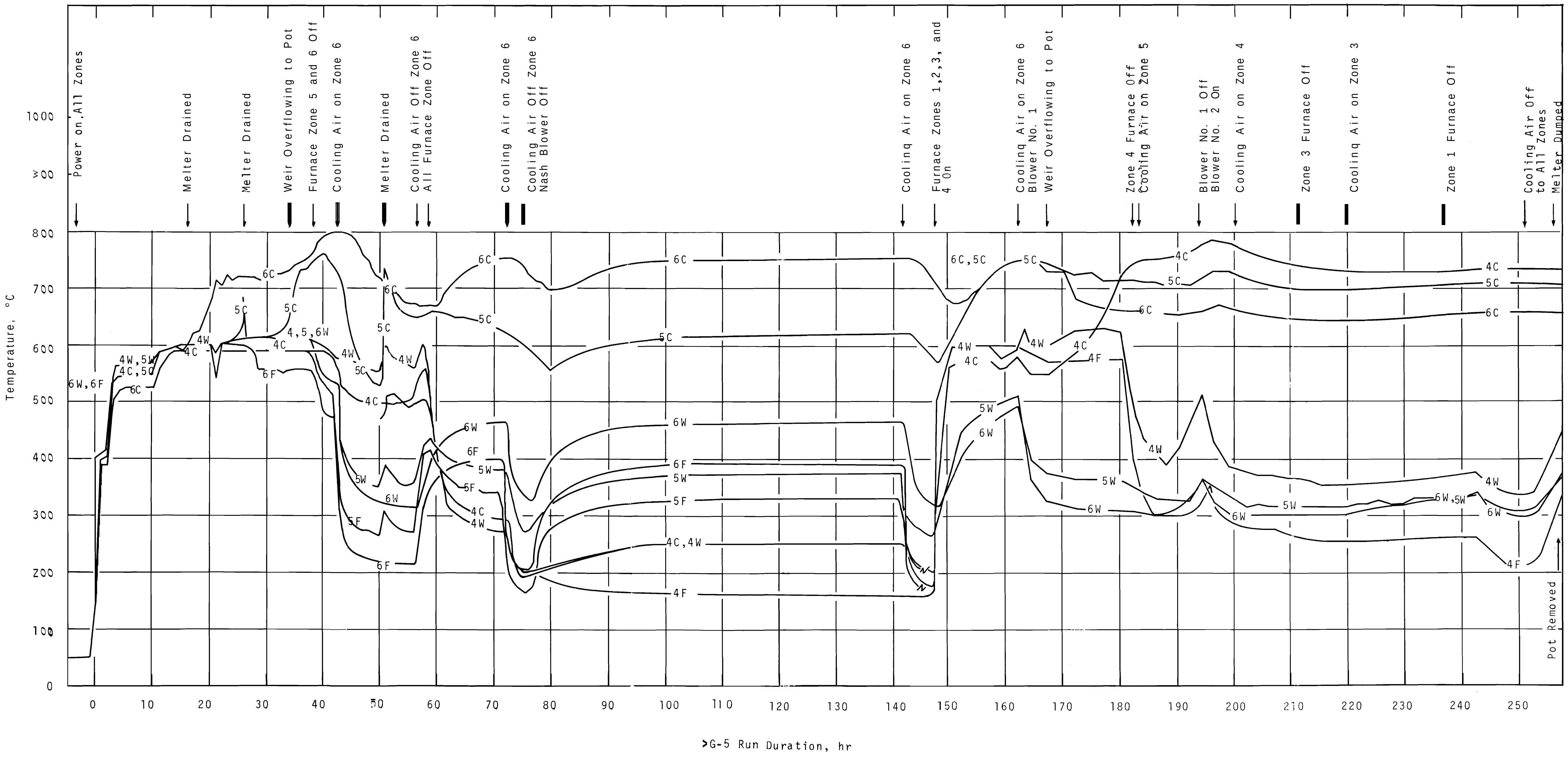


FIGURE 4.3 Run PG-5 Receiver Pot and Furnace Temperatures for Zones 4, 5, and 6

Pot Size	8 in.	12 in.
Material	Mild Steel or 304L SS Sch. Pipe	Mild Steel or 304L SS 0.310 in. Thick
OD in.	8.625	12.0
ID in.	7.981	11.38
Fill Height, in.	72	72
Fill Volume, liters	60	120
Thermowells Centerline	3/4 in. Sch.80 310 SS	
Intermediate	1/2 in. Sch.80 310 SS	

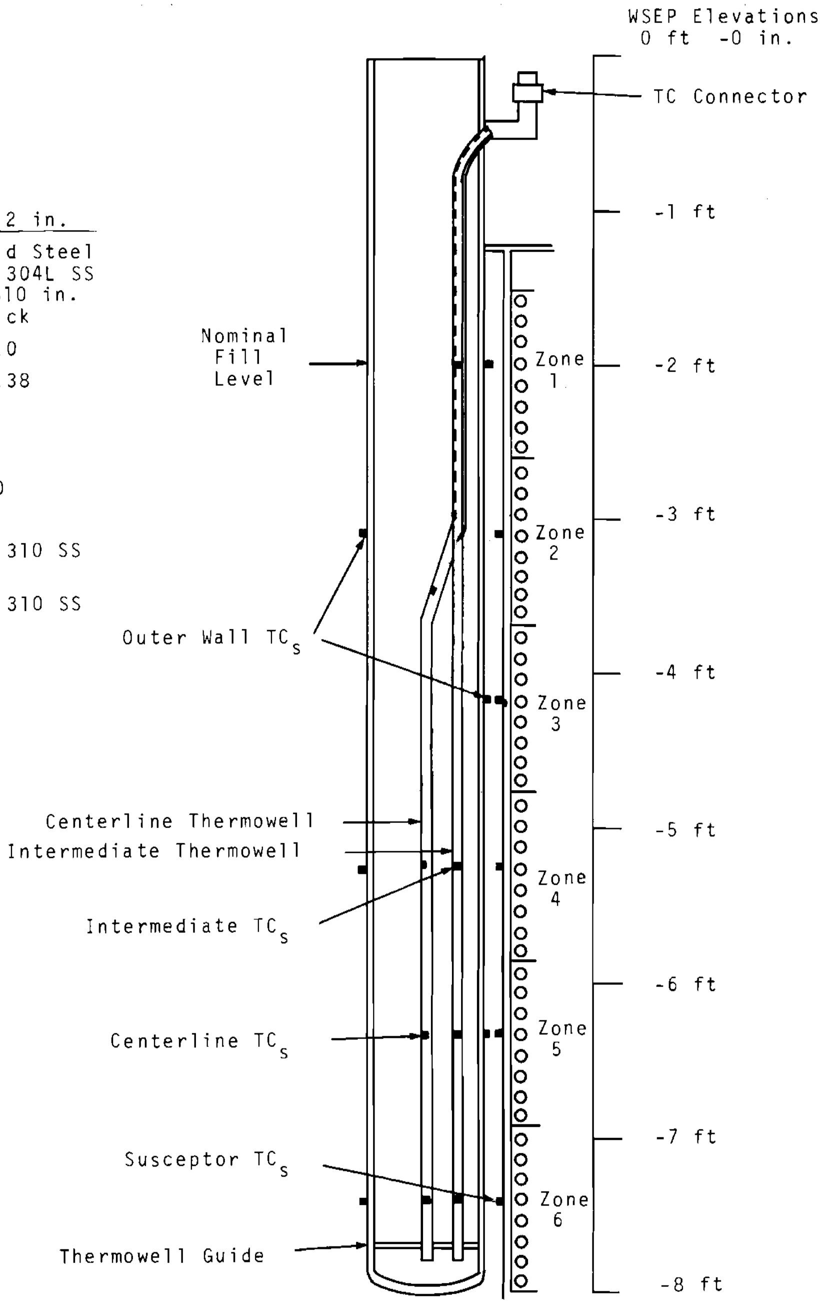


FIGURE 4.2 *Phosphate Glass Receiver Pot Thermocouple Arrangement*

while during the fourth run with PW-2 waste, the volume reduction was lower at 6.4. This lower value was caused by the 0.45M excess rare earths in the waste which required extra 0.5M $NaNO_3$ and 1.16M H_3PO_4 additions. During runs PG-5 and 6 where sulfate-free PW-1 waste was processed, the volume reduction factors were 3.5 and 4.0, respectively. These were a factor of about 2 less than during the PW-2 runs because of the additional chemical additives necessary to process the waste. See Table 9.1 for typical PW-1 and PW-2 waste compositions.

TABLE 4.4. *Volume Reductions*

PG Run	Feed Type	Denitrator-Evaporator Avg Liquid Temp °C	Overall Volume Reduction (a)	Estimate (e) Volume Reduction	Denitrator Concentration Factor (b)	Melter concentration Factor (c)	Measured Density of Product
1	PW-2	137	8.8	8.4	3.7	2.4	2.8
2	PW-2	137	9.1	8.2	3.2	2.8	2.9
3	PW-2	136	7.5	7.9	4.0	1.9	2.8
4	PW-2	137	6.4 (d)	5.7	2.2	2.9	2.9
5	PW-1	133	3.5	4.0	1.9	1.8	2.7
6	PW-1	132	4.0	3.5	1.8	2.2	2.8

---

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

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

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

d. Due to 0.45M excess rare earths, additional 0.5M Na and 1.16M PO_4 was added to the feed.

e. Estimate is based on density of product/total oxide weight in feed at 378 liters/tonne.

The unit volume of phosphate glass from PW-1 waste in a receiver pot (Table 4.5) was 93 and 102 liters/tonne of fuel for runs PG-5 and 6, respectively. For PW-2 waste, the volume ranged from 37 to 45 liters/tonne of fuel. The measured density of product averaged about 2.8 kg/liter and 2.9 kg/liter for PW-1 and PW-2 wastes, respectively. As a result of stalagmite formation during run PG-3, the volume of the melt could not be measured in the receiving pot because of voids in the product. The volume of product was calculated from the laboratory-measured density and the net weight in the pot.

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 6-foot depth
1	12	1600	258[a]	41.8	2.16	2.5
2	8	1700	100[b]	39.3	0.89	1.5
3	8	3300	98	50.0	0.69	1.2
4	8	4200	194	55.8	1.24	1.1
5	12	8800	306	103	1.04	1.2
6	8	9600	174	93.9	0.66	0.64

---

a. Does not include 17 kg startup additive.
b. Does not include 18 kg startup additive.

During the first four demonstration runs with sulfate-containing PW-2 waste, the typical denitrator-evaporator concentration factor (based on 378 liters/tonne) was 3.6, while the melter concentration factor averaged 2.6. An exception was during run PG-4 where the denitrator-evaporator concentration factor was 2.2 and the melter concentration factor was 2.9 for the reasons previously discussed. During runs PG-5 and PG-6 the concentration factors for the denitrator and melter were both about 1.9.

4.4 PERFORMANCE OF DENITRATOR-EVAPORATOR

The denitrator was started with an initial volume of 29 to 37 liters of 6M 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 was fed to the melter. Until the desired concentration was reached,-- and feeding of concentrate to the melter begun, the feed rate to the denitrator averaged 25 liters/hr for PW-1 waste and ranged from 11.0 to 21.6 liters/hr for PW-2 waste. The startup period required about 6 hours for all demonstration runs. The steady state feed rates averaged 10.8 liters/hr for PW-1 and varied from 7.5 to 16 liters/hr for PW-2 wastes. Processing rates are summarized in Table 4.2. The shutdown period involves dilution of the contents of the denitrator-evaporator with 6M nitric acid as feeding to the melter is continued and no waste is fed to the denitrator. During run PG-6, 100 liters of water and 6M nitric acid were used to dilute the denitrator. The use of water (versus nitric acid) caused no gelling of the hot concentrate.

The denitrator concentrate boiling temperature was held at about 132 and 137 °C for PW-1 and PW-2 wastes, respectively. The tube bundle steam to concentrate temperature difference varied from 12 to 24 °C for PW-1 waste and from 8 to 21 °C for PW-2 waste. See Table 4.6 for general operating parameters.

TABLE 4.6. *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 AT Steam-Liquid °C
1[b]	PW-2	138	136	37	45	1.8	200	52	148	10
2	PW-2	137	135	34	47	1.8	200	58	152	15
3	PW-2	136	136	35	47	1.8	200, 600	67	157	21
4	PW-2	137	110	35	55	1.9	200	45-60	145-153	8-16
5[b]	PW-1	133	110	35	48	1.8	200	45-70[b]	145-158	12-25
6	PW-1	132	109	29	45	1.8	200	65	156	24

---

a. At operating temperature
b. Average of two-part run
c. Saturated steam.

Significant denitration and concentration of the waste solution occurs at the boiling temperature of 132 to 137 °C. Nitric acid is distilled as well as displaced from the solution by the presence of excess phosphoric acid and sulfuric acid. During PW-1 demonstration runs, 60 to 70% of the nitrogen in the feed to the denitrator was driven off and condensed in the process condenser. About 90 to 95% denitration of the feed in the denitrator-evaporator occurred during the demonstrations with PW-2 waste. Both denitration ranges for PW-1 and PW-2 wastes agree with those from previous Design Verification tests and BNL pilot plant studies at the same boiling temperatures.

Plugging of the specific gravity and liquid level (weight factor) tubes was a continuous problem during the processing of PW-1 waste. This problem required hourly steam blow-downs to keep the dip tubes clear of granular solids.

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 9.1 through 9.7.

4.4.1 Volatilization and Entrainment

An important objective during the six phosphate glass runs was to characterize the path and behavior of ruthenium. Most of the ruthenium that is volatilized during the denitration-concentration step is collected in the WSEP auxiliary evaporator.

The ruthenium that volatilized from the denitrator-evaporator ranged from 0.2 to 3% during the WSEP runs. A nonradioactive test (Design verification Test CPG7) indicated that less than 3% of the ruthenium in PW-1 feed to the denitrator would volatilize from the denitrator. Table 4.7 lists

TABLE 4.7. *Volatilization and Entrainment from Denitrator-Evaporator*

PG Run	Mode	Feed Type	Denitrator Concentrate Volume, liters/tonne	Denitrator Concentrate Composition, M[(a)]						Additives	Foam Present	Average Feed Rate liters/hr	Boiloff Rate,[(c)] liters/hr	Percent ^{106}Ru Volatilized[(d)]	Percent ^{144}Ce-Pr Entrainment[(d)]
				Fe^{+3}	Al^{+3}	Na^{+}	SO_4^{-2}	PO_4^{-3}	Ru[(b)]						
1	A	PW-2	107	1.12	0.35	3.1	3.15	10.2	0.012	6M HNO_3	Yes	15.7	∿12.7	4.0	<0.1
	B	PW-2	96.6	0.975	0.94	2.76	3.68	13.2	0.014	6M HNO_3	Yes	13.9	∿11.9	0.5	<0.1
2	A	PW-2	117	0.70	0.78	3.2	2.78	10.8	0.012	6M HNO_3	Yes	18.0	∿15.7	0.9	0.02
3	A	PW-2	95.4	1.18	0.70	3.5	3.32	13.4	0.024	6M HNO_3	Yes	11.0	∿9.5	0.8	0.003
4	A	PW-2[(f)]	154	0.47	0.47	2.9	2.9	11.0	0.007	6M HNO_3 Antifoam	No[(e)]	9.4	∿11.1	0.2	0.001
5	A	PW-1	190	0.96	0.84	5.5	--	12.9	0.008	6M HNO_3 Antifoam	No	11.1	12.4	0.5	0.009
	B	PW-1	208	0.86	0.76	5.0	--	11.6	0.0072	6M HNO_3 Antifoam	No	12.8	13.5	0.5	NA
6	A	PW-1	212	1.89	0.29	5.2	--	11.5	0.0058	6M HNO_3	No	12.3	11.1	0.4	0.03

---

a. All molarities are at denitrator-evaporator average operating conditions. See appendix for feed concentration in the feed tank.
b. Chemical ruthenium.
c. Boiloff rate sometimes exceeds feed rate because of acid flushes to the denitrator.
d. Percent of total activity fed to the denitrator, which was found in the condensate from the denitrator. These values were calculated using stream samples.
e. Foaming occurred during startup prior to antifoam addition
f. Excess rare earths (0.45M) required additional sodium (0.5M) and phosphoric acid (1.16M) based on 378 liters/tonne.

ruthenium volatilization and cerium-praseodymium entrainment from the denitrator along with other variables that could affect volatilization.

Multiple startups and shutdowns apparently did not adversely affect the volatilization of ruthenium. During the first startup of run PG-1, 3% of the ruthenium delivered to the denitrator volatilized. After the second startup, 0.5% of the ruthenium fed to the denitrator was volatilized from the denitrator.

Entrainment of nonvolatile radioactivity from the denitrator ranged from 0.001 to 0.1% based on ^{144}Ce-Pr in condensate stream samples. These values were somewhat less than the 0.06 to 0.14% entrainment which occurred during the design verification tests using sodium and iron salts to represent nonvolatiles.(10) Feed composition had no apparent affect on either volatilization of ruthenium or entrainment of nonvolatiles. Figure 4.4 shows typical volatilization of ruthenium and entrainment of ^{144}Ce-Pr as a function of fraction of waste that was fed to denitrator-evaporator. The boiloff rates did not affect the entrainment markedly because the rates (less than 13 liters per hr) were considerably below the capacity of the denitrator (viz 35 liters/hr). Foaming that occurred in the denitrator during the first three radioactive runs contributed substantially to losses from the denitrator, but did not seem to affect entrainment or volatilization through the normal vent system. During PG-3, high foamover of concentrate through the denitrator seal pot caused bypassing of the denitrator vapors around the process off-gas condenser and into the melter condensate receiver.

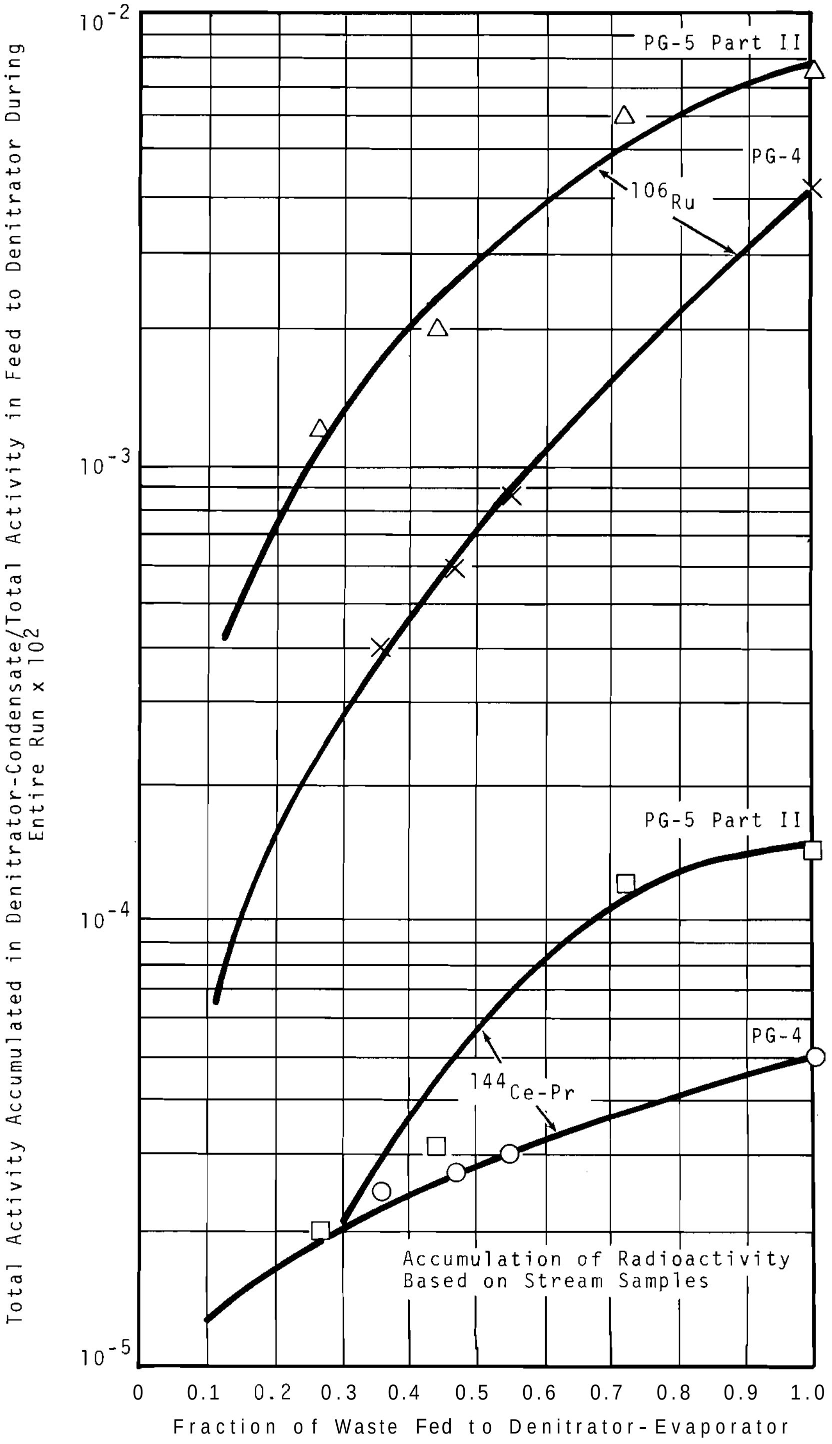


FIGURE 4.4. *Volatilization and Entrainment from the Denitrator-Evaporator*

4.4.2 Foaming

During the first three runs, foaming in the denitrator-evaporator was the most severe problem encountered. The primary indication of foaming during the runs occurred when the denitrator liquid and vapor temperature became equal (see Appendix, Figures 9.1 through 9.7.) Other indications of foaming were:

- Abnormal increases of specific gravity and liquid weight when 6M nitric acid was sprayed into the vapor space or when denitrator jacket cooling water was turned on causing foam to collapse.
- Increased liquid level (weight factor) readings in the denitrator overflow seal pot as foam entered.
- Abnormal increases in the liquid level (weight factor), specific gravity and temperature readings in the melter condensate receiver which receives overflows from the denitrator seal pot.

During run PG-3, two methods were tried to suppress the foam in the denitrator. These were (1) the use of cooling water in the denitrator jacket to cool and collapse the foam at the walls and (2) the use of increased agitation. The use of jacket cooling water beneficially suppressed foam losses. As soon as the cooling water was turned off, large surges of foam overflowed through the seal pot to the melter condensate receiver. The agitator speed was increased from 200 to 600 rpm and from 600 to 750 rpm; however, there was no evidence to show that the increased agitation reduced foaming. Also, during the first three runs the agitator was found to have been operating backwards. This agitated the liquid in the opposite direction to that of boiling.

After run PG-3, laboratory studies conducted with nonradioactive and radioactive PW-2 feed indicated that dibutyl phosphate (DBP) in the Purex waste used for feed preparation was the main foaming agent and that commercial silicone antifoam agents would successfully counteract the DBP-induced foaming.(11,13,15) It was concluded from these tests that the concentrations of antifoam in the denitrator-evaporator bottoms must be kept at about 100 ppm to adequately suppress foaming during the denitration-concentration of the phosphate glass feed.

During run PG-4, foaming was encountered as in previous runs, but the foam was successfully held to nondetectable levels for the first time by continuous addition of Dow Corning Antifoam B at a rate of 8.6 g/hr in 3.9 liters/hr of aqueous slurry to maintain the denitrator bottoms at 100 ppm of antifoam. Changing the feed entry point from below to above the liquid level suppressed the foam for 13 hr during startup, but did not reduce foaming to acceptable levels when the amount of foam-inducing DBP had reached steady state conditions prior to antifoam addition. In run PG-5, antifoam was first added at 17 g/hr in 2.6 liters/hr of solution to maintain the denitrator bottoms at 200 ppm antifoam B then reduced to 8.2 g/hr in 1.2 liters/hr to maintain the bottoms at 100 ppm antifoam B.

It is concluded that for runs in which the phosphate glass feed contains dibutyl phosphate, a suitable antifoam agent must be added to suppress the severe foaming in the WSEP denitrator-evaporator. The concentration of antifoam in the denitrator bottoms must be kept at approximately 100 ppm to successfully suppress the DBP induced foam, if Dow Corning Antifoam B is used.

4.4.3 Effect of Internal Heat Generation

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 13 to 16.8 W/liter for PW-1 waste and from 1.3 to 10.0 W/liter for PW-2 waste, increased the heat rate density in the denitrator until in run PG-6 the heat rate density was 68.9 W/liter in the denitrator concentrate. This heat-rate density accounted for about **32%** of the net heat requirement. (See Table 4.8.) Also, this concentrate remained at about 126 °C without heating or external cooling.

TABLE 4.8, Denitrator-Evaporator Internal Heat Generation Effects

PG Run	Feed Type	Average Feed Rate, liters/hr	Heat Rate Density in Feed, W/liter	Denitrator Average Holdup Volume, liters	Average Heat Rate Density in Denitrator Concentrate, W/liter	Internal Heat Generation(b) % of Denitrator Heat Requirement
1(a)	PW-2	15.7	1.3	48	5.9	2
	PW-2	18.0	3.9	47	19.5	7
	PW-2	11.0	10.0	47	48.0	26
4	PW-2	9.4	7.0	55	24.5	18
5(a)	PW-1	11.1	13.0	51	45.5	26
6	PW-1	12.3	16.8	45	68.9	32

---

a. Data from first part of a two-part run.
b. Based on evaporation of water.

4.4.4 Melter Feed System

The denitrated and concentrated waste is airlifted from near the bottom of the denitrator to an airlift pot from which part of the hot concentrate recirculates back to **the** denitrator and part overflows into the melter feed line.

The airlift transfer of concentrated waste from the denitrator-evaporator to the melter is limited to about 3 liters/hr because of the capacity of the melter to transfer heat into the incoming concentrated feed.

During the demonstration runs with PW-2 wastes (runs PG-1 through PG-4), the airlift used was the design shown in Figure 4.5. With the airlift operating smoothly, the feed rate to the melter cycled from about 3 to 5 liters/hr to zero, and averaged about 2.5 liters/hr. The feed rate to the melter was never constant. Some surges of feed to the melter caused

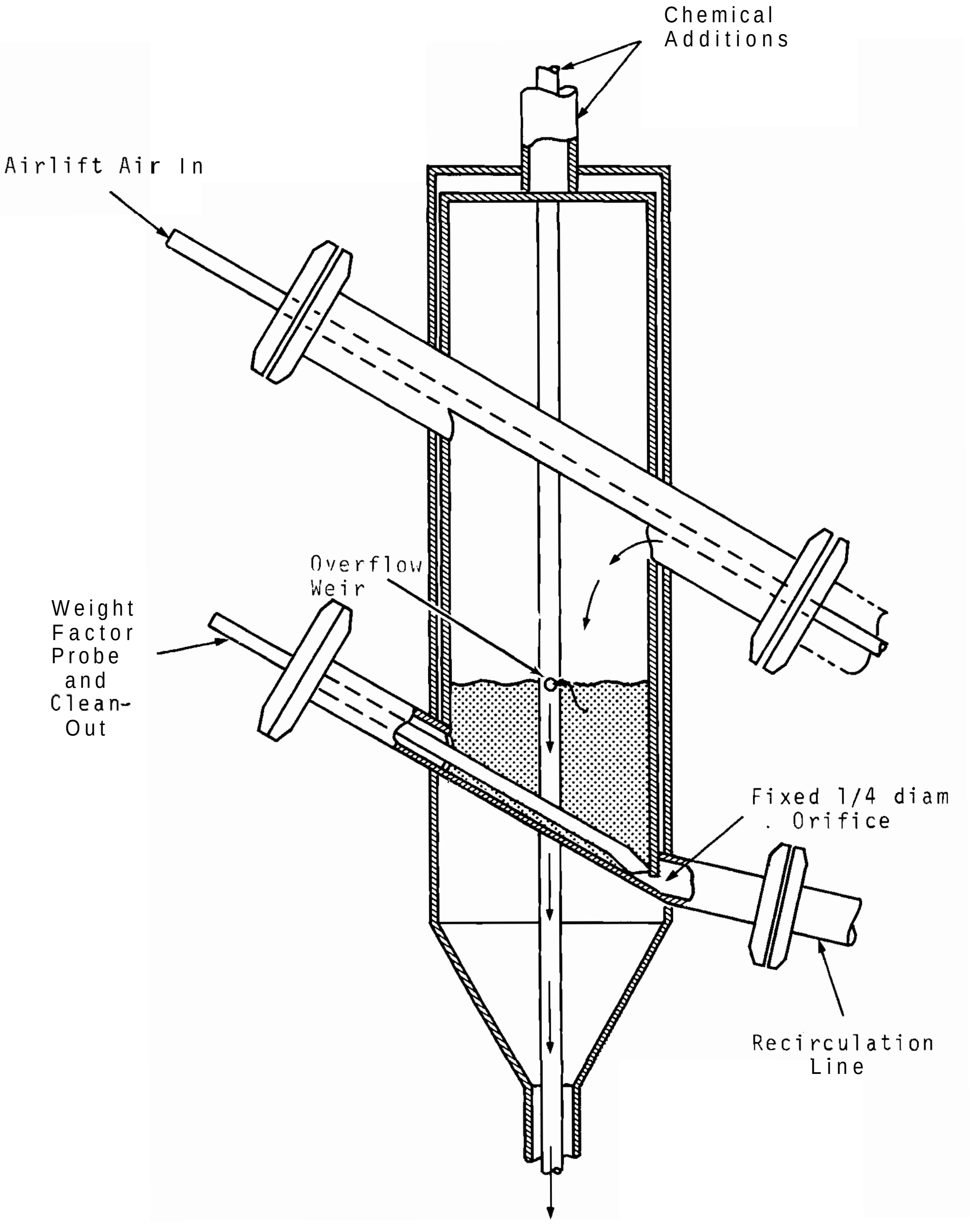


FIGURE 4.5. *Original Airlift Pot with Fixed Orifice*

increased foaming in the melter. At one period in run PG-4 the melter was sufficiently overfed to cause a high melt-foam level in the melter which resulted in restricting the melter vent line. No plugging in the airlift pot was encountered during the demonstration runs with PW-2 waste.

Prior to run PG-5 (the first run with PW-1 waste in the series), a new airlift pot (shown in Figure 4.6) was installed on the denitrator-evaporator.(1) The new airlift pot was necessary because of the increased solids plugging difficulties with PW-1 concentrate which would not permit satisfactory operation with the original unit. In the new unit, a movable plug valve is used to vary the orifice opening in the recirculation line from the airlift pot. In addition, variable airlift air is used to further improve control of the recirculation rate between the airlift pot and the denitrator. Movement of the plug valve also helps to remove solids buildup from the recirculation line. A rod through the plug valve is available to clean the recirculation line if the need arises. Provisions for chemical additions through the plug valve allows acid or steam addition through the recirculation line. Other chemical additives can be made through the airlift pot chemical addition nozzle into the melter feed line. The features of the new airlift pot proved to be very beneficial during runs PG-5 and 6. Many plugging problems occurred during these runs which required the remotable features of the new airlift pot.

During run PG-5 the melter feed line became plugged after 38 hours of operation resulting in no feed to the melter. The airlift pot internal temperature dropped from 125 to 104 °C, indicating no flow of hot concentrate through the airlift pot. The recirculation plug valve was moved in and out of the recirculation line, but with no success. A six molar solution of nitric acid was added through the melter feed line without any

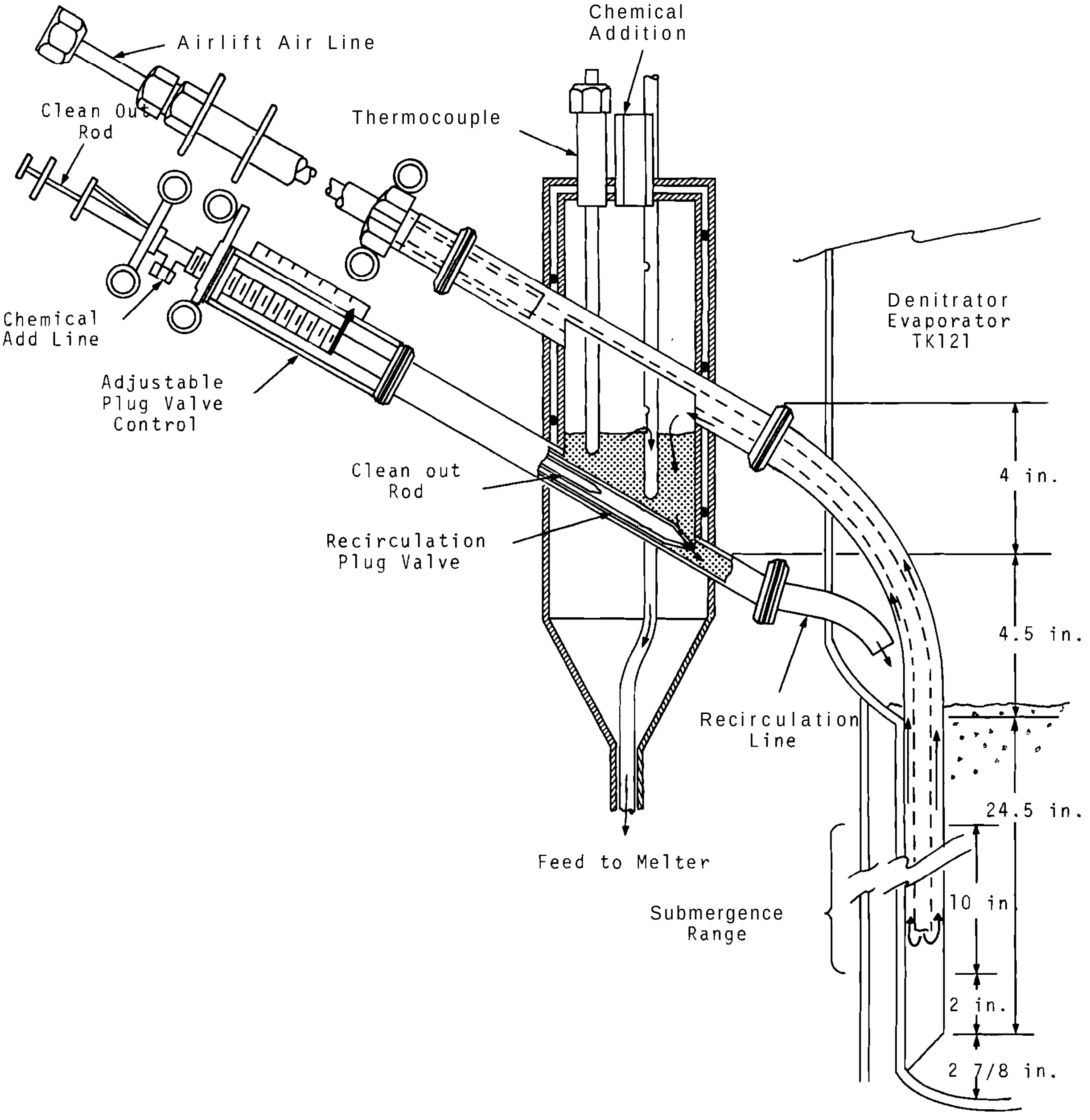


FIGURE 4.6. Airlift Pot with Variable Orifice Control

acid getting to the melter. These characteristics, along with the factsthat the airlift pot would only vent through the denitrator airlift recirculation line and that there was no circulation, indicated a restriction in the melter feed line. The airlift is normally operated so that the only way the airlift pot can recirculate the hot concentrate is for the pot to vent the incoming air through the melter feed line. When the airlift pot was finally vented to the cell, the airlift began to circulate very well. The restriction of concentrate in the melter feed line was removed by first rodding the solution feeder in the melter and then by gently tapping the melter feed line while it was heated with 25 psig steam in its jacket. This was followed with 6M nitric acid flushes through the line to insure that the line was clean.

During run PG-6, airlift pot plugging problems were more frequent and severe than in run PG-5. The airlift air supply line plugged twice during startup and once during shutdown. Steam was blown through the line to unplug it. During one period when steam was added, the airlift started to rapidly airlift concentrate from the denitrator which then overflowed to the melter. Air blowing the lines after steaming also caused too fast an airlift rate unless the recirculation valve was backed out. The airlift pot liquid level dip tube plugged shortly after startup of run PG-6 and was not unplugged until after the run. The airlift recirculation line required frequent (approximately five times/day) backing out of the plug valve as well as acid flushes to remove solids that were building up in this area.

In summary, the biggest difficulty inherent in the WSEP equipment design is the inability of the airlift pot to meter small flows (less than 3 liters/hr) of concentrate to the melter from the denitrator. Other difficulties were plugging of the airlift pot recirculation line and melter feed line. These plugs occur when solids settle out. Settling of solids is made worse by slow flow rates, and by overconcentration if the temperature of the solution is too high (greater than about 140 °C). Also, excessive cooling of the concentrate rapidly increases the concentrate's viscosity and resistance to flow. Therefore, the concentrate should be maintained between 100 °C and its boiling point in the airlift pot and in the solution feeder to the melter. Some of the main operating parameters for the airlift pot are shown in Table 4.9.

TABLE 4.9. Airlift Pot Operating Parameters

PG Run	Mode	Feed Type	Average Density Denitrator Bottoms, kg/liter	Average Concentrate Temp,		Average Air Supply Pressure, psig	Average Airlift Air Supply Rate, scfh	Average Airlift Pot Jacket Steam Pressure, psig
				Denitrator, °C	Airlift Pot, °C			
1	A	PW-2	1.81	137	NA[a]	7.4	1.6	12
	B	PW-2	1.83	138	NA	8.8	3.5	15
2	A	PW-2	1.80	137	NA	13.0	1.7	10
3	A	PW-2	1.83	136	NA	6.0	2.3	11
4	A	PW-2	1.90	137	NA	8.3	2.3	14
5	A	PW-1	1.79	134	126	9.6	2.4	10
	B	PW-1	1.80	132	125	6.1	1.7	15
6	A	PW-1	1.80	132	124	8.0	1.7	17

---

[a] Not available.

4.5 PERFORMANCE OF MELTER

Denitrator concentrate at 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 3 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 1 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 six runs proceeded smoothly except during short periods of foaming which sometimes followed excessive surges of feed to the melter. Before startup of runs PG-1 and 2, nonradioactive PW-2 phosphate glass was added to the melter to provide a seal in the internal overflow weir. This was done as a conservative precaution to permit better control of process vacuum by sealing the 2 melter discharge tubes. A modified startup procedure was used in run PG-3 and in all subsequent runs. In these cases, no initial sealing of the melter internal weir with nonradioactive glass was provided. Instead the melter vacuum was reduced from the normal 6 to 2 inches of water to minimize sucking air through the unsealed weir tubs 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.

The melter furnace was operated at an average temperature of 1220 °C during all six runs, and the resultant internal melt temperature ranged from 1050 to 1100 °C as measured near the bottom of the melter. Figure 4.7 shows typical melter temperature profiles for PW-1 and PW-2 wastes. No appreciable temperature difference was distinguishable between phosphate glass melts from PW-1 and FW-2 wastes. 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 controiling the 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 one 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

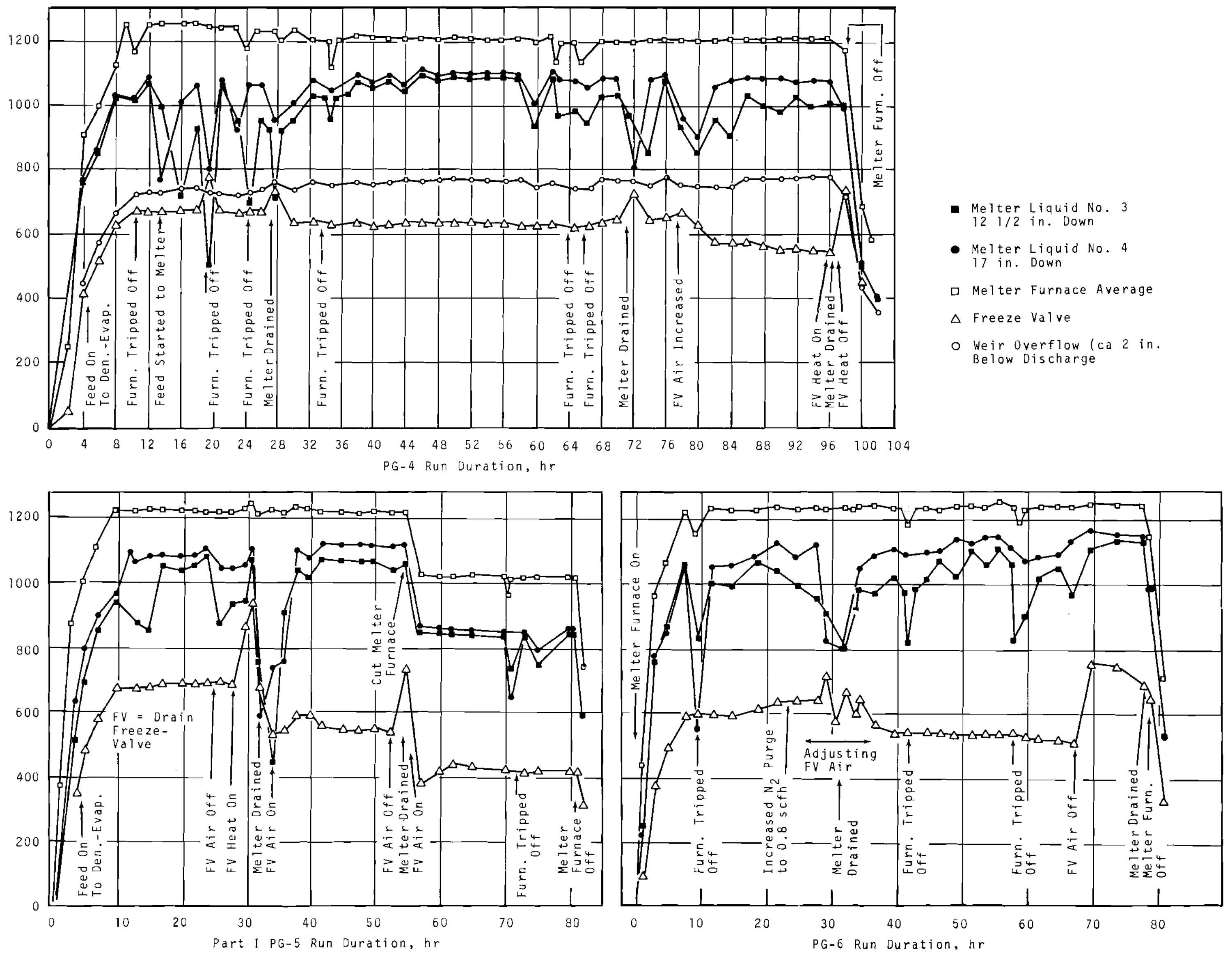


FIGURE 4.7. *Typical WSEP Melter Temperature Profile*

in the melter. The melt control temperature averaged between 750 and 900 °C during the six runs. An optimum would have been about 850 °C. 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. The weir heater became inoperable during PG-1 but was not required or used thereafter.

Since the limiting factor in process capacity was heat transfer in the melter, methods of increasing the melter capacity were investigated. Sparging nitrogen through the melt at a rate of 0.2 to 0.8 scfh apparently did not increase melting capacity (see Section 4.1).

4.5.1 Volatilization, Entrainment and Foaming

An important objective of the six radioactive demonstrations with the phosphate glass process was to characterize the path and behavior of ruthenium and other fission products. Ruthenium volatilized during the glass forming step must eventually be totally recycled to the denitrator-evaporator, waste evaporator or in the case of sulfate-containing waste must have further processing.

Design verification tests indicated that about 10% of the ruthenium fed to the melter would volatilize from the melter and that entrainment of nonvolatiles was less than 0.1%.(10) These values were corroborated during the six radioactive WSEP runs in which 1.3 to 10.4% of the ruthenium volatilized or entrained and 0.19 to 0.25% of the nonvolatiles were entrained from the melter. (See Table 4.10.)

During the first three runs with PW-2 waste, foaming in the denitrator-evaporator caused significant losses of concentrated feed via a seal pot to the melter condensate receiver. These foamover losses masked the radioactivity gained due to volatilization and entrainment from the melter. Consequently run PG-4 was the only demonstration performed with PW-2 waste where no such losses of concentrated feed occurred. During this run, 1.3% of the ruthenium and 0.23% of the ^{144}Ce-Pr (representing nonvolatiles) that was fed to melter accumulated in the melter condensate. Figure 4.8 shows the fraction of ruthenium accumulated in the melter condensate during runs PG-4, 5, and 6. Ruthenium volatilization during the runs with PW-1 waste (runs PG-5 and 6) ranged from 4.6 to 10.4% while entrainment of ^{144}Ce-Pr ranged from 0.19 to 0.25%, all of which again agreed with the nonradioactive design verification tests.

TABLE 4.10. *Volatilization and Entrainment from Melter*

PG Run	Feed Type	Average Internal Melt Temperature, °C	Melter Sparge Flow, scfh	Nitrogen Test Time, hr	Total Curies to Melter	Total Curies Ruthenium to Melter	Total Ruthenium Volatilized, %[a]	Total ^{144}Ce-^{144}Pr Entrained, %[a]
1	PW-2	1075	0.2	0	349,000	15,000	NA[b]	NA
2	PW-2	1080	0-0.8	8	419,000	20,300	∿8[c]	NA
3	PW-2	1100	0.5	8	604,000	11,000	NA	NA
4	PW-2	1100	0.45	8	1,100,000	30,900	1.3	0.23
5	PW-1	1050	0.2-0.8	50	2,180,000	43,200	10.4[d]	0.25
6	PW-1	1090	0.8	53	2,430,000	7,600	4.3	0.19

---

a. Percentage of total fed to the melter, as determined by that found in the total condensate from the melter.
b. NA: Not available
c. Estimated during the nonfoaming period of denitrator operation. (During foaming, denitrator contents overflowed via the seal pot to the melter condensate receiver.)
d. Severe foaming occurred in the melter at one point as caused by over feeding the melter. The run was separated into two parts by the need for removal of a solids plug in the melter feed line.

Foaming in the melter occurred during all the runs, but could be held to inconsequential limits by not overfeeding the melter (melter feed rate less than 5 liters/hr). 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-4, an excessive foam level partially plugged the melter off-gas line as a result of overfeeding the melter for about 0.5 hours. Successful control of foaming and melt level was accomplished by

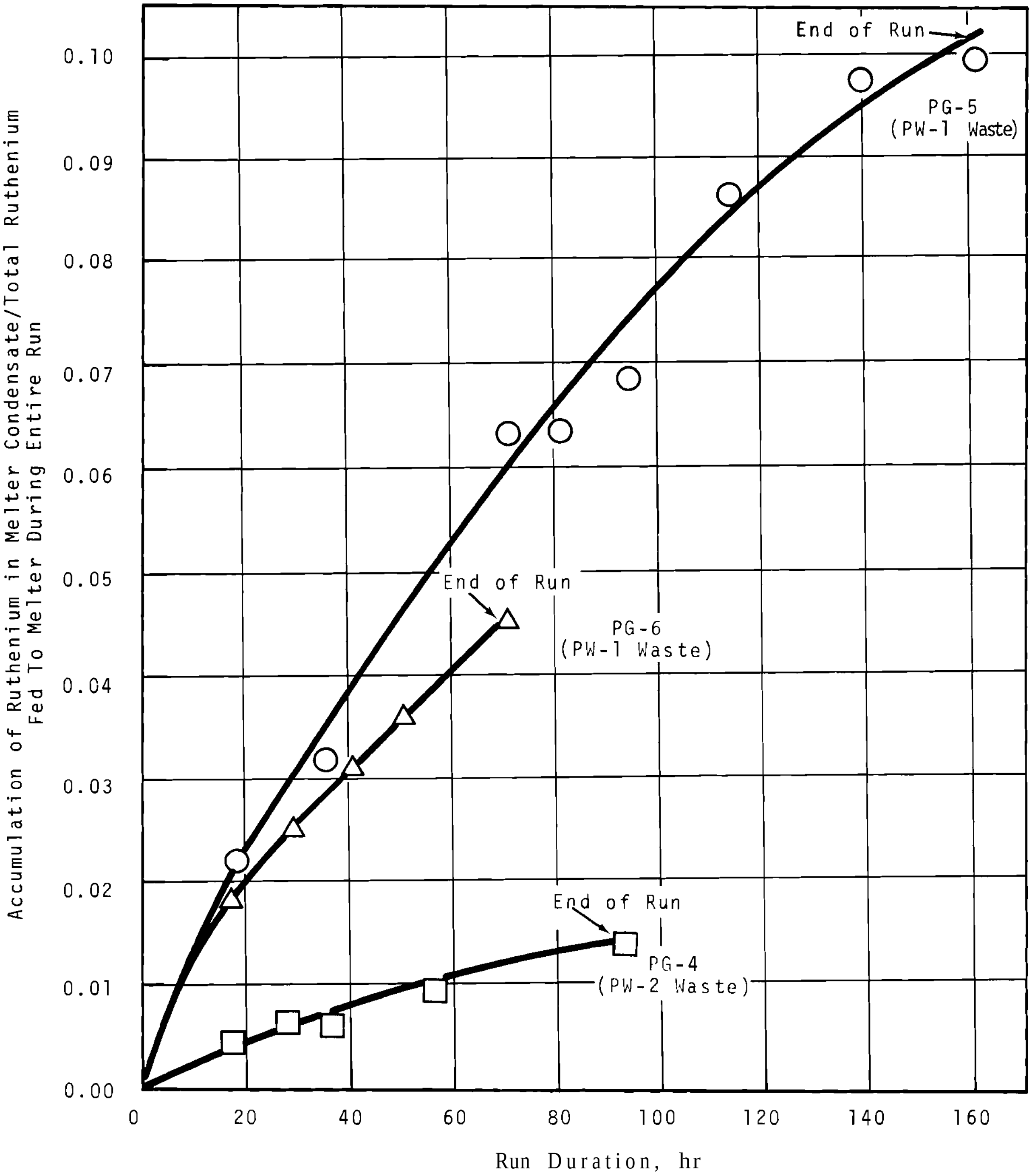


FIGURE 4.8. Ruthenium Accumulation in Melter Condensate

manually maintaining as steady a feed rate to the melter as possible and by always keeping some feed entering the melter. Foaming with PW-1 waste was greater than with PW-2 waste.

4.5.2 Drain Systems

During all the demonstrations, melt was discharged to the receiver 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. The contents of the melter were dumped at the end of each run to minimize the potential for stretching the melter due to different coefficients of thermal expansion of the glass and the platinum melter.

In the routine heating of the drain freeze-valve to thaw the melt plug during run PG-5, the electrical heater burned out. A propane-air torch was then used to directly heat the drain freeze-valve to drain the melter after runs PG-5 and PG-6.

4.5.3 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, and entrained materials are present. This stream is routed through a platinum and 5% iridium off-gas line to the melter-condenser. The temperatures of the gases passing through this line were maintained in the range of 300 °C to 460 °C in the six WSEP runs to prevent condensation and thereby minimize corrosion in the line.

In demonstration run PG-4, plugging of the off-gas line occurred due to an excessive feed rate to the melter for an extended time period (about 0.5 hour). The excessive feed rate caused melt to foam into the line. Following the run, the plug was removed remotely by alternating flushes of boiling nitric acid followed by a caustic flush. (Refluxing of acid was performed by boiling it in the melter and returning the condensate back through the pipe from the melter condenser.)

The gas temperatures at the inlet of the melter condenser were essentially the same as those of the off-gas line, or 300 °C to 460 °C, as shown in Table 4.11. The gas temperatures at the outlet of the condenser ranged from 30 °C to 49 °C, and were generally lower than the temperatures of the collected condensate which were 30 °C to 65 °C. Steam spray additions to the bottom chamber of the condenser and foamover of concentrated waste to the melter condensate tank were the primary reasons for the higher condensate temperatures. Condensate flow rates ranged from 1.1 liters/hr to 3.7 liters/hr, and averaged about 2.8 and 1.6 liters/hr for PW-1 and PW-2 wastes, respectively.

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[b] Rate of Melter Cond. Flow, liters/hr	Recovery of Melter Volatilized Sulfate, %
1	A	PW-2	390	48	47	2.5	6.5	1.8[c]	91
	B	PW-2	370	49	48	2.5	6.4	1.7[c]	90
2	A	PW-2	300-420	30	40-65	4.5	8.4	1.1[c]	92
3	A	PW-2	370	45	30-55	4.2	8.0	1.0	92
4	A	PW-2	320-360	30	35-42	2.1	6.2	2.1	72
5	A	PW-1	460	40	30-50	2.5	6.3	3.7	(a)
	B	PW-1	450	45	30-50	2.0	5.5	2.6	(a)
6	A	PW-1	425	40	38-46	2.0	63	2.5	(a)

---

a. Sulfate is not present in PW-1 wastes.

b. During period of continuous feeding to melter.

c. Foamover of denitrator-concentrate from the denitrator was occurring throughout the run. Foamover rates are included in this value.

Recovery of volatilized sulfate from PW-2 waste was 90 to 92% in the first three runs, but decreased to 72% in run PG-4. This low recovery in run PG-4 was directly attributable to the plug which developed in the melter off-gas line. Because of the plug in the melter off-gas line, much of the melter off-gas was vented directly through the melter seal pot and the melter condensate tank to the denitrator-evaporator process condenser. A decreasing liquid level in the melter seal pot and an abnormally sharp increase in the sulfate accumulation rate in the denitrator-evaporator condensate receiver (WSEP auxiliary evaporator) were noted during the plugging of the off-gas line.

Steam spray additions to the bottom chamber of the melter-condenser 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. Modification of the nozzle was necessary to avoid plugging of the orifice which occurred in the design verification tests. No plugging of the modified nozzle occurred during its use in the six radioactive runs. Because of the low steam pressures that prevailed during the demonstrations, the amount of steam spray that actually existed as steam (condensate) or a spray is in question. No conclusive evidence is available to determine the effectiveness of the spray in aiding the recovery of volatilized sulfate or ruthenium, or to determine the extent to which corrosion was inhibited.

---

* 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.

4.6 GENERAL PERFORMANCE AND OPERATING HISTORY

4.6.1 Waste Composition Effects

During WSEP phosphate glass solidification of highly radioactive aqueous wastes to solids, relatively few processing problems occurred. Two runs with PW-1 waste and four runs with PW-2 waste demonstrated performance with waste representing that from reprocessing spent fuel irradiated to 20,000 MWd/tonne at a power level of 15 MW/tonne. In the two runs with PW-1 waste, serious plugging of tubes was encountered due to granular solids in the waste. The problems were plugging of the specific gravity and liquid level dip tubes in the denitrator, of the airlift air line, of the airlift pot recirculation line, and of the feed line to the melter. Fewer plugging problems were experienced when hourly steam blowdown of dip tubes and airlift acid flushes were employed. Relatively few processing difficulties were encountered while concentrating and solidifying PW-2 waste.

One major overall problem was foaming in the denitrator-evaporator which was caused by the dibutyl phosphate present in the Purex waste used for makeup of the wastes. The same problem did not occur in run PG-5 with PW-1 waste because an antifoam agent was then used. A silicone-based antifoam agent successfully reduced foaming to a reasonable level.

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 (although sparging the melter contents with nitrogen had no effect).

Melt foaming was not appreciably affected by the chemical flowsheet, although melts with PW-1 waste foamed somewhat more readily than those with PW-2 waste. Excessive rates of feeding concentrate to the melter normally caused the foam to rise about 2 to 6 inches.

Waste compositions for the six runs, as well as other pertinent data on the feeds, are listed in Table 9.1 of the Appendix. General feed composition ranges for the six phosphate glass runs are shown in Table 4.12. Feeds to the phosphate glass solidification process were prepared using actual Purex high level waste and concentrated radiorare-earths (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, uranium, and rare earths compared to the standard PW-1 and PW-2 waste compositions, the actual composition of the wastes processed varied somewhat from the desired composition. (See Section 3.3 for the details of effects of these changes in composition.) The two PW-1 wastes contained from about 6 to 11% 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 partial substitute (17 to 45%) for the 0.93M iron during the runs with PW-1 waste. An excess of 0.06M rare earths in run PG-6 required additional H_3PO_4 (0.183M) be added to the waste to maintain the M/P equal to 1.0.

Feed compositions for PW-2 wastes varied in two ways: (1) the excess aluminum in the Purex 1WW was used as a partial substitute for iron, (2) the excess rare earths in PG-4 (0.45M) versus nominal (0.12M) required the addition of 0.5M sodium and 1.16M H_3PO_4.

TABLE 4.12. General Waste Composition Ranges(a)

Constituents	PW-1 Waste, M		PW-2 Waste, M	
	Nominal	Actual	Nominal	Actual
H^{+}(b)	3.7	2.1 -4.0	3.93	3.3 -3.5
Na^{+}	0.138	0.29-0.43	0.93	0.71-1.2
Fe^{+3}	0.93	0.48-1.1	0.45	0.19-0.32
Al^{+3}	0.001	0.16-0.42	0.001	0.24-0.10
SO_4^{-2}	0	0	0.87	0.83-1.20
NO_3^{-}	7.50	7.1 -7.5	5.37	4.4 - 5.0
$(Y+RE)^{+3}$	0.12	0.12-0.24	0.12	0.12-0.57
U^{+6}			0.01	0.01-0.02
Additives				
Na^{+}	2.47	2.46-2.47	0	0 -0.50
PO_4^{-2}	6.38	6.47-7.97	3.30	2.9 -4.5

---

a. All values are quoted at 378 liters/tonne.
b. Excludes H^{+} from disassociation of H_3PO_4 additive.

Chemical additives were added directly to the feed.

4.6.2 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.

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.

TABLE 4.13. Phosphate Glass Equipment Operating History

Equipment	Construction Material	Temp, °C	Pressure In-Water or Flow	Chemical	Operating Hours	Remarks
SC-Rack	Fe, SS, Monel	~50	-2 to -10	Liquid Nitrates, Sulfates, and Phosphate Slurries	873	--- --- --- --- ---
Melter	Platinum	800-1270	-2 to -10	Phosphate Melts	783	After 110 hr of CPG operation, the inadequately heated melter vent nozzle corroded and partially collapsed because of expansion stresses. It was replaced.
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	193	Used only during in-cell hot operation.
Melter Level Dip Tube	Platinum	800-1200	0 to 0.5 scfh	Air	473	Used only during in-cell hot operation.
Melter Furnace	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.
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	783	- - - - - - - - - - - - - - -
Melter Off Gas Line Heater	Nichrome Heating Wire	200-600	---	---	511	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-Monel Outer Shell-SS	40-180	-2 to -10	Sulfate and Nitrate Vapors	783	After 200 hr service, the SS line on the SC rack was changed to monel. For the in-cell runs (hot), the monel drain line jumper has been used 473 hr.
Melter Solution Feeder	Platinum	100-120	---	Purex Type Wastes	783	- - - - - - - - - - - - - - -
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 Fins)	120-140	-5 to +5	Purex Type Wastes	154	Installed prior to PG-5 to provide remotable feature.
Denitrator Evaporator (TK-121)	A-55 Ti	40-140	-2 to -10	Purex Type Wastes	873	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	873	- - - - - - - - - - - - - - -
Denitrator Agitator	SS Shaft, SS and Ti Impellers	40-140		Purex Type Wastes	843	After 330 hr the SS impeller was changed to A-55 Ti. The agitator ran backwards for PG-1 to 3.
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 binding. 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	2096	Also used as p o calciner furnace. Delaminated insulation was completely replaced with Ceroform at 1025 hr just before radio active service.

---

a. CPG = "Cold" phosphate glass runs.
b. PG = "Hot" phosphate glass runs.

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. During run PG-4, the seal pot successfully served its purpose by adequately venting the melter when the main melter off-gas line became plugged.

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. Although the overflow seal pot was never needed for emergency venting of the denitrator during the six runs, foam that occurred in runs PG-1 through 3 overflowed to the melter condensate tank by this route. If the overflow pot had not been available the foam would probably have forced its way into the top of the denitrator, then into the normal denitrator (and melter) vent system, and continued operation may not have been possible.

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 six phosphate glass runs. With additional air cooling inside the susceptor, 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.

P Condenser

The same process condenser is used for the vapors from all solidification processes in WSEP. A 304L SS 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 SS, 316L SS and Nionel. The coupons were inspected at the end of the first series of 6 pot calcination runs(3) and again after the 6 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.

5.0 AUXILIARY EQUIPMENT PERFORMANCE

Essential to any waste solidification facility will be the auxiliary systems in support of the solidification processes. In the final design of a solidification plant, equipment must be selected to assure the production of effluents acceptable for reuse or for low level waste treatment and release to the environment. For example, slightly contaminated acid can be recycled to the chemical reprocessing plant for fuel element dissolution. To obtain overall economy, integration of similar equipment functions in the reprocessing plant and the waste solidification process must be considered.

Process auxiliaries consist of the equipment necessary to:

- Prepare feed from waste solutions and feed the solidifier,
- Treat vapors or condensate effluents from the solidifier for recycle,[a] and
- Cleaning the off-gases and recover the acid.

Effluents directly from the phosphate glass process require recycling through auxiliaries since generally 0.08 to 5% of the ruthenium fed to the solidifier is volatilized and entrained from the denitrator. In addition, 0.001 to 0.03% of nonvolatile constituents are entrained. An additional 1.2 to 7.9% of the ruthenium is volatilized and entrained from the melter, and 0.2% of the nonvolatile constituents are entrained from the melter. Although melter condensate must be handled separately when it contains sulfate, it can usually be combined with the denitrator condensate[b] for treatment by the auxiliaries.

---

[a] Sulfate containing condensate from the phosphate glass melter cannot be directly recycled without treatment to remove the sulfuric acid or without very extensive cleanup to remove the radioactivity.

[b] If the denitrator decontamination factors were substantially greater than those for the melter (greater than about 10) then it may be beneficial to recycle the melter condensate back into the denitrator for additional decontamination.

The need to demonstrate how the condensate and acid can be recycled or otherwise disposed prompted the selection of three different operating modes in WSEP.

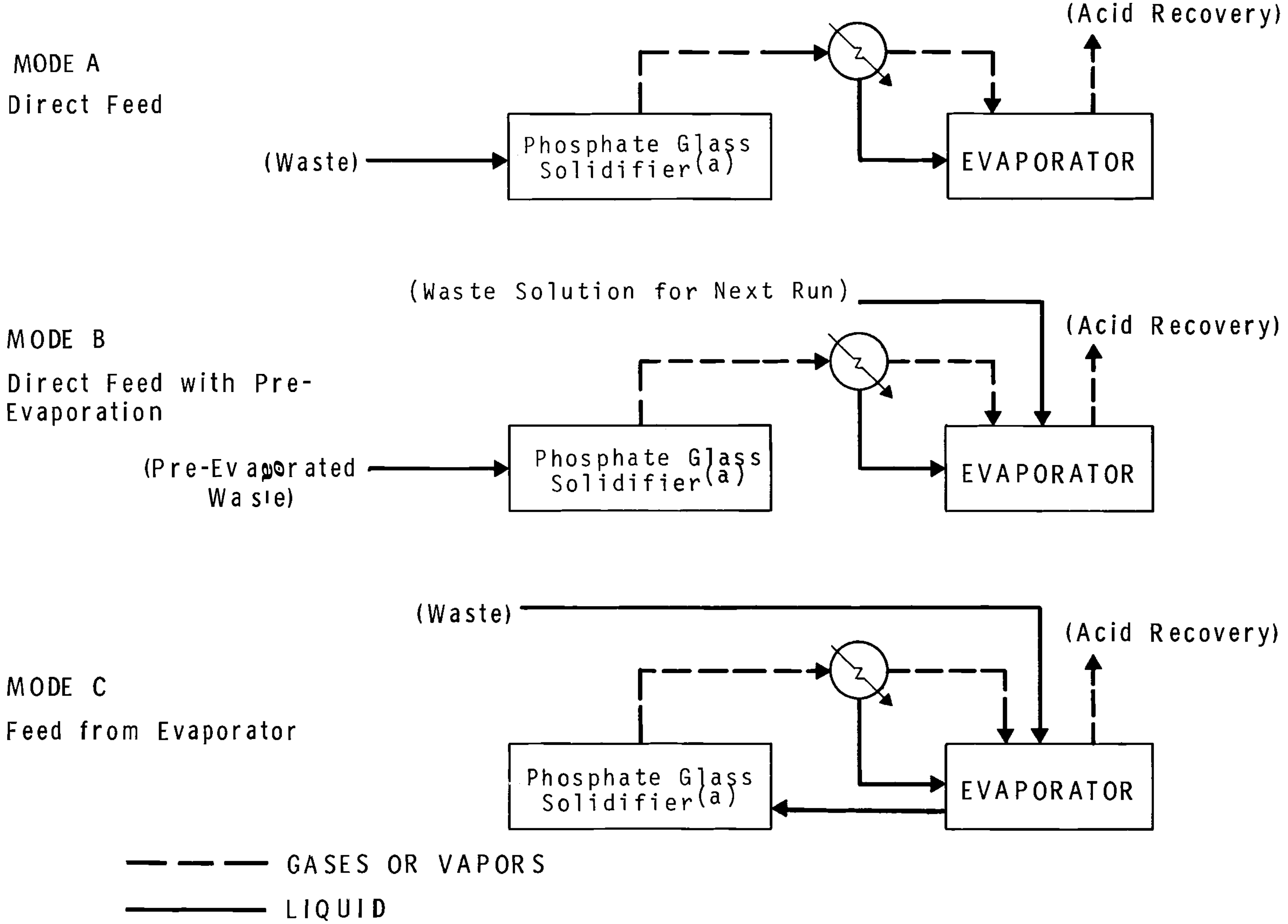
5.1 OPERATING MODES

Auxiliary equipment would likely be a part of the fuel reprocessing plant (e.g., a plant waste evaporator and acid recovery system) or it could be operated as a separate system independent of the reprocessing plant. In either case, the auxiliary equipment can be coupled to the phosphate glass process to produce three basic modes of operation: Mode A, Mode B, and Mode C (see Figure 5.1). So far, the first two of these modes were tested with the phosphate glass process, Mode C was not.

In Mode A, waste is fed directly to the solidifier without immediate preconcentration. The vapors from the solidifier are condensed and concentrated but are not recycled to the solidifier feed.

In Mode B, one batch of raw waste is preconcentrated in the evaporator simultaneously with the denitrator condensate while a previously prepared batch of waste is fed to the solidifier from a hold tank. (In a commercial plant which would not need the additional decontamination afforded by the auxiliary evaporator, the size of the denitrator could be designed to perform this required preconcentration.) During the phosphate glass Mode B demonstrations, the batch of wastes for concentration was not started into the auxiliary evaporator until the run was at least 50% completed.

In Mode C, the solidifier and evaporator can be operated as a close-coupled unit. Feed enters the evaporator where it is continuously mixed and concentrated with condensed vapors returning from the solidifier. This mixture of evaporator bottoms is continuously fed to the solidifier. Thus, the



a. Melter condensate to separate treatment if it contains sulfate.

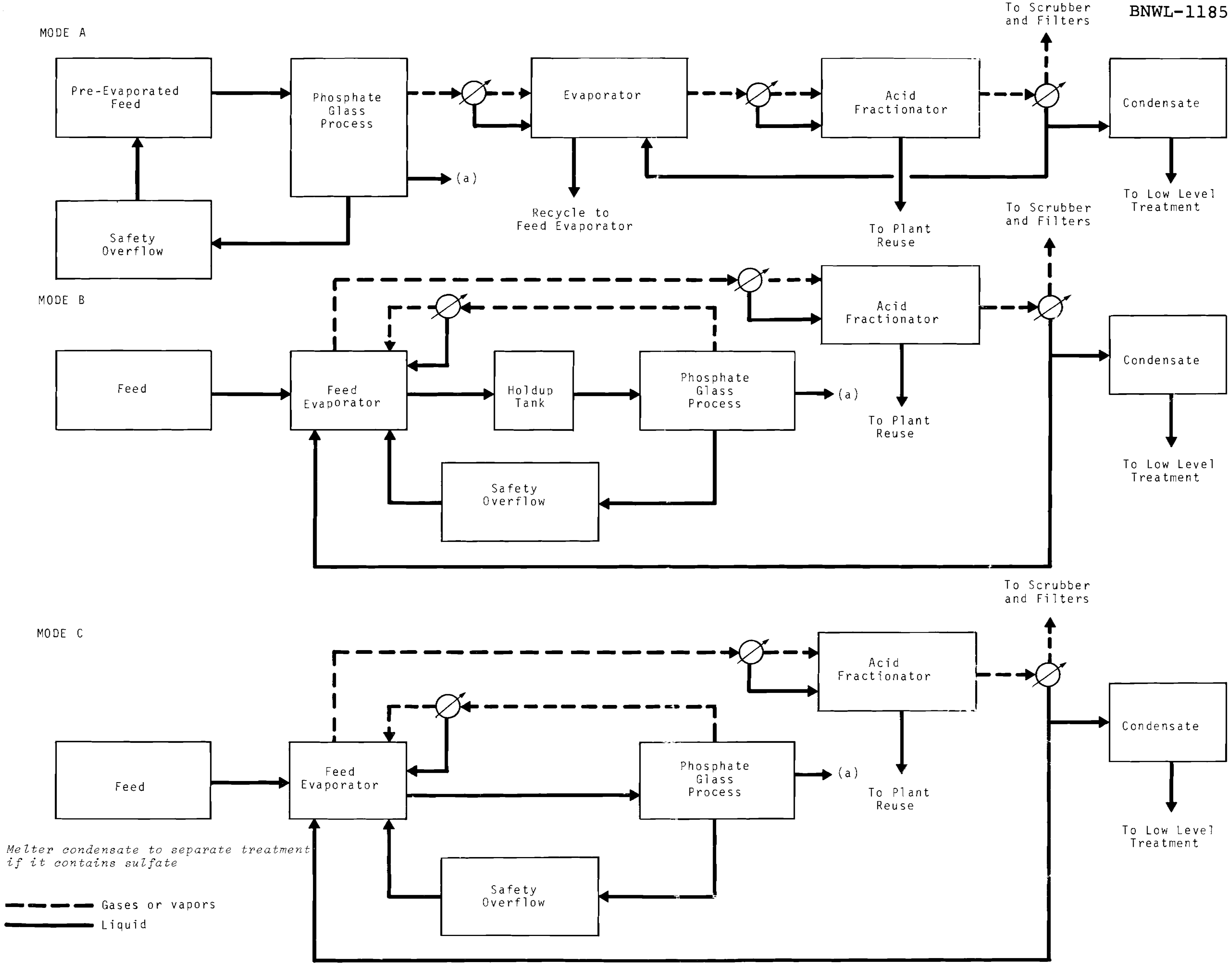
FIGURE 5.1. WSEP Process Options

nonvolatile constituents in the condensed vapors from the solidifier are continuously recycled. (This mode has not been tested to date with the phosphate glass process.)

Final applications of the modes are visualized as shown in Figure 5.2.

In WSEP, auxiliary treatment downstream of the auxiliary waste evaporator consists of condensing the overhead vapors from the evaporator and routing them to a fractionator which is used to further decontaminate the process noncondensible gases and to separate the vapors into a better decontaminated waste stream and a nitric acid stream (for potential reuse in a fuel reprocessing plant). In these tests the slightly acidic fractionator condensate was a low level waste. In all demonstrations, about 75% of this stream was recycled to the auxiliary evaporator to strip nitric acid from the evaporator while maintaining the evaporator bottoms at low acidity. The low acidity in the auxiliary evaporator bottoms and overhead streams help to minimize the volatilization of ruthenium from the evaporator. Noncondensible gases in the fractionator condenser are filtered, scrubbed, and filtered twice again prior to release to the atmosphere.

Performance of the auxiliary system was assessed by determining the decontamination factors at each stage in the system while using one of the three modes. Data on operating modes are presented in Table 5.1 as typical of the observed data. The fractionator bottoms during Mode A were nearly equal in radioactivity to that for Mode B for nonvolatile radioactivity and were less by a factor of 3 for ruthenium. The fractionator condensate during Mode A was lower in nonvolatile radioactivity by a factor of greater than 10 over Mode B operation. Ruthenium in the fractionator condensate during Mode A, however, exceeded that during Mode B by a factor of approximately 2. It would generally be expected that the radioactivity content in all



a. Melter condensate to separate treatment if it contains sulfate

FIGURE 5.2. *Operating Mode Applications*

TABLE 5.1. *Typical Effluents*[a] *During Operation with Modes A and B (First Six Phosphate Glass Runs)*

Stream	Operating Mode	Volume,[b] liters/ liter feed	Gross Radioactivity (less Ru), Ci/Ci in feed	Ru Radioactivity Ci/Ci in feed	Potential Disposal
Evaporator Bottoms	A	0.4[c]	1×10^{-5}	2×10^{-3}	Recycle to fuel processing plant waste concentrator
Fractionator Bottoms 9.5M HNO_3	A	0.5	3.1×10^{-7}	8.5×10^{-4}	Recycle to plant acid system
Fractionator Bottoms 10M HNO_3	B	0.4	2.8×10^{-7}	21×10^{-4}	
Fractionator Overhead 0.02M HNO_3	A	0.75	2×10^{-9}	2×10^{-6}	Low level treatment
Fractionator Overhead 0.02M HNO_3	B	1.4[d]	25×10^{-9}	0.7×10^{-6}	
Off-Gas	A	1000	2×10^{-12}	$<7 \times 10^{-11}$	To atmosphere
Off-Gas	B	1000	1×10^{-12}	$<4 \times 10^{-11}$	

---

a. Run PG-4 data were used as representative of Mode A and Run PC,-5 data were used as representative of Mode B. (See the Appendix, Table 9.4.)

b. Volumes include other additions to system (see the Appendix, Table 9.3). Because actual data were used, fractions do not add to 1.0.

c. Assumes working volume in WSEP evaporator of 300 liters. This volume is present at the start of a run. The stream can be recycled continuously or periodically on a batch basis.

d. Includes condensed vapors from PG-6 feed concentration during the Mode B operation.

streams would be lower in activity during Mode A than for other operating modes since the waste is one tank closer to the effluents when waste is in the auxiliary evaporator. The results for ruthenium, however, are more dependent on other factors including acid concentration in the auxiliaries and the fraction of ruthenium volatilized from the solidifier. Thus the differences in ruthenium in the effluent streams of the different operating modes can be minor. During Mode A operation, the evaporator bottoms is a side stream which must be recycled to the fuel reprocessing plant. In Mode B and Mode C operation, the evaporator bottoms are mixed with incoming waste.

Although there were differences in the radioactivity levels in the fractionator acid and fractionator condensate for the two modes tested, the radioactivity was similarly high enough that further treatment or disposal will be the same regardless of the operating mode. The fractionator condensate requires cleanup of ruthenium by factors of up to 100,000 if it cannot be used as makeup water (See Section 7, Table 7.4) in the reprocessing plant. The fractionator bottoms (about 10M HNO_3) can be used in the reprocessing plant for fuel element dissolution and thus will not require cleanup.

Mode C was not tested because it would have required continuous boiling of the phosphate glass feed. The degree of feed pre-evaporation which would be gained in the test is not needed because the denitrator-evaporator is available. Data from Mode C operation in a previous series of pot calcination runs indicates that Mode B and Mode C should produce similar effluents.

5.2 RUTHENIUM CONTROL

Data from extensive observations on ruthenium volatilization and its suppression in boiling nitric acid solutions has been plotted against nitric acid content in Reference 2. Although some correlations exist for very specific solutions, the range in volatilization for a constant distillate acidity ranges as much as five orders of magnitude. Such a range of values demonstrates the complex behavior of ruthenium chemistry in waste reprocessing. However, certain facts are known about ruthenium and its behavior. Ruthenium tetroxide (RuO_4) has been established(17) as the principle volatile form of ruthenium from boiling nitric acid solutions. Several general relationships apply to the volatilization of RuO_4.(2,18)

- Decreasing the concentration of nitrate in the bottoms and the corresponding overheads decreases the volatilization of ruthenium.
- Introducing other oxidants into the nitric acid solution increases ruthenium volatilization. Similarly, introducing reductants (e.g., sugar) into the solution suppresses volatilization.
- Increasing the temperature of acidic solutions up to the boiling point increases the vapor pressure of RuO_4 and, correspondingly, the volatilization of RuO_4.

By controlling the overheads concentration of nitric acid from the WSEP evaporator at less than 1.0M during the first six pot calcination runs volatilization of ruthenium was reduced.(3)

During the six phosphate glass runs, the auxiliary evaporator was operated at a bottoms concentration of 4 to 7M total nitrate to serve as a decontamination stage between the phosphate glass process and the nitric acid fractionator. Table 9.2 in the Appendix lists most of the average operating conditions for the evaporator as well as for the other auxiliaries. Part of the data for the evaporator is repeated in Table 5.2 to show the effects of evaporator contents,

TABLE 5.2. *Radioruthenium and Radiocerium Decontamination Factors*

PG Run	Mode	Solution in Evaporator	Additive	Evaporator Average Bottoms Acidity, M	Evaporator Average Overheads Acidity, M	Evaporator Cumulative Ruthenium DF(a)	Evaporator Cumulative Cerium DF(a)	Evaporator Instantaneous Cerium DF(b)	Fractionator Average Bottoms Acidity, M	Fractionator Average Overheads Acidity, M	Fractionator Cumulative Ruthenium DF(c)	Fractionator Cumulative Cerium DF(c)
1	A	Nitric Acid plus Denitrator Condensate	Strip Water	6	0.[illegible]	3.[illegible] × 10^3	----	10^4	11	0.02	2.1 x 10^2	----
1	B	Batch Waste plus Denitrator Condensate	Strip Water	6	0.6	42 x 10^3	33 x 10^5	---	14	0.09	7.2 x 10^2	----
2	A	Nitric Acid plus Denitrator Condensate	Strip Water	4	0.4	3.7 x 10^1	1 x 10^5	10^5	10	0.02	8.0 x 10^2	0.11 x 10^2
3	A	Nitric Acid plus Denitrator Condensate	Sugar and Strip Water	4	0.5	1.1 x 10^1	0.027 x 10^5	10^4	12	0.04	0.55 x 10^2	0.85 x 10^2
4	A	Nitric Acid plus Denitrator Condensate	Strip Water	5	0.4	3.2 x 10^1	3.1 x 10^5	10^6	10	0.02	4.3 x 10^2	33 x 10^2
5	A	Nitric Acid plus Denitrator Condensate	Strip Water	3	<0.2	9.7 x 10^1	0.94 x 10^5	10^6	9	0.02	10 x 10^2	----
5	B	Batch Waste plus Denitrator Condensate	Strip Water	7	0.7	3.9 x 10^1	2.1 x 10^5	10^6	11	0.02	60 x 10^2	33 x 10^2
6	A	Nitric Acid plus Denitrator Condensate	Strip Water	5	0.3	1.7 x 10^1	0.083 x 10^5	10^4	8	0.02	3.5 x 10^2	4.8 x 10^2

---

a. Total curies in evaporator at end of run/total curies gained in the fractionator.
b. Instantaneous concentration in evaporator/instantaneous concentration in condensed overhead vapor. See Figure 5.3 for instantaneous ruthenium DF versus acidity.
c. Total curies in fractionator at end of run/total curies passed to fractionator condensate.

overheads acid concentration, and chemical reductant (sugar) addition on the ruthenium DF. The ruthenium DF_c[a] across the evaporator varied from a low of 11 to a high of 420 under a variety of operating conditions. The lowest DF_c occurred in run PG-3 where sugar was added to improve the DF, and except for the two extreme values (DF_c of 11 and 420) the DF_c was nearly constant at 20 to 40. Overall, the ruthenium volatilized from the evaporator was about 3% of the ruthenium present in the evaporator. These data represent a factor of 30 decrease in performance over similar data obtained during the first six pot calcination runs.(3)

Generally, instantaneous ruthenium DF_i's[b] across the evaporator are directly related to the overheads acid concentration. When the evaporator overheads acidity was below 0.4M, the instantaneous ruthenium DF_i was equal to or greater than approximately 1000. Actual ruthenium DF_i's in the evaporator are shown by the data in Figure 5.3. Although the data show considerable scatter, the trend for each individual run (except for Runs PG-1 and PG-6) is a definite increase in DF_i with a decrease in overhead acidity. During PG-6 the samples did not have a sufficient spread in overheads and bottoms acidity (bottoms were 5.0, 5.2, and 5.1M HNO_3) to produce a meaningful trend. As with the earlier pot calcination runs(3) ruthenium DF_i's with feed in the evaporator were as high as any of the sets of individual run data. This is due to the definition used for DF_i** and to the fact that some of the entering activity in the gas stream from the solidifier is bypassing the evaporator bottoms. Reasons for this are discussed below.

---

[a] Total ruthenium curies in the evaporator at end of run from any source/total curies gained in the fractionator condensate.

[b] Instantaneous ruthenium concentration in the evaporator/ instantaneous concentration in the evaporator overheads.

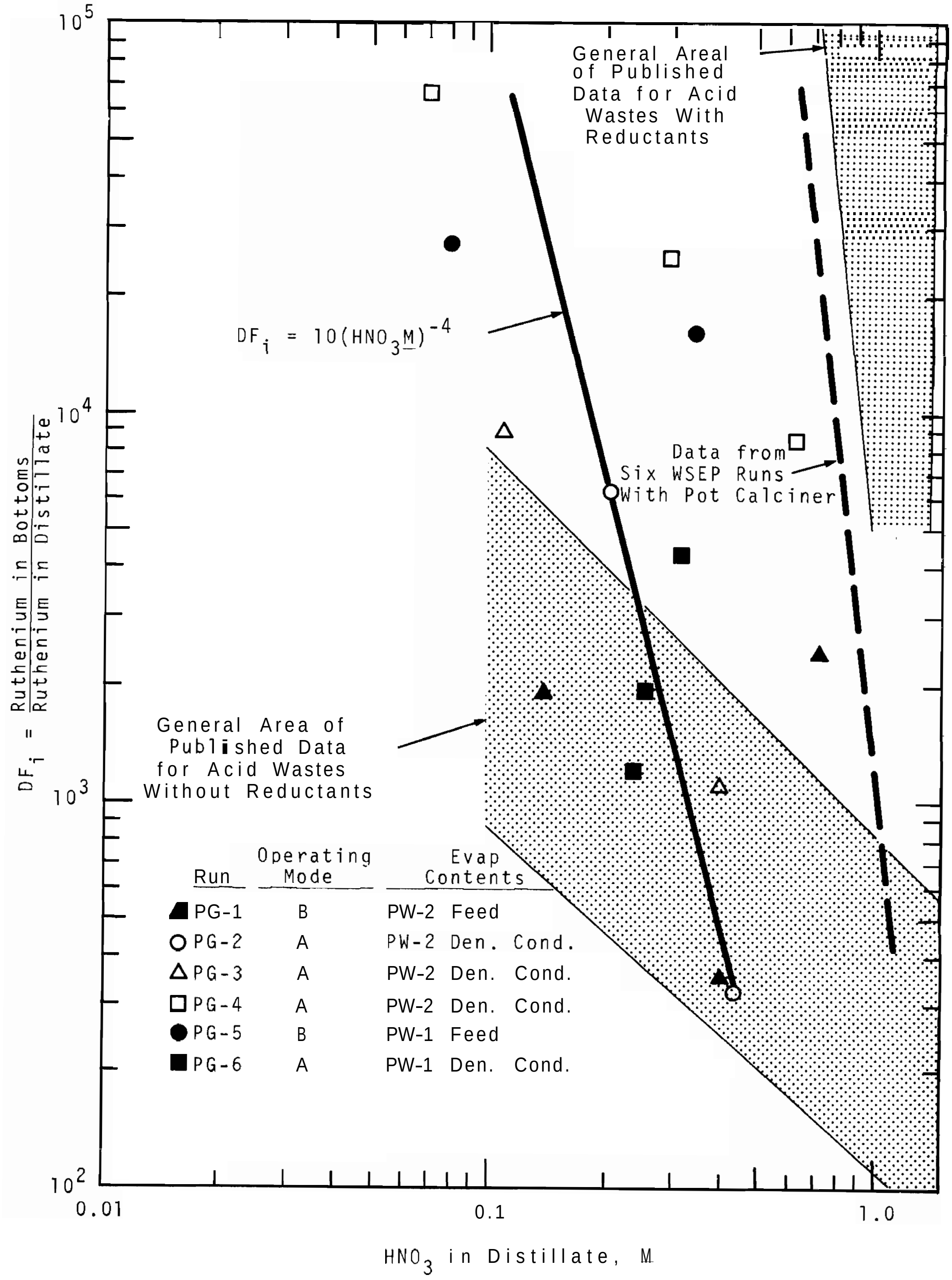


FIGURE 5.3. *Ruthenium Volatilization from the WSEP Auxiliary Evaporator*

The best fit of the data from Figure 5.3 gives the following equation for bottoms to overheads DF_i for ruthenium.

$$\text{Instantaneous } DF_i(\text{Ru}) = 10\ (\text{HNO}_3\ \underline{M})^{-4}$$

where

$\underline{M}$ = nitric acid molarity in the overhead over an applicable range of 0.1 to 0.5$\underline{M}$

In general, the DF_i for ruthenium was equal to or better than data in Reference 2 for wastes without reductants, but was somewhat less than that obtained during the first series of pot calcination runs.(3) The reason for this latter effect is due in part to a higher air flow (mostly due to inleakage) through the phosphate glass system. The 5 to 10 scfm air flow is considerably more than the 1 to 2 scfm encountered with the pot calcination system. Furthermore, in recent WSEP spray solidification demonstrations, it has been found that approximately 1% of the ruthenium volatilized in the solidifier bypasses the evaporator bottoms via the 15 scfm off-gas stream present in that system.(16) This same effect in the phosphate glass system would not be expected to be as significant, since the noncondensible gas flow and the percent of ruthenium volatilized from the phosphate glass system are less than for the spray solidifier.

Most of the ruthenium that escapes the evaporator to the overhead condensate is caught in the fractionator where additional decontamination occurs. Figure 5.4 is typical of the type of data obtained during the phosphate glass runs, and shows the accumulation of radioactivity in the evaporator condensate for a Mode B run where acidic waste is introduced to the evaporator after nearly 80 hours of Mode A operation. The addition of the acidic radioactive waste in the evaporator requires an increase in both boiloff rate and acid concentration

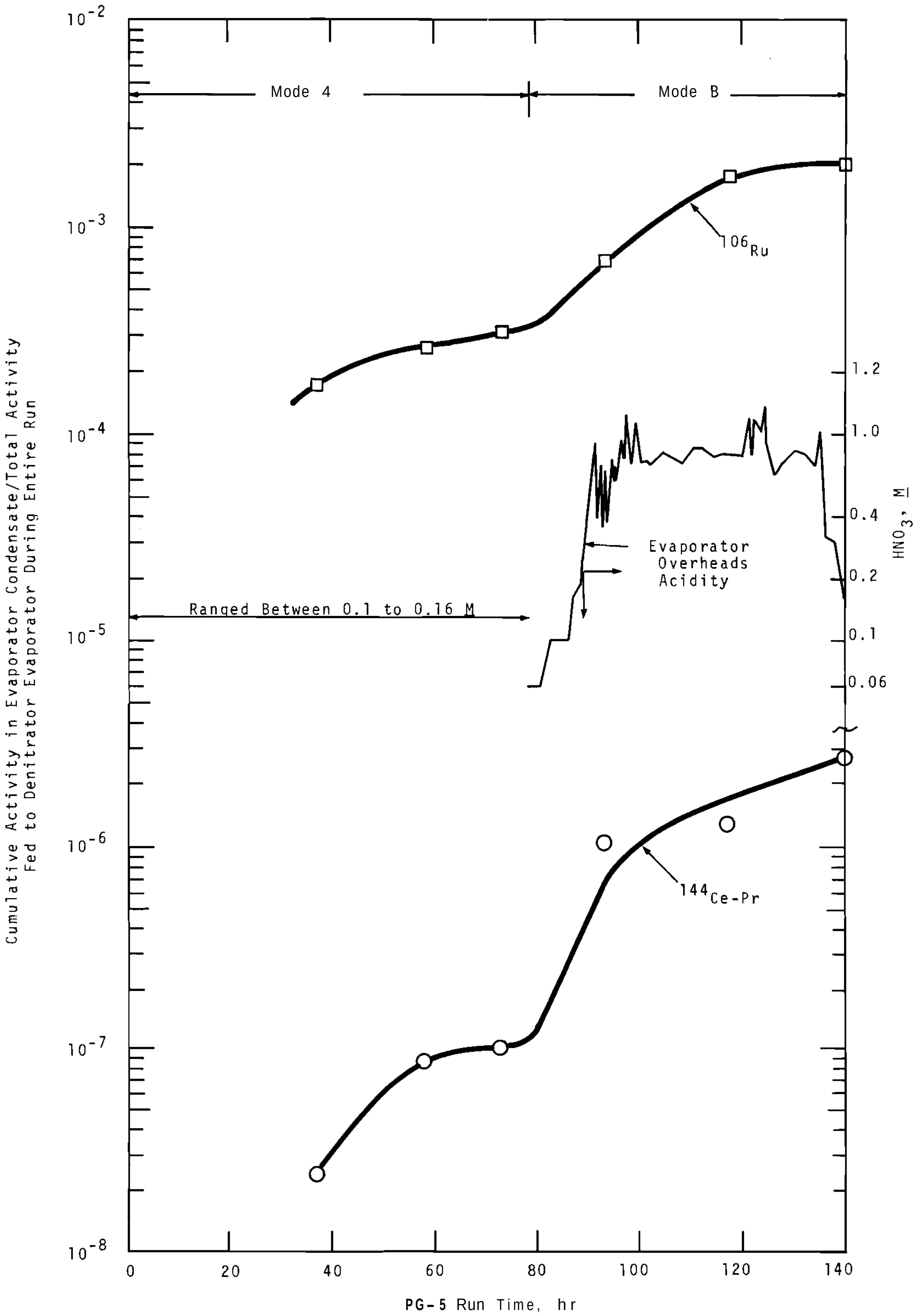


FIGURE 5.4. *Radionuclide Accumulation in the WSEP Auxiliary Evaporator Condensate (Fractionator bottoms)*

in order to strip nitric acid from both the waste and the incoming phosphate glass condensate. These two effects combined with the increase in radioactivity in the evaporator bottoms (from the entering radioactive waste) result in the increase in radionuclide accumulation in the evaporator condensate. Average strip water and boiloff rates for the evaporator for all runs are listed in the Appendix, Table 9.2.

Inleakage of air into the system (at 10 scfm) increased vapor velocities in the evaporator and fractionator towers by approximately 20% at an evaporator boiloff rate of 50 liters per hour.

For the six runs, the ruthenium DF_c across the fractionator (Table 5.2) varied from a low of 55 to a high of 6000. However, DF_c's of 200 to 1000 were more typical of the average data. Except for demonstration runs PG-1 and 3, the fractionator nitric acid concentration was maintained at approximately 9 to 11M, and the resulting fractionator overheads acidity was 0.02M using a fractionator tower internal reflux ratio of 0.1 to 0.2.

Ruthenium that escapes the WSEP fractionator to the overhead condensate is caught in the fractionator condensate tank. Figure 5.5 shows the accumulation of radioactivity in the fractionator condensate tank for the same typical Mode B run that was used for Figure 5.4. The fractionator DF_c for ruthenium for this demonstration run was equal to or better than the ruthenium data from any other run (Table 5.2).

5.3 CONTROL OF OTHER RADIONUCLIDES

Cumulative decontamination factors (DF_c) for nonvolatiles across the WSEP evaporator ranged from 2.7×10^3 to 3.3×10^6, but were typically about 10^5. Instantaneous DF's (DF_i) for nonvolatiles across the evaporator were calculated from radiocerium concentrations and ranged from greater than 10^4 to

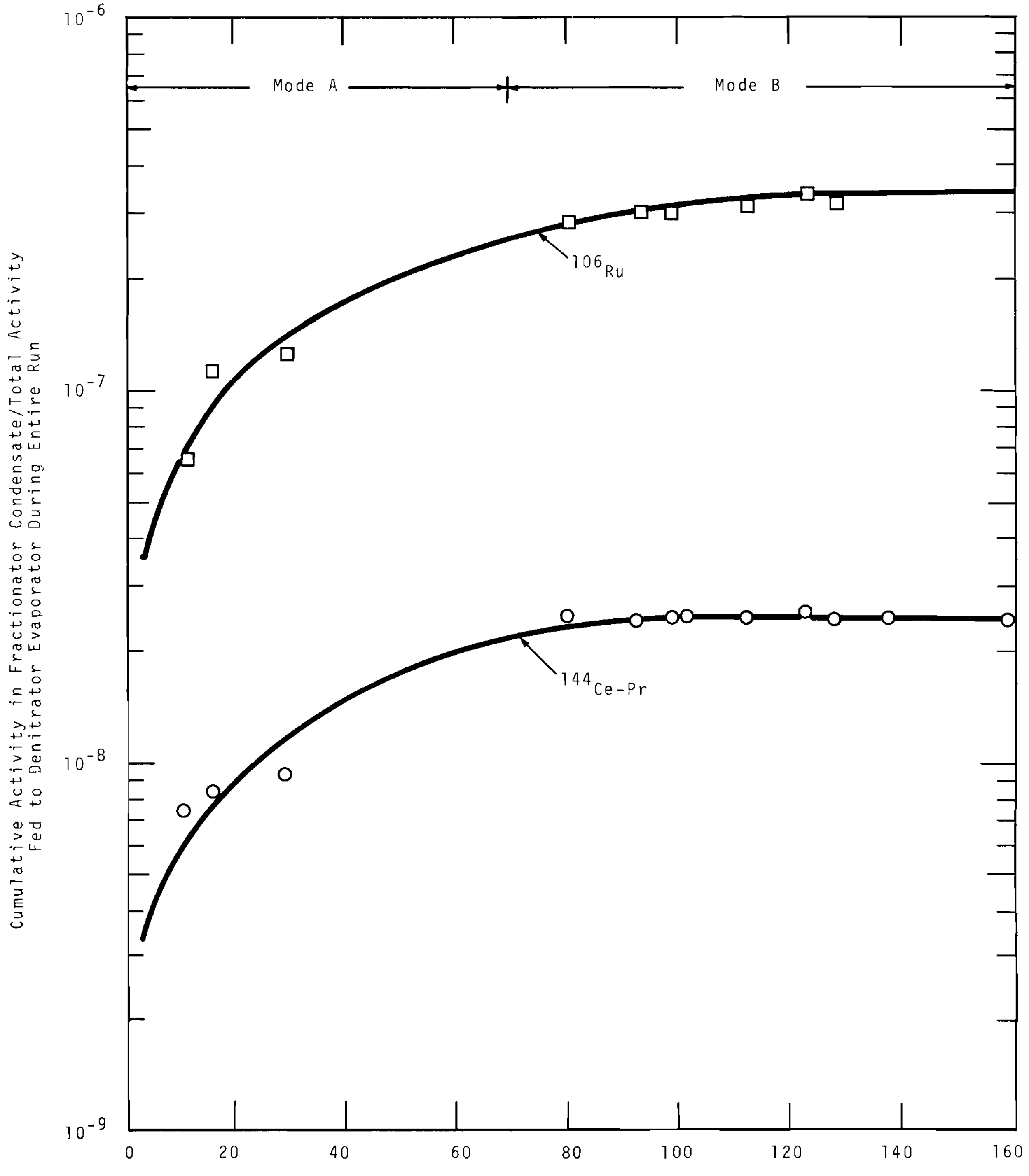


FIGURE 5.5. Radionuclide Accumulation in Acid Fractionator Condensate

greater than 10^6 (Table 5.2.) The data on nonvolatiles showed satisfactory operation and agree quite well with data from the first series of pot calcination runs.(3) There was essentially no difference in decontamination factors between runs, except that there were no low DF values when feed was in the evaporator. This effect was also noted in Reference 3. Figures 5.4 and 5.5 in Section 5.3 show the rate of accumulation of nonvolatile~(represented by ^{144}Ce-Pr) in the evaporator and fractionator condensates.

The phosphate glass process produces a relatively small quantity of noncondensable off-gas that must be decontaminated before it is released to the environs. The 5 to 10 scfm of inleakage at the process is significant, however, and should be reduced in commercial applications, if possible. The inleakage is primarily around the phosphate glass melter (viewing window, melter off-gas line flanges, etc.). In this first series of runs, no attempt was made to seal the system leaks because the system required operation at a very low vacuum (2 to 6 inches of water) to minimize sucking air backwards through the melt via the weir tubes. Also, some inleakage improved vacuum control. As discussed in Section 5.2, the high airflow through the system may be causing some ruthenium carry-over in the auxiliaries. The airflow apparently is not causing significant decontamination problems with nonvolatile constituents, since the data compare with Reference 3.

The airflow may have a slight adverse effect on the nitric acid stripping efficiency in the fractionator. Overheads concentrations of 0.02M are consistently produced when the bottoms is controlled at less than 11M HNO_3 (see Table 5.2 and Table 9.2 in Appendix). This is the same concentration produced with approximately 20% of the noncondensible gas flow as obtained during pot calcination tests.(3) Noncondensible off-gases from the process were approximately 1000 liters (STP) for each liter of aqueous feed. They were due almost entirely to air inleakage and instrument purge air. After off-gases left the fractionator, they were filtered, scrubbed, filtered twice again, and then discharged to the atmosphere. Their radioactivity concentration, after dilution by other C-MEL building and process air,[a] was well below detection limits and 10CFR20(1) release limits. The limit of detection for ruthenium is less than 2.4 x 10^{-6} Ci/week (calculated as ^{106}Ru) and for gross beta is less than 8.6 x 10^{-7} Ci/week (calculated as ^{90}Sr and ^{90}Y). Typical fractional losses of gross beta and ruthenium to the stack were 10^{-12} and 10^{-10}, respectively. The off-gas stream within the WSEP complex was not sampled during the phosphate glass runs, but samples are planned during the remaining phosphate glass tests. More recently, samples have been obtained of the WSEP off-gas as it leaves the scrubber. Initial data from these undiluted samples indicate that the off-gas at this point is approximately 50 times the 10CFR20 release limits.

Generally, decontamination of the process off-gas in the WSEP runs was at least as good as that achieved in the PNL hot cell phosphate glass tests where overall decontamination factors from feed to off-gas at the point of release to the atmosphere were 10^9 for both ruthenium and particulates.(20)

5.4 AUXILIARY HANDLING OF ACID PUREX WASTE

Fission product waste solutions contain precipitates which may interfere with liquid transfer or evaporation. While amorphous, noncaking precipitates can be reasonably handled at concentrations up to at least 30 volume percent, very small

---

[a] The 20 to 30 scfm of air exiting the WSEP scrubber (includes inleakage and motive air supply to the vacuum jet) is combined with other C-MEL building air to give a total flow of 120,000 scfm where it is monitored at the stack.

quantities of heavy, caking precipitate can plug pipes. Thus, proper design and operation requires a good knowledge of the precipitate characteristics. The precipitate present in a given waste solution depends on the chemical flowsheet used in the separations plant and the subsequent treatment of the waste. In general, the PW-1 and PW-2 solutions used in demonstration tests PG-1 through PG-6 were representative of 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 solids observed in actual samples of the feed solutions used in the six phosphate glass solidification runs varied from 108 in run PG-4 to 50% in run PG-3.

The main type of solids encountered in the phosphate glass feeds contains molybdenum, phosphorous, and zirconium and is probably a zirconium phosphomolybdate compound. The solid is a hydrous, amorphous precipitate which has never been observed to caked in the laboratory even after standing several months. In PW-1, the phosphomolybdate compound is predominant and the solids are gelatinous and noncrystalline. In the sulfate-bearing 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-1 waste is continuously boiled in the WSEP evaporator, the precipitate loses its gelatinous characteristics and becomes a very loose, easily-suspended (even after prolonged settling) precipitate. Continuous boiling of the PW-2 waste has not been attempted, and with this possible exception, the handling of phosphate glass feeds in feed tanks, evaporators and transfer lines is not considered as a major problem.

5.5 GENERAL PERFORMANCE OF AUXILIARIES

Auxiliary equipment performance was very satisfactory during the six phosphate glass demonstration runs except for some pump problems and a gradual deterioration of the electrical and instrument wiring within the cell. All six runs were successfully completed; only the first was interrupted during the operating period as the result of an auxiliary problem when a feed pump failed. Table 5.3 is a compilation of the general operating performance of the auxiliary equipment.

5.5.1 Pumps

The feed pump used at the start of the phosphate glass demonstration runs was the same pump used during the final pot calcination run.(3) The pump was a canned-rotor in-line pump(1) with boron carbide seals and boron carbide bearings with graphite thrust faces. Water lubricant to the bearings was recirculated through a small reservoir and a jacketed cooler, but was separated from the process fluid by a mechanical seal. After this type pump failed during the first phosphate glass demonstration (the shaft became bound), a modified in-line pump assembly using a conventional centrifugal pump was installed. The pump contained double mechanical, water-lubricated seals with graphite rotating rings. Isolation valves are required on the new type pump to prevent loss of feed if the seals fail. These valves also allow the pump to be changed out remotely in approximately 4 hours without transferring the feed out of the feed tank. Some pump failures have resulted with this new pump (see Appendix, Table 9.5) because of seal and bearing failures; however, the pumps have a longer life expectancy than the canned-rotor pumps if they are thoroughly flushed after each run. It appears that some of the difficulty with pump seal failures was caused by the seals drying out when the pumps were not being operated. An extended pump operating test has not been performed.

TABLE 5.3. *WSEP Auxiliary Operating Summary (Through phosphate glass run PG-6)*

Equipment	Construction Material	Normal Temp, °C	Pressure, in. $H_2O^{(a)}$	Chemical	Operating Hours	Remarks
Feed Tanks	304L SS	60	-5	Darex, Purex and TBP-25 type wastes	2398	Agitators used 1700 hours
Condensate Tanks	304L SS	25	-15 to -20	H_2O, Dilute HNO_3	2328	Submerged pump used 820 hours
Caustic Tank	304L SS	25-40	-2 to -20	Dilute NaOH	2328	Circulating pump used 1480 hours
Evaporator	A-55 Ti	110	-10 to -20	Boiling Waste	2198	Minor titanium corrosion caused by fluoride ion during early DVT runs
Fractionator	A-55 Ti	115	-10 to -20	8 to $12\underline{M}$ HNO_3	2178	
Solidifier Condenser	A-55 Ti	110	-5 to -20	HNO_3 Vapors	2328	Local vapor entry corrosion (up to 1/16 in.) during early DVT runs 3 and 4.
Feed Pumps	304L SS	60		Adjusted Waste	1255 428	During PG-1, changed from in-line pump to conventional pump. Prior to run PG-3 changed from a single pump set up to a dual pump jumper. See Appendix, Table 9.5.
Evaporator-Condenser	A-55 Ti	105	-10 to -20	HNO_3 Vapors		
Fractionator Condenser	304L SS	100	-10 to -20	HNO_3 Vapors		
Flowmeters						
a) Feed	Vitreous enamel liner, platinum seal and electrodes, Inconel flow tube	30-80		Waste Stream	1620	Occasionally intermittent due to lead wire failure. The meter also shows frequent shifts in calibration and loss of sensitivity.
b) Condensate, Magnetic	Vitreous enamel liner, platinum seal and electrodes, Inconel flow tube	25-40		Acid Stream	2302	Two units (1151 hr/unit) did not operate properly primarily due to lead wire failures.
c) Condensate, Electronic rotometer		30-80		Acid Stream	2178	Reliable meter for the clean final condensate.
Filters Absolute	Glass Asbestos with Al separators in 304L SS housing	50-70	-12 to -20	Predominately Air		The aluminum separators become seriously deteriorated after several weeks use.
Process Vent			-12 to -20		13,800	Filter has not been changed since radioactive operation began.
Feed Tank Vent			-10		13,800	Changed five times; 1800 hours was the shortest duration of any one filter.

---

a. First number is for phosphate glass operation, second number is for the other solidification processes.

5.5.2 Feed Control System and Flow Measurement

Operation of the feed control system over the range of 5 to 30 liters/hr was good. A 1/2-inch Hammel Dahl valve with a No. 5 spline trim was used for control of the feed to the denitrator-evaporator. Solids in the feed readily passed through the control valve. Special flushing procedures were used prior to and after feeding to keep the feed lines free of solids and to prevent possible calcination in the lines in the hot denitrator-evaporator.

Measurement of feed flow to the process with a magnetic flowmeter was often inadequate. Difficulties experienced with magnetic flowmeters in WSEP have included loss of signal, frequent shifts in calibration and wire insulation failure. The wire insulation failures are described below. Another obvious difficulty with magnetic flowmeters for metering wastes is the small hole size required for metering of the small flow rates in WSEP (5 to 30 liters/hr).

5.5.3 Evaporator and Acid Fractionator

The evaporator and acid fractionator performed satisfactorily. Specific gravity was used as the primary control for maintaining the desired bottoms concentration. Temperature was used on some occasions. Conductivity of the condensed evaporator overheads was used to control the strip water recycle flow to the evaporator to maintain a low nitric acid concentration in the overheads. The evaporator specific gravity and weight factor dip tubes would occasionally plug as they did during the first pot calcination runs.(3) Although most of the plugging was eliminated by alternately flushing the dip tubes with solutions of nitric acid and caustic between runs, the dip tubes will have to be made more reliable for continuous operation possibly by continuous or semicontinuous wet purging. More recently, promising results have been obtained by venting the dip tubes for approximately 10 out of every 15 minutes to allow the waste solution to rise into the dip tubes and in effect wash out the tubes.

To minimize fluoride-induced corrosion of the titanium evaporator and fractionator vessels, chemical complexants are added to the vessels before each run. Aluminum as $Al(NO_3)_3$ is added to the fractionator and to the evaporator if pure nitric acid is to be boiled. When waste is boiled in the evaporator, enough iron and zirconium and complexants are present in the waste to inhibit corrosion.

5.5.4 Filters

Performance of the high-efficiency filters was nearly the same as that experienced during the first pot calcination runs; the high-efficiency filters in the process ventilation system performed well, while those in the secondary feed tank vent system required several changeouts because of excessive pressure drops (greater than 10 inches of water). Failures with these secondary system filters have continued to be caused by their becoming wet with acidic vapors. Inadequate preheating upstream of the filter has not sufficiently "dried" the gases. The aluminum spacers between the filter material has also seriously deteriorated in all failed filters. Recently, the secondary feed tank vent system has been rerouted to ventilate through the WSEP waste vault vent system, and the original filter location has not been used.

5.5.5 Electrical and Instrument Wiring

The phosphate glass demonstration runs began at about the time that much of the hot cell wiring began failing (after 1 year of service). Most of the original wiring was insulated with linear polyethylene, a moderately radiation-resistant material. The linear polyethylene became brittle and caused wire breakage when the wires were bent. Less expensive Neoprene rubber has been more satisfactory for wire covering in WSEP. Neoprene remains more pliable than the linear polyethylene and has a useful life of at least two years.

5.5.6 Sampling

Contamination of the low-level radioactive aqueous Samples, (fractionator condensates and scrubber solutions) within the hot cell(3) was eliminated by routing the sample lines for sampling outside of the cell. Since representative samples of the WSEP evaporator and acid fractionator could not be obtained unless the two tanks were boiling, start and end of run samples for these two tanks were obtained when the tanks were boiling. Incorporation of the above improvements led to an improved sampling system by the end of the phosphate glass runs.

5.5.7 Material Balances

Material balances for the six phosphate glass demonstration runs are shown in the Appendix, Table 9.3. Except for ruthenium, the recovery of individual elements was good.

Analysis for ruthenium in the glassy product was, and still is, very unreliable, by either chemical or radiochemical analysis. Consequently, a total material balance for ruthenium is difficult to make. Analyses for ruthenium in the liquid streams in WSEP is easily obtained from radiochemical gamma energy analyses (GEA). No unusual material balance discrepancies have been found with the WSEP auxiliaries when it is operated with the phosphate glass solidifier.

The overall material balances (percent recovery) for the six phosphate glass demonstrations are shown in Table 5.4.

TABLE 5.4. Overall Material Balances for Phosphate Glass Runs

Run	Percent Recovery	
	vol%	wt%
1 (Part 1)	93	---
1 (Part 2)	100	100
2	90	92
3	---	---
4	98	96
5 (Part 1)	104	103
5 (Part 2)	116	111
6	101	105

6.0 FILLED RECEIVER POT PERFORMANCE

Evaluation of the receiving pot and glass product for interim and long-term storage constitutes an important part of the waste solidification program. The basic criterion for storage is that radionuclides do not enter the human environment beyond safe limits. A solids storage engineering test facility (SSETF)(21) was constructed for storing, monitoring, observing, and evaluating the products in several types of controlled environments as part of the WSEP Program. The initial and near-term behavior of the solidified wastes in their containers are being observed and evaluated in the product evaluation program and in the SSETF. Inasmuch as filled pots may be held in an interim storage facility until conditions (e.g., heat generation rate) are suitable for transferring them to a final storage site, it is very important to know what behavior to expect during the interim period.

The characteristics of the solidified waste which are of primary importance are good thermal conductivity, low leachability by water or air, good chemical stability and radiation resistance, and low corrosivity to product receiver pot.

6.1 EVALUATIONS

Most of the receiver pot performance characteristics of interest in the waste solidification program are concerned with changes which are expected to occur slowly, if at all. In fact, the extent of improved safety resulting from waste solidification hinges to a large extent on the absence of notable effects. In order to detect changes, the original conditions of the solidified waste must be determined.(22) Most of this section deals with the current progress and problems in determining the original conditions of the phosphate glass product from the 6 radioactive runs to date.

6.1.1 Maximum Temperatures

The temperatures produced in the receiver pot by the heat generating nuclides in the solidified waste are theoretically predictable from knowledge of the waste, its source and age. A major objective of WSEP demonstration runs was to determine the predictability of temperatures and the quantity of radionuclides required to produce the maximum allowable temperatures in a pot. The accuracy of predicting temperatures produced by radionuclide decay depends largely on the accuracy of properties such as thermal conductivity. If these properties are known, the general capability to process a waste by the phosphate glass process can be judged.

The temperature at the centerline of a heat generating cylinder is given by:

$$T_c = T_w + \frac{Q}{4\pi KL} \qquad (1)$$

where:

Q = heat generation rate (watts) in the cylinder (radionuclides are assumed to be uniformly distributed)
L = length of heat generating cylinder, meters
K = thermal conductivity, $W/(m^2)(°C/m)$
T_w = temperature at the cylinder wall, °C
T_c = temperature at the centerline of a solid cylinder of heat generating material, °C.

Equation (1) applies where the heat flow is perpendicular to the cylinder axis, as would be the case in cylinders with insulated ends or in sections of infinitely long cylinders. Thermal conductivity is assumed to be constant. The equation can be used to estimate maximum internal temperature in pots of solidified waste, if an "effective thermal conductivity" is used as explained below, even though the conditions required by the equation are not exactly met.

Equation (1) may be arranged to give:

$$\Delta T = \frac{Q}{4\pi K_e L} \tag{2}$$

where:

$AT = T_c - T_w$ (T_c is the maximum internal temperature and T_w is the wall temperature in the same zone.)

K_e = effective thermal conductivity.

Equation (2) shows that the temperature drop from the centerline of a pot to the outside wall is a function of the total internal heat generation rate from radionuclide decay. For a given internal heat generation rate, thermal conductivity and fill height, the temperature difference (AT) is the same for an 8-inch as well as for a 12-inch diameter pot. However, the allowable heat rate density for the solidified waste in an 8-inch diameter pot is a factor of 2 greater than that for a 12-inch pot. In Equation (2), Q is equal to $\frac{\pi d^2 L}{4}$ q where d is diameter and q is the heat generation rate density in the solid. For a given heat generation rate density in the solid, the temperature difference AT is a function of the square of the diameter. However, for this study, temperature as a function of the total heat generation rate is the major interest.

Graphical solutions to Equation (2) for several different values of K_e are presented in Figure 6.1. Centerline temperature estimates can be obtained by adding the ΔT from Figure 6.1 to the pot wall temperature, T_w, from Figure 6.2. Pot wall temperatures are shown in Figure 6.2 for 8- and 12-inch diameter pots cooled by natural convection and radiation in 38 °C (100 °F) air. The curves are derived from standard methods for convective and radiative heat transfer as given by McAdams.(23) An emissivity of 0.8 is used for the pot wall at all temperatures.

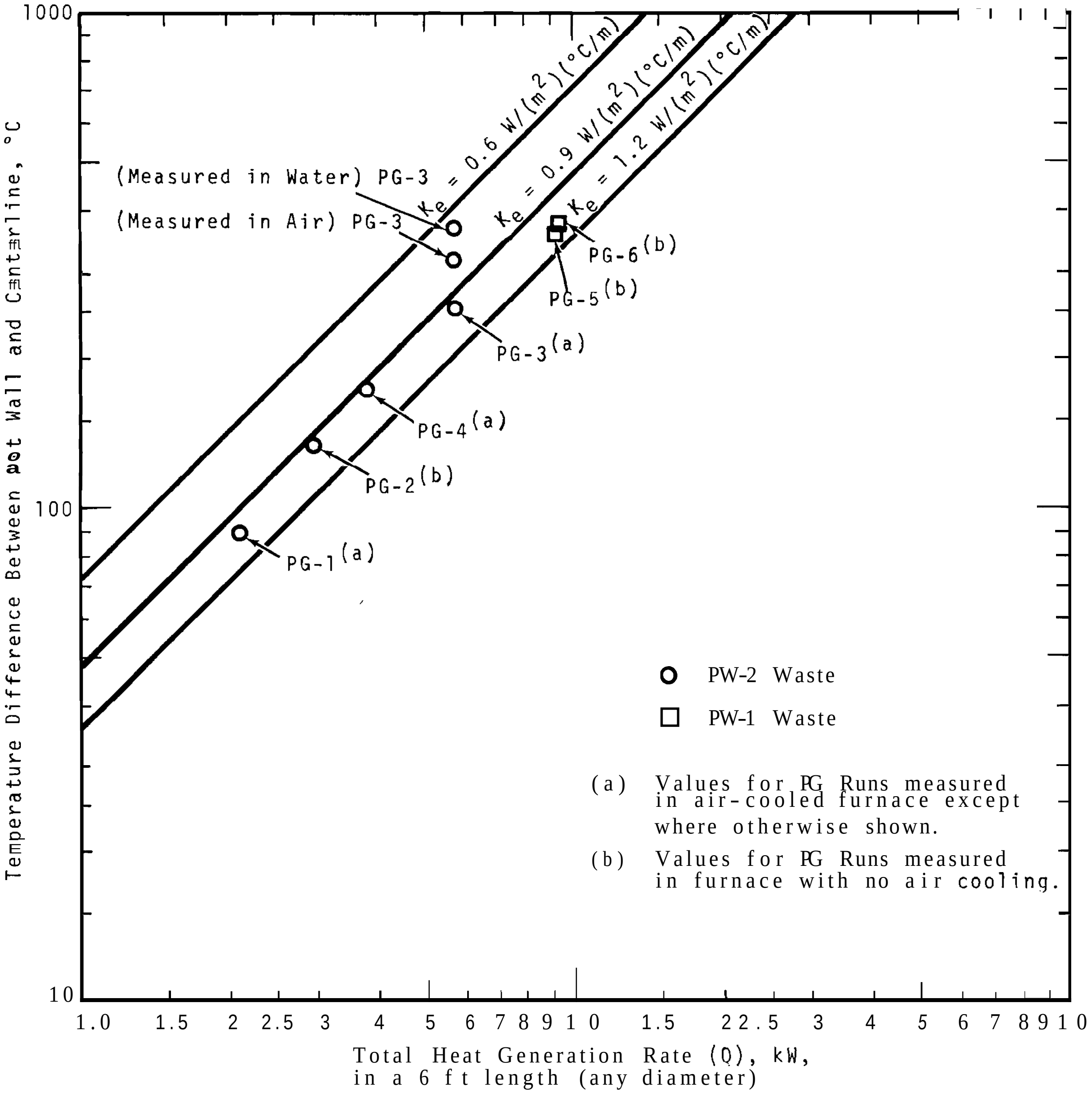


FIGURE 6.1. *Temperature Drop (Centerline to outside wall) in Receiver Pots Containing Solidified Waste*

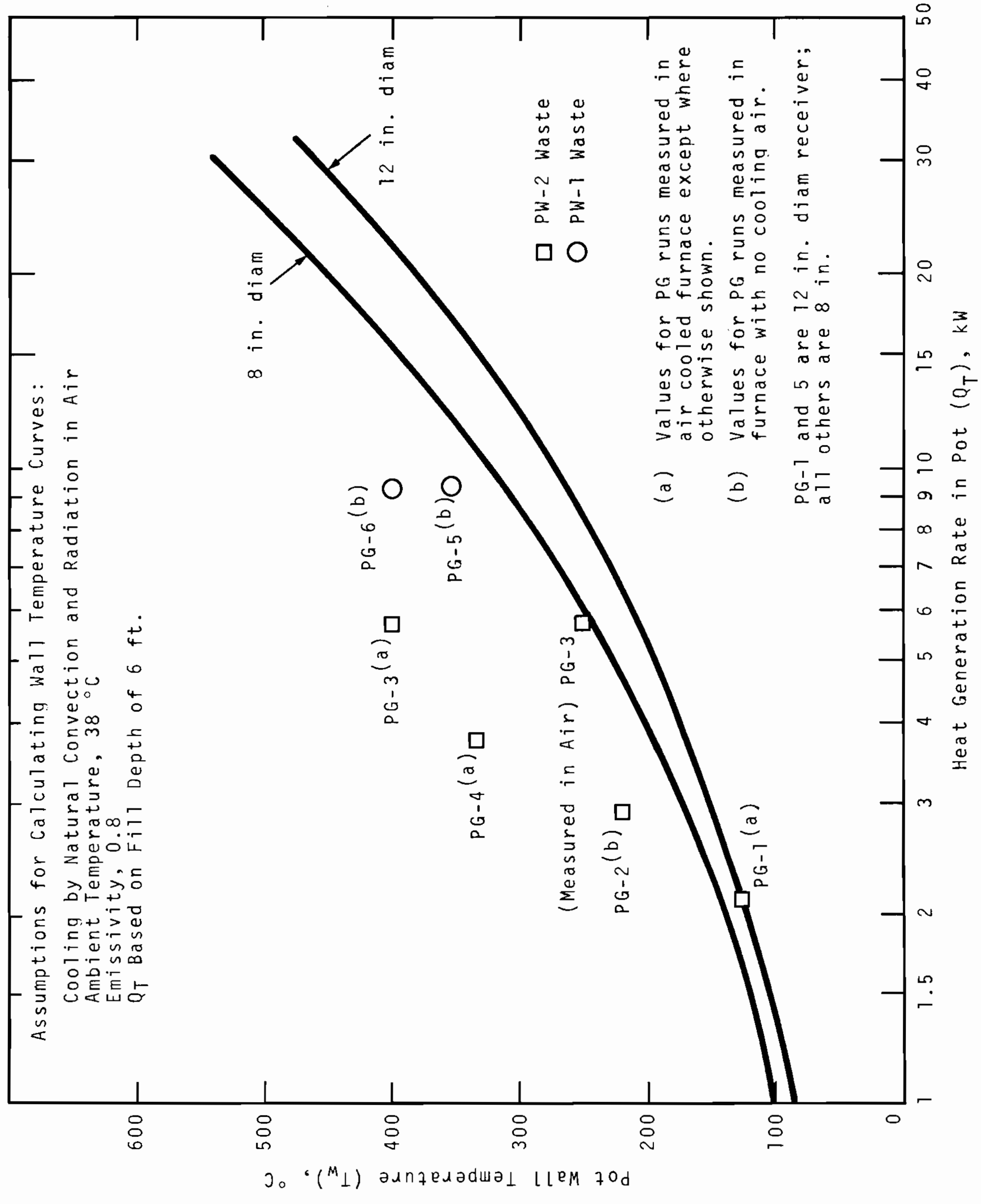


FIGURE 6.2. *Pot Wall Temperature in Air and in Air-Cooled Receiver Pot Furnace*

Figures 6.1 and 6.2 can be used to predict the maximum temperatures for the total heat generation rate in a pot. A trial and error technique is used to determine maximum conditions wherein both the wall and the centerline temperature are within allowable limits. First, the total heat generation rate in a pot is estimated; then a wall temperature is read from Figure 6.2. If this value of T_w is below the allowable limit (425 °C), a value of ΔT is read from Figure 6.1. Then T_c is determined from $T_c = T_w + \Delta T$. This procedure is repeated until either T_c or T_w has reached the allowable limits (900 °C for T_c). The value of Q at that point is the heat generation rate which will produce the maximum allowable temperatures.

In both Figures 6.1 and 6.2, experimental results from filled pot temperature measurements are shown. The observed pot wall temperatures are shown for the six runs in Figure 6.2, and pot-wall-to-centerline temperature differences are shown for the six runs in Figure 6.1. The measured wall temperature for the 8-inch pot of PG-3 was slightly higher than would be predicted from the curve. This difference may be due to the assumed value of emissivity, since a slight error toward low readings would be expected for thermocouples welded to the surface of the pot. In Figure 6.1, the location of experimental points indicates that thermal maximum estimates for phosphate glass material should be based on thermal conductivities of 0.94 to 1.13 $W/(m^2)$ (°C/m), [or 0.54 to 0.65 Btu/(hr)(ft^2)(°F/ft)] with solidified PW-2 waste tending toward the lower end of the range, and solidified PW-1 waste toward the higher end.

6.1.2 Effective Thermal Conductivity

The thermal conductivity for phosphate glass waste derived from the experimental data is essentially the true effective value for the central zones in the pot where heat flow is virtually radial. Earlier nonradioactive experiments have shown that phosphate glass produces a solid which normally fills the pot uniformly and homogeneously, so that heat generation is expected to be uniform throughout the cylinder. Effective values of thermal conductivity based on data from the PG runs are shown in Figure 6.1. These values are reasonable approximations for making temperature predictions in later runs with the same waste compositions.

In Figure 6.3, the relationship between effective thermal conductivity and the allowable heat generation rate to reach maximum temperatures is shown for 8-inch and 12-inch diameter pots. Twelve-inch pots filled to the 6 foot level, for example, would hold waste equivalent to 13 to 15 kilowatts at $K_e = 0.94$ and 1.13 $W/(m^2)(°C/m)$, respectively, without causing centerline temperatures above 900 °C or wall temperatures above 425 °C in air. For the range of K_e and pot diameters shown, the centerline temperature, rather than the wall temperature, is always the limiting temperature.

Thermal conductivities were calculated at different steady-state temperatures using heat-generation rates determined by calorimeter measurements on all runs except run PG-5 where the heat generation rate was based on analytical data in the aqueous waste. When these data are plotted against average phosphate glass temperatures, a trend for the waste showing a slight increase with temperature is obtained, as shown in Figure 6.4.

Thermal maximum pots intended for water storage* can be filled and safely handled in a plant that is designed to insure

---

* Thermal maximum in WSEP is the quantity of heat/unit volume of solidified waste which will produce a centerline temperature of 900 °C or a pot wall temperature of 427 °C when the pot is stored in either ambient temperature air or in water at 100 °C. Thermal maximum pots with molten cores are based on extrapolation of the thermal conductivity of the waste in the solid state to the hypothetical centerline temperature of 900 °C.

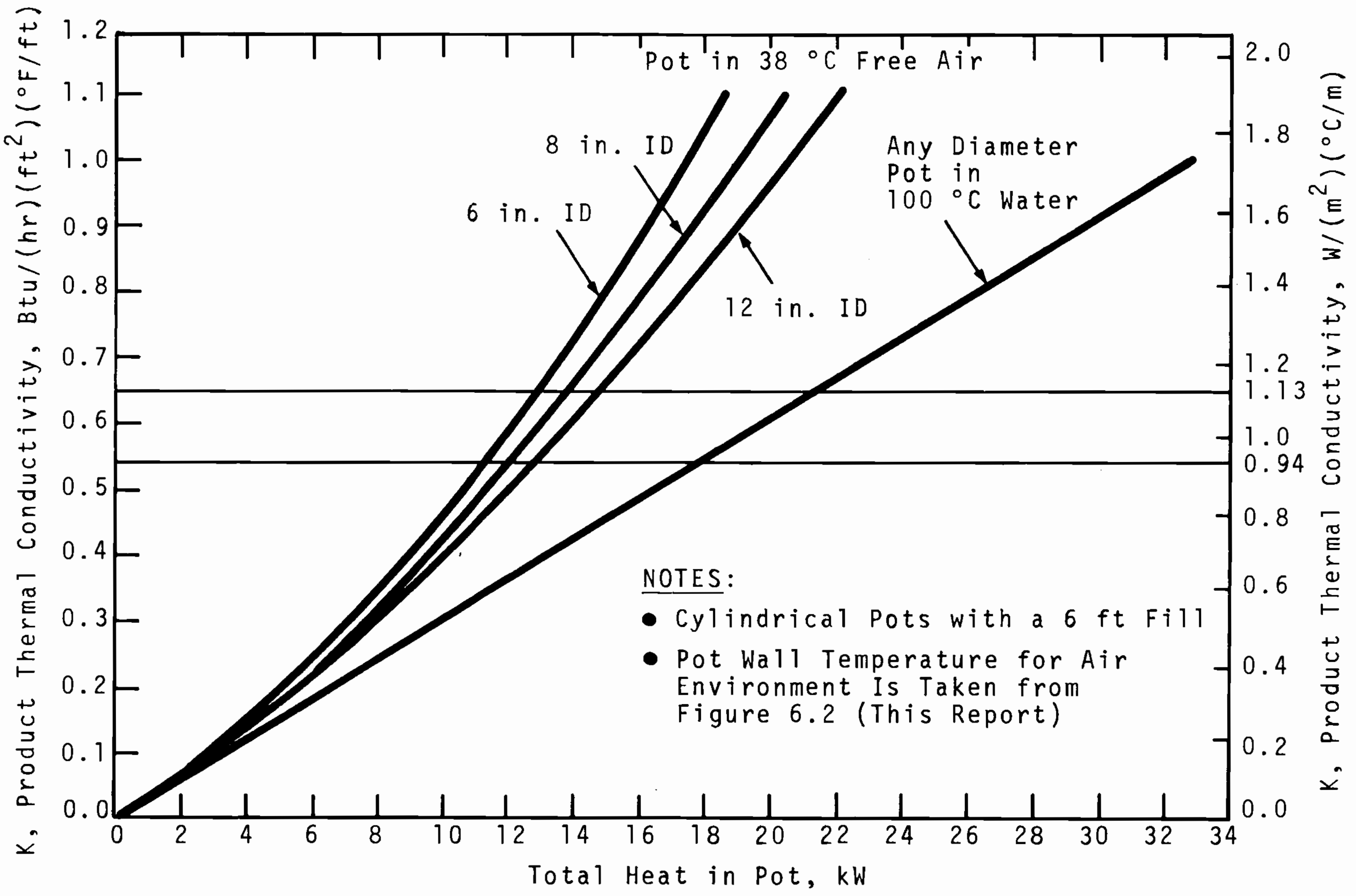


FIGURE 6.3. *Heat Required in a Cylindrical Pot to Attain a 900 °C Centerline Temperature*

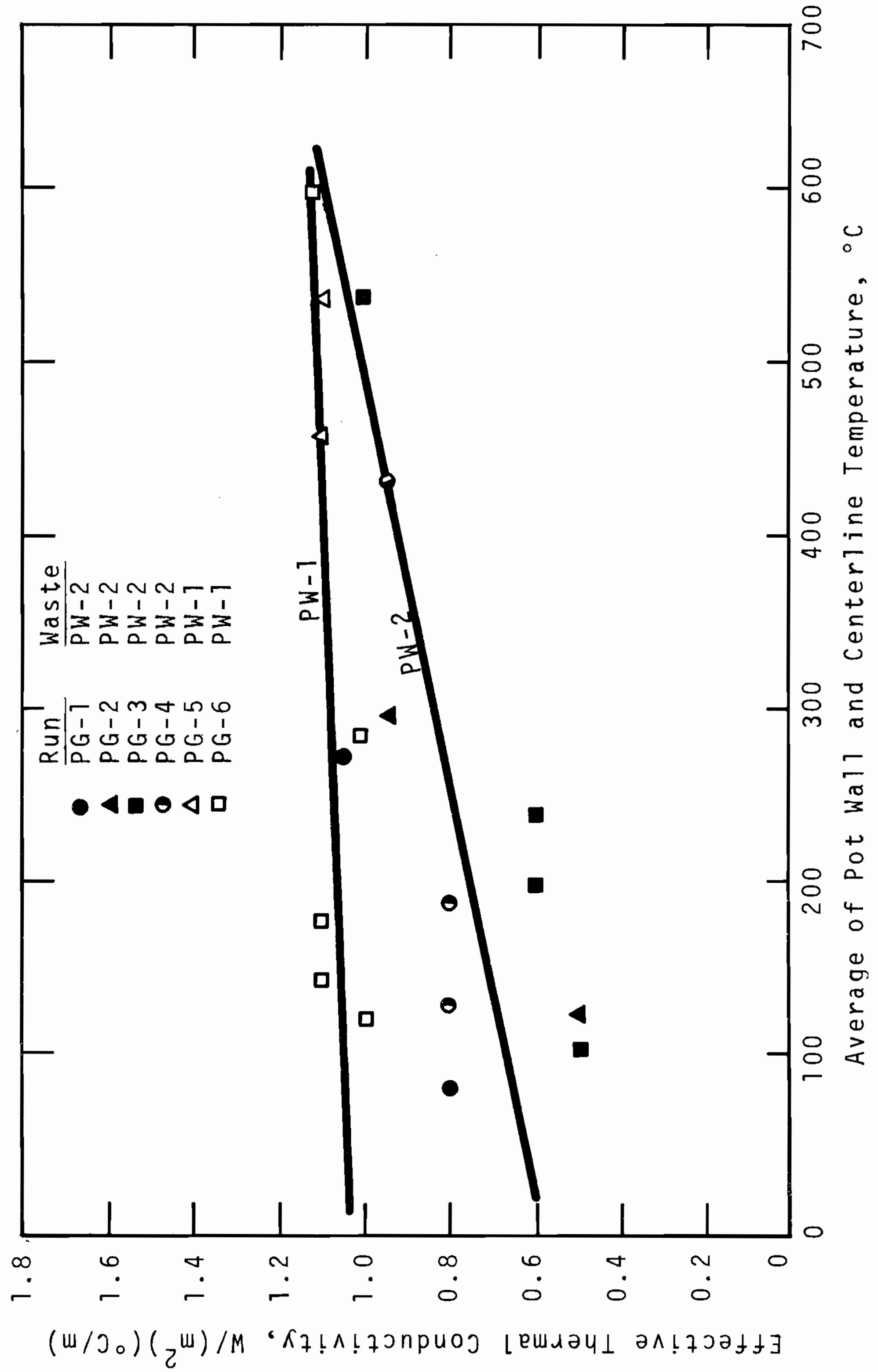


FIGURE 6.4. *Effective Thermal Conductivity of Radioactive Phosphate Glass*

water cooling of the pot during filling, pot transfers, and interim storage. The amount of heat generating fission products that can be safely handled in a pot is dependent on product thermal conductivity, product melting or remelt temperature, melt corrosiveness, pot geometry and pot environment during filling and interim storage. Indirect factors that must also be considered include product stability and fission product migration. More will be learned later about these two factors in long-term product storage tests. Filling pots while they are immersed in water is not considered a major problem.

Equations have been derived(24) for calculating frozen wall thicknesses in pots with molten cores. Graphs were also presented in an earlier report for this same purpose.(25) For cylindrical containers filled to a depth of 6 feet, Figure 6.3 shows the heat generation rate required at various product thermal conductivities in order for the pot centerline to reach 900 °C with no considerations for molten cores. Figure 6.5 gives the product frozen wall thickness as a function of remelt temperature. Figure 6.5 is for an 8-inch diameter pot containing waste with a heat rate content equal to the thermal maximum limit with water cooling for a centerline temperature of 900 °C taken from Figure 6.3.

One case is presented here to illustrate the considerations given to filling a pot with a high quantity of fission product heat. Suppose a pot containing a heat rate equal to the thermal maximum with water cooling (with 900 °C at the centerline) is desired for a product with a thermal conductivity of 0.7 Btu/(hr)(ft^2)(°F/ft). From Figure 6.3, the corresponding heat generation rate for 6 feet of glass is 23 kilowatts. If the product has a melting point of 700 °C, the frozen wall thickness during water storage is obtained from Figure 6.5, and is 2.0 inches. If the pot lost cooling water, but had the benefit of natural convection air cooling,

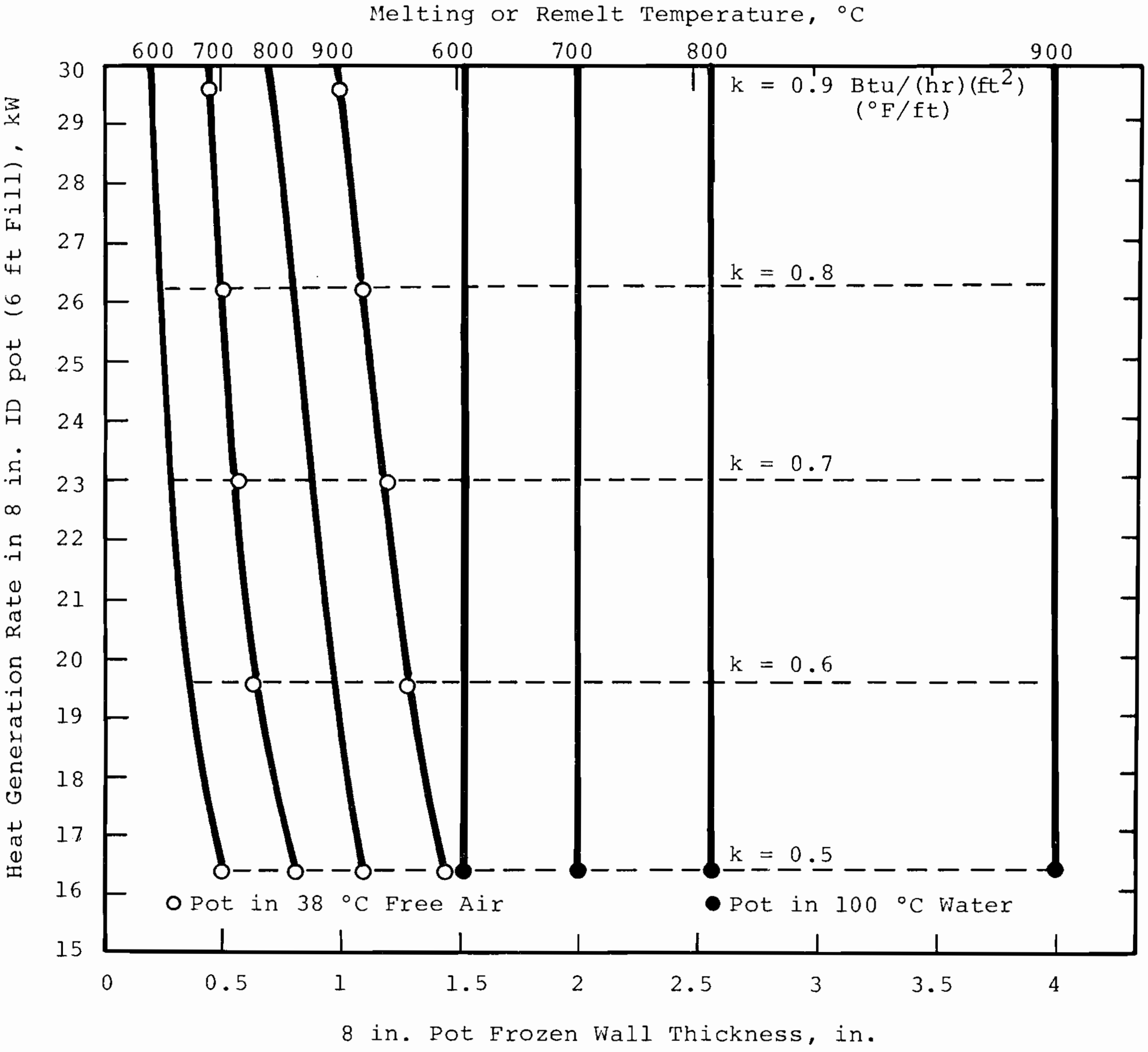


FIGURE 6.5. Product Frozen Wall Thickness for 8-Inch Thermal Maximum Pots (Receiver Pots Filled to Obtain a Hypothetical 900 °C Centerline)

the frozen wall thickness would decrease to about 0.5 inches. The wall temperature would increase to 480 °C and the centerline temperature would increase to 1300 °C, assuming no change in thermal conductivity. Obviously, the latter situation may give some cause for concern, and knowledge about the corrosiveness of the melt and the integrity of the frozen wall would be essential. Since the integrity of the frozen wall has not been fully evaluated, the minimum frozen wall thickness in WSEP has been limited to not less than one half the radius of the receiver. Each particular case will have to be evaluated according to its own characteristics by considering the items listed above.

6.1.3 Gamma Spectrum Analysis and Radiation Profiles

To get some idea of the solids deposition pattern, gross gamma radiation profile scans were made on each of the filled pots. The results of two scans are shown in Figure 6.6. Gamma radiation profiles were obtained simply by positioning an ionization chamber at a distance of about 6 inches from the pot and recording the radiation level at several points along the length of the pot. No collimation was attempted. In general, the profile was about what would be expected from the appearance of the contents of pots produced in earlier, nonradioactive runs. These profiles indicate that a uniform distribution of fission products probably exists, but the radiation measurements cannot be interpreted quantitatively. The pot centerline temperature profile for the pot from run PG-5 is also shown in Figure 6.6. As might be expected, the temperature and radiation profiles are quite similar; both reach a maximum in Zone 4.

A gamma spectrometer and multichannel analyzer system was designed and installed to measure gamma energy spectrum profiles of the filled pots. An indication was sought of the distribution of heat generating isotopes in the pot. However,

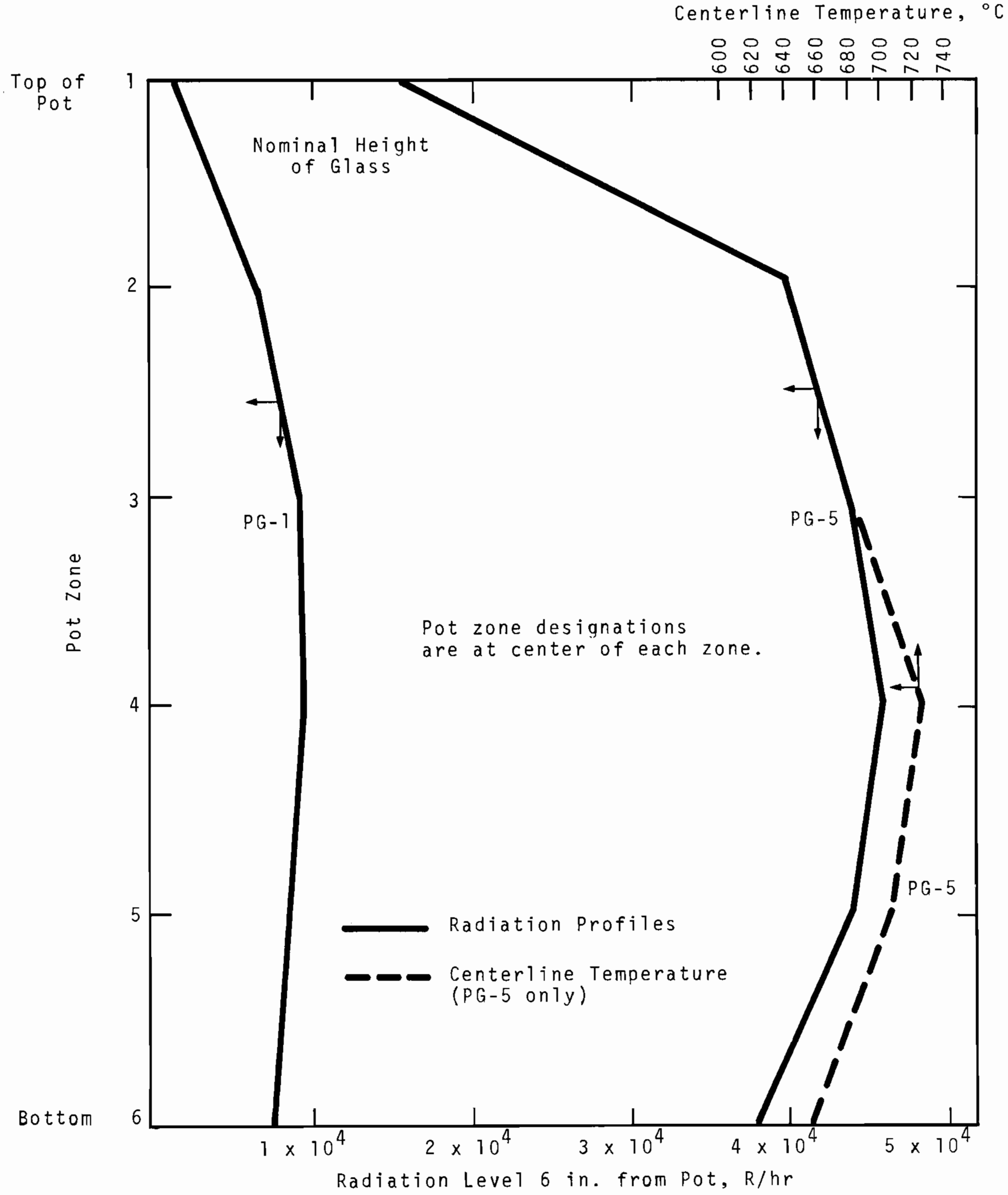


FIGURE 6.6. Radiation and Temperature Profiles of Receiver Pots Filled with Phosphate Glass

the system has not provided satisfactory measurements. The two major problems were: (1) the sodium iodide crystal became saturated in the high radiation field when using a 0.094-inch diameter collimation tube and (2) energy channels were not discernible due to distortion of the gamma energy spectrum by Compton scattering.

6.1.4 Pot Dimensions and Physical Data

After the processing cycle, no significant changes were detected in external pot dimensions of any of the six pots within the accuracy (±1/4 inch) of the remote in-cell measurements.

Before a pot was filled, it was subjected to tests and measurements to assure its integrity and to establish a basis for detecting changes which might occur during filling. Pot gross dimensions (length, diameter) were measured. As soon as possible after the pot was filled, the pot diameter was measured at three locations to see if any gross swelling or pot deformation had occurred. The measurements were confirmed by visual observations.

6.1.5 Leach Rates

Leach rates have been obtained on grab samples from four phosphate glass runs. Runs PG-5 and 6 were made with PW-1 waste, and runs PG-1 and 2 were made with PW-2 waste. The rates are in general agreement with those obtained on simulated nonradioactive samples,(26) being grouped around 10^{-6} g/(cm^2)(day). The melts with PW-1 waste are leached at rates about 5 times and 4 times those with PW-2 waste with respect to ^{137}Cs and ^{144}Ce, respectively. The difference is attributed to sodium that was added during processing of PW-1 wastes. This made the final melt about 25 mole % Na_2O versus 17% for the PW-2 melts.

Leach rates based on ^{137}Cs and ^{144}Ce analyses of the leach water are shown in Figure 6.7 for a grab sample from run PG-1 with PW-2 waste. The leach rates are based on a melt analysis calculated from the feed composition. The concentration of ^{137}Cs and ^{144}Ce calculated to be in the melt was usually about 1.3 times that found by actual analysis of the melt.

6.1.6 Internal Pressure

Bourdon tube gages were installed on filled pots as soon as the pots were sealed. For runs PG-4 and 6, the gages provided the only information as to how well the pots were sealed, since leak tests were not performed on these receivers. The pressure readings are shown in Table 6.1. The absence of positive pressure in the sealed pots from 4 of the runs indicates that the residual level of nitrate and other unstable or volatile constituents is as low as had been predicted. Three of the pots showed the subatmospheric pressures imposed on the receivers at the time of leak testing. Cooling reduced the pressure in the receiver of run PG-6 when it was stored in water after welding (cooling also occurs due to aging of the heat generating nuclides). The presence of 6.5 psig pressure in the pot of run PG-4 is believed to be a false reading from a damaged gage. Leak testing of the receiver of run PG-5 revealed a leaking Conoseal joint which accounts for the 0 psig reading on the gage.

6.1.7 Leak Testing

Helium leak testing of receiver pots in cell was accomplished by spraying the pots externally with helium after the pots were evacuated. Pot leakage for the first 3 runs (the only pots measured) varied from 1.1×10^{-8} to 4.6×10^{-8} and averaged 2.8×10^{-8} atm, cc/sec.

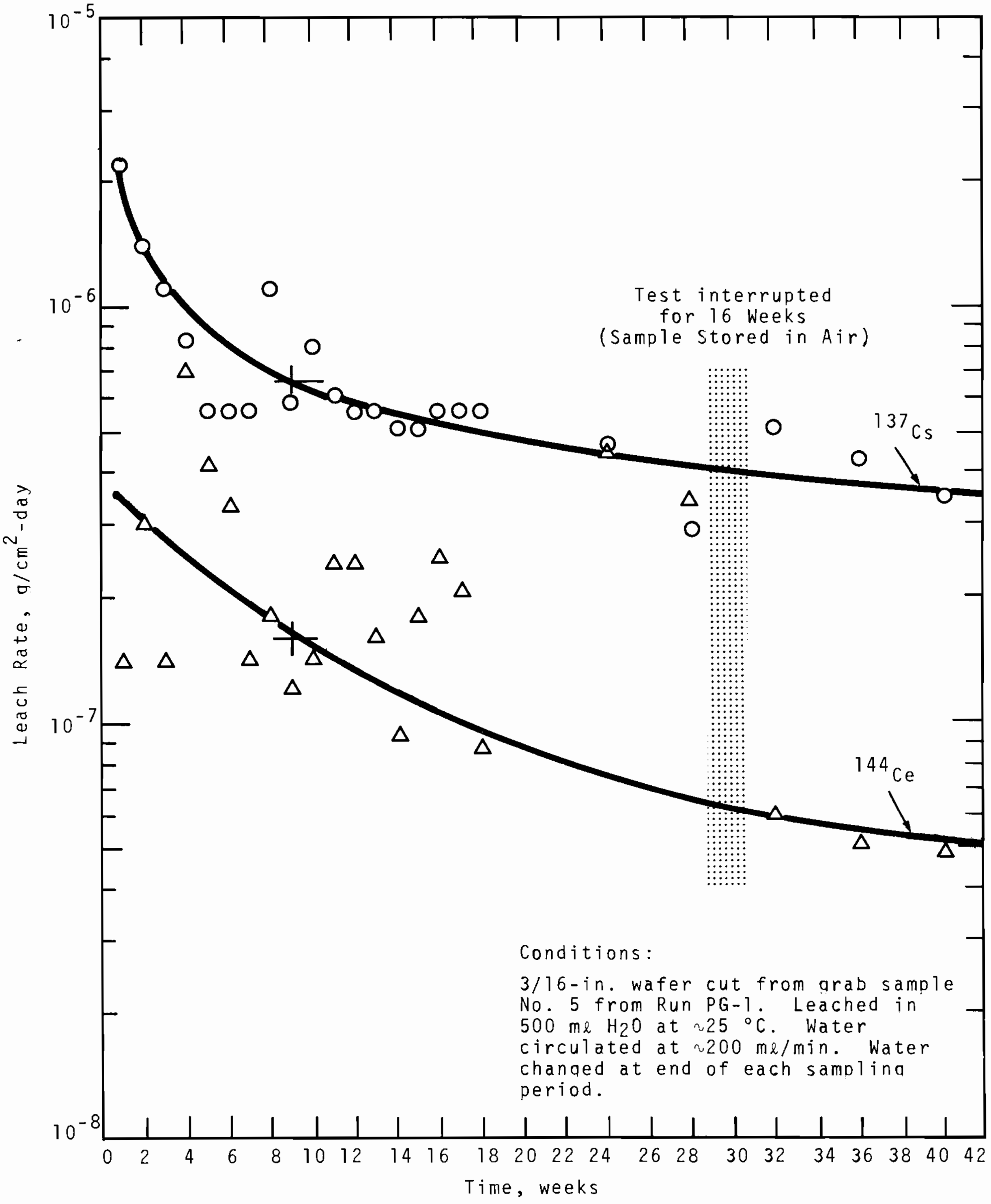


FIGURE 6.7. Leach Rates of Radioactive PW-2 Phosphate Glass

TABLE 6.1. *Receiver Pot Pressure Data*

Run No.	Time from Fill to Weld, days	Storage[a] Medium	Time from Weld to Pressure Reading, days	Storage[b] Medium	Pressure[c] Reading, psig	Pot Leakage, atm, cc/sec	Remarks
1	6	water	21	air	-14.7	1.1×10^{-8}	Pressure reading taken same day as leak check was made.
			165	air	-5.9		
			324	air	-9.8		
2	19	water	91	water	-14.7	2.4×10^{-8}	Leak check made on same day as welding.
3	5	water	62	air	-14.2	4.6×10^{-8}	Leak check made on same day as welding.
4	19	water	211	air	+6.5	-	Pressure reading was believed to be in error, due to a false reading of a damaged gage. No leak check was performed on receiver seal. Contents were not left under vacuum.
5	4	air	260	air	0	-	Conoseal joint leaked preventing seal leak check and preventing vacuum from being drawn in receiver.
6	90	water	67	water	-7.4	-	Receiver seal not leak checked after sealing. Vacuum due to cooling of receiver after immersion in water.
			96	water	-2.5		

---

a. Storage medium after filling and prior to welding.
b. Normal storage medium prior to and during pressure readings.
c. Receiver seal leak checked and contents left under vacuum except where noted.

A mass spectrometer and vacuum system on the nonradioactive side of the cell wall was connected through stainless steel tubing to the in-cell pot. A roughing pump was used to reduce system pressures to below 10 microns; a diffusion pump was used to further reduce the system pressure to less than 0.2 microns. Helium was sprayed in the regions to be tested for leaks and the detection of helium by the mass spectrometer indicated the extent of leaks.

6.1.8 Calorimetry

Heat generation in filled pots was measured in a calorimeter. The calorimeter used was a water-filled, insulated cylinder, equipped with a cooling coil. Cooling water flow rate and temperature rise under steady-state conditions provided a measure of the rate of evolution of heat from a pot immersed in the water. Operation of the calorimeter was quite satisfactory. The unit provided measurements precise to within 5% and comparable to feed data within an average of 10%.

6.1.9 Pot Corrosion

An ultrasonic wall thickness scanner was installed to measure corrosion of filled receiver pots. Reliable measurements have not yet been obtainable because of difficulty in maintaining proper alignment and contact between the receiver pot and the instrument.

6.2 POT HANDLING, CONTAMINATION CONTROL AND WELDING

Handling pots filled with phosphate glass proceeded with little difficulty. The handling system(1) provided for containment of the pot in a hood (which was vented to the cell through natural openings) during processing and until the pot was capped. The pot cap was placed on the pot before the hood was opened; the pot was then transferred to the welding station. This method of containment was designed to minimize the spread of contamination from an open pot. Experience with the handling and containment system led to two conclusions:

- Handling uncapped pots after filling did not cause a noticeable contamination problem in the cell. (However, the cell was badly contaminated from previous process leaks.)
- The press-in pot cap machined to accept a threaded pot plug successfully achieved simplicity in handling at reasonable pot fabrication costs.

Remote welding of the pot cap to the pot first required chucking the pot in the turntable and cleaning the pot lip with a damp swab. The pot cap was pressed in place and the plug then threaded into the center of the pot cap. The pot head runout* was checked by a dial indicator. The arc-head and torch were then positioned above the pot head. A weld test specimen was placed under the torch. Welding parameters were selected and set on the remote console, and a test weld was made to verify system operability. The torch was positioned over the weld joint at an angle of about 30 degrees to vertical, and the automatic weld cycle was started. Welding arc and weld puddle were continuously monitored through a spotting scope, and minor adjustments were made in torch position, as required, by operator control of the manipulator.

The pot cap and pot plug welds were inspected visually for cracks or other flaws. A helium leak check was then made using a mass spectrometer leak tester (as discussed previously).

Six phosphate glass pots [6 pot calcine pots(3) and 10 spray solidification pots(27)] have been welded remotely. A summary of the welding parameters for the phosphate glass pots is given in Table 6.2. The electrode diameter was

---

* Runout is the deviation from perfect form of a circle detected by full rotation of the part on a datum axis.

TABLE 6.2. Remote Pot Welding Experience

	Welding				
PG Run	Current, amps	Voltage, volts	Speed, in/min	Receiver Material[a]	Receiver Size,[b] in.
1	180	12	4.6	Mild Steel	12
2	170	12	↓	304L SS	8
3	180	12		Mild Steel	8
4	180	12		Mild Steel	8
5	180	12		Mild Steel	12
6	170	12		310 SS	8

---

a. All upper sections of pots and pot lids are constructed of 304L SS.

b. The pots have the same size opening and pot lids, about 8 inches in diameter.

1/8 inch. Argon was used at a rate of 20 scfh. Visual inspection has determined that all welds were of good quality. Experience with welding pots can be summarized as follows:

- The raised step weld joint gave good results. It is still recommended for remote welding of waste pots.
- Viewing of the weld was not one of the major problems in remote welding. A good quality lead-glass window and a spotting scope proved to be acceptable. However, if imperfect or radiation-damaged windows are used, periscopes would be preferred.
- Need for accurate chucking to avoid misalignment was eliminated or minimized by using a self-centering jig(1) mounted on top of the pot. The jig fastens to the pot and maintains positive joint and torch alignment.

7.0 PROJECTED FLOWSHEETS FOR PW-1 AND PW-2

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 the two generalized types of Purex acid wastes shown in Table 7.1 for initial demonstrations.

The initial phase of the program for WSEP demonstrations is 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. The resultant amounts of the more significant fission products are given in Table 7.2.

The heat generation rate by fission products in waste from one tonne of this fuel is presented in Figure 7.1. Both the initial heat generation rate levels of 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 an 8- and a 12-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,

TABLE 7.1. Compositions of PW-1 and PW-2

		Purex Waste-1 (PW-1)	Purex Waste-2 (PW-2)
H^+		3.6M	3.8M
Fe^{+++}		0.93	0.445
Cr^{+++}		0.012	0.024
Ni^{++}		0.005	0.010
Al^{+++}		0.001	0.001
Na^+		0.138	0.930
U^{+6}		0.010	0.010
Hg^{++}		<0.001	<0.001
$NO_3^- + NO_2^-$		6.5	5.37
$SO_4^=$		----	0.870
$PO_4^{\equiv}$		0.003	0.006
$SiO_3^=$		0.010	0.010
F^-		<0.001	<0.001
FP's(a) as M_{FP}^+ (b)		0.91	0.91
M_T^+ (c)		3.95	3.33
Volume		100 gal/tonne (378.5 liter/tonne)	100 gal/tonne (378.5 liter/tonne)
Heat Rate Density(d)	at 0.5 yr	22.7 W/liter	22.7 W/liter
	at 1 yr	12.2 W/liter	12.2 W/liter
	at 6 yr	2 W/liter	2 W/liter
Activity(e)	at 0.5 yr	4500 Ci/liter	4500 Ci/liter
	at 1 yr	2550 Ci/liter	2550 Ci/liter
	at 6 yr	580 Ci/liter	580 Ci/liter

---

a. See Table 7.2 for Fission Product (FP) distribution. In the summation of cation fission product equivalents, the elements Mo, Tc, Te have been considered as anions, and a valence of four has been assumed for Ru.

b. M_{FP}^+ is the summation of chemical equivalents of fission product cations.

c. M_T^+ is the summation of chemical equivalents of metallic cations including M_{FP}^+.

d. 20,000 MWd/tonne at 15 MW/tonne.

e. Includes ^{144}Ce daughter, ^{144}Pr.

TABLE 7.2. Fission Products from a Power Reactor Fuel Exposed to 20,000 MWd/tonne at 15 MW/tonne[a]

Element	Average Atomic Weight	Ci/tonne at 0.5 yr	g/tonne at 1 yr	Ci/tonne at 1 yr	g/tonne at 6 yr	Ci/tonne at 6 yr	At 6 yr, moles/tonne and moles/liter for 100 gal/tonne	
							moles/tonne	moles/liter
Rb	86	---	230	---	234	---	2.68	0.71×10^{-2}
Cs	134	1.3×10^{5}	1871	1.2×10^{5}	1755	6.7×10^{4}	13.10	3.45×10^{-2}
Sr	88	8.0×10^{4}	550	5.0×10^{4}	512	4.1×10^{4}	5.82	1.55×10^{-2}
Ba	138	---	908	---	1023	---	7.40	1.95×10^{-2}
Y	91	1.1×10^{5}	287	5.4×10^{4}	287	4.2×10^{4}	3.15	
La	139	---	766	---	766	---	5.50	
Ce	142	7.6×10^{5}[b]	1483	4.6×10^{5}[b]	1400	5.6×10^{3}[b]	9.85	
Pr	141	---	706	---	706	---	5.0	
Nd	148	---	2403	---	2475	---	16.70	11.85×10^{-2}
Pm	147	8.7×10^{4}	102	7.5×10^{4}	27	2.0×10^{4}	0.18	
Sm	147	---	463	---	537	---	3.65	
Eu	153	4.7×10^{3}	86	---	85	---	0.55	
Gd	156	---	26	---	28	---	0.18	
Zr	93	1.0×10^{5}	2266	1.5×10^{4}	2300	Neg	24.7	6.50×10^{-2}
Nb	95	2.0×10^{5}	Neg	3.0×10^{4}	Neg	Neg		
Mo	97	---	2135	---	2370	---	24.5	6.50×10^{-2}
Tc	99	---	523	---	523	---	5.3	1.40×10^{-2}
Ru	103	1.9×10^{5}	1286	1.2×10^{5}	1252	3.7×10^{3}	12.1	3.20×10^{-2}
Rh	102	2.3×10^{4}	285	---	285	---	2.8	0.74×10^{-2}
Pd	105	---	647	---	680	---	6.5	1.72×10^{-2}
Ag	109	---	33	---	33	---	0.3	0.08×10^{-2}
Cd	112	---	33	---	33	---	0.3	0.08×10^{-2}
Te	128	6.4×10^{3}	301	---	300	---	2.4	0.64×10^{-2}
Total Ci/tonne		1.7×10^{6}[c]		9.7×10^{5}[c]		1.9×10^{5}[c]		

---

a. Obtained from Computer Program Isogen - a Computer Code for Radioisotope Generation Calculations. Reference 28.

b. Includes ^{144}Ce daughter, ^{144}Pr.

c. Small contributors are not itemized but are included in total. Does not include trans-uranium and trans-plutonium elements.

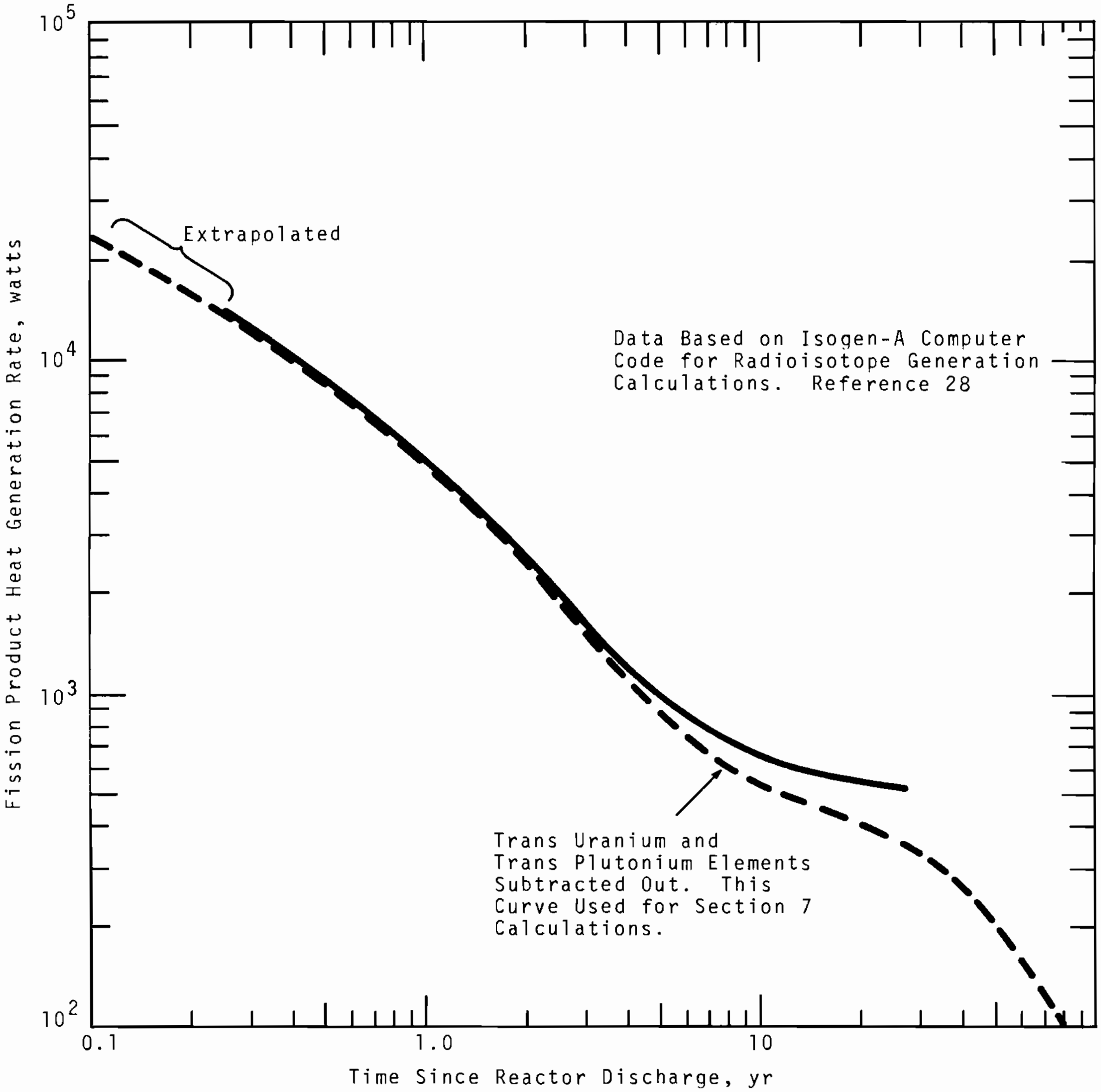
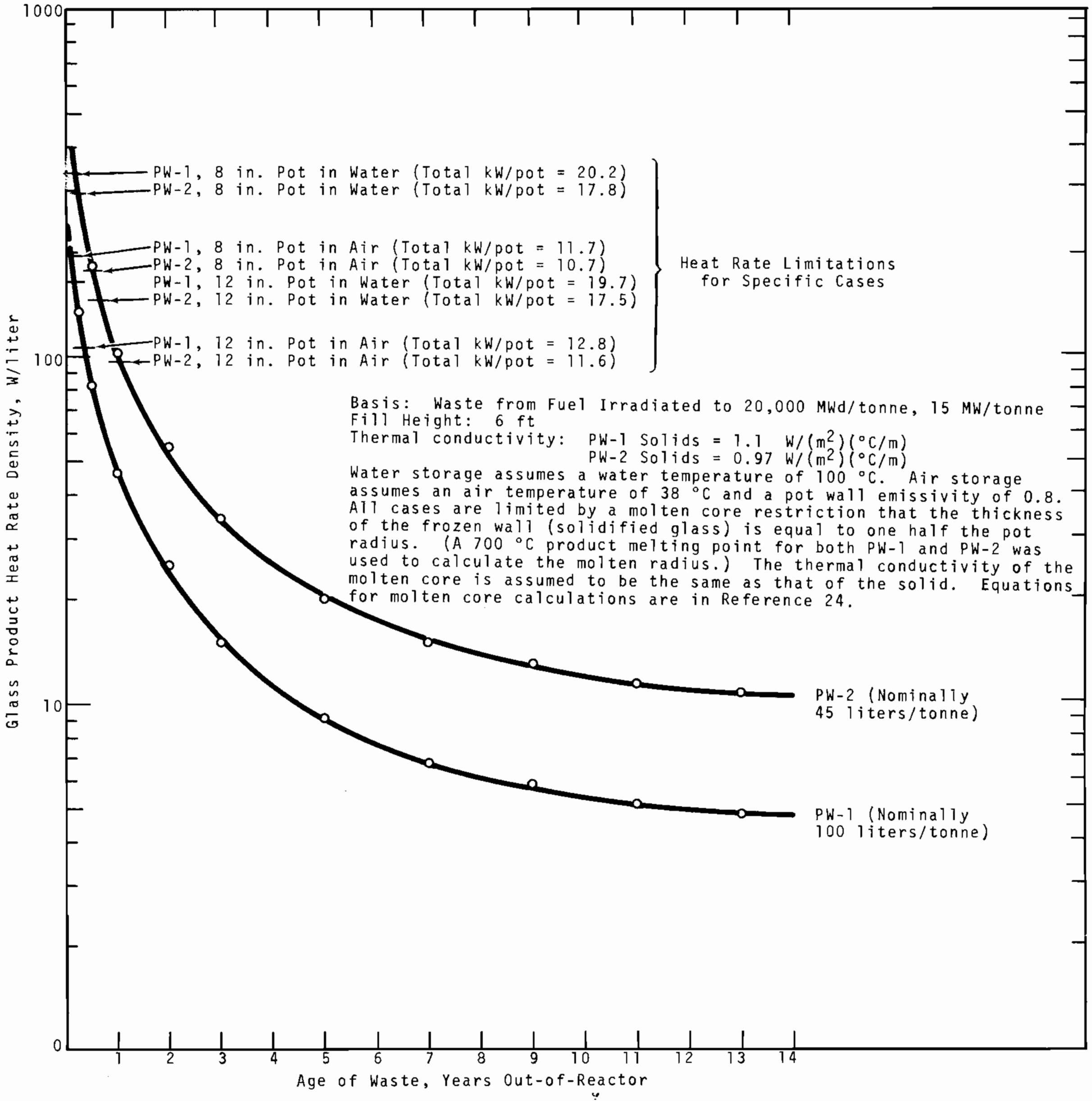


FIGURE 7.1. *Fission Product Heat Generation Rate with Time for One Tonne of Reactor Fuel Irradiated to 20,000 MWd/tonne at 15 MW/tonne.*

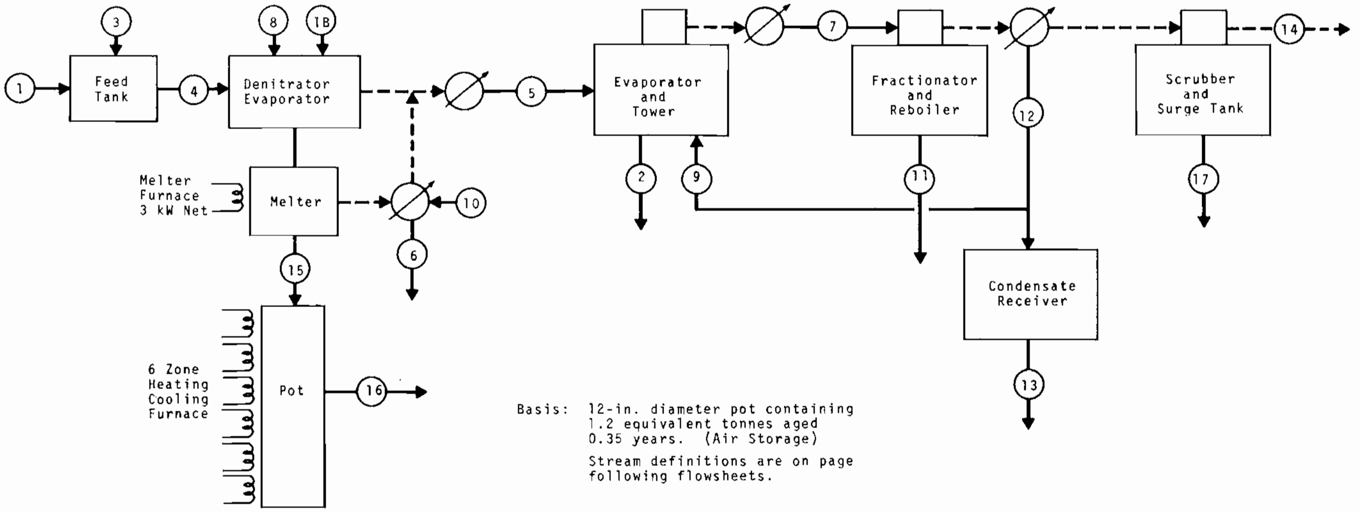


Basis: Waste from Fuel Irradiated to 20,000 MWd/tonne, 15 MW/tonne
Fill Height: 6 ft
Thermal conductivity: PW-1 Solids = 1.1 $W/(m^2)(°C/m)$
PW-2 Solids = 0.97 $W/(m^2)(°C/m)$
Water storage assumes a water temperature of 100 °C. Air storage assumes an air temperature of 38 °C and a pot wall emissivity 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-1 and PW-2 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 24.

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

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 (assuming K_e does not change considerably at higher temperatures). The aging before solidification of wastes depends on an economic choice. However, a proposed Federal Regulation(30) 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. Sufficient confidence in radioactive operation has been reached to specify most of the necessary details for flowsheets with both PW-1 and PW-2 wastes. Figure 7.3 is a Mode A flowsheet for PW-1 waste using a 12-inch diameter pot, and Figure 7.4 is a Mode A flowsheet for PW-2 using an 8-inch diameter pot. 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 heat rate density and maximum heat generation rate in a pot are, however, dependent on pot size. The two flowsheets presented are 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. For this condition, however, the out-of-reactor time approaches reactor discharge. The PW-2 waste is shown coming into the plant at a dilute 500 liters/tonne to minimize precipitation and plugging of lines by sodium rare earth sulfate solids.(3) However, after the phosphoric acid additive is added to the PW-2 waste, it can readily be handled at a concentration of 450 liters/tonne.

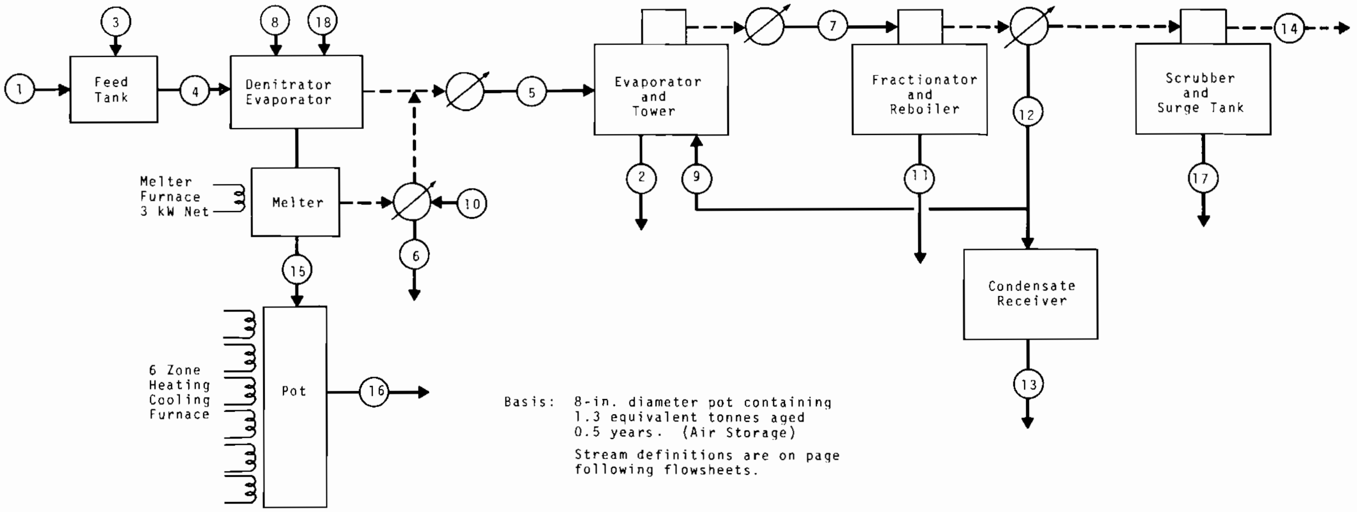


Basis: 12-in. diameter pot containing 1.2 equivalent tonnes aged 0.35 years. (Air Storage)

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	378	100	234	612	655	582	7000	136	6350	455	302	6734	343	7.6×10^5	100	100	-	136
Average Rate, liters/hr	Batch	Batch	Batch	6.7	7.2	6.4	76.9	1.5	70	5	Batch	74	Batch	8400	1.1	Batch	Batch	1.5
Gross Activity, Ci/tonne	2.3×10^6	3.2×10^4	-	2.3×10^6	3.2×10^4	4.2×10^3	193	-	-	-	193	-	0.56	$<5.9 \times 10^{-5}$	2.3×10^6	2.3×10^6	0.25	-
^{106}Ru, Ci/tonne	1.9×10^5	8.5×10^2	-	1.9×10^5	8.5×10^2	1.1×10^4	1.9×10^2	-	-	-	190	-	0.55	$<5.7 \times 10^{-5}$	1.7×10^5	1.7×10^5	0.25	-
^{90}Sr, Ci/tonne	4.8×10^4	9.6	-	4.8×10^4	9.6	9.6×10^1	0.07	-	-	-	0.07	-	1.6×10^{-4}	4.8×10^{-8}	4.8×10^4	4.8×10^4	3.8×10^{-5}	-
Ce-^{144}Pr, Ci/tonne	8.5×10^5	1.7×10^2	-	8.5×10^5	1.7×10^2	1.7×10^3	1.3	-	-	-	1.3	-	2.8×10^{-3}	8.5×10^{-7}	8.4×10^5	8.4×10^5	6.8×10^{-4}	-
Fission Product Heat Rate, W/tonne	1.1×10^4	9.8	-	1.1×10^4	9.8	126	1.9	-	∿0	-	1.9	∿0	∿0	∿0	1.07×10^4	1.07×10^4	∿0	-
Non-FP Oxides, kg/tonne	30.9	0.066	200	230.9	0.066	0.5	∿0	-	∿0	-	∿0	∿0	∿0	∿0	230.3	230.3	∿0	-
FP Oxides, kg/tonne	21.3	0.017	-	21.3	0.017	0.21	∿0	-	∿0	-	∿0	∿0	∿0	∿0	21.1	21.1	∿0	-
Total Oxides, kg/tonne	52.2	0.083	200	252.2	0.083	0.71	∿0	-	∿0	-	∿0	∿0	∿0	∿0	251.4	251.4	∿0	-
Nitrate, g-moles/tonne	2455	500	930	3385	3360	840	3500	816	127	-	3017	135	6.9	∿0	∿0	∿0	336	-

FIGURE 7.3. *Typical Flowsheet for Processing One Tonne of PW-1 Waste with Mode A Operation*



Basis: 8-in. diameter pot containing 1.3 equivalent tonnes aged 0.5 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	500	100	81	581	605	330	4630	75	4020	250	200	4425	405	4.2×10^5	45	45	-	75
Average Rate, liters/hr	Batch	Batch	Batch	11.6	12.1	6.6	92.5	1.5	80.4	5	Batch	88.5	Batch	8400	0.9	Batch	Batch	1.5
Gross Activity, Ci/tonne	1.7×10^6	1.2×10^3	-	1.7×10^6	1.2×10^3	5×10^3	144	-	-	-	144	-	3.4×10^{-1}	$<1.5 \times 10^{-5}$	1.7×10^6	1.7×10^6	1.3×10^{-1}	-
^{106}Ru, Ci/tonne	1.7×10^5	1.1×10^3	-	1.7×10^5	1.1×10^3	2×10^3	144	-	-	-	144	-	3.4×10^{-1}	$<1.2 \times 10^{-5}$	1.6×10^5	1.6×10^5	1.3×10^{-1}	-
^{90}Sr, Ci/tonne	4.8×10^4	3.8	-	4.8×10^4	3.8	9.6×10^1	0.015	-	-	-	0.015	-	9.6×10^{-5}	9.6×10^{-8}	4.8×10^4	4.8×10^4	1.9×10^{-4}	-
$Ce\text{-}^{144}Pr$, Ci/tonne	7.4×10^5	56	-	7.4×10^5	56	1.5×10^3	0.23	-	-	-	0.23	-	1.5×10^{-3}	1.5×10^{-6}	7.4×10^5	7.4×10^5	3.0×10^{-3}	-
Fission Product Heat Rate, W/tonne	8.6×10^3	10.6	-	8.6×10^3	10.6	46	1.4	-	∿0	-	1.4	∿0	∿0	∿0	8.5×10^3	8.5×10^3	∿0	-
Non-FP Oxides, kg/tonne	52.3	2.6	89.2	141.5	2.6	24.1	∿0	-	∿0	-	∿0	∿0	∿0	∿0	114.8	114.8	∿0	-
FP Oxides, kg/tonne	21.3	1.5×10^{-3}	-	21.3	1.5×10^{-3}	0.09	∿0	-	∿0	-	∿0	∿0	∿0	∿0	21.2	21.2	∿0	-
Total Oxides and Sulfates, kg/tonne	73.6	2.6	89.2	162.8	2.6	26.8	∿0	-	∿0	-	∿0	∿0	∿0	∿0	136.3	136.3	∿0	-
Nitrate, g-moles/tonne	2030	500	-	2030	2232	248	2315	450	80.4	-	2000	88.5	8.1	∿0	∿0	∿0	223	-

FIGURE 7.4. *Typical Flowsheet for Processing One Tonne of PW-2 Waste with Mode A Operation*

FLOW SHEET CODE FOR FIGURES 7.3 and 7.4

Stream Code Number

1. Incoming waste from processing 20,000 MWd/tonne at 15 MW/tonne power reactor fuel. (Also called "feed" to the solidifier.)

2. Evaporator bottoms. The bottoms must be recycled, either continuously or batchwise, to the feed or to another treatment process.

3. Nonradioactive chemical additives to the raw waste. Additives are phosphoric acid for PW-2 and sodium (sodium nitrate is used here) and phosphoric acid for PW-1.

4. Chemically adjusted feed to the denitrator. (See text regarding processing rates.)

5. Solidifier (primarily denitrator) condensate and noncondensibles. A total of 10% of the sulfate from the melter is assumed present in this stream. Totals of 70 and 90% of the total nitrate to the denitrator is assumed in this stream for PW-1 and PW-2, respectively.

6. Melter condensate. This is an intermediate level waste stream that contains most of the sulfate (90% is used here) when processing PW-2 waste. When sulfate free waste is processed, this stream can be routed to either the denitrator or the auxiliary evaporator for additional cleanup by evaporation.

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

Stream
Code
Number

8. Antifoam addition to the denitrator to suppress foam caused by foaming agents in the Purex wastes (6.75 g/ℓ).

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

10. Steam is sprayed into the melter condenser to dilute incoming vapors when sulfate is present in the waste, since the sulfate condensate is very corrosive when the nitrate concentration is low. The stream is also shown here for the sulfate free waste for dilution purposes. (A total of 5 liters/hr is used here.)

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 condensate.

13. Fractionator condensate; 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; 10% 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.)

Since the Purex reprocessing step requires the use of tri-butyl 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 2.5 liters/hr of combined melt and melter condensate. The BNL development melter has approximately twice this capacity. The increased capacity of the BNL melter results mainly from the higher BNL melter furnace temperature.

The primary control requirement for the auxiliaries is an evaporator overheads acidity of $0.5\underline{M}$ HNO_3 to minimize ruthenium volatilization. More continuous operating data should be obtained to better determine the degree of effect of overheads acidity on ruthenium volatility, since boilup flow rate requirements are inversely proportional to the overheads acidity.

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 20,000 MWd/tonne fuel, the radioactive fission product spectrum used did not represent that value. In order to project WSEP data to expected 20,000 MWd/tonne exposure, the same fractional distribution of radionuclides given in Table 9.4 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 Table 7.3. On this basis, approximately 200 curies of ruthenium, less than 1 curie of cerium-praseodymium-144 and less than 0.1 curie of strontium-90 are found in the fractionator bottoms per tonne of fuel processed. The gross $\beta + \gamma$ in the acid will range from 300 to 1500 μCi/mℓ. The higher ruthenium result for run PG-1 is not

TABLE 7.3. Calculated Curies in Fractionator Acid per Tonne of Fuel Irradiated to 20,000 MWd/tonne at 15 MW/tonne and Aged 0.5 Years[(a,b)]

Run	Mode	Cerium-Praseodymium-144	Strontium-90	Ruthenium (total)
1	A-B	---	---	1400
2	A	<0.1	<0.009	190
3	A	0.9	0.06	74
4	A	0.3	0.02	160
5	A-B	0.1	0.009	390
6	A	0.8	0.05	190

---

a. Calculated from radionuclide distribution fractions in run data in the Appendix, Table 9.4, with both cerium-praseodymium and strontium represented by the cerium-praseodymium values. These fractions are applied to the product of the tonnes processed and the selected Ci/tonne values in Table 7.2.

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<u>M</u> HNO_3/tonne of fuel processed.

typical and was probably due to inadequate agitation of the fractionator bottoms when the end of run sample was taken.

The nitric acid produced in the fractionator in WSEP was 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 containing approximately 200 curies of ruthenium per tonne of fuel could be recycled to the reprocessing plant for fuel dissolution or other reprocessing steps.

The ratio of the radionuclide concentration in the final condensate to 10CFR20 release limits was obtained by projecting run data as shown in Table 7.4. While strontium and cerium-praseodymium concentrations are approximately 1000 to 10,000 times the 10CFR20 release limits, ruthenium is the controlling constituent at approximately 100,000 times its limit. Another simple distillation of the condensate would, in general, bring all values, except possibly ruthenium, to below 10CFR20 limits. The bottoms from the redistillation step would be recycled to the high level waste evaporator.

TABLE 7.4. Projected Radionuclides in Condensate from the Acid Fractionator per Tonne of Feed Processed[a]

Nuclide	Feed Ci/tonne	10CFR20[b] Limit, μCi/mℓ	Projected Condensate,[c] μCi/mℓ	Ratio, Projected Condensate to 10CFR20 Limit
^{144}Ce-Pr	7.4×10^{5}	2×10^{-5}	4.7×10^{-3} to 60×10^{-3}	230 to 3000[d]
^{90}Sr	4.8×10^{4}	3×10^{-7}	3.2×10^{-6} to 40×10^{-6}	1100 to 13,000[d]
^{106}Ru	1.7×10^{5}	1×10^{-5}	3.7×10^{-1} to 8	37,000 to 800,000
Others	7.4×10^{5}	9×10^{-6}[e]	5×10^{-3} to 60×10^{-3}	550 to 6700

---

a. Values are calculated for 1 tonne of 0.5-year-old, 20,000 MWd/tonne fuel irradiated at 15 MW/tonne.

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

c. Values are based upon radionuclide distribution fractions from runs PG-2 through PG-6 and as they are listed in the Appendix, Table 9.4, with all nuclides except ruthenium represented by the cerium (nonvolatile) values. A condensate volume of 300 liters is used but actual volumes depend on feed type, etc. Condensate volumes will actually vary from 200 to 400 liters/tonne.

d. Larger values are from PG-5, a mode B run.

e. The limiting value (that for ^{134}Cs) is applied to all remaining nuclides.

8.0 FUTURE WORK

In order to fulfill the objectives of the WSEP technical program for the phosphate glass process, additional information is needed with respect to chemical process requirements and product characterization.

8.1 WASTE TYPES

To complete requirements that would adequately demonstrate solidification of PW-1 or PW-2 type wastes, thermal maximum should be demonstrated for one of these wastes. Such a demonstration would also provide a receiver full of phosphate glass with a molten core for evaluation.

The solidification of two other waste types should also be demonstrated to ascertain tolerable limits of fission products and heat for forthcoming nuclear power cycles. These wastes are currently scheduled for demonstration. One of the wastes is typical of a low-salt, high-fission product waste from thermal reactor fuel (exposed to 45,000 MWd/tonne at 15 MW/tonne) produced by "clean" Purex reprocessing (i.e., low iron, low sodium, and no sulfate). The other waste is from reprocessing spent core fuels from Liquid Metal Fast Breeder Reactors. Optimum chemical flowsheet requirements for these wastes should also be obtained.

8.2 EQUIPMENT AND PROCESS REQUIREMENTS

Frequent plugging of transfer lines and liquid level and specific gravity dip tubes associated with the denitrator-evaporator indicates a need for a more reliable means of transferring denitrator-evaporator product. Samples of the denitrator-evaporator product should be provided to confirm steady state characteristics as a function of boiling points for processing plant wastes.

Development of methods for reducing the reliance on visual access for monitoring melter operation would be desirable. The governing mechanism which affects melter capacity must be established to provide information for scale-up. The apparently nonexistent effects of the addition of antifoam agents on the platinum melter over an extended period of time should be confirmed.

8.3 AUXILIARIES

Effluent cleanup efficiency should be determined with Mode B operation with waste containing high concentrations of fission products.

If reasonably possible, direct quantitative measurement of the amount of ruthenium in the final phosphate glass product should be sought.

Although effluent acid and condensate contained acceptably low levels of radioactivity, methods to improve their cleanup through the evaporator and acid fractionator are desirable for demonstration. Additional performance data on de-entrainment and filters are desirable to determine if a caustic scrubber is needed. Data from gas sampling of the effluent stream at various points in the auxiliary system would be desirable to define better the characteristics of the radioactivity in the effluents. In addition, sampling the final process effluent gas stream is desirable to determine the radionuclide content in the process stream without dilution and without contributions from other streams.

Separation and decontamination of the sulfate component of the melter condensate of a PW-2 waste should be demonstrated in engineering scale equipment.

8.4 FILLED POT PERFORMANCE

Observations so far are confirming the expectations that initial and short-term effects would be small in pots filled by the phosphate glass solidification process. Since the "oldest" pot is less than 2 years old, very little can be concluded about long-term effects. Future work in this area is outlined in the product evaluation program.(21)

Under the product evaluation program, filled pots will be placed in controlled environments and will be examined at intervals to determine the effects of age, temperature, feed type, pot material, and radioactivity on product stability and pot wall corrosion. Both destructive and nondestructive tests will be made. Some pots will be stored at elevated temperatures corresponding to those which would be experienced in pots containing significantly higher levels of heat-producing radionuclides. Others will be stored at lower temperatures for use as control references.

An assessment of the magnitude of hazards associated with the rupture of a pot in air or water is desired to assure a properly balanced emphasis on safeguards measurements.

9.0 APPENDIX

9.1 RUN DESCRIPTION

WSEP radioactive runs PG-1 through PG-6 are briefly described. General information for all runs on feed compositions, operating parameters and results, material balances, fission product distribution, and decontamination factors are shown in Tables 9.1 to 9.5, respectively, at the end of this section. A schematic of equipment arrangements is shown in Figures 9.1a and 9.1b. Solution parameters versus run time for the six phosphate glass runs are shown in Figures 9.2 to 9.7. (Figures 9.1 through 9.7 precede the tables at the end of this section.)

Run PG-1

The first engineering scale conversion of highly radioactive aqueous wastes to glass by the phosphate glass solidification process was successfully completed in WSEP during November 1967. In 92 hours of operating time, a total of 1103 liters(a) of adjusted, sulfate-containing, PW-2 waste (Table 9.1) was reduced to 92 liters(b) of phosphate glass containing 349,000 curies of radioactivity including 13,000 curies of radioruthenium with an internal heat rate density of 17 W/liter. This demonstration was equivalent to solidifying wastes generated from the processing of 2.2 tonnes of 7.5 year-old, 20,000 MWd/tonne power reactor fuel at 15 MW/tonne. The 274 kilograms(c) of glass product, containing a heat generation rate of 1600 watts from radionuclide decay, were collected in a 12-inch diameter, 8-foot long mild steel receiver.

---

a. 709 liters at a concentration of 480 liters/tonne.
   394 liters at a concentration of 580 liters/tonne.
b. Does not include startup additive.
c. In-cell weight including 17.2 kg startup additive.

Run PG-1 was conducted in two parts because failure of a feed pump necessitated a shutdown of the run which had been in progress for 61.4 hours. During the first part of the run, a mode A auxiliary equipment arrangement was used, shown in Figure 9.1a. The mode B arrangement, shown in Figure 9.1b, was used in the second part of the run. During this period, 1140 liters of Purex waste, containing 600,000 curies of radioactivity were prepared for subsequent use in Run PG-2. During the period of mode B operation, frequent dip tube plugging occurred in the auxiliary evaporator. This plugging was caused by solids accumulation in the evaporator bottom.

In the first part of the run, 964 liters of PW-2 feed (at 480 liters/tonne) were fed to the denitrator-evaporator at an average feed rate of 15.7 liters/hr. In the second part of the run, 431 liters of diluted feed, (at 580 liters/tonne) were introduced to the denitrator-evaporator at an average feed rate of 13.9 liters/hr. During the interruption of the run, nitric acid was added to the denitrator-evaporator to remove most of the concentrate. The remaining condensate and acid flushes of the equipment were combined with remaining feed, thus resulting in the more dilute feed that was used in the second part of the run.

As expected from laboratory tests, aluminum was successfully substituted for 22 and 54 mole percent of the nominal iron concentration in Batch 1 and Batch 2, respectively, as shown in Table 9.1.

A total of 438,000 curies of radioactivity, which included 19,700 curies of radioruthenium, was fed to the denitrator-evaporator. Feed rates to the denitrator-evaporator during steady-state operation averaged 14.6 and 13.0 liters/hr while the liquid temperature was maintained at an average of 137 °C and 138 °C for Parts 1 and 2, respectively. Startup of the evaporator required 9.0 hours in Part 1 and 5.0 hours in

Part 2. Steady state operation was 52.4 and 26.0 hours in Parts 1 and 2, respectively. The feed was concentrated by factors of 4.5 and 6.0, respectively, in Parts 1 and 2 which are concentration factors of 3.5 and 4.7, respectively, based upon the waste at a concentration of 378 liters/tonne. Denitrator-evaporator solution parameters such as liquid and vapor temperatures, volume, and specific gravity versus run time are shown in Figure 9.2.

Foaming occurred in the denitrator-evaporator during startup when the boiling temperature of the concentrate was between 122 and 135 °C. Indications of foaming were above normal vapor temperatures (113-127 °C) and below normal specific gravity readings (1.52-1.67) for a concentrate within the boiling point temperature interval (122-135 °C). Foaming during this period was satisfactorily controlled by reducing feed rates to between 5 and 10 liters/hr. Later, severe foaming occurred in the denitrator-evaporator for approximately 4 hours between the 18th and 22nd hour of the denitrator-evaporator feeding period when concentrate equivalent to about 50 liters of feed overflowed to the melter condensate tank (TK-117) via the seal pot. Although the foaming was aggravated by an increased feed rate which approached 32 liters/hr at one point, the primary cause, as subsequently established in other runs, was the accumulation of partially degraded tri-butyl phosphate present in the Purex waste stock. The overflow accounted for approximately 15% of the total feed to the melter condensate tank and 13% of the total feed to denitrator-evaporator at this time. Mild foaming occurred throughout the remainder of the run because of the foaming agent, and was responsible for a continuous overflow of approximately 3% of the total denitrator feed. Liquid level detection by means of the specific gravity and weight factor tubes was adequate.

The airlifting of concentrated feed from the denitrator-evaporator to the melter through the airlift pot, which was maintained at 117 °C and 122 °C during Part 1 and Part 2, respectively, proceeded without difficulty during most of the run. Cyclic flows of concentrate to the melter provided for periods of smooth operation, but difficulty was encountered in re-establishing cyclic patterns once they were interrupted. Fluctuating denitrator-evaporator liquid levels, foam, periodic nitric acid additions to the denitrator-evaporator and venting of the airlift pot through the melter feed line, combined with the natural difficulty of trying to meter a high temperature viscous slurry at 3 liters/hr were responsible for the inability to maintain desired, stable flow rates.

Melter operation proceeded smoothly throughout the run except during short periods of foaming which followed excessive surges of feed to the melter. At startup, a charge of 17 kilograms of nonradioactive PW-2 phosphate glass product was introduced into the melter to provide a seal in the overflow weir. This was done as a precaution in the first 2 runs to permit better control of process vacuum. Smooth, cyclic drainage of melt occurred from the unheated weir tube which was maintained at 750 °C by the melt. The weir heater was inoperable. The average operating liquid level of the melt was approximately 6 inches. Liquid level control in the melter was dependent on both visibility into the melter and interpretation of thermocouple readings since actual melt levels did not always correspond directly to those indicated by control thermocouple readings. On several occasions, the thermocouple used to control the feed rate to the melter gave high readings (approximately 900 °C) when the melter was very dark (viz. less than 700 °C). The reason was that the melt level had increased above the control thermocouple which became shielded from the incoming concentrated feed (approximately 100 °C) at the melt surface. At the end of the run, the melter was completely emptied through the freeze valve by raising the temperature of the air-cooled freeze valve from a normal, steady-state operating temperature of 450 °C to 900 °C by turning off the cooling air and turning on the heater. This was done at the end of each run to minimize the potential for stretching the melter due to differences in thermal expansion between the glass and platinum. The final volume of melt (approximately 5 liters) was held in the melter a minimum of 30 minutes after feed was stopped and after flushing was discontinued to assure glass formation. This procedure was also used at the end of each run and deviations occurred only in the length of time the melt was held in the melter. The temperature of the melt averaged 1075 °C and 935 °C at the bottom and at the top of the melter, respectively, while the furnace temperature was 1230 °C. Average glass production rates were 29.1 and 21.0 liters/day in Parts 1 and 2, respectively.

The melter receiver pot, held at 570 °C on the wall in a furnace maintained at 590 °C, filled uniformly with radioactive glass with no signs of melt spattering or stalagmite formation.

The solidified product, which had a melting point of 825 °C and an estimated slump point of 550 °C, was a homogeneous, dark green glass with a bulk density of 2.7 kg/liter. The 1600 watt internal heat generation rate in the glass was sufficient to produce a centerline temperature of 316 °C and a centerline-to-wall ΔT of 89 °C with the receiver in the furnace with no cooling air. A centerline temperature of 140 °C and a centerline-to-wall ΔT of 108 °C was recorded with the receiver in water. The effective thermal conductivity of the glass was calculated to be 1.02 W/(m^2)(°C/m) [0.59 Btu/(hr)(ft^2)(°F/ft)] in the furnace and 0.69 W/(m^2)(°C/m) [0.40 Btu/(hr)(ft^2)(°F/ft)] in water. The unit volume of glass was 42.0 liters/tonne of equivalent fuel. The volume reduction factor from waste to glass was 8.8 and from adjusted feed to glass, 12.0. The receiver gross radiation reading at 6 inches was 9500 R/hr.

Several attempts to control the tube bundle steam rate, the denitrator feed rate, and the melter feed rate automatically during parts of the run did not prove satisfactory, and manual control became necessary to maintain satisfactory operation. Operating parameters of the denitrator-evaporator, airlift pot, melter, receiver, and auxiliary process equipment for all runs are shown in Table 9.2.

Radioactivity distributions in the melter condensate Tank-117, auxiliary evaporator Tank-113, fractionator Tank-115, and fractionator condensate receiver Tank-116, are shown in Table 9.4. The results were not typical because the samples taken to provide the information were either nonrepresentative because of incomplete solution agitation and sample recirculation, or contaminated because samples were exposed to entrained radioactivity in the cell. In later runs it was found that representative startup and shutdown samples of the auxiliary evaporator and fractionator could only be obtained with the tanks at boiling. A material balance for all PG runs is shown in Table 9.3.

Run PG-2

The second successful phosphate glass solidification demonstration run was completed during December 1967. In run PG-2, 520 liters of adjusted PW-2 waste (at 586 liters/tonne) equivalent to that generated from the processing of 0.89 tonnes of 2.5 year-old, 20,000 MWd/tonne power reactor fuel, were converted to 34.7 liters of glass weighing 102 kilograms. An 8-inch diameter, 8-foot long, 304L stainless steel receiver was used to receive the glass which contained a total internal heat generation rate of 1700 watts and an internal heat rate density of 49 W/liter.

The denitrator-evaporator was fed 873 liters of PW-2 feed containing 670,000 curies of radioactivity, including 33,000 curies of radioruthenium, in 49 hours of mode A operation at an average feed rate of 18 liters/hr. The feed rate during steady-state operation averaged 14 liters/hr. The nominal iron concentration was replaced by 54 mole% aluminum which produced no noticeable change in the expected processing characteristics. A concentration of the feed by a factor of 5 was realized in the denitrator-evaporator, which was equivalent to a concentration of 3.2 for the nominal waste. Startup time required 10 hours, and steady-state operation was 32 hours.

Again, as in run PG-1, modest foaming in the denitrator-evaporator occurred throughout this run, causing a continuous overflow of concentrate to the melter condensate tank via the denitrator seal pot. An excessive feed rate, surpassing 40 liters/hr, again contributed to severe foaming for 10 hours during the last part of the run. Approximately 27% of the total feed introduced into the denitrator-evaporator overflowed to the melter condensate tank due to the foaming. Denitrator-evaporator solution parameters versus run time are shown in Figure 9.3. No problems were encountered in airlifting concentrated feed to the melter through the manually controlled airlift pot held at 114 °C, when the liquid level in the denitrator-evaporator was maintained above 26 inches. Liquid levels below 26 inches hindered smooth air lift operation. Internal heat rate density in the feed was 3.9 W/liter which increased to 20 W/liter in the denitrator-evaporator after being concentrated. There were no noticeable effects on the performance of the denitrator-evaporator due to the increased heat rate of the feed. However, because increased heat rate of the feed required a greater quantity of radioactive waste, the concentration of foam-inducing organic, dibutyl phosphate, was also increased. The increased accumulation of foaming agent produced increased foaming in the denitrator-evaporator in this run.

Melter operation proceeded smoothly as in run PG-1. A 16 kilogram charge of nonradioactive glass to seal the melter weir was again used during startup. The melt satisfactorily overflowed from the weir tube which was sustained at 740 °C by the melt. The air-cooled freeze valve temperature was raised to 700 °C to empty the melter at the end of the run. The melter furnace temperature during the run was 1230 °C while the internal melt temperatures at the bottom and at the top of the melter averaged 1055 °C and 825 °C, respectively.

During the run a test was made to determine if the capacity of the system could be increased by sparging the melter with nitrogen. At a sparge rate of 0.6 scfh the melter internal temperature increased by approximately 20 °C, indicating a slight increase in melt circulation. However, no increase in the feed rate to the melter or denitrator-evaporator was achieved during this period. The average glass production rate for this run was 14.9 liters/day, which is lower than the previous run PG-1. This reduced rate is due to the reduced feed rate to the melter caused by the increased foamover of concentrated feed to the melter condensate tank.

Uniform filling of the heated melter receiver with radioactive glass was accomplished during the run at normal melt flow rates (1 liter/hr) from the weir, and also at fast melt flow rates (approximately 1 liter/min) encountered during batch dumping of the melter through the freeze valve. Heating the melt receiver at 580 °C maintained the wall temperature at 535 to 575 °C. The solidified product had an initial melt formation temperature of 800 °C (which was lower than that in run PG-1) and an estimated slump point temperature of 650 °C. The measured density was 2.85 kg/liter, or essentially the same as in run PG-1. The 1700 watt internal heat generation rate in the glass was sufficient to produce a centerline temperature of 355 °C and a steady-state centerline-to-wall ΔT of 135 °C with the receiver in the cooled furnace. The effective thermal conductivity of the glass under these circumstances was calculated to be 0.94 $W/(m^2)(°C/m)$ [0.54 $Btu/(hr)(ft^2)(°F/ft)$], slightly lower than in run PG-1. A maximum radiation reading of 48,000 R/hr was recorded at 6 inches from the wall of the receiver. The volume reduction factor from waste to glass was 9.1, and the unit volume of the glass was 40 liters/tonne.

No difficulties were encountered during Mode A operation of the WSEP auxiliary evaporator Tank-113 with the exception of a 1.5 hour period in the first 10 hours of operating run time in which the overhead acidity exceeded 0.7$\underline{M}$. The high acid condition was corrected by the increased recycle of strip water from the fractionator. The acidity was thereby maintained at an average of 0.35$\underline{M}$ throughout the remainder of the run.

Data indicating fission product distribution during normal running conditions were again difficult to obtain because of continuous mild foaming during the run and severe foaming at the end of the run. Contamination of samples from WSEP evaporator Tank-113 due to residual activity from the previous run also complicated the evaluation. The high percentage of ruthenium found in the melter condensate receiver (41% as shown in Table 9.4) does not reflect the true extent of ruthenium volatilization and entrainment, since denitrator-evaporator overflow combines with melter condensate. The 9% value determined after 40 hours of operation, but before the period of severe foaming, does coincide more closely with values obtained during cold runs, although it too is slightly inflated because of the mild foaming constantly present throughout the run. Approximately 0.1% of the total nonvolatiles and 0.9% of the total ruthenium in the feed to the denitrator-evaporator accumulated in the WSEP evaporator Tank-113 throughout the entire run. About 0.1% of the total ruthenium in the feed to the denitrator-evaporator was collected in the fractionator Tank-115 and of this amount, approximately 36% accumulated in the first 10 hours of the run when a high overhead vapor acidity of 1<u>M</u> was recorded in the WSEP auxiliary evaporator Tank-113.

Run PG-3

In January 1967, the third phosphate glass solidification run was successfully completed in WSEP after 318 liters of PW-2 feed (at 458 liters/tonne) were converted to 35 liters of phosphate glass containing 604,000 curies of radioactivity, including 10,200 curies of radioruthenium. Nuclear wastes, equivalent to those generated in the processing of 0.7 tonnes of 1 year-old, 20,000 MWd/tonne power reactor fuel were solidified to 98 kilograms of phosphate glass containing a heat generation rate of 3300 watts in an 8-inch diameter, 8-foot long, mild steel receiver. Internal heat rate density of the glass measured 95 W/liter, an increase of 46 W/liter over PG-2.

In 63 hours of mode A operation, 16 hours of which were at steady-state operation, 697 liters of adjusted PW-2 waste were fed to the denitrator-evaporator at an average rate of 11 liters/hr. Uncontrolled foaming of the concentrated feed in the denitrator-evaporator which occurred over a period of 34 hours during the run was responsible for the overflow of 245 liters of equivalent feed to the melter condensate receiver. Attempts were made to eliminate the foaming problem by introducing new operating techniques. One technique used during the run was circulation of cooling water instead of steam in the denitrator-evaporator jacket to cool and collapse the foam at the walls. Foam losses were reduced during application of this technique, but were not completely eliminated. Another technique used to attempt to control foam was increasing the agitator speed. However, no beneficial effects resulted. Spray additions of nitric acid to the top of the denitrator-evaporator were also made and momentary suppression of foam was noted by an increase in the specific gravity reading and a lowering of the vapor thermocouple reading. This technique suggested moving the point of feed entry from the bottom of the denitrator-evaporator to the top for the next run. Laboratory studies, described in Section 7, were also initiated and identified the cause of foaming and aided in the selection of a suitable antifoam agent. The feed (at 458 liters/tonne) was concentrated by a factor of 4.0 in the denitrator-evaporator. Startup time required 13 hours.

Difficulty was encountered in maintaining a satisfactory water seal in the overflow pot because of the continuous foam-over of concentrate from the denitrator-evaporator. These temporary losses of a seal caused the denitrator-evaporator vapors to follow the foam into the melter condensate receiver. The reduced amount of denitrator-evaporator process off-gases in the auxiliary evaporator and fractionator, coupled with rerouting of concentrate because of foaming, prevented truly meaningful determinations of ruthenium and fission product volatilization and entrainment from the process equipment. In addition, the effectiveness of adding sugar to WSEP auxiliary evaporator Tank-113 for this run could not be determined because of the significant reduction of nitric acid in the auxiliary system.

Stable flow rates of concentrate from the denitrator-evaporator to the melter through the airlift pot were difficult to maintain because of the variations of operating conditions tested in attempts to control the excessive foam. The frequent nitric acid additions caused the liquid level in the denitrator-evaporator to fluctuate by 5 inches which contributed directly to unstable airlift pot operation.

The startup procedure of the melter was changed during run PG-3. No initial sealing of the melter overflow weir with cold phosphate glass was provided for. Instead, the melter vacuum was decreased to 3 inches of water from 6 inches of water to minimize back-sparging of air through the unsealed weir while concentrate was delivered to the melter. When molten glass was observed dripping into the receiver, the vacuum was returned to 6 inches of water. During most of the run, a layer of foam, 1/2 to 2 inches thick, was present on the surface of the melt except for a circular area, 2 to 4 inches in diameter, in the center of the pool where concentrate was deposited. The thicker layers of foam developed after surges of concentrate entered the melter during periods of unstable airlift operation.

Sparging of the melter with nitrogen gas through 3 available sparger dip tubes was again initiated to determine the effect on melter capacity. During 6 hours of sparging at 0.5 scfh, no detectable effect on capacity was noted. The average glass production rate was 13 liters/day, which was much lower than in runs PG-1 and PG-2. Overflow of feed to the melter condensate receiver caused by foaming was directly responsible for the low glass production rate.

The melter was deliberately drained twice through the freeze valve during the run to minimize growth of a stalagmite in the top of the 300 °C receiver. After each drain, the melter freeze valve was resealed by air-cooling. The discharge of melt through the overflow weir was also re-established after each drain through the freeze valve. During the final drain at the end of the run, the melter overflow weir was deliberately back-sparged to clear it of melt by increasing the melter vacuum. The freeze valve tube was again resealed by cooling, in preparation for the next run. The melter furnace was maintained at 1230 °C while internal melt temperatures ranged from 850 °C at the top of the melt to 1100 °C at the bottom.

Attempts to fill the receiver while maintaining the wall temperature at 300 °C led to persistent stalagmite formation in the top of the receiver as viewed in the sample chamber. Efforts to dislodge stalagmites by increasing receiver wall temperatures to as high as 750 °C were unsuccessful, since the major portion of the stalagmite was above the heated portion of the receiver. Mechanical shattering knocked down the stalagmite, but never completely succeeded in dislodging the base of the stalagmite from its anchorage. Increased pot furnace temperatures reduced the growth rate of stalagmites during the last part of the run. Quick drains of the melter through the freeze valve also did not prevent stalagmite formation.

Following the run, visual observation of the inside of the receiver revealed the presence of a 1/2-inch diameter, 30-inch long stalagmite anchored to a level indicator tab located in zone number 2 of the receiver (second zone from top). Uneven filling of the receiver was also noted at this time. Since no stalagmite problems were encountered in receivers with wall temperatures maintained at 580 °C in runs PG-1 and PG-2, low receiver wall temperatures were considered to be responsible for stalagmite formations in run PG-3. The melting point of the glass product was 850 °C, higher than in both PG-1 and PG-2, and the estimated slump point was 650 °C.

The 3300 watts of internal heat generation rate contained in the 34.5 liters of glass product was sufficient to produce a centerline temperature of 655 °C and a centerline-to-wall ΔT of 255 °C with the pot located in the cool furnace. An effective thermal conductivity of 0.98 W/(m^2)(°C/m) [0.57 Btu/(hr)(ft^2)(°F/ft)] was calculated for the product and was lower than that calculated in run PG-1, but higher than in run PG-2. The volume reduction factor from waste to glass was 7.5, which is lower than in runs PG-1 and PG-2, and the unit volume of the glass product was 50.7 liters/tonne. The presence of voids in the receiver due to stalagmite formation is the reason for the high unit volume recorded for the product in this run. A radiation profile of the receiver in addition to a sketch of the contents of the receiver is shown in Figure 9.8. The uneven filling of the receiver due to stalagmite formation accounts for the uneven radiation profile. The maximum receiver radiation reading at a distance of 6 inches was 41,000 R/hr.

The feed used in run PG-3 differed from the nominal PW-2 feed in that 39% of the iron was replaced by aluminum, the ruthenium concentration was doubled to 0.0064$\underline{M}$, and the uranium concentration was 70% higher than the nominal 0.01$\underline{M}$. The feed contained a suspended solids content of 50% by volume and again no operating difficulty from these flocculent solids was apparent.

The distribution of radioactivity for the auxiliary equipment was not typical because of the foaming which detoured part of the process vapors to the melter condensate Tank-117. Part of the radioactivity (shown in Table 9.4) found downstream of the auxiliary evaporator was originally in the evaporator bottoms and did not come from the solidifier. Feed waste is routinely concentrated in the auxiliary evaporator before each run and retains an appreciable amount of activity (about 10,000 curies) at startup even after considerable flushing.

Run PG-4

In run PG-4, conducted in February and March 1968, wastes equivalent to those generated in the processing of 1.3 tonnes of 1.6-year-old 20,000 MWd/tonne power reactor fuel were successfully converted to 213 kilograms (73 liters) of phosphate glass with an internal heat rate density of 57 W/liter in an 8-inch diameter mild steel receiver. The 4200 watt internal heat generation rate in the glass was sufficient to produce a centerline temperature of 510 °C and a centerline-to-wall ΔT of 175 °C with the receiver in an unheated furnace with no cooling air. An effective thermal conductivity of the glass was calculated to be 0.94 W/(m^2)(°C/m) [or 0.54 Btu/(hr)(ft^2)(°F/ft)], which was lower than those calculated for runs PG-1 and PG-3 and the same as in run PG-2.

The denitrator was fed 725 liters of adjusted PW-2 waste (at 540 liters/tonne) in 77 hours at an average feed rate of 9.4 liters/hr. The feed, containing 1,200,000 curies of radioactivity including 34,000 curies of radioruthenium, was concentrated in the denitrator-evaporator by a factor of 3.1, which represents a concentration factor of 2.2 from PW-2 waste at a concentration of 378 liters/tonne. Startup of the denitrator-evaporator required 12 hours, thereby leaving 65 hours of steady-state operation. The feed rate during this period was 7.5 liters/hr. Once again aluminum was substituted for 43 mole % of the nominal iron concentration. Because of the excessive rare earth content in the feed stock solution, the rare earth content was greater by a factor of 4.75 in this feed over the nominal 0.12$\underline{M}$. The nominal sodium concentration was increased by a factor of 1.3 to reduce the temperature of melt formation by the 50 °C increase caused by the increased rare earth content. The phosphoric acid concentration was increased to 4.5M to maintain a final M/P of 1.0. The amount of suspended solids was 20% by volume in this feed.

Although foaming was encountered in the denitrator-evaporator as in previous runs, it was successfully held to nondetectable levels for the first time by continuously adding an antifoam agent. Dow Corning Antifoam B was added at a rate of approximately 100 ppm/hr (3.9 liters of 0.22 wt% solution/hr). Changing the feed entry point from near the bottom of the denitrator to one above the liquid level at the top definitely suppressed the foam for the first 13 hours, but it did not reduce foaming to acceptable levels at steady-state conditions. Prior to use of the antifoam agent, overfeeding of concentrate to the melter occurred because foaming caused an increase in the concentrate level. Attempts to prevent the overfeeding by gradually shutting off feed to the denitrator-evaporator were not successful and only served to intensify the foam and overfeeding since the top entry of the feed had been suppressing the foam. The overfeeding resulted in a temporary overfilling of the melter and probably caused a restriction in the melter vent line 48 hours later. Following the run, the restriction was successfully removed by flushing the line with alternating batches of nitric acid and caustic.

Operation of the airlift pot was adversely affected by elimination of foam in the denitrator-evaporator, since the liquid level dropped to 25 inches of all liquid instead of 30 inches with part foam. The foam had actually aided operation of the airlift in transfer of concentrate via the airlift pot to the melter in this and the previous runs. The undesirably high 30-inch liquid level was maintained in the denitrator-evaporator for the remainder of the run. Lengthening of the transfer air tube in the denitrator-evaporator after the run eliminated the need for operating at a high liquid level in the ensuing runs.

Startup of the melter with an unsealed weir was again successfully demonstrated as in the previous run PG-3. Splattering and foaming did not occur because of the control of vacuum to limit the pulling of air through the weir into the melter. Melt overflowed dropwise from the unheated weir with no problems throughout the run. The melter was completely emptied through the drain tube by heating the freeze valve at the end of the run. Premature drainage of the melt, which drains at 800 °C, was prevented by air cooling the freeze valve to below 640 °C. Throughout most of the run, feed from the denitrator entered the melter as viscous bubbles, but caused no major difficulties. A melter sparge test was again tried to determine if melter capacity increased, but no marked changes were noted after sparging the melter for 8 hours at a rate of 0.45 scfh with nitrogen gas. The melter furnace temperature was 1220 °C while the internal melt temperature ranged from 840-1100 °C, depending on the feed rate to the melter.

The receiver was fairly uniformly filled with glass at a rate of 0.79 liters/hr or 19 liters/day. The receiver temperature was maintained at 570 °C which prevented stalagmite formation. However, at the end of the run, the receiver was filled above the heated zone, which permitted the formation of small stalagmites at this time. The stalagmites were easily broken off mechanically as they formed. The unit volume of glass in this run was 59 liters/tonne. This was higher than in previous runs because of the increased amounts of phosphoric acid and sodium required. A maximum radiation dose rate of 37,000 R/hr was measured at 6 inches from the receiver wall.

The specific gravity and weight factor dip tubes of the auxiliary evaporator continuously plugged throughout the run, even though it was operating on condensate from the denitrator. A highly concentrated solution in the evaporator bottoms caused most of the dip tube plugging. Although steam blowdowns were used to clear the dip tubes, they remained unplugged for only short periods of time (about 2 hours). This problem had been prevented in previous runs by flushing the dip tubes with alternate nitric and caustic flushes prior to each run and after the feed concentration had been performed. The only other difficulty encountered during the evaporator operation was that of the inoperable condensate conductivity probe which prevented monitoring of the overheads acidity from the evaporator. However, liquid temperatures showed that the evaporator overheads acidity became greater than 1$\underline{M}$ for an 8-hour period early in the run and for a 5-hour period after 52 hours of running time.

Over the length of the run, 1.3% of the radioruthenium fed to the melter was volatilized or entrained. Entrainment from the melter was 0.23% of the total nonvolatile activity in the feed to the melter.

Ruthenium volatilization and entrainment from the denitrator-evaporator during the run amounted to 0.2%, while nonvolatile entrainment was 0.001%. Semi-continuous dip tube plugging in the auxiliary evaporator resulted in somewhat unreliable volume calculations and made data analysis of radioactivity levels difficult.

The run was temporarily interrupted after 68 hours when the feed pump P-114-1, developed a leak in the impeller housing gasket. A standby pump was valved in, but proved to be faulty, requiring a return to the first pump. The last 9 hours of the run were completed after a shutdown of a few minutes.

Run PG-5

In April 1968, the fifth phosphate glass run was demonstrated in WSEP. For the first time, a sulfate-free PW-1 waste was used. Waste equivalent to that produced by processing

1.04 tonnes of 0.5 year-old power reactor fuel (20,000 MWd/tonne at 15 MW/tonne) was processed to produce 306 kilograms of phosphate glass. The 113 liters of radioactive glass, contained in a 12-inch diameter mild steel receiving pot, produced an internal heat rate density of 78 W/liter. An overall volume reduction of nominal PW-1 waste to glass of 3.5 was achieved.

Run PG-5 was conducted in 2 parts because of an interruption of the run after 38 hours of operation by a plug that developed in the melter feed line. The restriction was removed by gently tapping the line while it was heated with 25 psig steam in its jacket. Following removal of the plug, the run was restarted using a mode B operation.

During the first part of the run, 420 liters of adjusted PW-1 waste (at 666 liters/tonne) were fed into the denitrator-evaporator at an average feed rate of 11 liters/hr. During a 32-hour period of steady-state operation, the average feed rate was 10 liters/hr. The adjusted feed, containing 1,290,000 curies of radioactivity, including 23,600 curies of radioruthenium, was concentrated by a factor of 3.5. Continuous addition of Dow Corning Antifoam B at a rate of 10 g/hr (2.6 liters/hr of 0.67 wt% antifoam solution) to the denitrator-evaporator again kept foam to nondetectable levels. This amount represented 200 ppm of the denitrator contents/hr.

In the second part of the run, 842 liters of adjusted PW-1 waste (at 1143 liters/tonne) were fed to the denitrator-evaporator at an average feed rate of 12.8 liters/hr. The feed used in the second part of the run was made more dilute by the addition of nitric acid. The acid was added to aid in partial removal of feed from the denitrator-evaporator during interruption of the first part of the run. Water flushes used after transferring concentrate from one tank to another were also added to the feed which subsequently was used for the second part of the run. The dilute feed for the second part of the run, containing 1,570,000 curies of radioactivity, including 32,600 curies of radioruthenium, was concentrated in the denitrator by a factor of 5.5. However, because of the diluteness of the feed used, the equivalent concentration factor when applied to the PW-1 waste is 1.81. Dow Corning Antifoam B was again continuously fed to the denitrator-evaporator, but at the reduced rate of 8 g/hr (1.2 liters/hr of 0.67 wt% solution which was sufficient to prevent foaming. A concentration of 180 ppm was maintained in the denitrator. In addition to processing the dilute feed, 771 liters of waste containing 3,500,000 curies of radioactivity including 35,000 curies of radioruthenium were concentrated by a factor of 4 in the auxiliary evaporator to demonstrate the mode B operation.

Prior to run PG-5, a new airlift pot (shown in Figure 4.6) was installed on the denitrator-evaporator. The new pot features a hollow, moveable, tapered plug valve equipped with a cleanout rod and chemical additives line to minimize anticipated accumulation of more rapidly settling PW-1 solids in the recirculation line. The valve also provided an added control of feed rate to the melter by controlling the recirculation rate between the airlift pot and the denitrator. The new unit proved its need by being used successfully in several instances during the second part of the run to aid in the removal of plugs that had started to form in the recirculation line from the airlift pot.

Plugging of the denitrator-evaporator specific gravity and weight factor dip tubes occurred frequently as anticipated for PW-1 feed due to the increase in granular, heavier solids content and the tendency for drying the solids at the end of the dip tubes. Although plugging was initially prevented by continuous low pressure steam purges (about 0.75 kg/hr, at 1 psig) some indications were evident that the steam purges eventually contributed to the formation of plugs. Subsequently, semi-continuous purges every 2 hours with steam as high as 120 psig were used to prevent plugs from completely stopping up the lines. In order to prevent feed from being drawn into the dip tube lines by partial vacuums created by condensing steam, air purging of the lines was required after each steam purge.

By maintaining close vacuum control (less than 4 inches of water in the melter) successful startup of an empty melter was again demonstrated as in runs PG-3 and PG-4, thus eliminating the need for introducing a preliminary charge of glass into the melter at startup to prevent splattering due to sparging of gases up into the unsealed melter weir tube. Concentrated feed entered the melter as a gummy, bubbly material as in run PG-4, but did not cause any difficulties. Attempts to prevent this condition by flushing the solution feeder with nitric acid temporarily (for a few minutes) succeeded in correcting the situation.

Sparge tests in the melter were again tried to substantiate an apparent increase in melter capacity observed during design verification testing. Using nitrogen purges at rates up to 0.8 scfh in both parts of the run produced no increase in melter capacity. The sparging effects immediately observable were increased foaming, increased melt temperatures (approximately 20 °C) and possible increased entrainment indicated by clouding of the melter sight glass located in the top of the melter. Foaming occurred in the melter whenever the flow rate of concentrated feed to the melter was increased beyond approximately 3.0 liters/hr. The melter furnace operated at 1220 °C with an internal melt temperature of 1050 °C. The average control temperature was 825 °C at which temperature the optimum feed rate was 2.6 liters/hr.

Draining of the melter through the freeze valve tube at the end of the first part of the run proceeded without difficulty. Attempts to drain the melter after the second part of the run encountered difficulty, even though the freeze valve was heated to 1015 °C. In the course of heating the freeze valve, the heater burned out. A propane-air flame from a torch was then applied directly to the freeze valve, thereby permitting melter drainage at 870 °C. The reason that increased heat was required during attempts to drain the melter for this run was probably the presence in the drain tube of unmelted material from the plug that had been dislodged from the melter feed line. The unmelted material probably had a different composition and required a high temperature to form a melt before it would drain.

The receiver pot wall was maintained at an average temperature of 575 °C with the average furnace temperature at 600 °C. The receiver fill rates averaged 1.2 and 0.86 liters/hr for Parts 1 and 2, respectively. No stalagmites were formed in the receiver during either part of this run. The 113 liters of glass did not protrude above the heated zones of the furnace. The 8800 watts of internal heat generation rate was sufficient to produce a centerline temperature of 712 °C and a centerline-to-wall temperature difference of 352 °C with the pot in the air-cooled furnace. These values yielded an effective thermal conductivity of 1.13 $W/(m^2)(°C/m)$ [or 0.65 $Btu/(hr)(ft^2)(°F/ft)$]. The unit volume of the glass was 108 liters/tonne. The required addition of 2.47$\underline{M}$ Na and 6.47$\underline{M}$ phosphoric acid was responsible for the increase in unit volume for PW-1 waste. A maximum radiation dose rate of 47,000 R/hr was measured at 6 inches from the pot wall.

The WSEP auxiliary evaporator performed satisfactorily at boiloff rates of 20 liters/hr and of 88 liters/hr during the first and the second parts of the run, respectively. Plugging of the specific gravity and of the weight factor dip tubes did not occur, thereby permitting accurate control of the solution parameters. As in previous runs, the conductivity of the condensed overheads from the evaporator was used to maintain a low acid concentration in the overheads.

During the entire run, 8% of the radioruthenium fed to the melter was volatilized or entrained. This was a factor of 6.7 greater than was observed in run PG-4 using PW-2 waste. Entrainment from the melter was 0.25% of the total nonvolatile activity introduced into the melter. This value was in close agreement with the value obtained in run PG-4. A total of 0.5% of the radioruthenium present in the feed introduced into the denitrator-evaporator was volatilized.

Run PG-6

The sixth phosphate glass run was completed in May 1968 using a sulfate-free PW-1 waste for the second time. In 50 hours of operating time, including startup, 584 liters of PW-1 waste (at 889 liters/tonne) were converted to 62 liters of phosphate glass with an internal heat rate density of 155 W/liter. This waste was equivalent to that generated from the processing of 0.66 tonnes of 0.2 year-old 20,000 MWd/tonne power reactor fuel. The 174 kilograms of glass product containing 9600 watts of internal heat generation rate from radionuclide decay were collected in an 8-inch diameter, 8-foot long 304L stainless steel receiver.

A total of 616 liters of PW-1 feed containing 2,560,000 curies of radioactivity, including 8000 curies of radioruthenium, was fed to the denitrator-evaporator in 50 hours at an average rate of 12.3 liters/hr. During a 43 hour period of steady-state operation, the feed rate averaged 10.5 liters/hr. Concentration of the feed by a factor of 4.2 was realized in the denitrator-evaporator, or the equivalent volume reduction factor of 1.8 for waste at a concentration of 378 liters/tonne. Manual control of tube bundle steam permitted close control of the denitrator-evaporator solution parameters. The feed rate to the denitrator and to the melter were controlled manually without significant operating problems.

The feed used for run PG-6 was prepared using a radiocerium solution as the only source of radioactivity. As a result of using this feed which was devoid of Purex waste, no foaming occurred in the denitrator-evaporator even though the antifoam agent, Dow Corning Antifoam B, was not used. This test conclusively established that the accumulation of small quantities of partly degraded tributyl phosphate which is normally present in Purex waste stock was responsible for the foaming problems encountered in the first 3 runs.

The specific gravity and liquid level dip tubes in the denitrator-evaporator were kept free of plugs by hourly steam purges followed by 2-minute air purges. The tendency to plug, however, was not eliminated, and was particularly troublesome in the airlift pot and airlift air supply line to the air lift. The air line plugged twice during startup and once during shutdown. Steam was successfully used to unplug the airline in each instance. Air purging of the air line following the steam addition resulted in abnormally high air lifting rates which in turn caused excessive feed rates to the melter. This sequence required repositioning the plug valve to allow a faster recirculation rate and a lesser flow to the melter. Frequent (approximately 5 times per day) backing out of the plug valve accompanied by acid flushes were necessary to remove accumulated solids in this area. A plug which developed shortly after startup in the airlift pot liquid level tube could not be removed until after the run. With careful operation, no significant trouble resulted from the absence of liquid level instrumentation. Laboratory tests performed just prior to the run showed that a batch addition of 10% by volume water to the boiling denitrator concentrate (at 135 °C) did not cause any jelling problems. Consequently, for the first time, water flushing the denitrator-evaporator during the dilution and shutdown period was attempted and successfully demonstrated.

The melter was again started successfully with an unsealed weir by controlling the vacuum at less than 4 inches of water. Mild foaming in the melter was observed periodically, but did not cause any appreciable problems in the operation of the melter. Premature draining of the melter through the freeze valve tube occurred twice during the run. Additional cooling air was required to reseal the freeze valve. To drain the melter at the end of the run, a propane-air torch was again used to heat the freeze valve to 890 °C before drainage was initiated. The reason for the high temperature requirement to initiate drainage was the accumulation of calcined feed or melter foam with a different composition in the drain tube that had not been converted to a melt. The melter furnace temperature was 1220 °C, while the melt temperature was typically 1090 °C at the bottom center of the molten glass pool. A glass production rate of 26 liters/day was achieved during the run.

Holding the receiver wall at a temperature of 575 °C prevented stalagmite formation. The 62 liters of glass product having a density of 2.8 kg/liter and a melting point of 800 °C contained 9600 watts of internal heat generation rate. This rate was sufficient to produce a centerline temperature of 780 °C and a centerline to wall temperature difference of 380 °C. From these values, the effective thermal conductivity was calculated to be 1.1 $W/(m^2)(°C/m)$ [or 0.61 $Btu/(hr)(ft^2)(°F/ft)$] which compares well with that from run PG-5.

The auxiliary evaporator Tank-113 operated without appreciable difficulty throughout the run. The liquid level and specific gravity tubes did not become plugged at any time. This performance was the result of operating on clean condensate and maintaining the bottoms at a low specific gravity.

During run PG-6, 4.3% of the radioruthenium in the feed to the melter was volatilized or entrained. This was less than the 8% obtained in run PG-5, but more than the 1.2% for run PG-4. Entrainment from the melter was 0.19%, as determined from ^{144}Ce evolution. This compared favorably with the 0.23% and 0.25% values determined in runs PG-4 and PG-5, respectively. A total of 0.4% of the ruthenium in the feed delivered to the denitrator-evaporator was volatilized or entrained. This was more than the 0.2% reported for run PG-4 and less than the 0.5% recorded in run PG-5. Entrainment of nonvolatiles from the denitrator was 0.03% which was greater than the 0.009% in run PG-5, and greater than the 0.001% reported in PG-4.

9.2 STARTUP PROCEDURE FOR PHOSPHATE GLASS SOLIDIFICATION PROCESS

The startup sequence for the phosphate glass solidification equipment involves feeding and gradual concentration of waste in the denitrator-evaporator Tank-121 to specified conditions without feeding the melter, while bringing the melter and later the melt receiver up to operating temperature by starting up the melter and receiver furnaces.

9.2.1 Denitrator-Evaporator (Tank-121)

Steam to the denitrator-evaporator tube bundle is turned on and slowly increased to start a previously added 6M nitric acid solution to boil at 15 liters/hr. The denitrator-agitator is then turned on to 200 rpm. Water feed is started at 15 liters/hr when the liquid level has been reduced to 20 inches. Radioactive feed is then started while the water is slowly turned off. Melter feed airlift air is turned on along with the airlift weight factor purge. Recirculation of feed in the airlift pot is started without feeding the melter. Steam to the melter feed airlift pot jacket is set to maintain a temperature of 125 °C. The liquid level in the denitrator is raised slowly to 25 inches. The steam and feed rate to the denitrator are adjusted to give the desired liquid boiling point. When the evaporator is at specified conditions, automatic operation of the tube bundle steam, temperature control loops and liquid level control loops can be initiated. Automatic operation was suspended during the first run and was not used in subsequent runs.

9.2.2 Melter Solution Feeder and Off-Gas Line

While the evaporator is being brought to its steady-state operating condition, cooling water to the reflux condenser of the melter solution feeder is turned on and the solution feeder cooling jacket is filled with water to just below the reflux cooling coils. Prior to feed startup, the melter off-gas line heater is turned on and adjusted to maintain a temperature between 400 and 500 °C.

9.2.3 Melter and Melter Furnace

One hour before feed is turned on to the denitrator-evaporator, the melter furnace is started up. The melter temperature controller is turned on and periodically adjusted in 200 °C intervals to permit furnace temperatures to rise to 1230 °C in about 4 to 6 hours. An automatic set point is fixed to maintain the furnace at that temperature. Nonradioactive phosphate glass, which had been previously processed in cold runs, was loaded into the melter prior to the startup of this unit for runs PG-1 and 2 to prevent backsparging of air through the melter weir overflow and the freeze valve during initial melter feeding. This practice was discontinued for the remaining four runs when backsparging was held to a minimum by close control of process melter vacuum. A steam spray is turned on to the melter condenser prior to feeding the melter. This is done primarily when processing sulfate wastes to improve sulfate scrubbing and recovery in the condenser, and to dilute the condensate for improved corrosion control in the condensate collection system.

9.2.4 Receiver Furnace

Just before feed is turned on to the denitrator-evaporator, the receiver furnace is turned on. Temperature controllers are set to maintain furnace temperatures below 600 °C.

9.3 NORMAL OPERATING PROCEDURE

9.3.1 Denitrator-Evaporator

During operation of the denitrator-evaporator at specified conditions (usually 26 inches liquid level at a temperature of approximately 135 °C), the tube bundle is sprayed once each 1 to 4 hours with 1 to 2 liters of 6 M nitric acid. The spray washes away accumulation of muddy scale on the top baffle of the tube bundle. The temperature and specific gravity and the level of the concentrated feed are closely monitored and controlled during operation. To change evaporator conditions appropriate changes are made in the tube bundle steam pressure, airlift rate and melter furnace temperature if necessary.

9.3.2 Melter Operation

The temperature of the melt pool near the bottom of the melter is usually maintained at about 50 to 100 °C below the melter furnace temperature. A temperature near the melt surface is maintained at 850 to 900 °C (with the melter furnace at 1230 °C) and is thereby used to control the melter feed rate. Visual observation of the melt dripping into the melter receiver is made periodically. Visual observations also provide for estimating melter feed and discharge rates, and melt temperature and viscosity. Catch samples of the dripping melt are collected at specified times. The solution feeder temperature is maintained at 100 ± 10 °C temperature at all times by the periodic addition of 100 to 200 milliliters of water to its cooling jacket. Melt level in the melter is maintained at 6 inches. Cooling air is constantly directed to the freeze valve, thereby maintaining a frozen plug of glass in the tube.

9.3.3 Melt Receiver

During filling of a receiver, the wall temperature is maintained at or just below 600 °C by the six zone induction-heated furnace. The melt centerline temperature is limited to a maximum of 850 °C. The temperature profile of the contents of the receiver serves as an indicator of the melt level within a zone of the receiver. As each of the six receiver zones becomes filled, furnace heat to the zone is discontinued. Cooling air is available for direct or indirect application to the receiver wall to confine temperatures within prescribed limits. The contents of the receiver are visually checked for possible stalagmite formation.

9.4 SHUTDOWN PROCEDURES

The shutdown sequence for the phosphate glass equipment involves a gradual dilution of the contents of the denitrator-evaporator while feeding the melter, cooling of the diluted concentrate for idle or jetting out, draining of the melter contents, and finally, shutdown of the melter furnace and the melter receiver furnace.

9.4.1 Evaporator-Denitrator (Tank-121)

The contents of the denitrator-evaporator are slowly diluted by the addition of diluted feed, water, or nitric acid at the end of the run while feeding the melter with boiling concentrate. This dilution is continued until a concentrate with a boiling point less than 122 °C is attained. The evaporator dilution is then terminated and the feed lines and pump are flushed. Airlift of the dilute denitrator feed to the melter is continued until the level drops to the point that the airlift will not function (approximately 22 inches). The air supply to the airlift is turned off, the airlift pot is flushed with 6M HNO_3 and then the melter airlift pot steam is turned off. The level of liquid is again increased to 26 inches in the denitrator by the addition of 6M HNO_3 sprays. The steam to the tube bundle and jacket is turned off, and the contents are cooled to less than 75 °C. The contents are jetted to Tank-112 and the agitator shut off when the level reaches 15 inches. The denitrator is flushed by filling it to 40 liters with 6M HNO_3 sprays. The steam and agitator are again turned on and the solution is heated to 100 °C and agitated for a minimum of 30 minutes. This step may be repeated and the contents, except for a 20 liter heel, are again jetted to Tank-112, and the agitator is turned off. Tank-121 was diluted only with water in run PG-6.

9.4.2 Melter

After the jacket steam for the melter airlift pot has been turned off, the cooling air to the melter freeze valve is also turned off. The melter freeze valve heater is turned on, and the valve is heated to 900 °C to melt the frozen glass plug, thus releasing the contents of the melter. To remove the melt from the melter overflow weir during final draining of the melter, the melter vacuum is increased to 12-15 inches of water until sparging within the melter is noted. The melter furnace is shut off when the contents of the melter have been emptied. The melter off-gas line heater is turned off when dilution of the denitrator-evaporator is completed. The steam spray addition to the melter condenser is turned off. When the melter furnace temperature decreases to below 50 °C, the melter reflux condenser cooling water is shut off.

9.4.3 Melt Receiver

At the end of a run, after the contents of the melter have been emptied into the receiver, all heat to the receiver is discontinued. Cooling air is turned on to bring receiver temperatures to steady state. The receiver is then removed from the furnace and stored in air. Water storage is available to confine wall or centerline temperatures within prescribed limits. For storage, maximum permissible wall temperatures are lowered to 427 °C but maximum centerline temperatures are still limited to less than 850 °C.

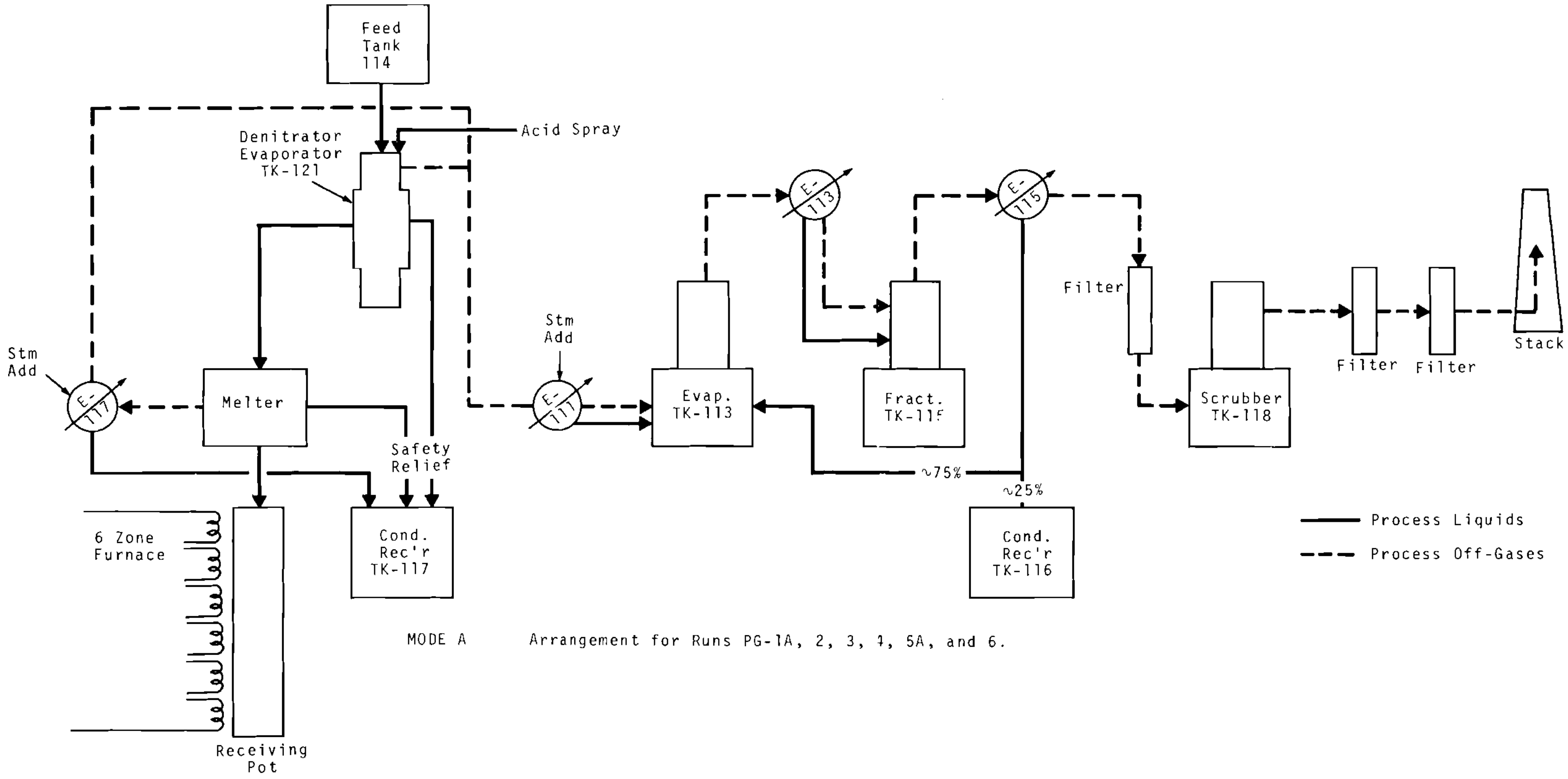
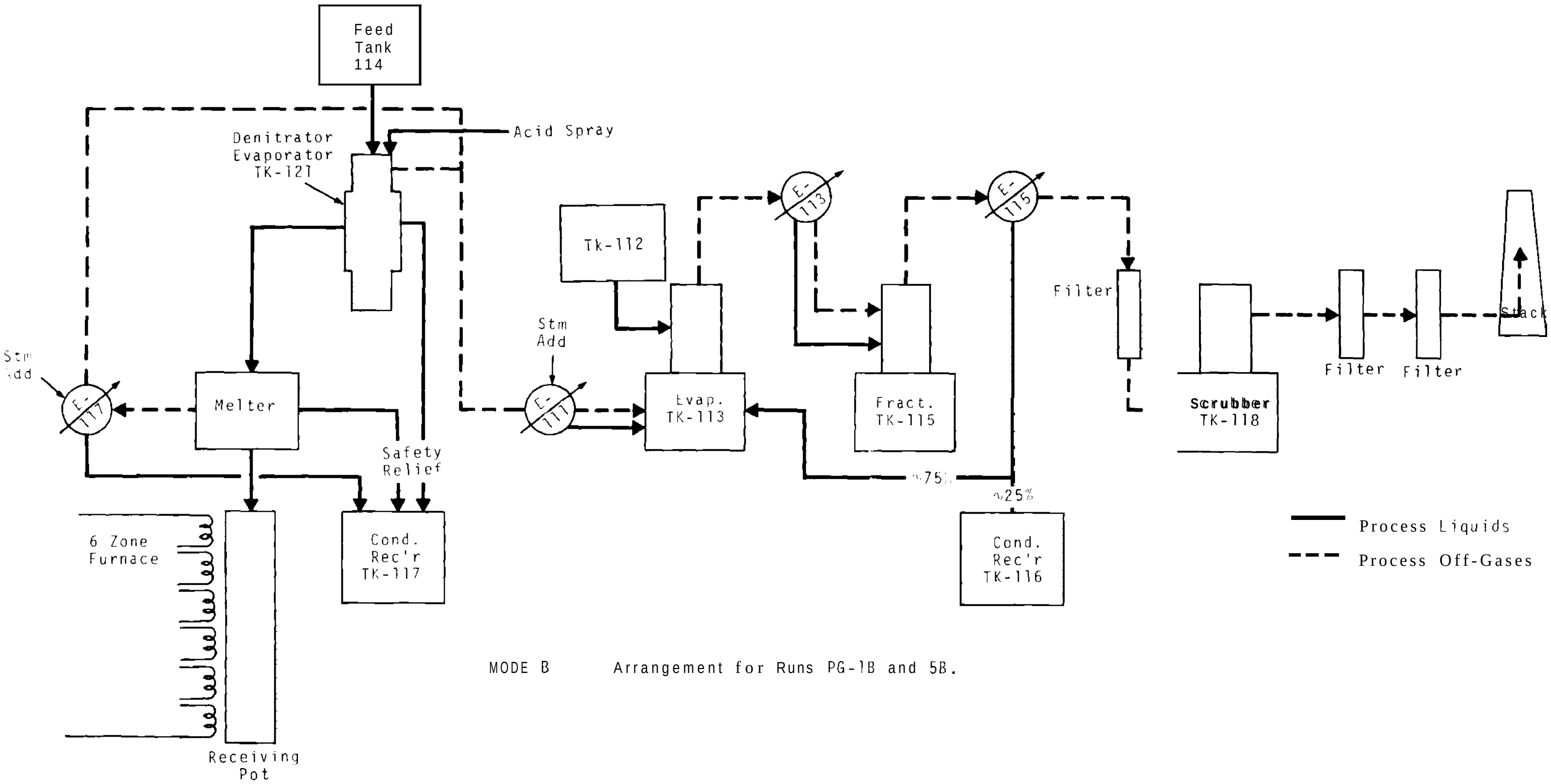


FIGURE 9.1a. *Equipment Arrangement for Mode A Phosphate Glass Runs*



MODE B Arrangement for Runs PG-1B and 5B.

FIGURE 9.1b. *Equipment Arrangement for Mode B Phosphate Glass Runs*

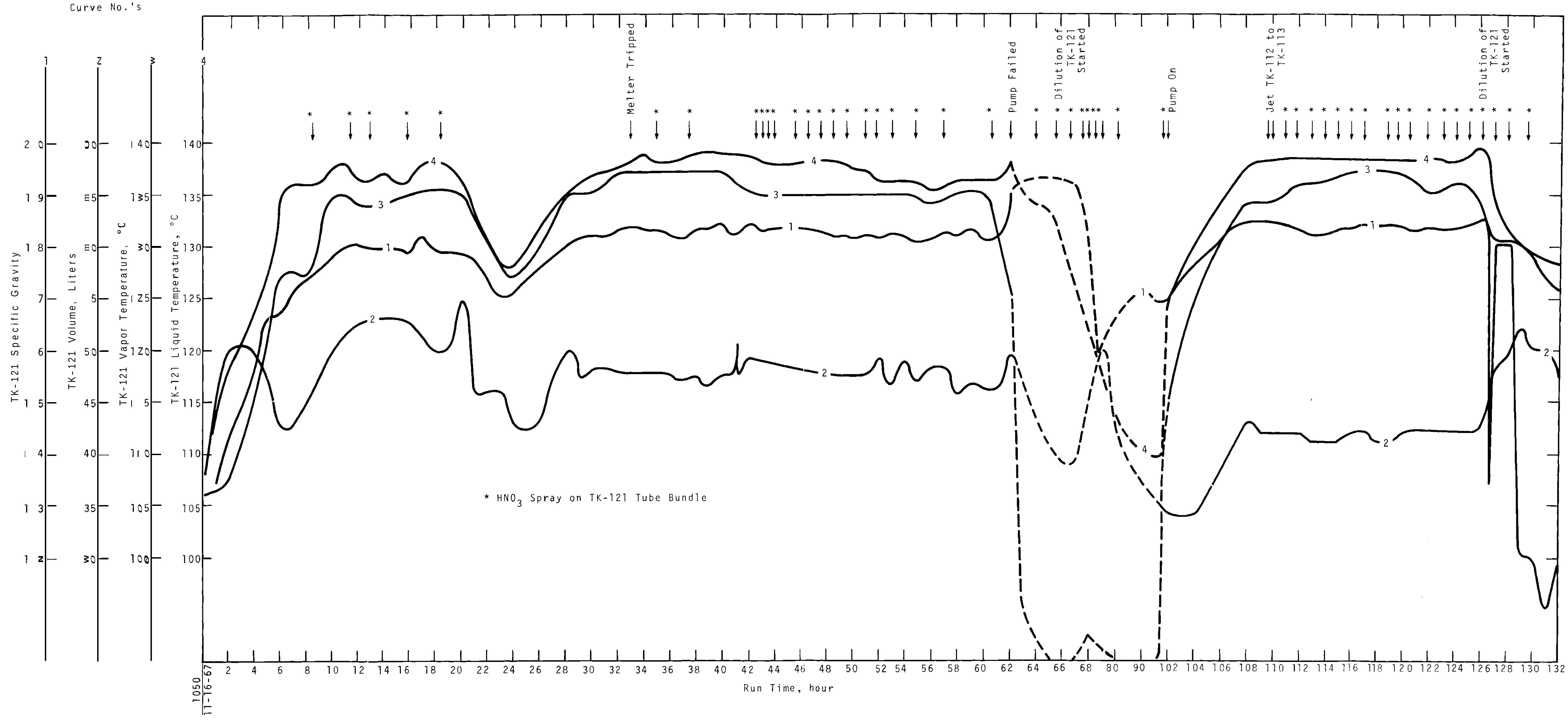


FIGURE 9.2 *Denitrator-Evaporator (TK-121) Solution Parameters During Run PG-1*

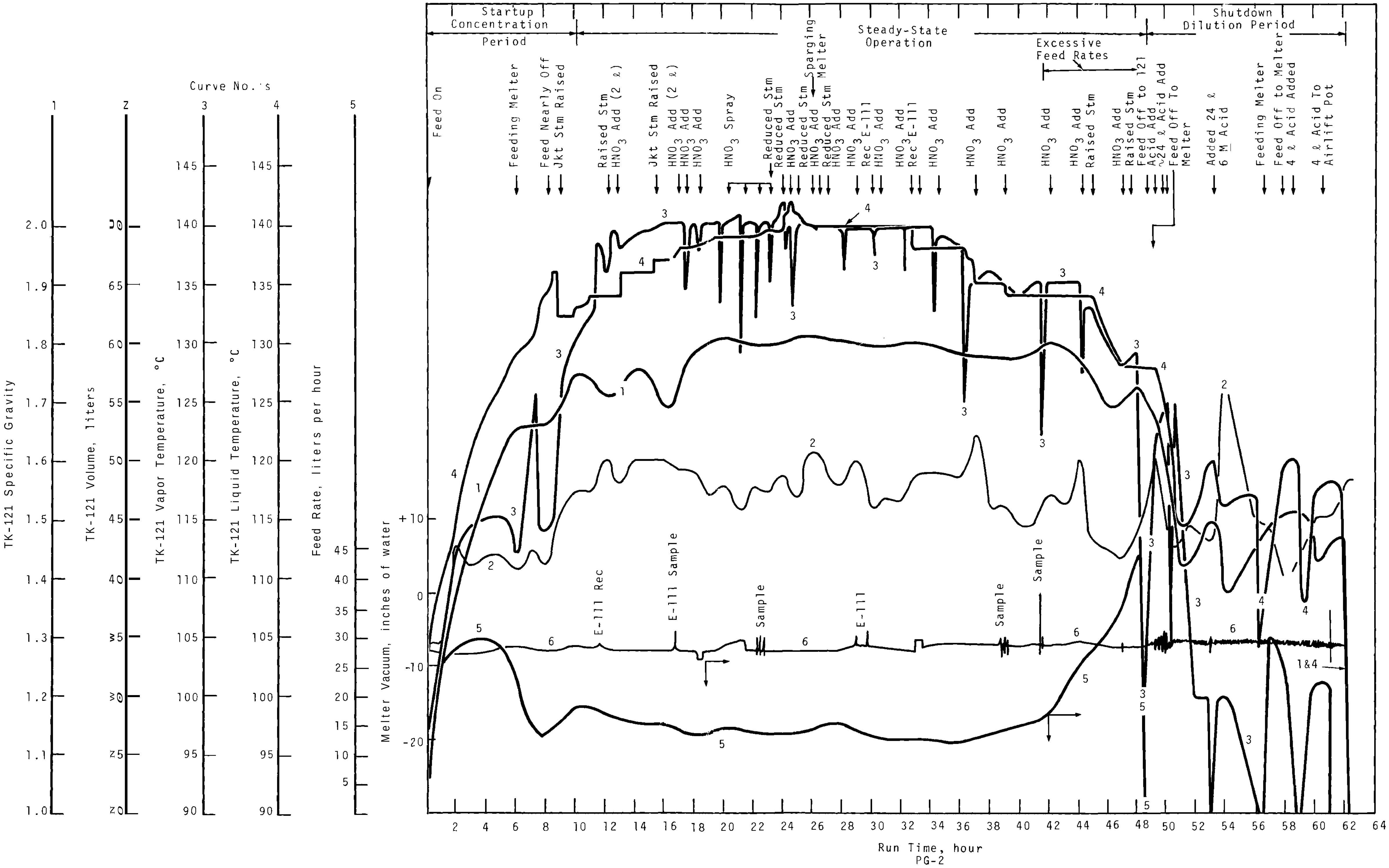


FIGURE 9.3 *Denitrator-Evaporator (TK-121) Solution Parameters During Run PG-2*

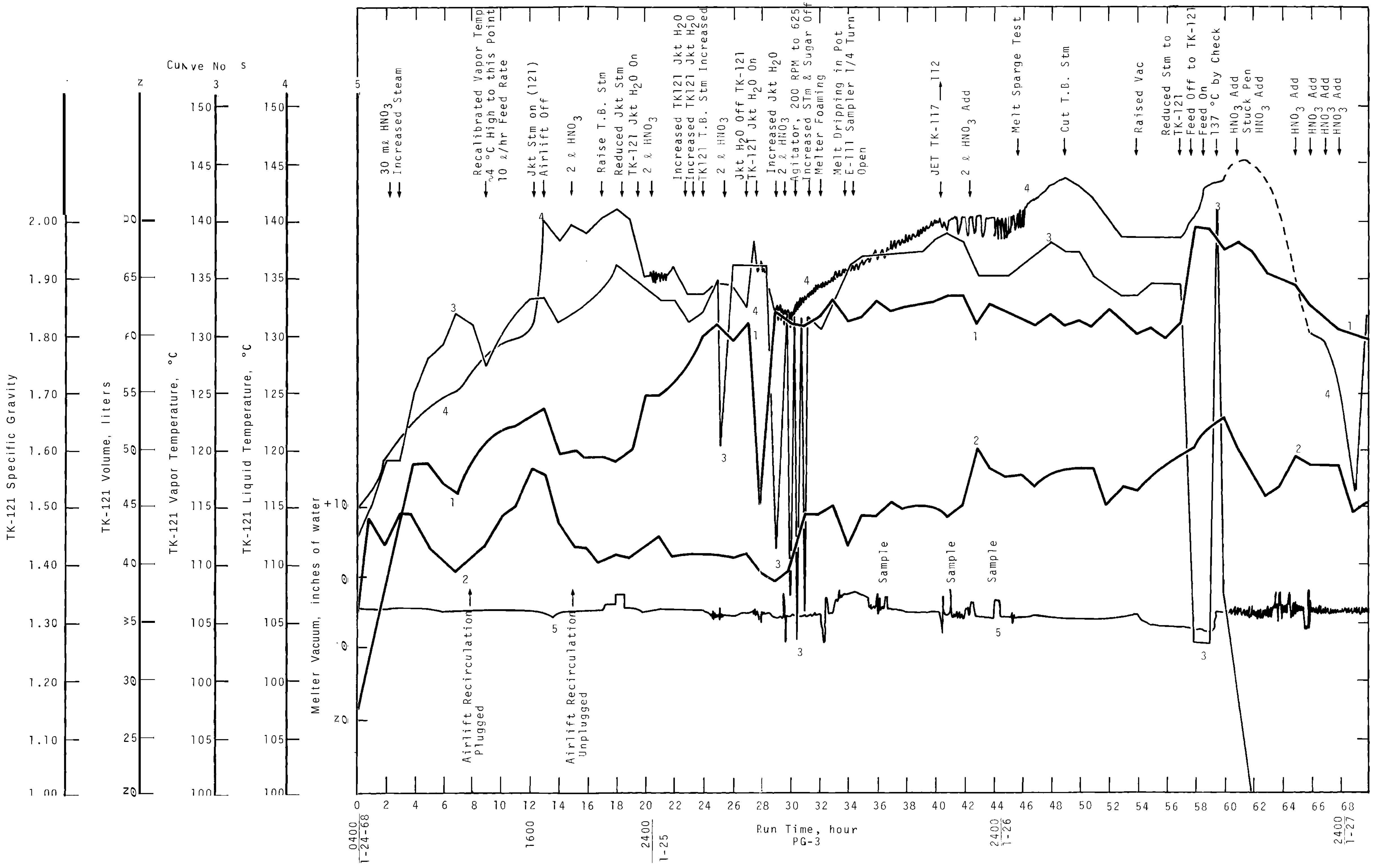


FIGURE 9.4a *Denitrator-Evaporator (TK-121) Solution Parameters During Run PG-3*

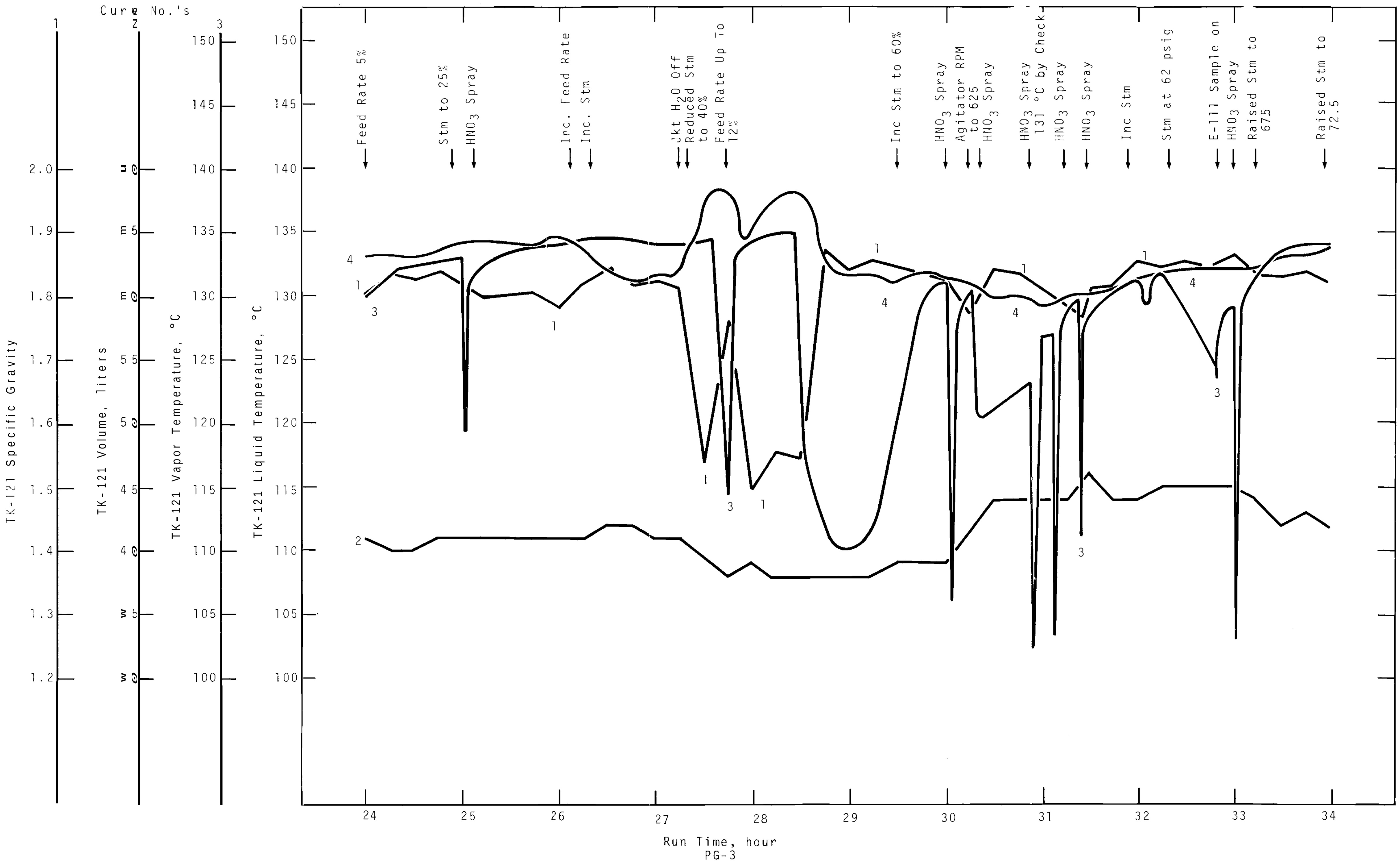


FIGURE 9.4b *Denitrator-Evaporator (TK-121) Solution Parameters During Part of Run PG-3.*

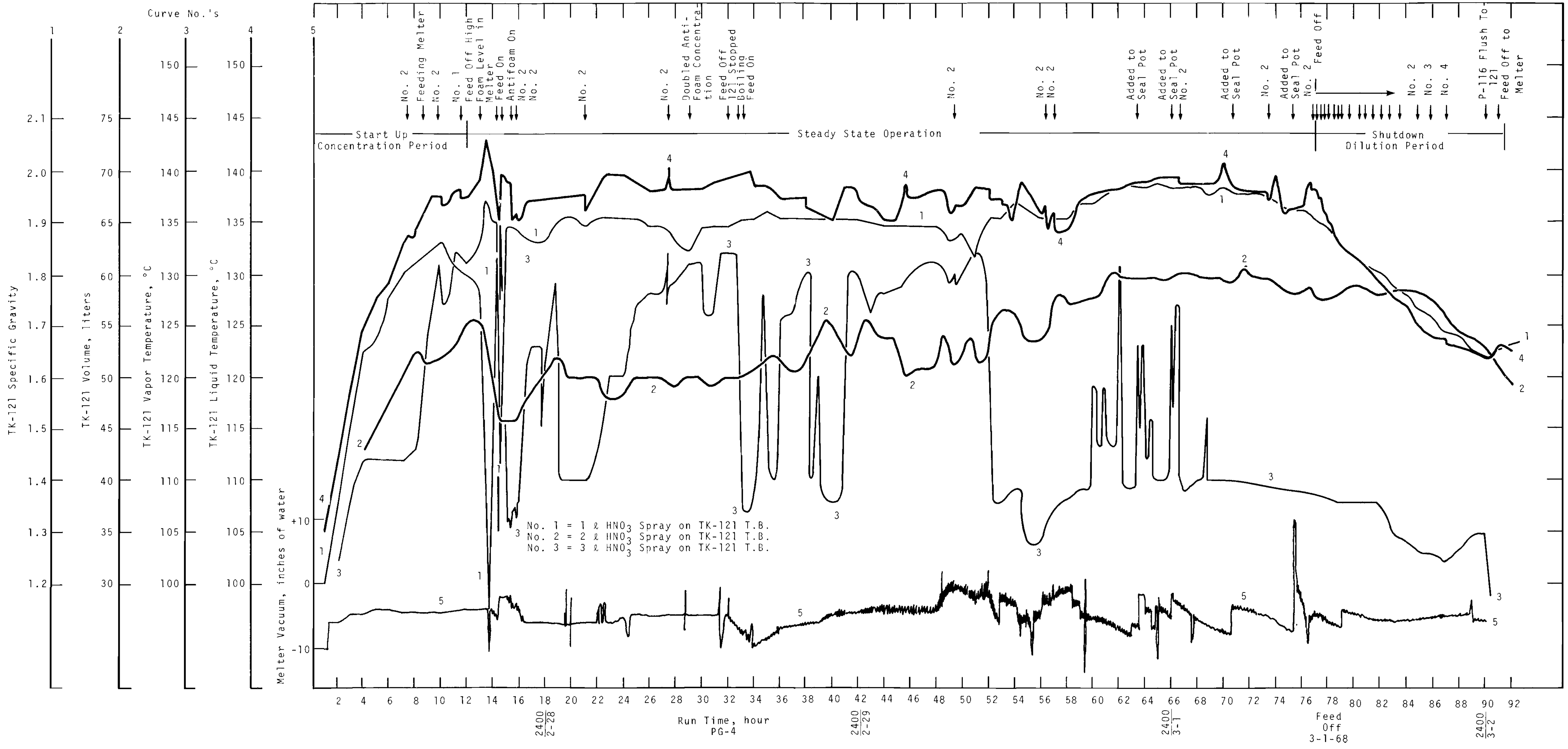
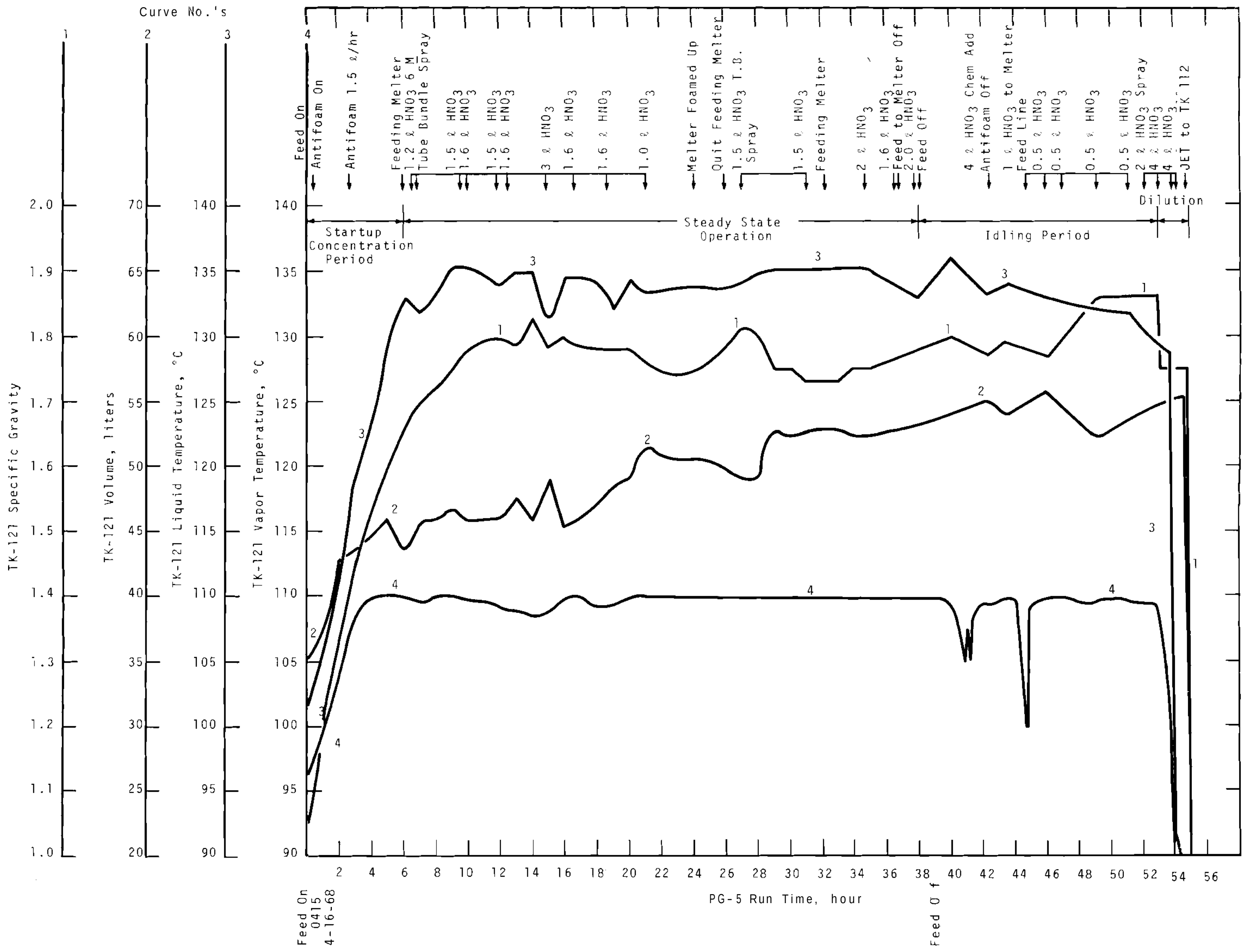


FIGURE 9.5 *Denitrator-Evaporator (TK-121) Solution Parameters During Run PG-4*



<u>*FIGURE 9.6a*</u>*. Denitrator-Evaporator (TK-121) Solution Parameters During Run PG-5, Part 1*

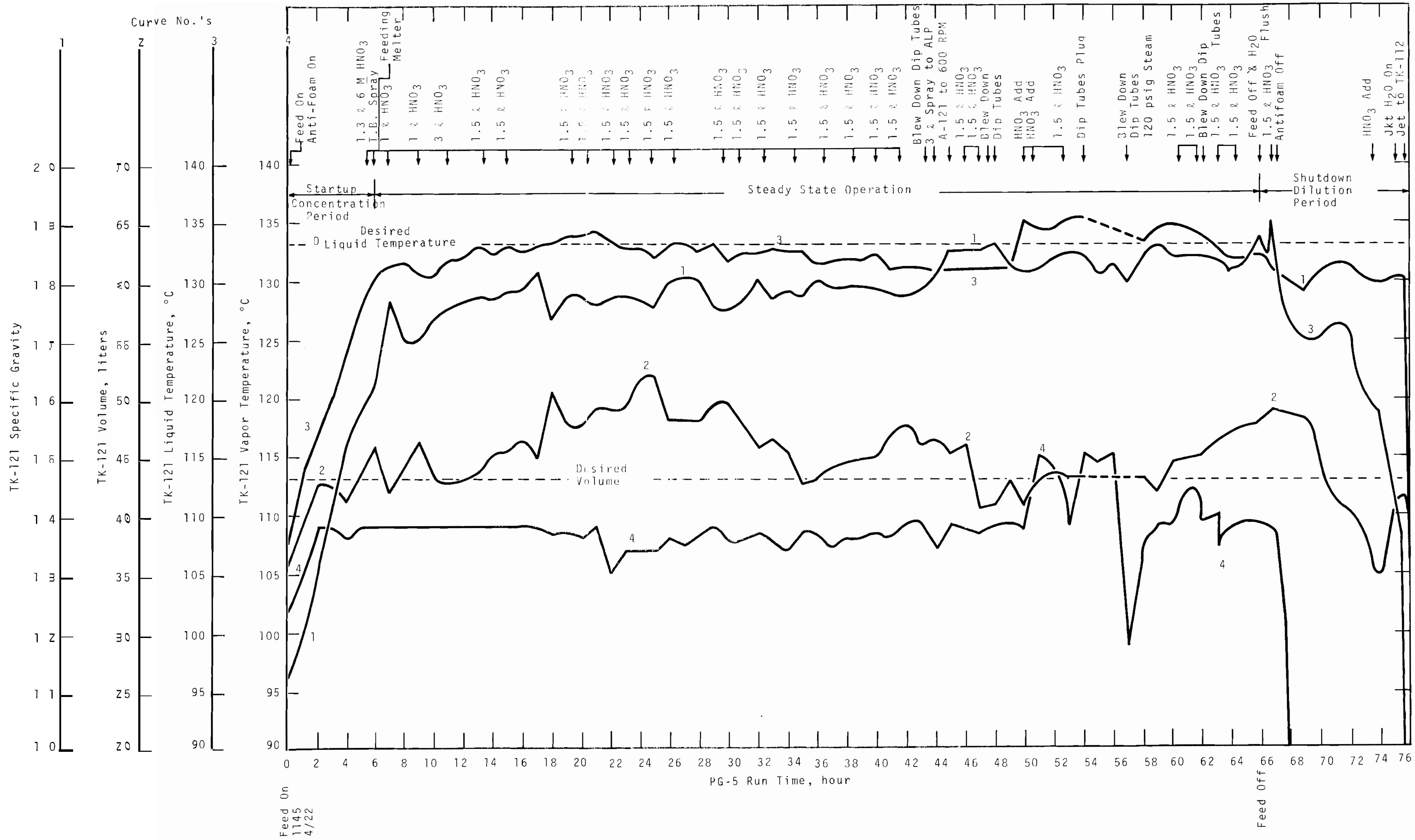


FIGURE 9.6b. Denitrator-Evaporator (TK-121) Solution Parameters During Run PG-5, Part 2

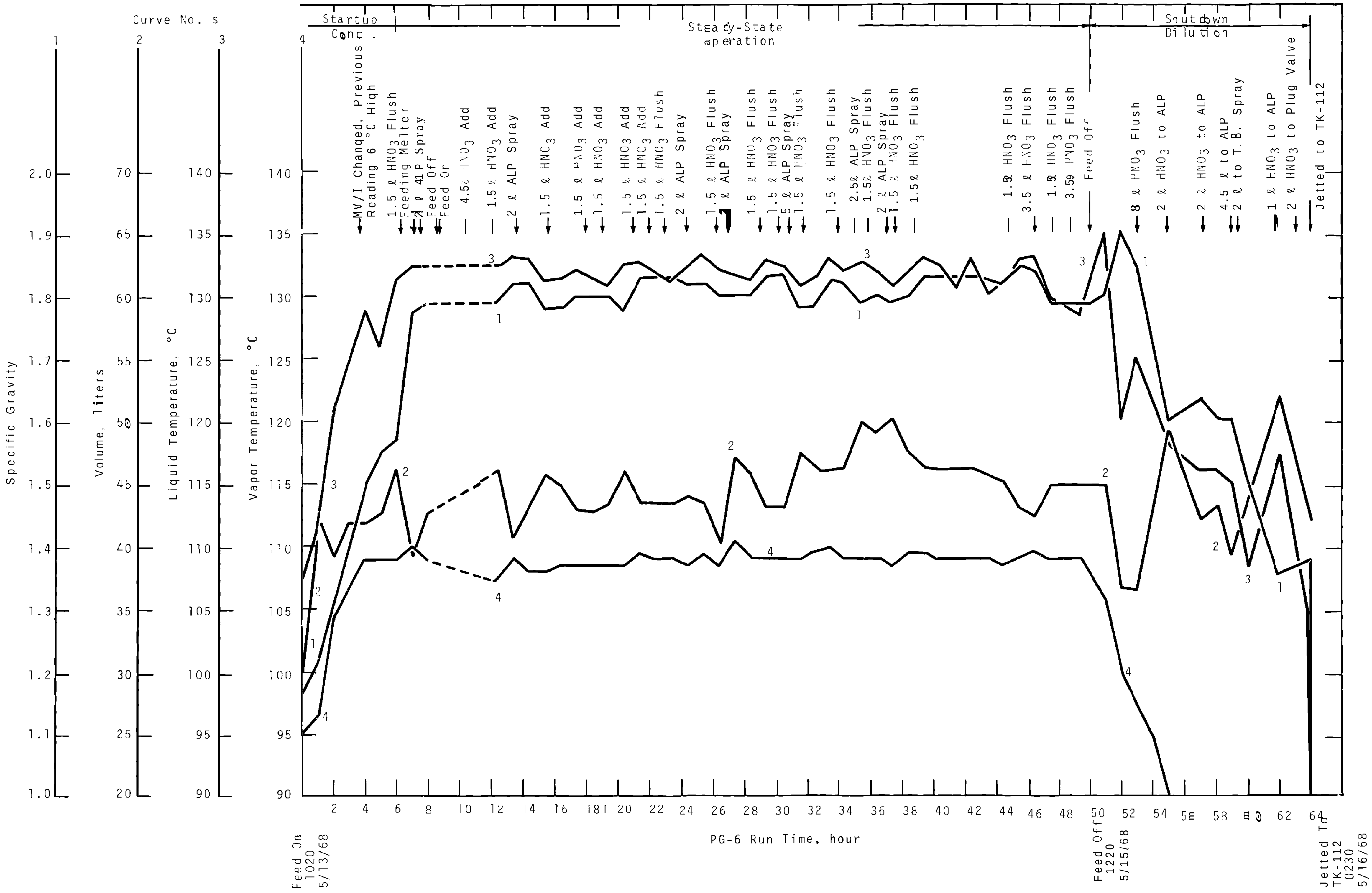


FIGURE 9.7. *Denitrator-Evaporator (TK-121) Solution Parameters During Run PG-*

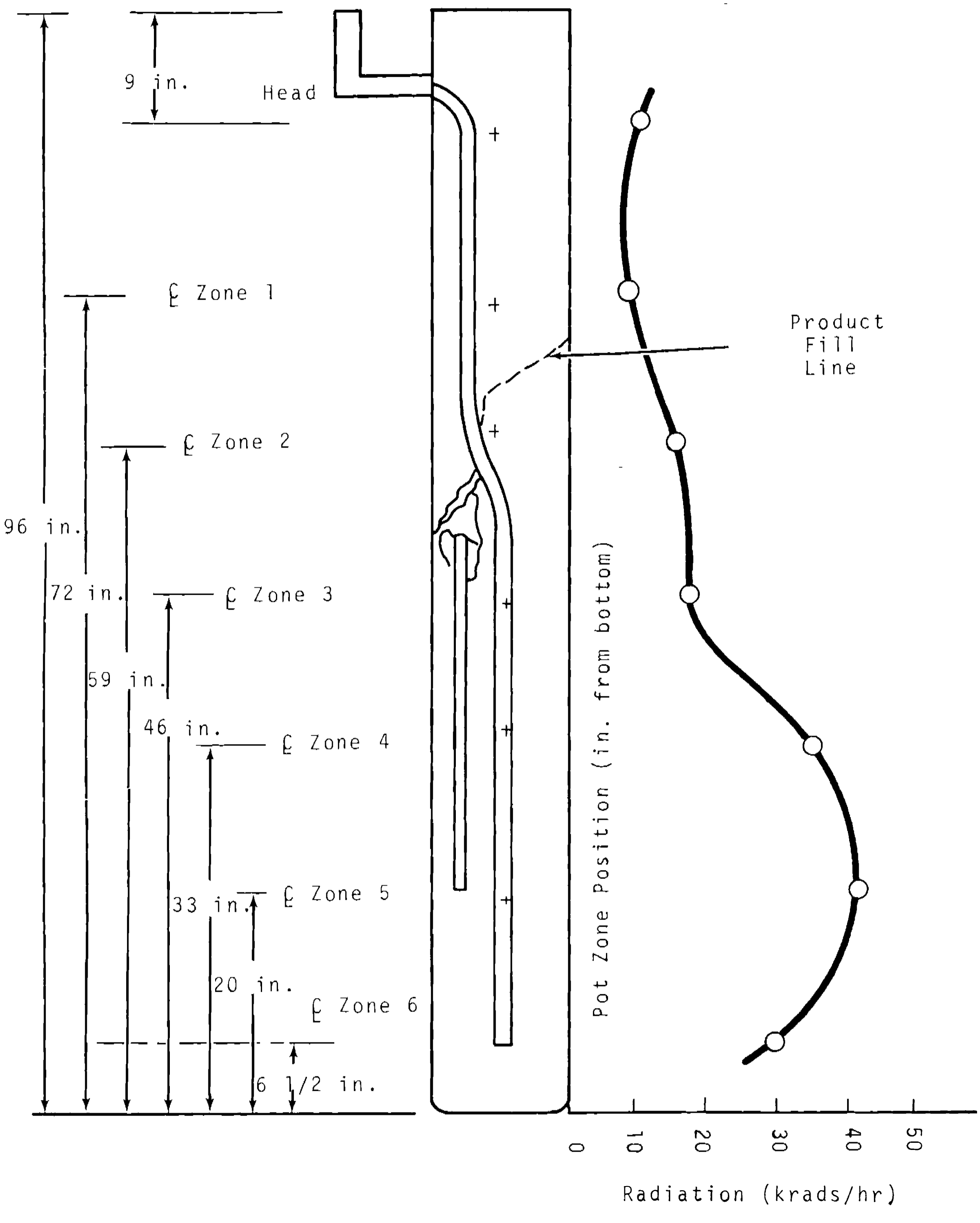
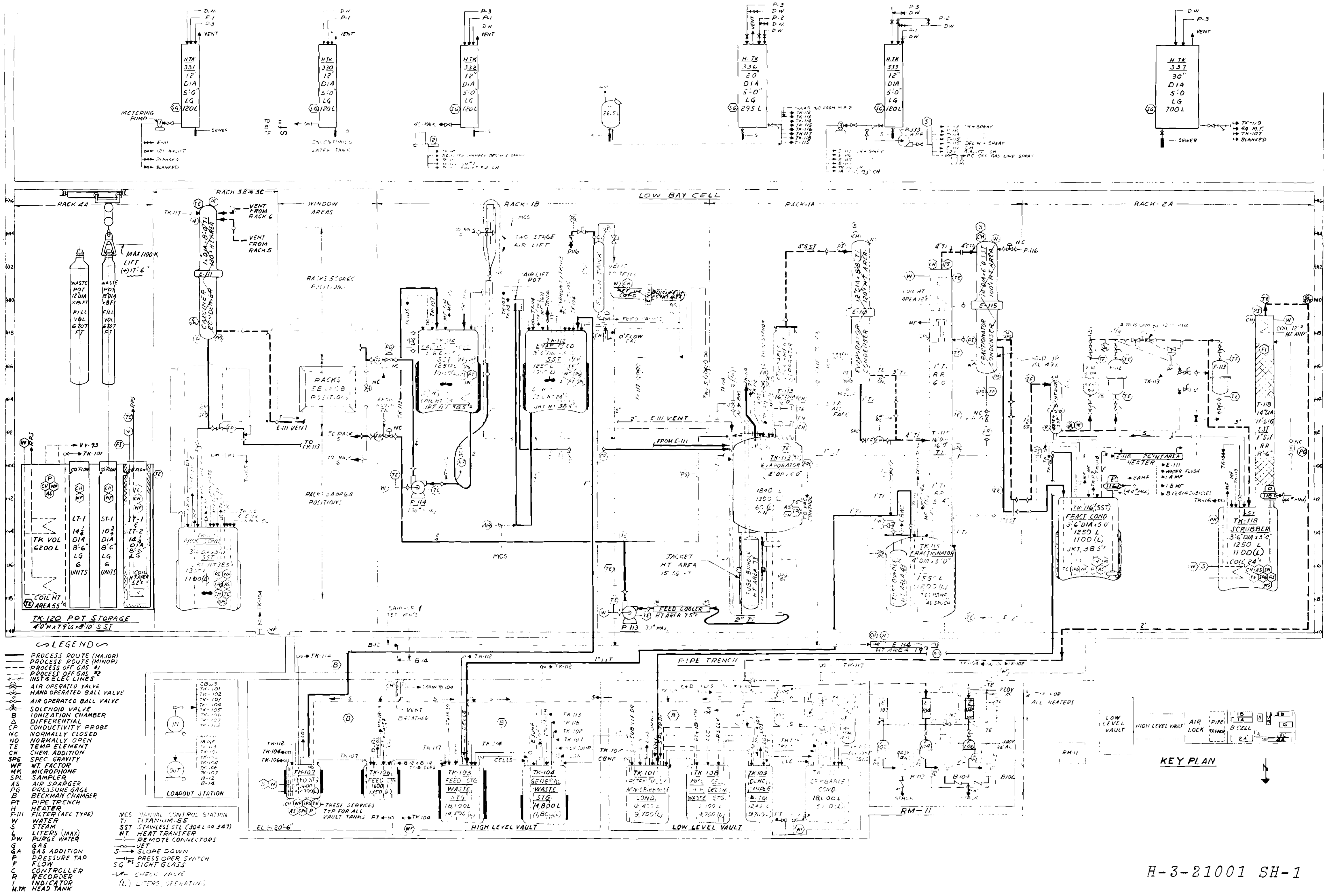
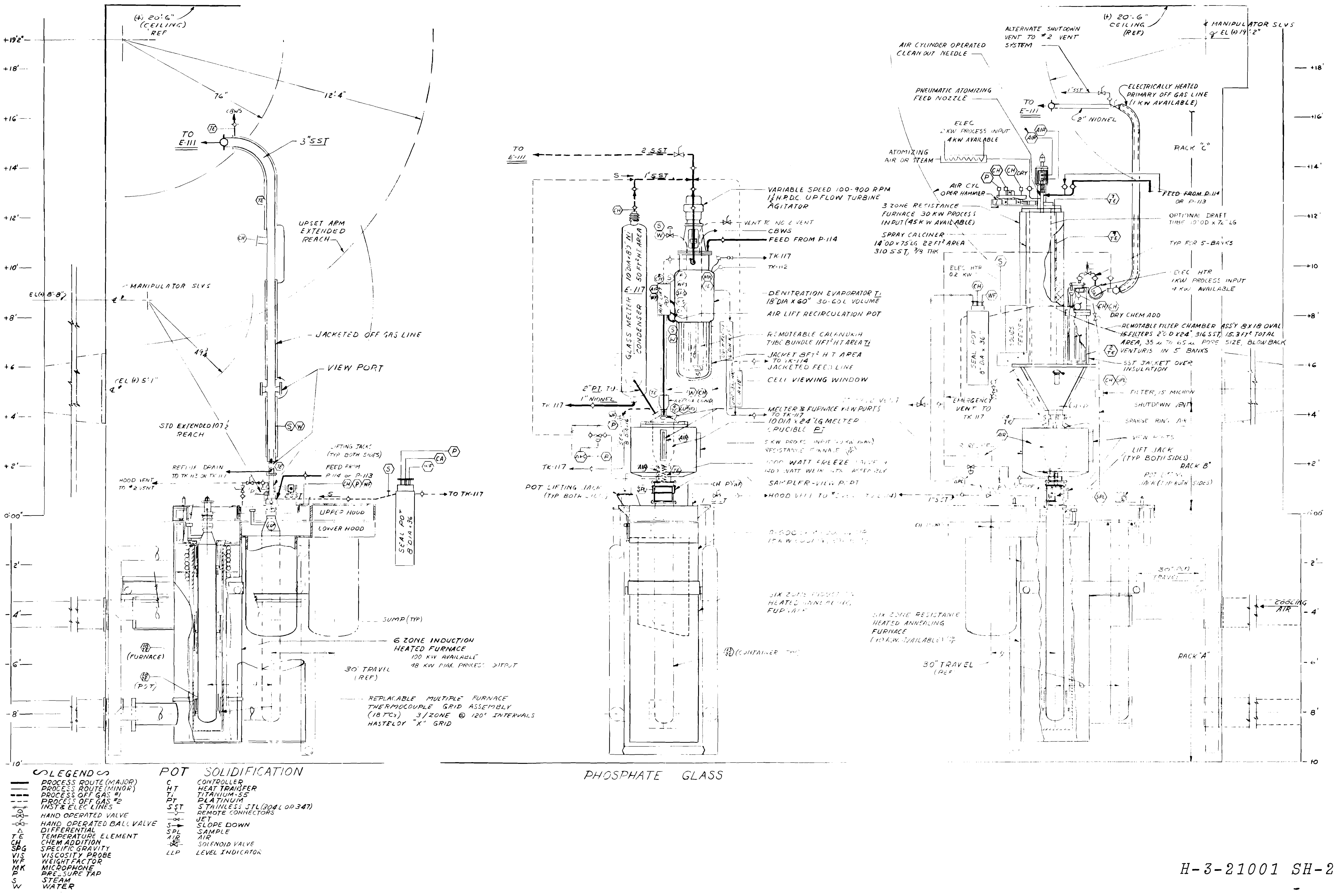


FIGURE 9.8 *Run PG-3: Pot Radiation Profile at 6-Inches from Wall*



H-3-21001 SH-1

FIGURE 9.9. WSEP Auxiliary Equipment Flow Diagram



H-3-21001 SH-2

FIGURE 9.10. WSEP Solidification Equipment Flow Diagram

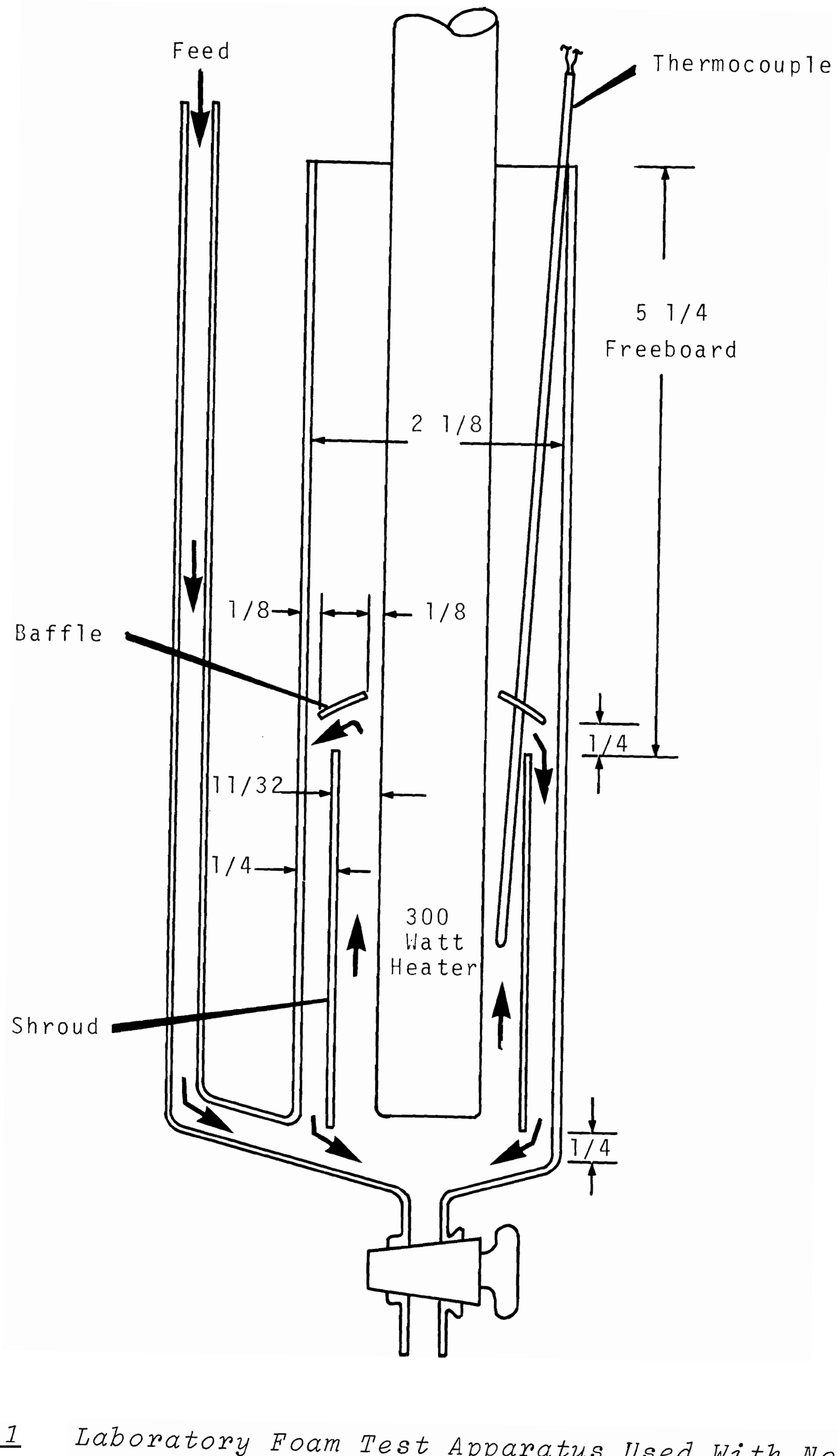


FIGURE 9.11 *Laboratory Foam Test Apparatus Used With Nonradioactive Feed*

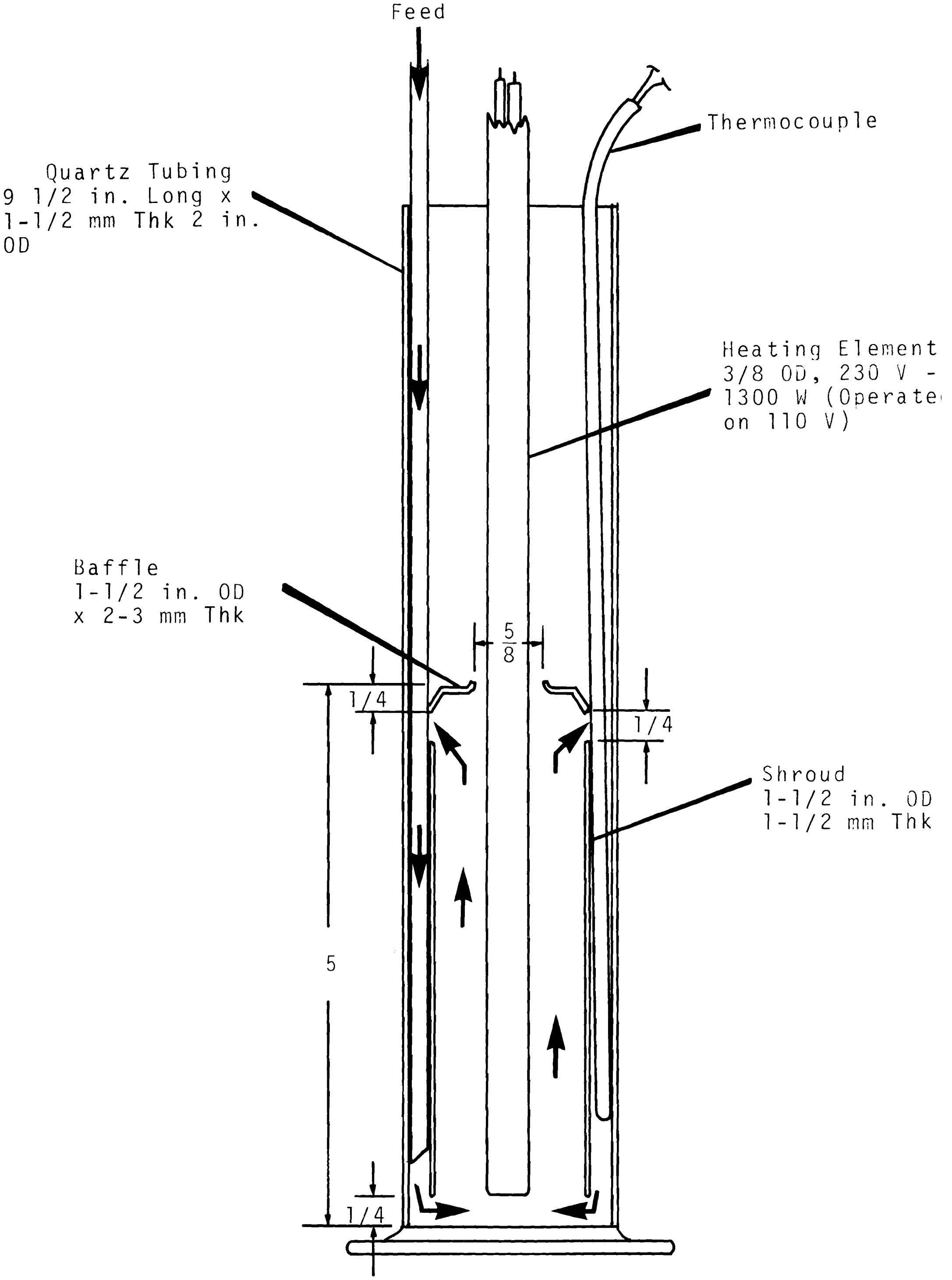


FIGURE 9.12. *Laboratory Foam Test Apparatus Used with Radioactive Feed*

TABLE 9.1. Nominal and Actual Feed Compositions Used in Phosphate Glass Runs PG-1 Through PG-6

	Composition, moles/liter(a)									
		PW-2 Actual						PW-1 Actual		
	PW-2	PG-1					PW-1			
Component	Nominal	Batch 1	Batch 2	PG-2	PG-3	PG-4	Nominal	PG-5		PG-6
H^+	3.33	8.9(h)		6.5(h)	6.4(h)		3.7	8.6(h)		12(h)
Fe^{+3}	0.445	0.320(d)	0.249(d)	0.22(d)	0.294(d)	0.191(d)	0.93	0.48(d)		1.05
Cr^{+3}	0.024						0.012			
Ni^{+2}	0.010						0.005			
Al^{+3}	0.001	0.101(d)	0.240(d)	0.243(d)	0.176(d)	0.191(d)	0.001	0.416(d)		0.16(d)
Na^{+1}	0.930	0.895	0.705	0.99	0.88	1.2	0.138	0.29		0.43
U^{+6}	0.010				0.017		0.010	0.05(f)		
NO_2, NO_3^{-1}	5.37	4.68	4.37	4.85	4.5	4.33	7.5	7.1		7.5
SO_4^{-2}	0.87	0.9	0.94	0.87	0.83	1.2	--			
PO_4^{-3}	0.006						0.003			
SiO_3^{-2}	0.01						0.010			
Cs^+ (added K)	0.042						0.042			
Sr^{+2}	0.0155						0.0155			
Ba^{+2}	0.0195						0.0195			
$(Y + RE)^{+3}$	0.120				0.115	0.57(g)	0.120			0.24(i)
ZrO^{+2}	0.065						0.065			
MoO_4^{-2} +Tc as MoO_4^{-2}	0.130			0.079		0.079	0.130	0.079		
Ru^{+4}	0.0032	0.0035	0.0036	0.0037	0.006	0.003	0.0032	0.004		
Ru^{+4} (Added as Fe^{+3})	0.0288						0.0288			
Rh^{+2} (Added as Co^{+2})	0.0074						0.0074			
Pd^{+2} (Added as Ni^{+2})	0.0172						0.0172			0.0222
Ag^{+2} + Cd^{+2} (Added as Cu^{+2})	0.0016						0.0016			
TeO_4^{-2} (Added as SO_4^{-2})	0.0064						0.0064			
Additive To Feed								Part I	Part II	
Na^+	0					0.5	2.47	2.47		2.46
PO_4^{-3}	3.30	2.92	3.36	3.43	3.36	4.5	6.38	6.47		7.97
ΣM^+_T	3.30	3.1	3.11	3.32	3.25	4.64	6.38	6.59		8.01
$\Sigma M^+_T/P$	1.0	1.06	0.93	0.97	0.97	1.03	1.0	1.02		1.0
Sp. Gr. at 25 °C(b)		1.36		1.3	1.37	1.43		1.46	1.33	1.37
% Solids(b)		13	31	25	50	10		16	22	12
Concentration, liters/Te		483	470	586	458	540		666	1143	889
Radioactivity										
Total Ci/liter		215	518	790	2,520	1,590		3070	1860	4160
Ru Ci/liter		11	21	38	53	46		56	39	13
Heat W/liter		1.3(c)	1.3(c)	3.9	10(e)	7		13	8	16.8

---

a. Values are reported on a 378 liters/tonne basis.
b. Values reported for samples as taken.
c. Values obtained from pot calorimetry data.
d. Aluminum substituted for part of the iron.
e. By heat rise test assuming Cp = 0.9 kcal/kg -°C for concentrated wastes only.
f. U^{+6} is factor of 5 greater than nominal 0.01M; 0.24M H_3PO_4 added because of excess U^{+6}
g. The rare earths were ∿6 times the nominal 0.12M R.E.
h. Includes H^+ from H_3PO_4.
i. Excess of rare earths over nominal 0.12M caused need for 0.183M H_3PO_4 addition to the nominal 6.38M H_3PO_4.

TABLE 9.2. Operating Parameters and Results of Phosphate Glass Solidification Demonstration in Runs PG-1 Through PG-6 in WSEP

Phosphate Glass Run Number	PG-1		PG-2	PG-3	PG-4	PG-5		PG-6
	Part 1	Part 2				Part 1	Part 2	
Date	11/16/67-	11/21/67	12/12/67-12/14/67	1/24/68-1/26/68	2/27/68-3/1/68	4/16/68-	4/25/68	5/13/68-5/15/68
Operating Mode	A	B	A	A	A	A	A,B	A
Feed Type	PW-2	PW-2	PW-2	PW-2	PW-2	PW-1	PW-1	PW-1
Denitrator-Evaporator								
Adjusted Feed Conc, liter/tonne	480	580	586	458	540	666	1143	889
Total Run Feed Time, hr	61.4	31.0	48.5	57	77	38	66	50
Startup Time (concentration period), hr	9.0	5.0	10	13	12	6	6	7
Steady State Operation, hr	52.4	26.0	32	16	65	32	60	43
Shutdown Time (dilution period), hr	11.7	15.0	14	14.4	13	2	10	14
Avg. Feed Rate, liter/hr	15.7	13.9	18	11.0	9.4	11.1	12.8	12.3
Avg. Feed Rate During Startup, ℓ/hr	21.6	19	22	11	20	25	25.8	23.6
Avg. Feed Rate During Steady State Operation, liter/hr	14.6	13.0	14	16	7.5	10	11.5	10.5
Total Feed to Denitrator-Evaporator, liter	964	431	873	697	725	420	842	616
Total Feed, Tonne Equivalents	1.97	0.75	1.52	1.52	1.34	0.63	0.74	0.69
Total Feed to Melter, liters	709	394	520	318	669	271	728	584
Adjusted Feed: Solid Volume Ratio	12		13	9.1	9.1	6.1	10.5	9.4
Waste: Solid Volume Ratio	8.8		9	7.5	6.4	3.5		4.0
Denitrator-Evaporator Conc. Factor	4.5	6.0	5	4.0	3.1	3.5	5.5	4.2
Denitrator-Evaporator Equivalent Conc. Factor	3.5	4.71	3.2	4.0	2.2	2.0	1.8	1.8
Avg. Liquid Temperature, °C	137	138	137	136	137	134	132	132
Avg. Vapor Temperature, °C	135	136	135	136	110	110	110	109
Avg. Specific Gravity	1.8	1.8	1.8	1.8	1.9	1.79	1.8	1.8
Holdup Volume, liter	48	42	47	47	55	51	45	45
Agitator RPM	200	200	200	600	200	200	200	200
Tube Bundle Steam Pressure, psig	52	51	58	67	45-60	45-70	45-70	65
Nitric Acid Spray (6M), liter/hr	1	1	0.7	1.5	0.8	1.3	1.6	1.5
Total Nitric Acid Spray (6M) Added, liter	65	82	31	20	57	58	32	102
Total Grams Antifoam B Added	0	0	0	0	532	502	328	0
Antifoam B Solution Addition, liter/hr				0	3.9[a]	2.6[b]	1.2[b]	0
Total Curies to Denitrator-Evaporator,	438,000		670,000	1,540,000	1.2×10^6	1.29×10^6	1.5×10^6	2.56×10^6
Total Curies Ru in Feed	19,700		33,000	30,000	34,000	23,600	32,600	8,000
Steam Pressure on Jacket, psig	0		10	0	0	0	0	0
Airlift								
Avg. Air Supply Rate, scfh	1.6	3.5	1.7	2.3	2.3	2.4	1.7	1.7
Avg. Air Supply Pressure, psig	7.4	8.8	13	6.0	8.3	9.6	6.1	8.0
Avg. Jacket Steam Pressure, psig	12	15	10	11	14	10	15	17
Solution Feeder (Melter)								
Reflux Solution (Coolant)	Water		Water	Water	Water	Water	Water	Water
Reflux Temperature, °C	101	102	105	97	95	103	103	100
volume, mℓ	~200	–200	200	200	200	200	200	200
Melter								
Furnace Temperature, °C	1230	1220	1230	1230	1220	1220	1220	1220
Internal Melt Control Temperature (Weir Overflow), °C	940	930	750-900	850	800-900	825	825	880
Internal Melt Temperature. (Bottom of Melter), °C	1075	1075	1080	1100	1100	1050	1050	1090
Melt Discharge Method	Unheated Weir		Unheated Weir	Unheated Weir	Unheated Weir	Unheated Weir		Unheated Weir & Freeze Valve
Weir Temperature, °C(L)	750	750	740	760	750	NA		NA
Freeze Valve Temperature While Frozen, °C	450	470	460	330	640	570	570	690
Freeze Valve Cooling Air, psig								15-26
Melter-Receiver ΔP, inches water	3.3	3.3	2-6	3	6-10	6-10	6-10	6-10
Startup Additive (Freeze Valve Seal), kg Glass	17.2		16	<1.0	0	0	0	0
Average Liquid Level, inches	~6	~6	6	6	6	~6	~6	~6
Sparger Nitrogen Flow, scfh	0.2		0-0.8	0.5	0.45	0.2-0.8		0.8
Length of Sparger Test, hr	0		8	8	8	50		53
Steady State Processing Rate, tonnes/day	0.61	0.44	0.38	0.21	0.34	0.28	0.20	0.28
Steady State Processing Rate, liters of melt/day	29.1	21.0	14.9	10.5	19.0	28.8	20.6	26.0
Process								
Vacuum, inches water	2-6		2-6	2-6	2-6	2-6		2-6
Off-gas Flow (inleakage), scfm	~5		6	-	-	9		5
Product Receiver								
Receiver Material	Mild Steel		304-L	Mild Steel	Mild Steel	Mild Steel		304-L
Receiver Diameter, inches	12		8	8	8	12		8
Furnace Temperature, °C	590		580	310	600	600	600	600
Receiver Wall Temperature, °C	590		535-575	300	550-590	575	575	575
Depth of Glass in Receiver, inches	66.5[c]		49.5[d]	41.4	80.4	68		74
Leakage, atm-cc/sec	1.1×10^{-8}		2.35×10^{-8}	4.6×10^{-8}	NA	NA		NA
Product								
Weight, kg	274[c]		118[d]	98	194	119	187	174
Volume, liters	98[c]		41[d]	35	73	44	69	62
Bulk Density, kg/liters	2.7		NA	NA	NA	2.8		NA
Measured Density, kg/liters	2.8		2.9	2.8	2.9	2.7		2.8
Equivalent Waste, tonnes	2.16		0.89	0.69	1.24	1.04		0.66
Equivalent Decay Time, years	7.5		2.5	1.0	1.45	0.53		0.22
Fission Product Heat, watts	1600		1700	3300	4200	8800		9600
Total Radioactivity, curies	349,000		419,000	604,300	1.1×10^6	2.2×10^6		2.43×10^6
Total Radioruthenium, curies	13,000		20,300	10,200	30,912	42,200		8000
Centerline Temperature, °C	316[e]	140[i]	355[f]	655[e] 570[g] 430[h]	510[e]	712[f]		780[f]
Centerline-To-Wall ΔT, °C	39[e]	108[i]	135[f]	255[e] 320[g] 370[h]	175[e]	352[f]		380[f]
Effective Thermal Conductivity, k_e, [W/(m^2)(°C/m)]	1.03[e]	0.69[i]	0.94[f]	0.98[e] 0.78[g] 0.68[h]	0.94[e]	1.13[f]		1.07[f]
Radiation Reading at 6 inches, R/hr	9.5×10^3		4.8×10^4	4.1×10^4	3.7×10^4	4.7×10^4		NA
Melting Point, °C	825		800	850	850	800	800	800
Expected Slump Point, °C	550		650	650	700	700	700	~700
Internal Heat Density, W/liter	17[j]		[illegible][j]	95	57	78		155
Unit volume, liters/tonne	42[j]		40[j]	51	59	108		94
Melter Condenser TK-117								
Inlet Gas Temperature, °C	390	370	300-420	370	320-360	460	450	425
Condenser Off-Gas Temperature, °C (outlet)	48	49	30	45	30	40	45	40
Steam Spray Pressure, psig	2.5	2.5	4.5	4.2	2.1	2.5	2.0	2.0
Steam Spray Rate, liters/hr	6.5	6.4	8.4	8.0	6.2	6.3	5.5	6.3
Auxiliary Process Equipment Average Operating Conditions								
Evaporator (TK-113)								
Bottoms Nitrate, M	6	6	4	4	5	3	7	5
Overheads Acidity, M	0.6	0.6	0.4	0.5	0.4	<0.2	0.7	0.3
Boilup Rate, liters/hr	70	160	53	70	~50	20	88	68
Strip Water Addition, liters/hr	60	125	41	65	~40	12	61	56
Waste Addition Rate, liters/hr, Mode B	0	50[k]	0		0	0	50[k]	0
Total Curies Waste Concentrated, Mode B	0	590,000	0		0	0	3.5×10^6	0
Total Liters Waste Concentrated, Mode B	0	1,140	0		0	0	770	0
Sugar (0.128M) Addition Rate, liter/hr	0	0	0		0	0	0	0
Fractionator (TK-115)								
Bottoms Acidity, M	11.0	14	10	12	9	9	11	8
Overheads Acidity, M	0.02	0.09	0.02	0.04	0.02	0.02	0.02	0.02
Reflux Ratio, Upper Section	0.1	0.1	0.1-0.2	0.25	0.1-0.2	0.1-0.2	0.1-0.2	~0.2
Boilup Rate, liters/hr	70	150	47	70	~45	20	83	69
Fractionator Condensate (TK-116) Acidity, M	0.02	0.09	0.02	0.04	0.02	0.02	0.02	0.02
Scrubber (TK-118)								
Circulation, liters/min	20	20	20	20	20	20	20	20
Bottoms NaOH, M	0.82	0.45	1	1.1	0.9	0.5	0.3-0.03	1.0

---

a. Contains 0.22% by weight of Antifoam B.
b. Contains 0.67% by weight of Antifoam B.
c. Includes 17.2 kg (6 liters) of startup additive nonradioactive glass.
d. Includes 16.3 kg (5.8 liters) of startup additive nonradioactive glass.
e. Receiver sitting in an unheated furnace with no cooling air on.
f. Receiver sitting in an unheated furnace with cooling air on.
g. Receiver suspended in approximately 40 °C air.
h. Receiver sitting in 30 °C water.
i. Based on data recorded 3 months after filling of receiver. Fission product heat had decayed to 1300 W.
j. Does not include additive startup glass.
k. Batchwise addition.
l. Temperature between weir tube shield and weir heater.

TABLE 9.3. *Material Balances for Phosphate Glass Runs PG-1 Through PG-6 in WSEP*

			PG-1		PG-2	PG-3	PG-4	PG-5		PG-6
			Part 1	Part 2				Part 1	Part 2	
Feed To Denitrator-Evaporator (TK-114)	liters/ρ	Initial	1454/1.36	603/1.26	979/1.3	739/1.37	858/1.43	978/1.46	958/1.33	666/1.37
		Final	492	171	106	179	133	558	116	50
	Net change, kg	Volume	-962	-432	-873	-560	-725	-420	-842	-616
		Weight	-1283.4	-546	-1124	-811	-1040	-580	-1137	-806
		Na	-15.85	-5.27	-12.9	-11.4	13.4	--	--	--
		Fe	-13.71	-4.53	-7	-9.14	5.3	--	--	--
		Al	-3.03	-1.74	--	-2.61	--	--	--	--
		P	-75.85	-30.1	-60.2	-60.1	71	--	--	--
		S	-20.68	-8.01	-14	-16.6	13	--	--	--
		N	-52.37	-19.1	--	-32.18	36.1	--	--	--
		Ru	-285.1	-110.2	--	-0.36	--	--	--	--
Denitrator-Evaporator (TK-121)	liters	Initial	42	34	35	38	36	35	36	29
		Final	34	43	46	33	48	55	41	42
	Net change, kg	Volume	-8	9	11	-5	12	20	5	13
		Weight	-8.1	10	41	-6	45	66	34	24
		Na	2.3	-0.62	1.5	--	1.1	--	--	--
		Fe	1.95	-0.54	0.8	--	0.4	--	--	--
		Al	0.75	-0.21	--	--	--	--	--	--
		P	13.00	-3.58	6.9	--	5.4	--	--	--
		S	3.45	-0.95	1.6	--	1.4	--	--	--
		N	0.41	-0.5	--	--	2.7	--	--	--
		Ru	47.5	13	--	--	--	--	--	--
Melter Condensate (TK-117)	liters	Initial	119	890	137	168	115	176	710	119
		Final	890	1115	907	508	812	710	1489	795
	Net change, kg	Volume	771	225	770	340	697	590	779	674
		Weight	848.2	231	803	350	697	599	779	691
		Na	1.7	0.60	5.7	0.81	0.3	--	--	--
		Fe	1.5	0.51	3.4	0.12	0.2	--	--	--
		Al	0.2	0.20	--	0.51	--	--	--	--
		P	7.6	3.42	25.7	3.1	1.7	--	--	--
		S	15.9	8.96	14.3	6.73	6.3	--	--	--
		N	9.6	6.22	--	34.3	2.2	--	--	--
		Ru	50	20	--	0.025	--	--	--	--
Auxiliary Evaporator Feed (TK-112)	liters	Initial	--	1035	--		--	--	771	--
		Final		125	--		--	--	110	--
	Net change, kg	Volume	--	-910	--		--	--	-849	--
		Weight	--	-1113	--		--	--	-996	--
		Na	--	-11.7	--		--	--	--	--
		Fe	--	-8.2	--		--	--	--	--
		Al	--	-6.6	--		--	--	--	--
		P	--	-6.2	--		--	--	--	--
		S	--	-0.3	--		--	--	--	--
		N	--	-39.1	--		--	--	--	--
		Ru	--	-270	--		--	--	--	--
Flush Water to TK-113	Addition, liter		--	--		--	--	--	189	--
Water Addition to TK-113	Addition, liter		--	--	--	--	--	--	70	--
Dilution Water to Denitrator Evaporator (TK-121)	Addition, liter									100
	Net change	Volume	--	--	--	--	--	--	-70	-100
		Weight	--	--	--	--	--	--	-70	-100
Evaporator (TK-113)	liters	Initial	662	244	340	361	166	213	133	320
		Final	244	428	177	217	340	132	326	290
	Net change, kg	Volume	-418	184	-163	-144	174	-81	193	-40
		Weight	-427	380	-163	-182	174	-84	240	-19
		Na	--	13.5	0.2	--	0.7	--	--	--
		Fe	--	12.8	-0.04	--	0.1	--	--	--
		Al	--	9.5		--	--	--	--	--
		P	0.4	-10.3	-0.2	0.2	0.3	--	--	--
		S	1.3	-0.6	-0.7	0.34	4.5	--	--	--
		N	6.6	19.2	--	-16.3	-6.2	--	--	--
		Ru	--	330	--	--	--	--	--	--
Fractionator (TK-115)	liters	Initial	438	460	440	386	343	424	493	420
		Final	460	826	779	421	696	493	893	500
	Net change, kg	Volume	22	366	339	35	353	69	400	80
		Weight	27.7	456	394	101	445	104	561	118
		P	41.1	49.6	--	25.7	50.3	--	--	--
		Ru	--	40	--	--	--	--	--	--
		S	--	--	--	0.07	--	--	--	--
Fractionator-Condensate (TK-116)	liters	Initial	210	365	212	226	214	256	636	195
		Final	1247	1276	590	644	764	670	2038	800
	Net change, kg	Volume	1036	911	378	418	550	414	1392	605
		Weight	1036	911	378	418	550	414	1392	605
		N	0.3	0.7	--	0.33	--	--	--	--
		Ru	10	91	--	--	--	--	--	--
Scrubber	liters	Initial	495	38	361(1)	473	544(1)	503(1)	453(1)	533(1)
		Final	338	280	276	444	226	453	325	483
	Net change, kg	Volume	-157	-58	-85	-29	-226	-55	-129	-50
		Weight	-157	-58	-85	-20	-226	-55	-129	-50
		S	--	0.5	--	--	--	--	--	--
		N	4.1	0.3	--	4.61	--	--	--	--
Evaporator Reductant Addition	Addition	Volume	--	--	--	82	--	--	--	--
	Net change	Volume	--	--	--	-82	--	--	--	--
		Weight	--	--	--	-84	--	--	--	--
Melter Condenser Steam (E-117)	Addition	Volume, L	500	283	533	830	600	456	510	450
	Net Change	Volume	-500	-283	-533	-830	-600	-456	-510	-450
		Weight	-500	-283	-533	-830	-600	-456	-510	-450
Head Tank Additions	liters	Initial	72	43	31	648	57	58	32	102
		Final		0						
	Net change, kg	Volume, L	-72	-43	-31	-648	-57	-58	-59	-102
		Weight, kg	-86	-51	-36	-736	-68	-69	-66	-112
		N	--	--	--	43.6	-4.8	--	--	--
Process Condenser Steam (E-111)	Addition	Volume, L	--	--	90	--	36	--	--	--
	Net change	Volume	--	--	-90	--	-36	--	--	--
		Weight	--	---	-90	--	-36	--	--	--
Product	liters	Initial	6.2	76		0				
		Final	76	111		34				
	Net change, kg	Volume, L	70	35	41	34	73	44	69	62
		Weight, kg	194	97	118	98	213	119	187	174
		Equiv, te	1.5	0.75	--	--	--	--	--	--
		Na, kg	11.8	5.3	6.4	5.75	11.8	--	--	--
		Fe	10.2	4.56	3.8	4.41	5.3	--	--	--
		Al	2.0	1.75	--	1.24	--	---	--	--
		P	55.2	30.3	26	24.1	59.6	--	--	--
		S	--	--	0.04	0.01	0.03	--	--	--
		N	--	--	--	--	--	--	--	--
		Ru, g	180	105	--	0.059 kg	--	--	--	--
Net Change		Volume, L	-218		-151	--	199	47	407	126
		Weight, kg	--	40	-226	--	-88	38	312	75
		Na, kg	--	1.8	0.5	0.68	0.5	--	--	--
		Fe	--	4.6	0.98	-0.58	0.7	--	--	--
		Al	--	2.9	--	0.57	--	--	--	--
		P	--	4.1	-1.8	-8.2	-4	--	--	--
		S	--	-0.4	+2.3	0.75	-0.8	--	--	--
		N	3.7	13.7	--	-6.0	8.1	--	--	--
		Ru, g	--	218.8	--	0.086	--	--	--	--
Percent Recovery		Volume	93	100	90	--	98	104	116	101
		Weight	--	100	92	--	96	103	111	105
		Na	--	110	104	106	104	--	--	--
		Fe	--	135	114	94	113	--	--	--
		Al	--	134	--	120	--	--	--	--

		S	15.9	8.96	14.3	6.73	6.3	--	--	--
		N	9.6	6.22	--	34.3	2.2	--	--	--
		Ru	50	20	--	0.025	--	--	--	--
Auxiliary Evaporator Feed (TK-112)	liters	Initial	--	1035	--		--	--	771	--
		Final		125	--		--	--	110	--
	Net change, kg	Volume	--	-910	--		--	--	-849	--
		Weight	--	-1113	--		--	--	-996	--
		Na	--	-11.7	--		--	--	--	--
		Fe	--	-8.2	--		--	--	--	--
		Al	--	-6.6	--		--	--	--	--
		P	--	-6.2	--		--	--	--	--
		S	--	-0.3	--		--	--	--	--
		N	--	-39.1	--		--	--	--	--
		Ru	--	-270	--		--	--	--	--
Flush Water to TK-113	Addition, liter		--	--	--	--	--	--	189	--
Water Addition to TK-113	Addition, liter		--	--	--	--	--	--	70	--
Dilution Water to Denitrator Evaporator (TK-121)	Addition, liter									100
	Net change	Volume	--	--	--	--	--	--	-70	-100
		Weight	--	--	--	--	--	--	-70	-100
Evaporator (TK-113)	liters	Initial	662	244	340	361	166	213	133	320
		Final	244	428	177	217	340	132	326	290
	Net change, kg	Volume	-418	184	-163	-144	174	-81	193	-40
		Weight	-427	380	-163	-182	174	-84	240	-19
		Na	--	13.5	0.2		0.7	--	--	--
		Fe	--	12.8	-0.04		0.1	--	--	--
		Al	--	9.5		--	--	--	--	--
		P	0.4	-10.3	-0.2	0.2	0.3	--	--	--
		S	1.3	-0.6	-0.7	0.34	4.5	--	--	--
		N	6.6	19.2	--	-16.3	-6.2	--	--	--
		Ru	--	330	--	--	--	--	--	--
Fractionator (TK-115)	liters	Initial	438	460	440	386	343	424	493	420
		Final	460	826	779	421	696	493	893	500
	Net change, kg	Volume	22	366	339	35	353	69	400	80
		Weight	27.7	456	394	101	445	104	561	118
		N	41.1	49.6	--	25.7	50.3	--	--	--
		Ru	--	40	--	--	--	--	--	--
		S	--	--	--	0.07	--	--	--	--
Fractionator-Condensate (TK-116)	liters	Initial	210	365	212	226	214	256	636	195
		Final	1247	1276	590	644	764	670	2038	800
	Net change, kg	Volume	1036	911	378	418	550	414	1392	605
		Weight	1036	911	378	418	550	414	1392	605
		N	0.3	0.7	--	0.33	--	--	--	--
		Ru	10	91	--	--	--	--	--	--
Scrubber	liters	Initial	495	38	361(I)	473	544(I)	503(1)	453(1)	533(1)
		Final	338	280	276	444	226	453	325	483
	Net change, kg	Volume	-157	-58	-85	-29	-226	-55	-129	-50
		Weight	-157	-58	-85	-20	-226	-55	-129	-50
		S	--	0.5	--	--	--	--	--	--
		N	4.1	0.3	--	4.61	--	--	--	--
Evaporator Reductant Addition	Addition	Volume	--	--	--	82	--	--	--	--
	Net change	Volume	--	--	--	-82	--	--	--	--
		Weight	--	--	--	-84	--	--	--	--
Melter Condenser Steam (E-117)	Addition	Volume, L	500	283	533	830	600	456	510	450
	Net Change	Volume	-500	-283	-533	-830	-600	-456	-510	-450
		Weight	-500	-283	-533	-830	-600	-456	-510	-450
Head Tank Additions	liters	Initial	72	43	31	648	57	58	32	102
		Final		0						
	Net change, kg	Volume, L	-72	-43	-31	-648	-57	-58	-59	-102
		Weight, kg	-86	-51	-36	-736	-68	-69	-66	-112
		N	--	--	--	43.6	-4.8	--	--	--
Process Condenser Steam (E-111)	Addition	Volume, L	--	--	90		36	--	--	--
	Net change	Volume	--	--	-90		-36	--	--	--
		Weight	--	---	-90	--	-36	--	--	--
Product	liters	Initial	6.2	76		0				
		Final	76	111		34				
	Net change, kg	Volume, L	70	35	41	34	73	44	69	62
		Weight, kg	194	97	118	98	213	119	187	174
		Equiv, te	1.5	0.75	--	--	--	--	--	--
		Na, kg	11.8	5.3	6.4	5.75	11.8	--	--	--
		Fe	10.2	4.56	3.8	4.41	5.3	--	--	--
		Al	2.0	1.75	--	1.24	--	---	--	--
		P	55.2	30.3	26	24.1	59.6	--	--	--
		S	--	--	0.04	0.01	0.03	--	--	--
		N	--	--	--	--	--	--	--	--
		Ru, g	180	105	--	0.059 kg	--	--	--	--
Net Change		Volume, L	-218	4	-151	--	199	47	407	126
		Weight, kg	--	40	-226		-88	38	312	75
		Na, kg	--	1.8	0.5	0.68	0.5	--	--	--
		Fe	--	4.6	0.98	-0.58	0.7	--	--	--
		Al	--	2.9	--	0.57	--	--	--	--
		P	--	4.1	-1.8	-8.2	-4	--	--	--
		S	--	-0.4	+2.3	0.75	-0.8	--	--	--
		N	3.7	13.7	--	-6.0	8.1	--	--	--
		Ru, g	--	218.8	--	0.086	--	--	--	--
Percent Recovery		Volume	93	100	90	--	98	104	116	101
		Weight	--	100	92	--	96	103	111	105
		Na	--	110	104	106	104	--	--	--
		Fe	--	135	114	94	113	--	--	--
		Al	--	134	--	120	--	--	--	--
		P	--	110	97	87	95	--	--	--
		S	--	96	115	105	94	--	--	--
		N	106	122	--	96	117	--	--	--
		Ru	--	158	--	77	--	--	--	--
Antifoam Addition(2) to TK-332	Addition	Volume	0	0	0	0	242	75	101	0
	Net change	Volume	--	--	--	--	-242	-75	-101	--
		Weight	--	---	--	--	-242	-75	-101	--

---

1. Not included in material balance.
2. Included in material balance.

Definitions for Table 9.2

Operating Mode - WSEP equipment arrangement, see Section 3 and Figure 9.1

Feed Type - PW-1, 2 = Purex Waste - 1 or 2, See Appendix Table 9.1, and Tables 7.1 and 7.2

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 power reactor fuel from which the waste processed would be derived

Total 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

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

Denitrator-Evaporator Concentration Factor - Concentration factor from liquid feed 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-cc/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, 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 power reactor 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 power reactor 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 AT, °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 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. Distribution of Radioactivity for Phosphate Glass Runs PG-1 Through PG-6

Process Vessel	Radio-nuclides	Fraction of Total Activity Fed to System in Run No.:							
		PG-1		PG-2		PG-3	PG-4	PG-5	PG-6
		Part 1	Part 2						
Melter Condensate TK-117. 10^{-3}	Ru	200	200	410	90[b]	410	12	79	43
	Ce-Pr	30	30	270	46	490	2	2.5	1.9
	Cs	100	200	280	48	690	2.8	12	--
	Sr	--	--	--	--	620	--	--	--
	Zr-Nb	50	100	300	68	590	--	--	--
	T-Ru	100	200	270	46	500	2	2.5	1.9
Process Condensate TK-113, 10^{-5}	Ru	4,000[a]	500[a]	900		NA	2,200	6,100	1,700
	Ce-Pr	<100	<100	580		NA	350	1,600	1,300
	Cs	100	80	--		NA	1,500	1,100	--
	Zr-Nb		---	--		NA	1,400	1,500	--
	T-Ru	1	320	580		NA	350	1,600	1,300
Fractionator TK-115, 10^{-7}	Ru	100,000	16.000	10,000		3,900	8,500	21,000	10,000
	Ce-Pr	--	--	<1.2		7.9	3.1	2.8	15
	Cs	500	--	--		--	53	510	--
	Sr	--	--	--		18	--	--	--
	Zr-Nb	--	--	--		24	--	--	--
	T-RU	10	--	1.2		8.6	3.1	28	15
Fractronator Condensate TK-116, 10^{-9}	Ru	16.000	7,800	1,300		14,000	2,000	670	2,900
	Ce-Pr	1,800	4,600	11		9.6	2	25	3.3
	Cs	480	340	--		--	--	--	--
	T-Ru	1,800	6,500	11		9.6	2	25	3.3
Scrubber Bottoms TK-118, 10^{-10}	Ru	--	--	90,000		93,000	7,500	13,000	--
	Ce-Pr	--	--	400		--	40	8	--
	Cs	2,000	52,000	--		--	--	--	--
	T-Ru	--	--	--		--	40	8	--
Stack Off-Gas 10^{-12}	Ce-Pr	--	--	5.8		--	--	--	--
	T-Ru	4.1	3.1	5.8		0.54	2	1	1
Ratio of Radioactivity in Fractionator Condensate to That in 10CFR20[d], 10^{1}	Ru	1,450	760	1,000		6,600	780	180	320
	Ce-Pr	1,647	4,570	77		110	40	180	55
	Cs	10.3	8	--		--	--	--	--
	T-Ru	1,725	6,850	--		--	--	--	
Ratio of Activity in Process Off-gas After Dilution by Building Air[g] to That in 10CFR20[d][h], 10^{-4}	Total a (^{239}Pu)[e]	8,000		1,500		<970	<490	850	<490
	T-Ru[e][h]	8.5		8.9		8.1	23	21	26
	Ru	<68		<68		<68	<68	<68	<68

---

a. Values obtained from stream samples; initial tank samples were contaminated (nonrepresentative).
b. Sample taken at 40 hr into run during period before severe foaming occurred.
c. Based on Part 1 (Mode A).
d. Code of Federal Regulations, Title 10, Part 20, Appendix B, Table 2, Column 2.
e. Particle filter.
f. Gas Scrubber
g. The 20-30 scfm of off-gas exiting the WSEP scrubber (includes inleakage and vacuum control jet air) combines with other C-MEL building air to give a total flow of 120,000 scfm where it is monitored at the stack.
h. (T-Ru) Based on ^{90}Sr, (Ru) Based on ^{106}Ru. Radioactivity monitored in 1.2 x 10^{5} scfm. Stack gas flow including the ~15 scfm gas flow from WSEP solidifier.

TABLE 9.5. Feed Pump Experience During WSEP Phosphate Glass Runs

Pump No.	Service (Runs)	Feed Type	Hours	Run Date	Remarks
P-4	PG-1 (Part 1)	PW-2	(Previous Run time 20 hr) 64 84 Total	11-16-67	Pump installed during PC-6 Pump failed 2/3 through Run PG-1
P-7	PG-1 (Part 2)	PW-2	34	11-22-67	P-7 is the first of the Deanline ® Pumps to be used.
P-7	PG-2	PW-2	64 98 Total	12-12-67	After Run PG-2, P-7 pump was removed.
P-8	PG-3	PW-2	79 79	1-24-68	A new design dual pump jumper was installed with one Deanline Pump as primary and the second as secondary - P-8 is primary. P-9 is secondary.
P-8	PG-4	PW-2	90	2-27-68	
P-8	PG-5	PW-1	83 252 Total	4-16-68	
P-9	PG-5	PW-1	33 Total	4-23-68	P-8 started leaking feed during PG-5, switched over to pump P-9. P-8 was changed out after the run.
P-10	PG-6	PW-1	64 Total	5-13-68	

® Dean Brothers Pumps, Inc.

10.0 ACKNOWLEDGMENTS

Successful demonstrations of six 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.

The principal participants who contributed to the successful efforts were:

BNL

L. C. Emma
J. J. Fedelem
L. P. Hatch
G. Strickland
E. J. Tuthill
G. C. Weth

PNL

A. G. Blasewitz
C. R. Cooley
H. D. Cross
G. V. Fitzpatrick
B. O. Kahle
V. P. Kelly
M. G. Krisher
F. L. Mourich
A. M. Platt
M. O. Rankin
G. Rey
M. R. Schwab
M. E. Spaeth
D. H. Siemens
R. J. Thompson
J. S. Wallner

AEC

C. B. Bartlett
W. G. Belter
W. H. Regan
I. C. Roberts
A. D. Toth

REFERENCES

1. K. J. Schneider and V. P. Kelly. Waste Solidification Program Volume 11, 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 I, Process Technology - Pot Spray and Phosphate Glass Solidification Process, BNWL-1073. Battelle-Northwest, Richland, Washington, August 1969.
3. 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 IV, Pot Solidification Performance During the First Radioactive Tests in WSEP, BNWL-814. Battelle-Northwest, Richland, Washington, December 1968.
4. E. J. Tuthill, G. G. Weth, L. C. Emma, Gerald Strickland, and L. P. Hatch. "Brookhaven National Laboratory Process for the Conversion of High Level Radioactive Wastes to Phosphate Glass," proceedings of the Symposium on the Solidification and Long-Term Storage of Highly Radioactive Wastes. February 14-18, 1966, Richland, Washington, CONF-660208: Available from Clearinghouse for Federal Scientific and Technical Information, Springfield, Virginia.
5. J. N. Hartley and M. R. Schwab. "Phosphate Class Solidification Process," Waste Solidification Program Vol. 1, Process Technology, Pot, Spray and Phosphate Glass Solidification Processes, K. J. Schneider, editor, BNWL-1073. Battelle-Northwest, Richland, Washington, August 1969.
6. U. L. Upson, Battelle Memorial Institute, Pacific Northwest Laboratory, G. G. Weth, Brookhaven National Laboratory, Associated Universities Incorporated. "Fixation of High-Level Radioactive Wastes in Phosphate Glass," Proceedings of the Symposium on the Solidification and Long-Term Storage of Highly Radioactive Wastes, February 14-18, 1966, Richland, Washington, CONF-660208. Available from Clearinghouse for Federal Scientific and Technical Information, Springfield, Virginia.
7. G. G. Weth, G. Strickland, and E. J. Tuthill. "Platinum for High Temperature Crucibles Used in Processing Radioactive-Waste," Proceedings of the Symposium on the Solidification and Long-Term Storage of Highly Radioactive Wastes, Februaru 14-18, 1966, Richland, Washinaton, CONF-660208. Available from Clearinghouse for Federal Scientific and Technical information,-spring field, Virginia.

8. G. Strickland, E. J. Tuthill, and R. F. Drager. "Phosphate Glass Process: Evaporator Studies with Simulated Purex Wastes," Proceedings of the Symposium on the Solidification and Long-Term Storage of Highly Radioactive Wastes, February 14-28, 1966, Richland, Washington, CONF-660208. Available from Clearinghouse for Federal Scientific and Technical Information, Springfield, Virginia.

9. R. F. Drager, L. C. Emma, J. J. Fedelem, L. P. Hatch, G. Strickland, E. J. Tuthill, and G. G. Weth. Development of the Phosphate Glass Process for Ultimate Disposal of High Level Radioactive Wastes, BNL-50,130. Brookhaven National Laboratory, Upton, Long Island, New York, January 2968.

10. D. L. Scott, M. E. Spaeth, and K. J. Schneider. Unpublished Data. "Waste Solidification Engineering Prototypes, Design Verification Testing of the Phosphate Glass Process," November 1968. Battelle-Northwest, Richland, Washington, 1968.

11. Unpublished Data from WSEP, Battelle-Northwest, Richland, Washington, Run Summary Reports.

PG-1	December	2968	M. R. Schwab
PG-2	March	2968	J. N. Hartley
PG-3	October	2968	M. R. Schwab
PG-4	June	1968	J. N. Hartley
PG-5	September	1968	J. N. Hartley
PG-6	October	1968	J. N. Hartley

12. M. R. Schwab, J. N. Hartley, and K. J. Schneider. "Phosphate Glass Solidification (Radioactive Demonstration Runs PG-1, 2, and 3)" Quarterly Progress Report, Research and Development Activities, Fixation of Radioactive Residues, A. M. Platt, editor, BNWL-771. Battelle-Northwest, Richland, Washington, November-January 1968.

23. J. N. Hartley and J. L. McElroy. "Phosphate Glass Solidification (Radioactive Demonstration Runs PG-4 and PG-5)" Quarterly Progress Report, Research and Development Activities of Radioactive Residues, A. M. Platt, editor, BNWL-824. Battelle-Northwest, Richland, Washington. February-April 1968.

14. J. L. McElroy, J. N. Hartley and M. R. Schwab. "Phosphate Glass Solidification (Radioactive Demonstration Run PG-6)" Quarterly Progress Report, Research and Development Activities, Fixation of Radioactive Residues, A. M. Platt, editor, BNWL-889. Battelle-Northwest, Richland, Washington, May-July 1968.

15. J. E. Mendel. "Phosphate Class Solidification (Foaming in the Denitrator-Evaporator)," Quarterly Progress Report, Research and Development Activities, Fixation of Radioactive Residues, A. M. Platt, editor, BNWL-889. Battelle-Northwest, Richland, Washington, February-April 1968.

16. P. C. Owxarski. "Highlights in Spray Solidifier Runs SS-5, SS-6, and SS-7," Quarterly Progress Report, Research and Development Activities, Fixation of Radioactive Residues, A. M. Platt, editor, BNWL-1003. Battelle-Northwest, Richland, Washington, Fabruary 1969.

17. S. M. Stoller and R. B. Richards. Reactor Handbook, Interscience Publishers Inc., New York, 1961. Chapters 3 and 24, Second Edition, vol. II.

18. A. S. Wilson. "Ruthenium Volatilization in the Distillation of Nitric Acid," J. Chem. Eng. Data, vol. 5, no. 4. October 1960.

19. United States Atomic Energy Commission Code of Federal Regulations, Title 10, Part 20, Standards For Protection Against Radiation, Appendix B, Table 2, Column 2.

20. U. L. Upson. Fixation of High-Level Radioactive Wastes in Phosphate Glass - Bot Cell Glass Experiment, BNWL-200. Battelle-Northwest, Richland, Washington, January 1966.

21. V. P. Kelly. Waste Solidification Program, Volume 111, Design Features of the Facilities and Equipment for the WSEP Product Evaluation Program. BNWL-832. Battelle-Northwest, Richland, Washington, December 1968.

22. W. V. DeMier. Unpublished Data. Battelle-Northwest, Richland, Washington, October 2967. (Product Evaluation Plans)

23. W. H. McAdams. Heat Transmission, McGraw-Hill, New York, 1954. Third Edition, Chapters 4 and 7.

24. J. D. Kaser. "Estimation of Molten Core Size in Waste Storage Vessels and Frozen Wall Waste Matters," Quarterly Progress Report, Research and Development Activities, Fixation of Radioactive Residues, November, December, 1968, January 1969, A. M. Platt, editor, BNWL-1003. Battelle-Northwest, Richland, Washington, February 1969.

25. W. V. DeMier. "Measurements, Techniques, and Equipment," Quarterly Progress Report, Research and Development Activities, Fixation of Radioactive Residues, April-June 1967, A. M. Platt, editor, BNWL-507. Battelle-Northwest, Richland, Washington, August 1967.

26. E. J. Tuthill, G. G. Weth, L. C. Emma, G. Strickland, and L. P. Hatch. "Phosphate Glass Process for Disposal of High Level Radioactive Wastes," Ind. Eng. Chem., Process Design Development, vol. 6, pp. 314-321. July 1967.

27. K. J. Schneider. Unpublished Data from WSEP Demonstrations. Battelle-Northwest, Richland, Washington, June 1969.

28. H. H. Van Tuyl. ISOGEN - A Computer Code for Radioisotope Generation Calculations, HW-83785. Available from Clearinghouse for Federal Scientific and Technical Information, Springfield, Virginia, September 1964.

29. E. J. Tuthill, G. G. Weth, and A. Abriss. "Studies on Ion Exchange and Glass Formation as Applied to Ultimate Waste Disposal in Fixation of Radioactivity in Stable Solid Media," Report of the Second Working Meeting, Idaho Falls, Idaho, September 1960, TID-7613, Book I, P310-338, February 1961.

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

DISTRIBUTION

No. of Copies	
OFFSITE	
1	AEC Chicago Patent Group G. H. Lee
1	AEC Dayton Area Office P. O. Box 66 Miamisburg, Ohio, 45342 E. A. walker, Chief Operations Branch
178	AEC Division of Technical Information Extension
2	AEC Division of Materials Licensing 4915 St. Elmo Avenue Bethesda, Maryland 20014 John A. McBride R. B. Chitwood
1	AEC Division of Naval Reactors R. S. Brodsky
1	AEC Division of Operational Safety Alex F. Perge
1	AEC Division of Production W. L. Lennemann
5	AEC Division of Reactor Development and Technology C. N. Bartlett W. G. Belter W. H. McVey A. J. Pressesky W. H. Regan
1	AEC Division of Space Nuclear Systems F. C. Schwenk
2	AEC Idaho Operations Office P. O. Box 2108 Idaho Falls, Idaho 83401 K. K. Kennedy B. L. Schmalz

No. of
Copies

1 AEC Oak Ridge Operations Office
C. S. Shoup

1 Allied Chemical Corporation
Nuclear Fuels Department
P. O. Box 35
Florham Park, New Jersey 07932
R. L. Newman
A. Schneider

3 Argonne National Laboratory
S. Lawroski
J. Loeding
R. C. Vogel

1 Argonne National Laboratory
East Area EBR - 2
National Reactor Testing Station
Scoville, Idaho
P. Fineman

1 Atomic Energy Commission
Minister of Defense
Rehovoth, Israel
Yehuda Feige

4 Atomic Energy of Canada Limited
C. A. Mawson
I. L. Ophel
L. C. Watson
J. Woolston

5 Atomic Energy Research Establishment
Harwell, Didcot, Eerks, England
R. H. Burns
H. J. Dunster
W. H. Hardwick
K. D. B. Johnson
W. Wild

3 Australian Atomic Energy Commission
Research Establishment
Private Mail Bag
Sutherland, New South Wales, Australia
M. G. Bailie, Chemical Engineering Section
R. C. P. Cairns
L. Xeher

No. of
Copies

3 Brookhaven National Laboratory
L. P. Hatch
E. J. Tuthill (2)

5 Center for Nuclear Studies
P. O. Box 6, Fontenay-aux-Roses
(Seine), France
R. Bonniaud
F. Laude
J. Pomerola
P. J. Regnaut
J. Sauteron

1 Center for Nuclear Studies
P. O. Box 269
Grenoble (Isere), France
M. G. Wormser, Chemistry Division

Center for Nuclear Studies
P. O. Box 2, Saclay
Gif-sur-Yvette
(Seine-et-Oise), France
C. Gailledreau
A. Menoux
Andre J. Raggenbass

2 Center for Study of Nuclear Fnergy (C.E.N.)
Mol, Belgium
L. Raetsle
P. Dejonghe

Commissaire Boite
Postale No. 149
Paris (15 3m3), France
F. Dumahel

1 Comitato Nazionale per l'Euergia Nucleare
Divisione di Protezione Sauitaria e Controlli
Viale Regina Margherita 125
Roma, Italy
Ferruecio Gera

1 Commissariat a L' Rnergie Atomique
Cadarache, France
P. E. Pottier

1 Dow Chemical Company (AEC)
D. L. Ziegler

No. of
Copies

6 duPont Company, Aiken (AEC)
R. M. Girdler
C. H. Ice
L. H. Meyer
C. M. Patterson
E. B. Sheldon
D. S. Webster

1 duPont Company, Wilmington (AEC)
J. R. Thayer

1 The E. F. MacDonald Company
Touramerica Division
New York, New York
Fred Rerber-Oettgen

1 EURATOM
Cassella Postale No. 1
Ispra, Italy
M. Lindner

1 EURATOM
53 Rue Belliard
Brussels, Belgium
Pierre Kruys

2 Eurochemic Library
Mol, Belgium

1 European Nuclear Energy Agency
38 Boulevard Suchet
Paris 16, France
I. G. K. Williams, Deputy Director

1 Federal Water Pollution Control Administration
Division of Applied Science and Technology
Washington, D.C. 20242
W. J. Lacy

1 General Electric Company
Fuel Recovery Operation
175 Curtner Ave.
San Jose, Calif. 95125
R. G. Barnes

2 General Electric Company, Pleasanton, California
W. H. Reas

No. of
Copies

1 General Electric Co.
Morris, Illinois
S. G. Smolen

1 George Washington University
Washington, D. C.
C. R. Naeser

1 Geotechnical Corporation
Box 28277, Dallas, Texas
D. W. B. Heroy

1 Grupo de Combustibles Irradiados
Junta de Energia Nucl.
Div. de Mat, Civdat Univ.
Madrid 3, Spain
Federico de Lova Soria

1 Gulf General Atomic
P. O. Box 608
San Diego, California 92112
J. J. Shefcik

1 Hahn-Meitner Institut
100 Glienicker Street
1 Berlin 39, Germany
Hans W. Levi

1 Harvard University
Cambridge, Massachusetts
H. A. Thomas, Jr.

3 Idaho Nuclear Corporation
J. A. Buckham
B. R. Wheeler

1 Illinois State Geological Survey Division
Urhana, Illinois
J. C. Frye

3 India Atomic Energy Establishment
Trombay Engineering Hall No. 5
Bombay 73, India
Keshave Chandra
Jitender D. Sehal
K. T. Thomas

No. of
Copies

1 International Atomic Energy Agency
P. O. Box 645
A 1011 Vienna, Austria

3 Johns Hopkins University
513 Ames Hall
Baltimore, Md. 21218
J. Geyer
W. A. Patrick
A. Wolman

1 Kansas State Health Department
Topeka, Kansas 66601
S. J. Reno

1 Karlsruhe Nuclear Research Center
Decontamination Dept.
75 Karlsruhe
Siemensallee 83, West Germany
Helmut Krause

1 Karlsruhe Nuclear Research Center
Waste Storage Dept.
Leopoldshafen/Bd.
Max-Plandk-Str. 12,
West Germany
H. F. Ramdohr

1 KFA
Director of Waste Treatment
Juelich, Germany
S. Rottay

1 Lawrence Radiation Laboratory, Berkeley (AEC)
Technical Information Division Library

1 Lawrence Radiation Laboratory, Livermore (AEC)
Technical Information Division Library

1 Los Alamos Scientific Laboratory (AEC)
C. W. Christenson

1 Mining Academy Clausthal
Petrology, Minerology
& Economics Geology, Dept.
Siemensalle, West Germany
H. F. A. Borchert

No. of Copies	
1	Minister of Federal Property Const. Dept Bad Godesberg, West Germany G. M. K. Klinke
2	Mound Laboratory (AEC) S. Freeman J. J. Goldin
1	MPR Associates, Inc. 815 Connecticut Avenue, N. W. Washington, D.C. 20006 Theodore Rockwell, III, Chairman, AIF Safety Task Force
1	National Lead Company 111 Broadway New York, New York 10006 Stephen Brown
1	National Research Council 2101 Constitution Avenue Washington, D.C. 20418 Dr. Cyrus Klingsberg Tech. Secretary National Academy of Scientists
1	N. Y. State Atomic & Space Development Authority 230 Park Ave. New York, N. Y. O. Townsend, Director
1	William A. Nixon 656 South Illinois Street Arlington, Virginia 22204
2	Nuclear Fuel Services, Inc. P. O. Box 124 West Valley, N. Y. 14171 J. P. Duckworth W. G. Urban
1	Nuclear Materials and Equipment Corporation (AEC) Nuclear Design and Development M. Selman, Manager
1	Nuclear Safety Associates 1055-9-Rockville Pike Rockville, Md. 20852 W. A. Rodger

No. of
Copies

1 Nuclear Reactor Des. Sect.
Nuclear Power Plant Dept.
Bitachi, Ltd., Bitachi Works
Hitachi-Shi Ibaraki-Ken, Japan
A. Shimozato

4 Oak Ridge National Laboratory (AEC)
Central Research Library,
Document Reference Sect.
Central Research Library,
ORNL
Laboratory Records Dept.,
ORNL
Laboratory Records Dept,,
ORNL-RC

1 Phillips Petroleum Company
Water Reactor Safety Program Off.
P. O. Box 2067
Idaho Falls, Idaho 83401
W. Lyle Slagle

1 Plutonium Extraction Plant
Marcoule, France
C. J. Jouannaud

1 Princeton University
Princeton, New Jersey 08540
H. H. Hess

2 Radiation Protection Dept.
Luisenstrasse 46,
Bad Godesberg, West Germany
H. M. Holtzem
G. Straimer

1 Tokai Refinery
At. Fuel Corp.
Tokai-Mura
Ibraki-Ken, Japan
M. Ichikawa

8 Union Carbide Corporation (ORNL)
P. S. Baker
R. E. Blanco
J. O. Blomeke
W. C. Clark
F. M. Empson
H. B. Godbee
J. C. Suddath
M. E. Whatley

No. of
Copies

1 University of Arizona
Tucson, Arizona
E. S. Simpson, Professor of Geology

1 University of Minnesota
Environmental Health Research
and Training Center
Room 1108, Mayo Building
School of Public Health
Minneapolis, Minnesota 55455
C. P. Straub

1 University of North Carolina
Chapel Hill, North Carolina
H. C. Thomas

1 University of Texas
Austin, Texas 75712
E. R. Gloyna

1 University of Wisconsin
Madison, Wisconsin 53715
H. Gladys Swope

2 U. S. Bureau of Mines
Washington, D.C.
J. E. Crawford
J. W. Watlcins

1 U. S. Geological Survey
Washington, D. C.
R. L. Nace

1 U. S. Public Fealth Service
Winchester, Massachusetts
D. Moeller

1 USDA National Agricultural Library
Current Serial Record (G)
Washington, D. C. 20250

1 Vanderbilt University
Nashville, Tennessee
P. A. Krenkel

No. of
Copies

ONSITE-HANFORD

1 AEC Chicago Patent Group
R. K. Sharp (Richland)

6 AEC Richland Operations Office
J. T. Christy
O. J. Elgert (2)
J. F. Goodwin
C. L. Robinson
W. E. Lotz

2 AEC RDT Site Rep., Richland
P. G. Holsted
A. D. Toth

3 Atlantic Richfield Company
P. O. Box 370
Richland, Washington 99352
S. J. Beard
H. C. Rathvon
L. L. Zahn

15 Atlantic Richfield Hanford Company
M. H. Campbell
J. B. Fecht
W. M. Harty
R. E. Isaacson
H. H. Hopkins
L. M. Knights
W. P. McCue
R. W. McCullough
G. C. Oberg
H. P. Shaw
P. W. Smith
R. E. Smith
R. E. Tomlinson
J. H. Warren
File Copy

3 Battelle Memorial Institute

2 Douglas United Nuclear, Inc.
T. W. Ambrose
DUPJ File

1 Jersey Enterprises, Inc.
Joseph Building
Richland, Washington
L. B. Torobin

No. of Copies	
70	Battelle-Northwest
	G. J. Alkire
	A. G. Blasewitz (2)
	W. R. Bond
	D. W. Brown
	R. E. Burns
	J. J. Cadwell
	C. R. Cooley
	D. R. de Halas
	G. M. Dalen
	V. L. Hammond
	J. N. Hartley
	M. M. Hendrickson
	G. Jansen
	J. D. Kaser
	J. H. Kleinpeter
	F. J. Leitz
	J. L. McElroy
	J. E. Mendel
	J. D. Moore
	R. L. Moore
	F. L. Mourich
	T. J. Owen
	H. M. Parker
	D. W. Pearce
	L. D. Perrigo
	A. M. Platt
	K. J. Schneider (30)
	M. R. Schwab
	R. J. Thompson
	C. J. Touhill
	E. E. Voiland
	W. K. Winegardner
	M. G. Wittenbrock
	Technical Information Files (5)
	Technical Publications (2)