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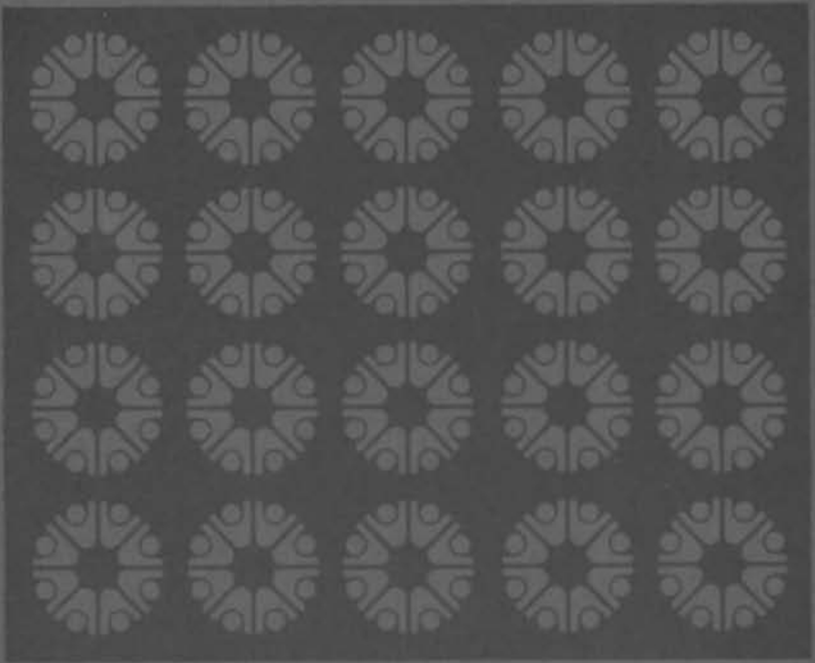
AEC Research and Development Report

WASTE SOLIDIFICATION PROGRAM
VOLUME 9
POT SOLIDIFICATION PERFORMANCE DURING FINAL RADIOACTIVE TESTS IN WASTE SOLIDIFICATION ENGINEERING PROTOTYPES

January 1972



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Waste Disposal
and Processing

WASTE SOLIDIFICATION PROGRAM
VOLUME 9
POT SOLIDIFICATION PERFORMANCE DURING FINAL RADIOACTIVE TESTS IN WASTE SOLIDIFICATION ENGINEERING PROTOTYPES

By

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January 1972

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ABSTRACT

Battelle-Northwest has successfully completed demonstration of solidification of high-level radioactive waste by the pot solidification processes. Approximately 4 million curies of radionuclides were processed and collected in 6 and 8-inch diameter containers during the final three engineering-scale runs in the Waste Solidification Engineering Prototypes (WSEP) at the Pacific Northwest Laboratory. The maximum self-generating heat rate density within an 8-inch diameter pot of solidified calcine was established at approximately 90 W/liter. The solidified calcine within a full 8-inch diameter pot represented 1.3 tonnes of power reactor fuel for PW-1 waste (irradiated to 20,000 MWd/tonne at a power level of 15 MW/tonne) and 0.74 tonnes in a 6-inch diameter pot for PW-4m waste (irradiated to 45,000 MWd/tonne at a power level of 30 MW/tonne). High level aqueous radioactive waste was fed to the pot at average overall rates of 10 to 13.7 liters/hr. The equivalent processing rates ranged from 0.31 to 0.64 tonnes/day of original fuel. During one run the rising level glass process was demonstrated by solidifying PW-4m into a borosilicate glass.

Approximately 10% of the total ruthenium fed to the solidifier was volatilized from the solidifier; entrainment of nonvolatiles was generally less than 1%. The WSEP auxiliary equipment, consisting of an evaporator, an acid fractionator, filters, and a caustic scrubber, 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 10^9 for nonvolatiles and greater than 10^3 for radioruthenium to concentrations acceptable for recycle to a fuel reprocessing plant or low-level treatment processes. The sealed containers of radioactive solids are undergoing further testing in the Solids Storage Engineering Test Facility.

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

K. J. Schneider, Editor, Waste Solidification Program, Volume 1, Process Technology - Pot, Spray and Phosphate Glass Solidification 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.

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

J. L. McElroy, J. N. Hartley, M. R. Schwab, and R. J. Thompson, Waste Solidification Program, Volume 7, Phosphate Glass Solidification Performance During Final Radioactive Tests in Waste Solidification Engineering Prototypes, BNWL-1541 Battelle-Northwest, Richland, Washington, January 1971.

W. R. Bond, J. N. Hartley, J. E. Mendel, J. L. McElroy, and R. J. Thompson, Waste Solidification Program, Volume 8, Spray Solidification Performance During Final Radioactive Tests in Waste Solidification Engineering Prototypes, BNWL-1583, Battelle-Northwest, Richland, Washington, June 1971.

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1.0 INTRODUCTION

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1.0 INTRODUCTION

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

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 on techniques for solidification of high level wastes has taken place in the past 15 years and is still progressing. Four processes for solidification of high level liquid wastes have been developed

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

in the USA to the point of radioactive demonstrations on an engineering scale. The four processes are pot calcination, spray solidification, phosphate glass solidification, and fluidized bed calcination. Two waste solidification methods under development abroad are 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 solidified waste 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), have been demonstrated at the Pacific Northwest Laboratory on an engineering scale with full radioactivity levels for the Atomic Energy Commission. The purpose of the 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 from the reprocessing of nuclear fuel. Battelle-Northwest, in cooperation with Oak Ridge National Laboratory and Brookhaven National Laboratory, is carrying out this demonstration program in the Waste Solidification Engineering Prototypes (WSEP).

The WSEP is a pilot plant that was 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 Material Engineering Laboratory facility has been previously reported.(1) An up-to-date summary of the technology of the pot, spray and phosphate glass solidification processes has also been reported.(2)

This report presents results and analyses of the final 3 radioactive demonstration runs with the pot solidification system in WSEP. (Similar results for the first 6 radioactive demonstrations with the pot solidification system in WSEP were reported in Reference 3, and for the spray and phosphate glass solidification systems in References 4 and 5, respectively. The final phosphate glass and spray solidification runs were reported in References 6 and 7, respectively.) Also included are results of the performance of the associated auxiliary equipment and measurements on the solidified waste. Where pertinent, results are compared to previous nonradioactive data. Detailed descriptions of each demonstration run are presented in the Appendix.

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

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

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

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

5. J. L. McElroy, J. N. Hartley, K. J. Schneider and R. F. Drager (BNL). Waste Solidification Program, Volume 5, Phosphate Glass Solidification Performance During the First Radioactive Tests in the Waste Solidification Engineering Prototypes, BNWL-1185. Battelle-Northwest, Richland, Washington, November 1969.

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7. W. R. Bond, J. N. Hartley, J. E. Mendel, J. L. McElroy and R. J. Thompson. Waste Solidification Program, Volume 8, Spray Solidification Performance During Final Radioactive Tests in Waste Solidification Engineering Prototypes, BNWL-1583. Battelle-Northwest, Richland, Washington, June 1971.

2.0 SUMMARY

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2.0 SUMMARY

Solidification of high level aqueous radioactive wastes containing approximately 4 million curies was successfully completed in three demonstration runs using the pot solidification process in the WSEP. Major accomplishments in the demonstrations were as follows:

- Heat generation from fission products produced temperatures in the solidified waste at the maximum contemplated for the process as prescribed in WSEP. Adequate heating and cooling control of the pots was demonstrated during filling to prevent excessive temperatures during the solidification cycle.
- Aqueous radioactive wastes were solidified and encapsulated in stainless steel pots with minimal corrosion and without pressurization or distortion of the pots.
- The rising level glass (RLG) modification of the pot calciner (wherein the waste was fused directly in the final storage pot) was demonstrated.
- Off-gases passing from the auxiliary effluent treatment equipment and the facility to the atmosphere were decontaminated from radionuclides to levels well below government regulations.
- Aqueous effluents (the fractionator distillate and bottoms) from the auxiliary effluent treatment equipment contained sufficiently low quantities of radionuclides to permit recycle to a fuel reprocessing plant; however, improved cleanup of these streams is desirable to improve the efficiency of their reuse.

2.1 POT SOLIDIFIER PERFORMANCE

The principle objectives for the last three runs were to determine allowable heat generation rates in the solidification pots, to demonstrate pot calcination in 6-inch diameter pots, to demonstrate the rising level glass technique, and to test two waste compositions.

A maximum radioactive decay heat-rate density of 93 W/liter in an 8-inch diameter pot (5600 watts of decay heat from 1.4 million curies) produced a calcine centerline temperature of 1025 °C, in excess of the maximum 900 °C specified for WSEP, with no adverse effects. A heat-rate density of 310 W/liter was obtained in a 6-inch diameter rising level glass pot with no adverse effects.

Two aqueous waste compositions simulating that which would result from the Purex reprocessing of spent power reactor fuels were fed to the pot solidifier at average rates of 9.4 to 13.7 liters/hr. The waste compositions were denoted as PW-1* (a high iron-containing waste from thermal reactor fuels irradiated to 20,000 MWd/tonne** at 15 MW/tonne) and PW-4m* (a "clean" waste from thermal reactor fuels irradiated to 45,000 MWd/tonne at 30 MW/tonne).

The overall processing rates ranged from 0.31 to 0.41 tonne/day for PW-4m waste with 6-inch diameter rising level glass and pot calcination pots, respectively. For PW-1 waste a processing rate of 0.64 tonne/day was obtained during an 8-inch diameter pot calcination run.

The overall volume reduction factor for pot calcination was 8.2 for both PW-1 and PW-4m based on aqueous waste at 378 liters/tonne. For the rising level glass run a volume

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* For detailed chemical compositions see Appendix Table 9.1.

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

reduction of 13 was obtained with a waste composition that contained 50 wt% waste oxides (predominantly fission products). These volume reductions produced solid waste volumes in the range of 32 to 46 liters/tonne. General conditions for each pot run are summarized in Table 2.1.

Although the pot calcination process appears ready for use as a commercial process, the rising level glass process requires additional engineering scale testing before it can be used.

During the pot calcination runs phosphate was successfully used as an additive in place of sulfate to suppress volatilization of alkali metals. This also reduced the concentration of sulfate in the feed and prevented solids precipitation problems which were encountered during the first series of pot runs. The continuous addition of a silicone antifoam agent during the pot calcination runs appeared to stabilize pot calciner foaming, a tendency which was frequently noted during the first series of runs.

Difficulties encountered with the rising level glass process included poor feed control to the RLG pot and calcine plugging of the pot throat. The feed to the RLG pot was fed as a film down the pot centerline thermocouple well in order to increase the heat transfer area and boiloff capacity by a factor of approximately three. This was necessary since the expected capacity would have been less than the WSEP feed system minimum continuous operational rate of approximately 5 liters/hr. Although an average feed rate of 10 liters/hr was attained, the feed also unexpectedly ran onto the intermediate thermocouple well, making feed and temperature control difficult.

Ruthenium volatilization from the two pot calcination runs was 6.1 and 11% of the total amount fed to the solidifier.

TABLE 2.1. Pot Solidification Runs in WSEP

Run	Waste Type	Receiver Pot		Radioactivity Processed, MCi	Heat Generation Rate in Receiver Pot		Equivalent Tonnes to Receiver Pot		liters/ tonne	Equivalent Age(b) of Waste, years
		Diameter, in	Material		Total, kW	Density, W/liter	Actual	100% Fill(a)		
PC-7	PW-1	8	304L SS	1.4	5.6	93	1.3	1.3	46	3.0(c)
PC-8	PW-4m	6	304L SS	1.2	4.8	141	0.74	0.74	46	2.0(d)
PC-9(RLG)	PW-4m	6	310 SS	1.4	5.6	310	0.58	1.16	32	1.2(d)

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a. The equivalent tonnes of waste actually collected normalized to a fill height of 6 feet in the receiver pot.
b. Out-of-reactor time for fuel with the same heat generation rate.
c. Based on fuel exposed to 20,000 MWd/tonne at 15 MW/tonne.
d. Based on fuel exposed to 45,000 MWd/tonne at 30 MW/tonne.

Fifteen percent of the ruthenium was volatilized during the RLG run. Entrainment from the three runs ranged from 0.15 to 1.2%, and approximately 0.6% of the cesium in the feed to the RLG pot appeared to have volatilized.

2.2 AUXILIARY PROCESS SYSTEMS PERFORMANCE

The process off-gas from the pot solidifier is treated by the WSEP auxiliary system (i.e., condensers, evaporator, fractionator, scrubber and filters) where the effluent is separated into streams of cleaner nitric acid, water, and noncondensable gases.

To evaluate the performance of the auxiliary system, fission product decontamination factors (DF's) were determined at each stage of the system. From the original aqueous waste through the auxiliary system to the recovered nitric acid in the fractionator, the DF's were typically 10^2 to 10^3 for radioruthenium and 10^5 to 10^6 for radiocerium. Comparable DF's to the recovered water (accumulated fractionator distillate) were greater than 10^3 for radioruthenium and greater than 10^9 for radiocerium. The DF's to the recovered water were a factor of 10 to 100 lower than expected and were apparently caused by internal contamination of the system. The overall DF's to the off-gas scrubber were 10^3 to 10^4 for radioruthenium. There was no detectable gain of radiocerium in the scrubber. Comparable DF's to the off-gas leaving the scrubber were 10^6 to 10^8 for radioruthenium and 10^8 to 10^9 for radiocerium. Comparable DF's for the final off-gas to the stack were typically 10^8 to 10^9 for radioruthenium and 10^{11} to 10^{12} for gross beta less radioruthenium.

The radioruthenium concentration in the final aqueous effluent (fractionator distillate) was greater than 10^5 (10^3 to 10^4 if adjusted for probable contamination) above allowable values in 10CFR20. Consequently, additional cleanup would be necessary before discharging to the environment unless the effluent is recycled in a fuel reprocessing plant. The nonvolatile radionuclide concentrations in the final effluent would require considerably less cleanup than the ruthenium.

Gaseous effluents from the solidifier condenser, evaporator condenser, fractionator condenser, high efficiency filter, and off-gas scrubber were sampled for both particulate and volatile forms of radioactivity by routing a side stream of the gas through a glass fiber filter and KOH scrubber. Ruthenium DF's across the process condensers ranged from 10^2 to 10^3, while cerium DF's ranged from a low of 50 (fractionator condenser) to a high of 1.2×10^4 (solidifier condenser).

The process off-gas leaving the scrubber contained a concentration of radionuclides above 10CFR20 discharge limits by factors of 22 to 390 for ruthenium and 94 to 430 for nonvolatiles. The radioruthenium in the final stack gas was less than detectable (except for Run PC-8) after the off-gas leaving the scrubber was filtered twice more and combined with building ventilation air. Run PC-8 stack gas ruthenium concentration was 2% of the 10CFR20 limit. All remaining beta radioactivity in the building stack gas was assumed to be ^{90}Sr and was well below 10CFR20 release limits.

During the last series of pot solidification runs, automatic control of the auxiliaries was successfully demonstrated. The process control computer used as a WSEP data logging device was programmed to set the set point on the controllers for the steam flow to the evaporator and fractionator tube bundles.

2.3 FILLED POT PERFORMANCE

Nine pots have now been filled by the pot solidification process. The performance of the waste pots from these demonstration runs is encouraging. None of the pots have indicated any pressurization and none have suffered any measurable change in external pot dimensions through warpage, hot spots, or corrosion during processing or storage. Long term effects up to five years after fill and beyond are not known but are being studied and evaluated in controlled environment tests in the Solids Storage Engineering Test Facility (SSETF).

Stainless steel pots have proven to be satisfactory for pot solidification, and the pots have been seal welded remotely by WSEP developed techniques with existing equipment. Leak checking to 1×10^{-7} atm cm^3/sec or better using a helium mass spectrometer can only be accomplished after prolonged vacuum pumping due to off-gassing of the residual nitrate in the calcine.

Temperature profile measurements and analytically determined heat generation rates have provided the basis for effective thermal conductivity calculations. The effective thermal conductivity calculated for the pot calcine was 0.35 $W/(m^2)$ (°C/m) over a temperature range of 100 to 700 °C. The effective thermal conductivity of the rising level glass borosilicate product is temperature dependent and increases from 1.1 to 1.35 $W/(m^2)$(°C/m) over the range of 250 to 600 °C. Above 650 °C the effective thermal conductivity increases sharply due to remelting of the glass.

Gross axial radiation profiles and axial temperature profiles have shown that the fission products are uniformly distributed in the pot solidified product. Continued observations of the filled pots and core-drilled samples will be used to verify and further establish product uniformity.

Waste pot wall thickness measurements after filling indicate that no corrosion problem exists.

2.4 STATUS OF POT SOLIDIFICATION

The pot solidification runs in WSEP have been completed and the pot calcination process is ready for commercial use. Wastes equivalent to those from power reactor fuels irradiated up to 45,000 MWd/tonne have been demonstrated. A fission product heat generation rate of approximately 90 W/liter is the maximum for PW-1 and PW-4m calcined solid in an 8-inch diameter pot (stored in 38 °C air) when the WSEP restriction of limiting the product temperature to 900 °C is considered. Using the same limit a heat generation rate of 225 W/liter is the maximum for borosilicate glass in an 8-inch rising level glass pot. These restrictions require that a PW-4m waste be cooled 2.1 years before solidification by the RLG process (using 50 wt% waste oxides in solid) or 3.5 years by pot calcination. These times can be reduced by using smaller diameter pots, by dilution of the solids with additives, or by modifying the pot design to include fins or an annulus.

Some individual nuclides (e.g., ruthenium) were not at the levels expected for the fuel exposures tested. 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 in these runs, several general conclusions can be made about the expected operation of the solidifier, the auxiliary evaporator, and the fractionator during processing of full level radioactive wastes:

- Approximately 10% of the ruthenium will be volatilized from the pot calciner to the evaporator during processing of PW-1 and PW-4m wastes. Based on one run, 15% of the ruthenium will be volatilized during the rising level glass process. The evaporator bottoms (concentrated solidifier condensate) can be recycled back to the fuel reprocessing plant high level waste system or the solidifier feed system.

- Less than 1% of the total ruthenium fed to the solidifier will reach the acid fractionator, and the nitric acid produced in the acid fractionator (approximately 150 to 250 liters/tonne of 8 to 12<u>M</u> acid) will contain approximately 400 to 1500 μCi/ml of total β radioactivity. Radioruthenium will be the principle contaminant.
- The ruthenium DF from solidifier feed to the fractionator distillate can be expected to be 10^4 to 10^5 with the ruthenium concentration in the fractionator distillate 10,000 to 100,000 times higher than the concentrations in 10CFR20 when solidifying actual 45,000 MWd/tonne wastes. There will be about 200 to 400 liters of distillate per tonne of fuel processed. Ruthenium-106 is the radionuclide in the final aqueous effluent with the highest concentration ratio to the concentrations in 10CFR20, followed by ^{90}Sr and ^{144}CePr.
- The recovered acid and water are sufficiently low in volume and radioactivity that they can be reasonably recycled for use in fuel element dissolution and/or for use in solvent extraction scrub streams.
- As an alternative to recycling, the radioactivity level of the fractionator distillate is acceptable for additional low-level treatment such as by distillation to concentration limits for discharge of the water to the environment.
- Solidifier product from acidic wastes will have a volume of 29 to 42 liters/tonne of spent fuel for the types of thermal reactor wastes demonstrated. These volumes represent 2 to 3 liters/1000 MWd_e for fuel irradiated to 45,000 MWd/tonne at 30 MW/tonne.

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

3.0 BACKGROUND, PROCESS DESCRIPTION, AND PROCESS TECHNOLOGY

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3.0 BACKGROUND, PROCESS DESCRIPTION, AND PROCESS TECHNOLOGY

3.1 BACKGROUND

The pot calcination process, as developed at Oak Ridge National Laboratory, is suitable for the calcination of a variety of high-level radioactive wastes containing nitrate and sulfate salts and can also be used to incorporate wastes in glassy solids of decreased leachability. The process features simplicity, which is advantageous for remote operation.

Nonradioactive studies of pot calcination were made at ORNL in both laboratory and engineering-scale equipment.(1,2,3,4) Simulated Purex, TBP-25, Darex, and Thorex wastes were solidified in these studies. Subsequently, eight bench-scale tests (six of them with actual Purex waste) were made in a hot-cell at PNL to study fission product behavior as a function of feed additives and off-gas equipment.(5) Eight engineering-scale runs were made during the design verification tests of the WSEP equipment using simulated Purex, Darex, and TBP-25 wastes.(6) The first, third and fourth, and sixth, seventh, and eighth radioactive runs made in the WSEP were demonstrations of the pot calcination process at a rate equivalent to processing wastes from about 1 tonne/day of spent fuel.(7) These WSEP runs with radioactive PW-1 and PW-2 waste compositions culminated an eight-year program of development for the pot calcination process. They demonstrated that the process was essentially ready for commercial application to certain high-level wastes.

The three WSEP runs described in this report were designed to further define process operability and to demonstrate a glass-forming process modification.

3.2 PROCESS DESCRIPTION

3.2.1 Pot Calcination

In the pot calcination process, as demonstrated in the WSEP, 6-, 8-, or 12-inch diameter stainless steel pots, 8 feet long, are filled to approximately 75% of capacity with a cake of calcined waste. The major process equipment consists only of a pot and a zoned furnace to heat the pot to 900 °C.

A complete cycle of operations for pot calcination consists of four rather distinct stages: feeding, calcination, cooling, and pot changeout.

Feeding - The radioactive waste solution is normally pre-evaporated prior to feeding to decrease its volume as much as possible without undue precipitation of solids. In the pot calcination process, as developed at ORNL, the evaporator is operated close-coupled to the pot (Figure 3.1). Most of the pot runs in WSEP were not operated in this way but instead had direct feed from a feed tank with the pot condensate routed to a separate evaporator. The calciner off-gas stream is decontaminated primarily by condensing the acid vapors and absorbing the nitrogen oxides in the calciner condenser. Over 99% of the volatilized ruthenium (which is 3 to 30% of that fed to the calciner) is also absorbed at this point and returned to the evaporator with the condensate.

In WSEP the acid condensate is re-evaporated in the evaporator and passed through a de-entraining tower to an acid fractionation column along with uncondensed nitrogen oxides from the calciner. The acid fractionation column produces concentrated nitric acid and an overhead distillate which is a dilute, low-activity nitric acid. About 75% of the fractionator distillate is recycled to the evaporator to strip nitric acid and control the evaporator acidity. This technique is

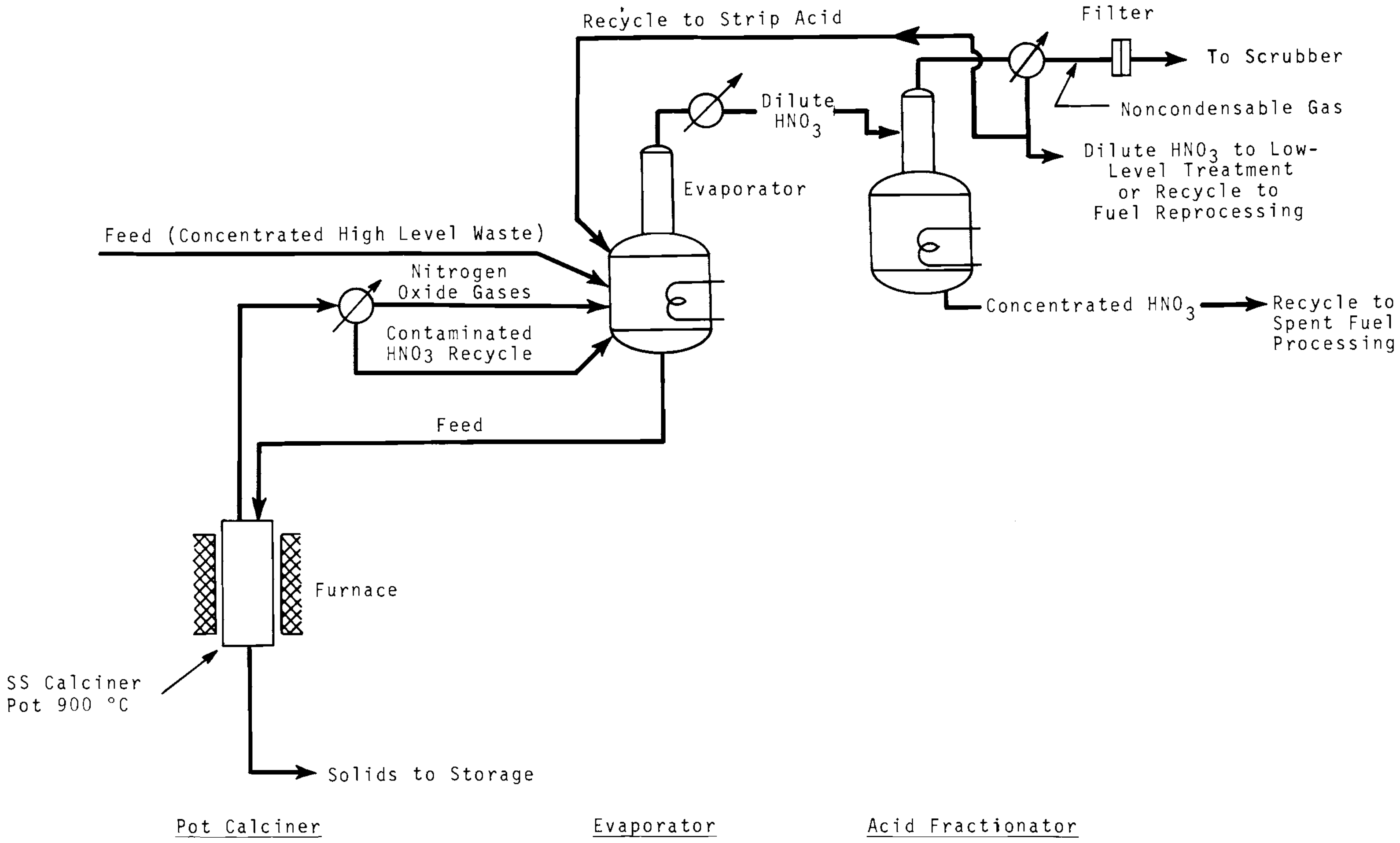

FIGURE 3.1. A Typical Pot Calcination Setup for Solidifying High-Level Wastes

used to maintain the overhead concentration of nitric acid from the evaporator at less than 1.0M, to suppress volatilization of ruthenium.

In WSEP a special self-cleaning off-gas line was used with the pot calcination process. Approximately 10 to 20% of the liquid boiled-up from the pot was continually refluxed in the vertical off-gas line to keep it washed of entrained calcine. The reflux was not returned to the pot but was routed to the evaporator where it was recombined with the remainder of the pot condensate from the process condenser.

The rate at which waste solution is fed to the pot exerts a major influence on operation of the pot calciner. The preferred feeding procedure, based on ORNL and PNL experience, is to keep the level of boiling waste constant at about 2 feet below the top of the pot. At startup, the pot is partially filled with water (from flushing of the pot vent line and fill head assembly between runs). Heating is started and waste is added to increase the liquid volume and then maintain the desired level. As the waste is concentrated in the pot, salts precipitate from solution and form a deposit on the bottom and walls of the pot. The deposit, in the form of a scale or cake, grows progressively inward and upward. As the cake thickens, the heat-transfer rate to the pot contents is reduced, and the pot wall temperature approaches the furnace operating temperature (900 °C). Boilup rates decrease. Finally, the feed rate must be reduced to a point where it is no longer practical to continue feeding. This point is ideally determined by an economic balance between pot costs on the one hand and operating costs on the other.(8) In the WSEP tests, and in most previous development work, feeding was terminated at rates of about 5 liters/hr.

Calcination - Even before feeding is stopped, calcination of the cake deposited near the pot walls is well underway. Internal power generation from radioactive decay accelerates the rate at which calcination proceeds. Excessive temperatures in the calcine are prevented by decreasing the control temperature in the lower zones of the furnace as the calcine level increases. Ultimately, forced air cooling of the lower zones is required. In the WSEP runs, heating of the top zones had to be continued about 8 hours after cessation of feed to obtain complete calcination of the pot contents.

Cooling - After calcination of the pot contents is completed, forced air is applied to the entire pot wall (indirectly via a susceptor). This prevents excessive pot centerline temperatures and reduces the wall temperature to below about 425 °C to allow normal remote handling of the pot without the need for special precautions. It should be noted that the forced air cooling used to counteract the heat generation due to radioactivity in the lower part of the pot before the end of the run decreased the cooling air time needed at the end of the run. In this way the internal radioactive heat generation rate increased overall processing rates.

Pot Changeout - In the WSEP, pot removal and replacement consisted simply of loosening the clamp on the pot off-gas lines, lowering the pot about 6 inches, and rolling the furnace forward 30 inches. After mechanical capping, the pot was picked up by a cell crane and another pot was placed in the furnace. Later, the cap was welded to make the final seal.

3.2.2 Rising-Level Glass

The rising-level glass process produces a coherent glassy product, with a relatively high thermal conductivity, in the same equipment used for the pot calcination process. The process has been demonstrated in laboratory and pilot-plant-scale nonradioactive tests(3,4,6) and in one full-level radioactive pilot-plant test [WSEP Run PC-9(RLG)].

In the RLG process, as in the pot calcination process, the waste solution is concentrated as much as is practical before being fed to the pot. Glass-forming additives, such as borates, and any glass modifiers required are added to the waste solution in the feed tank. In some cases it is desirable to add part of the glass-forming additives as an aqueous solution or slurry at a "T" just above the pot. Silica is generally added in this manner since it is very abrasive to most feed pumps. The silica addition to WSEP Run PC-9(RLG) was made in this way.

At equilibrium three operations are occurring simultaneously within the pot: evaporation, calcination, and melting. At the start of the run the liquid level in the pot is kept quite low until some of the first feed solution has been dried, calcined, and melted. The aqueous feed rate is then adjusted so that the rate of calcine melting just equals the rate at which calcine is formed. Thus, as the run continues, there is a constantly rising pool of melt (hence, rising-level glass) covered by a relatively thin layer of calcine which is in turn topped by a layer of boiling liquid waste. In PC-9(RLG), and in most of the development studies, levels in the pot were determined by thermocouples located at various positions in the pot. Other methods which have been investigated briefly are the use of electrical and thermal conductivity probes.(10)

Processing rates can be increased by a factor of approximately three by increasing the surface area of the liquid in the pot. This is accomplished if the waste solution is fed via film flow down a central pipe in the heated pot. Film flow down the centerline thermocouple well was used in WSEP Run PC-9(RLG) and in one DVT* run.(6)

The effective thermal conductivity of the molten RLG product is about 2.5 W/(m^2)(°C/m). This is sufficiently high that forced air cooling, such as is required in the latter parts of pot calcination runs to counteract radioactive heating in the pot, is not essential to prevent excessive centerline temperatures in 6- or 8-inch diameter RLG pots. Except for reduced cooling requirements, the pot changeout operations for the RLG process are similar to those for the pot calcination process.

3.3 PROCESS TECHNOLOGY

3.3.1 Waste Compositions

Solidification of two different high-level radioactive waste compositions, PW-1 and PW-2, was demonstrated in the first series of pot calcination runs.(7) Solidification of PW-1 and a third waste composition, PW-4m, were demonstrated in the final series of runs, described in this report. The nominal chemical composition of PW-4m is shown in Table 3.1.

Waste type PW-4m was designed to be representative of the wastes from processing of power reactor fuel with an integrated exposure of 45,000 MWd/tonne at a power level of 30 MW/tonne. "Clean" Purex processing was assumed, so the waste was essentially a solution of fission products in nitric acid.

Combinations of Hanford Purex plant waste, selected fission products, and inert chemicals were used to prepare the PW-4m solutions used for the WSEP runs. The Hanford Purex plant waste supplied the complete spectrum of fission products;

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* DVT = Design Verification Test

trace quantities of mercury, silicon, and fluorine; and larger quantities of sodium, iron, chromium, nickel, and aluminum. Large quantities of radioactive cerium from the Hanford Waste Management Process were added to achieve the desired heat rate density in the waste. Inert chemicals were used, as required, to make up the final PW-4m concentrations of all constituents. Some chemicals were prohibitively expensive; substitutions were made in these cases, using cheaper but chemically similar elements. (The substitutions are shown in Table 3.1).

TABLE 3.1. Chemical Composition of PW-4m Liquid Waste for WSEP Demonstrations

Concentration, Molarity at 378 liters/tonne			
Inert Materials		Fission Products (a)	
H	0.50	Mo	0.130
Fe	0.050	Tc (Mo)	0.031
Cr	0.012	Sr	0.036
Ni	0.008	Ba	0.041
Al	0.001	Cs (K)	0.078
Na	0.10	Rb (K)	0.014
U	0.010	Y+RE (b)	0.27
Hg	<0.001	Zr	0.14
NO_3	2.4	Ru (Fe)	0.082
PO_4	0.003	Rh (Co)	0.013
SiO_3	0.010	Pd (Ni)	0.043
F	<0.001	Ag (Cu)	0.0016
		Cd (Cu)	0.0025
		Te (S)	0.014
kg oxide/ tonne	4.6		49.0

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a. Substitute elements used in WSEP solutions are shown in parentheses.

b. RE is rare earth elements.

3.3.2 Pot Calcination Processing Considerations

The pot calcination process converts nitrate salts to oxides, which are more stable toward chemical and radiolytic degradation. Temperatures of at least 800 °C are required to assure complete (>99.7%) nitrate decomposition.

Sulfate volatility problems can occur during pot calcination of sulfate-containing wastes unless suitable precautions are taken. If SO_3 is allowed to evolve, severe corrosion can result; and a sulfate-containing sidestream is generated which requires further treatment. Volatilization of sulfate can be practically eliminated by insuring that sufficient alkali or alkaline earth equivalents are present to exceed the stable anion equivalents ($SO_4^{=}$, PO_3^{-}, BO_2^{-}, $SiO_3^{=}$.) by approximately 10%.(7)

Chemical adjustments are also used to reduce volatilization of several other waste constituents during pot calcination. Volatilization of the alkali metals sodium, cesium, and rubidium is controlled by assuring that there are sufficient nonvolatile anions present to stoichiometrically balance the alkali metal cations. Sulfate was used for this purpose in the first set of WSEP pot calcination runs and phosphate in the second set of runs. The use of phosphate reduced solids plugging problems which occurred during the first set of runs. Ruthenium volatility can be suppressed, but not prevented entirely, by the use of reducing agents. Among the reducing agents which have been found of some benefit are formaldehyde, sugar, and H_3PO_3. No method has been found to prevent mercury volatilization. The most practical approach is to remove mercury from the waste before solidification. Procedures in which mercury is replaced in solution by a more active metal such as copper or aluminum have been shown to remove as much as 99% of the mercury.(11) Problems associated with the possible volatilization of fission products tellurium, selenium, bromine, and iodine during pot calcination have not been evaluated.

3.3.3 Rising-Level Glass Processing Considerations

Most of the RLG process development work was done with phosphate glass formulations.(3,4,6) Phosphate glass formulations were considered desirable because all additions to the wastes could be made as easy-to-handle solutions and any precipitates that formed were flocculent and easily handled. Phosphate melts had the added advantage that the melts did not foam as much as borate melts and homogeneous melts were possible with high sulfate wastes. On the other hand, phosphate melts were known to be more corrosive than borosilicate melts. Furthermore, the corrosion rates proved to be somewhat unpredictable.(9) Ultimately, the decision was made to use a borosilicate formulation for the WSEP high-level RLG demonstration run, PC-9(RLG).

Borosilicate RLG Additives - The borosilicate additive formulation developed at Oak Ridge National Laboratory for use in Run PC-9(RLG) was designed to maximize fission product density in the final melt. Further, an enhancement of thermal conductivity was sought by operating at a low temperature so that the final product contained a dispersion of undissolved oxides in a glassy matrix. (Actually, the thermal conductivity of the PC-9(RLG) product, 1.1 to 1.3 $W/(m^2)(°C/m)$, was in the same range as BNL phosphate glass and in-pot melting borosilicate glass products; however, thermal conductivities as high as 2.1 $W/(m^2)(°C/m)$ have been achieved at ORNL with dispersions.)(12) Some sacrifice in product leachability was accepted to achieve the preceding goals.

The RLG process is similar to the English FINGAL process(13) in that borosilicate waste products are prepared in a rising-level pot system. However, the operating temperature, the type of waste solid, and the off-gas processing system are completely different.

The additives, and the nominal melt composition, for the WSEP demonstration run of the ORNL rising-level glass process were:

Additives (Molarity at 378 liters/tonne)	B_2O_3	0.84M
	$NaNO_3$	0.84
	SiO_2	0.76
Product Composition	B_2O_3	23 wt%
	Additive Na_2O	10
	SiO_2	17
	PW-4m Oxides	50

The B_2O_3 and $NaNO_3$ were added to the PW-4m solution in the feed tank. The solution was diluted to 700 liters/tonne and held at 60 °C to avoid precipitation of boric acid. Silica was added as Ludox® (49 wt% colloidal silica) solution in a separate stream just above the pot.(14) The addition of Ludox to the feed tank was not considered since failures of centrifugal feed pumps of the type used in WSEP had been experienced in past tests with silica-containing feeds. The combined waste and silica streams were fed to the pot by film flow down the outside surface of the central thermowell. Additional heat transfer obtained in this manner increased the processing rate by a factor of approximately three.

Originally it was planned to combine all additives and feed them separately to the pot; however, when the additive was prepared from 105 g/l B_2O_3, 71 g/l $NaNO_3$ and 66 g/l $SiO_2 \cdot xH_2O$ (76.5 wt% SiO_2), there were excessive solids present that were difficult to suspend and that would not dissolve on heating to 75 °C. When Ludox (49 wt% colloidal

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silica) was used in place of the $SiO_2 \cdot xH_2O$, there were crystals present that dissolved when the solution was heated to 60 °C but reprecipitated with only slight cooling. This composition would have required insulating the entire feed additive system (partly inaccessible) to prevent solids from precipitating in the pot feed lines.

RLG Melting Characteristics - The RLG process with the ORNL borosilicate formulation did not receive as much development on a nonradioactive basis as was accorded other WSEP solidification techniques, particularly in the area of engineering-scale tests. Some foaming occurs with the RLG process which can be troublesome in the long narrow pots. Foaming can interfere with liquid level determinations, making operational control during the run more difficult. Foaming is associated with gassification of residual nitrates into the viscous initial melt at 650 to 700 °C. The amount of foaming is lessened by increased operating temperatures and increased waste to flux ratio. Tests showed that the 50 wt% PW-4m formulation used in PC-9(RLG) foamed much less than a melt containing 30 wt% PW-4m.

Type 310 stainless steel is superior to 304L stainless steel as a material of construction for RLG pots as shown by the following corrosion data.

	Corrosion Rates, mils/month[a]	
	310	304L
900 °C	2 (12) 105 (16)	13-41 (15) 235 (16)
950 °C	200 (17)	425 (17)
1000 °C	6 (12) 400 (17)	223-352 (15) 808 (17)

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[a] Reference sources of data are shown in parentheses.

Severe pitting of the 304L surfaces was reported; pitting of the 310 surfaces was much less marked. Although a wide range of 310 stainless steel corrosion rates have been reported, all assure safe operation for the approximately 50 hours at 900 °C nominally required for a RLG run. The English FINGAL tests were made at 1050 °C with a stainless steel very similar to 310.(13)

The pitting attack noted above may be due to a second phase which was present in minor amounts in the RLG melts. The second phase, known to be appreciably more corrosive than the melt proper, occurs in fission product melts containing silica. This second phase was investigated somewhat more thoroughly in connection with the borosilicate in-pot melting WSEP demonstrations described in Reference 18. It should be noted that the second phase is apparently due to fission product molybdenum. Sulfur, another element normally present as an anionic species, also forms a separate phase in borosilicate melts.

Ruthenium evolution during PC-9(RLG) was about 15% of that fed to the pot. Evolution from the FINGAL RLG tests made at 1050 °C averaged about twice this amount.(13) Evolution of other volatile elements was not studied.

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4.0 POT SOLIDIFICATION PERFORMANCE

CONTENTS

4.0 POT SOLIDIFICATION PERFORMANCE

The final three radioactive demonstration runs with the pot solidification process were completed in the WSEP. The major objectives were to demonstrate the solidification of PW-4m waste, to determine the maximum allowable heat generation rate in a calcine pot, to demonstrate the rising level glass technique on a radioactive basis and to determine the solidifier performance coupled with the auxiliary off-gas treatment equipment. Major variables of the runs are shown in Table 4.1.

TABLE 4.1. Major Demonstration Run Variables

PC Run	Mode[a]	Pot Diameter, in.	Waste Type	Total Radioactivity Processed, Ci	Equivalent Tonnes Processed	Heat Rate Density, W/tonne	Equivalent[b] Age, yr.
7	A	8	PW-1	1,400,000	1.3	4300	3.0
8	A	6	PW-4m	1,200,000	0.74	6500	2.0
9 (RLG)	A	6	PW-4m	1,400,000	0.58	9700	1.2

a. See Figure 5.2 for WSEP operating modes.

b. Out-of-reactor time for fuel with the same heat rate density. Based on fuel exposed to 20,000 MWd/tonne at 15 MW/tonne for PW-1 and 45,000 MWd/tonne at 30 MW/tonne for PW-4m.

There were no major problems encountered during this second series of runs with the pot calcination process. Problems encountered during the first series of runs with sodium rare earth sulfate solids precipitating in the feed system and with a tendency for foaming in the pot calciner were eliminated during this series of runs. The sulfate precipitates were reduced by having substantially less sulfate in the calciner feed. In addition, phosphate was used in place of sulfate as an additive to suppress alkali metal volatilization. The foaming was minimized by continuously adding a small stream of silicone antifoam to the calcine pot. The maximum allowable heat generation rate in an 8-inch diameter calcine pot was again established at approximately 5 kilowatts (air cooling by natural convection).

Some operating difficulties were experienced during the single rising level glass (RLG) run and additional testing is required before it can be used commercially. Problems were encountered with feed control to the RLG pot and with calcine plugging the pot throat prior to the off-gas line.

4.1 OVERALL PROCESSING RATES

Overall processing rates (including feeding, calcining and cooling times) were 0.64 tonnes/day for PW-1 waste using an 8-inch pot, 0.41 tonnes/day for PW-4m waste using a 6-inch pot and 0.31 tonnes/day for PW-4m using a 6-inch rising level glass pot.

Establishing the maximum overall processing rate for pot calcination was not a major objective of the WSEP runs. Hence, the general factors affecting rates were not rigorously investigated and results are somewhat qualitative. Feed composition, pot size, and internal power were the major variables which affected the processing rates. Startup procedure, initial feed rate, feed rate at feed shutoff, available furnace power and interruptions also affected the processing rates for a given feed composition, pot size, and internal power level.

Other factors which influenced the rates slightly were:
1) Approximately 1 kg/hr of steam was added to the pot to purge the pot weight factor dip tube during the feeding period.
2) Five to ten liters of condensed pot vapors were returned to the pot during the run to wash the lower section of the pot vent line and the pot throat. 3) A run was started with 10 to 30 liters of water accumulated in the pot from a vent line

flush. 4) During this last series of runs approximately 1 kg/hr of antifoam solution was added to the pot to stabilize foaming.

Since startup and operating conditions can affect rates, a consistent startup procedure was used. Rather than allow high and random feed rates during the early stages of the runs, which could affect the data, the 8-inch pots were limited to a maximum rate at startup of approximately 30 liters/hr and the 6-inch pots to approximately 20 liters/hr. These rates minimized entrainment by limiting the vapor velocity in the pot to approximately 1.2 ft/sec. Maximum feed rates to 12-inch pots in the first series of runs(1) were limited to 50 liters/hr, but they could probably be operated at 60 liters/hr without significantly increasing entrainment.

Table 4.2 summarizes the data on processing rates for the last pot runs. Only one 8-inch run (PC-7) was made to compare with earlier runs;(1) the remaining two runs were a 6-inch pot calcination run and a 6-inch RLG run. The feed and processing rates during PC-7 were slightly lower than previous 8-inch pot runs and can be compared as shown in Figure 4.1. For the WSEP pot calcination runs it can be seen that the average feed rate to the pot calciner increases substantially with pot diameter. The overall processing rate increase is less sensitive to pot diameter because the calcination and cooling time (final bake-out period after feeding is terminated) increases significantly for large diameter pots. Typical pot feed rate curves were described in Reference 1 and actual feed rate curves for PC-7 through PC-9(RLG) are shown in the Figure 4.2.

The effect of internal heat generation rate on the overall processing rate (i.e., feeding, calcining, and cooling) was apparent in that the calcining and cooling cycle following

TABLE 4.2. WSEP Pot Solidifier Processing Rates

PC Run	Feed Type	Pot Diameter, in.(f)	Furnace Net Power Input, kW	Feed Conc., liters/tonne	Feed Heat Rate Density, W/liter	Product Heat Rate Density, W/liter	Total Feed, liters	Drying and Cooling Time, hr(a)	Total Run Time, hr	Avg. Feed Rate at Feed Off, liters/hr	Overall Average(b) Feed Rate, liters/hr	Overall Processing Rate, liters/hr	
												liters/hr	tonnes/day
7	PW-1	8	24	385	11.2	93	500	8	46.5	5	12.8	10.7	0.64
8	PW-4m	6	20	460	14.2	141	340	7	43	3	9.4(e)	7.9	0.41
9(RLG)	PW-4m	6	NA	705	14.3	310	433(c)	NA	43.2(d)	NA	10.0(c)	10.0(c)	0.31

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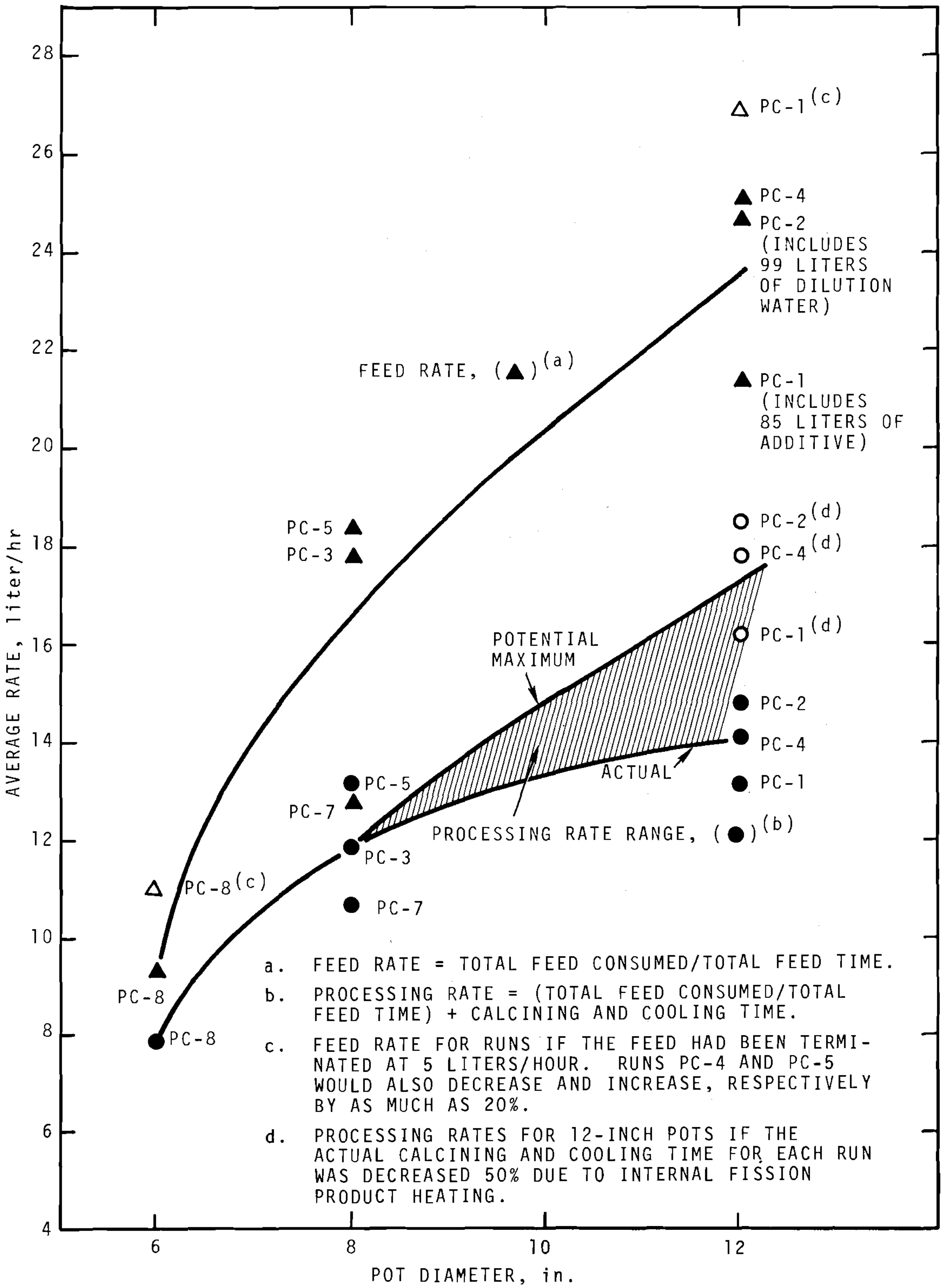
a. Time required after feed off to bake calcine and cool the pot for removal from the furnace.
b. Antifoam was also added during Runs PC-7 and PC-8 at 0.8 and 1.0 liters/hr respectively.
c. Includes 40 liters of additive.
d. Does not include down time during run.
e. Rate would have been 11 liters/hr if the feed was shut off at 5 liters/hr (315 liters processed).
f. Standard Schedule 40 pipe.
NA Not Applicable



a. FEED RATE = TOTAL FEED CONSUMED/TOTAL FEED TIME.

b. PROCESSING RATE = (TOTAL FEED CONSUMED/TOTAL FEED TIME) + CALCINING AND COOLING TIME.

c. FEED RATE FOR RUNS IF THE FEED HAD BEEN TERMINATED AT 5 LITERS/HOUR. RUNS PC-4 AND PC-5 WOULD ALSO DECREASE AND INCREASE, RESPECTIVELY BY AS MUCH AS 20%.

d. PROCESSING RATES FOR 12-INCH POTS IF THE ACTUAL CALCINING AND COOLING TIME FOR EACH RUN WAS DECREASED 50% DUE TO INTERNAL FISSION PRODUCT HEATING.

FIGURE 4.1. Pot Calciner Processing and Feed Rate Dependence on Pot Size

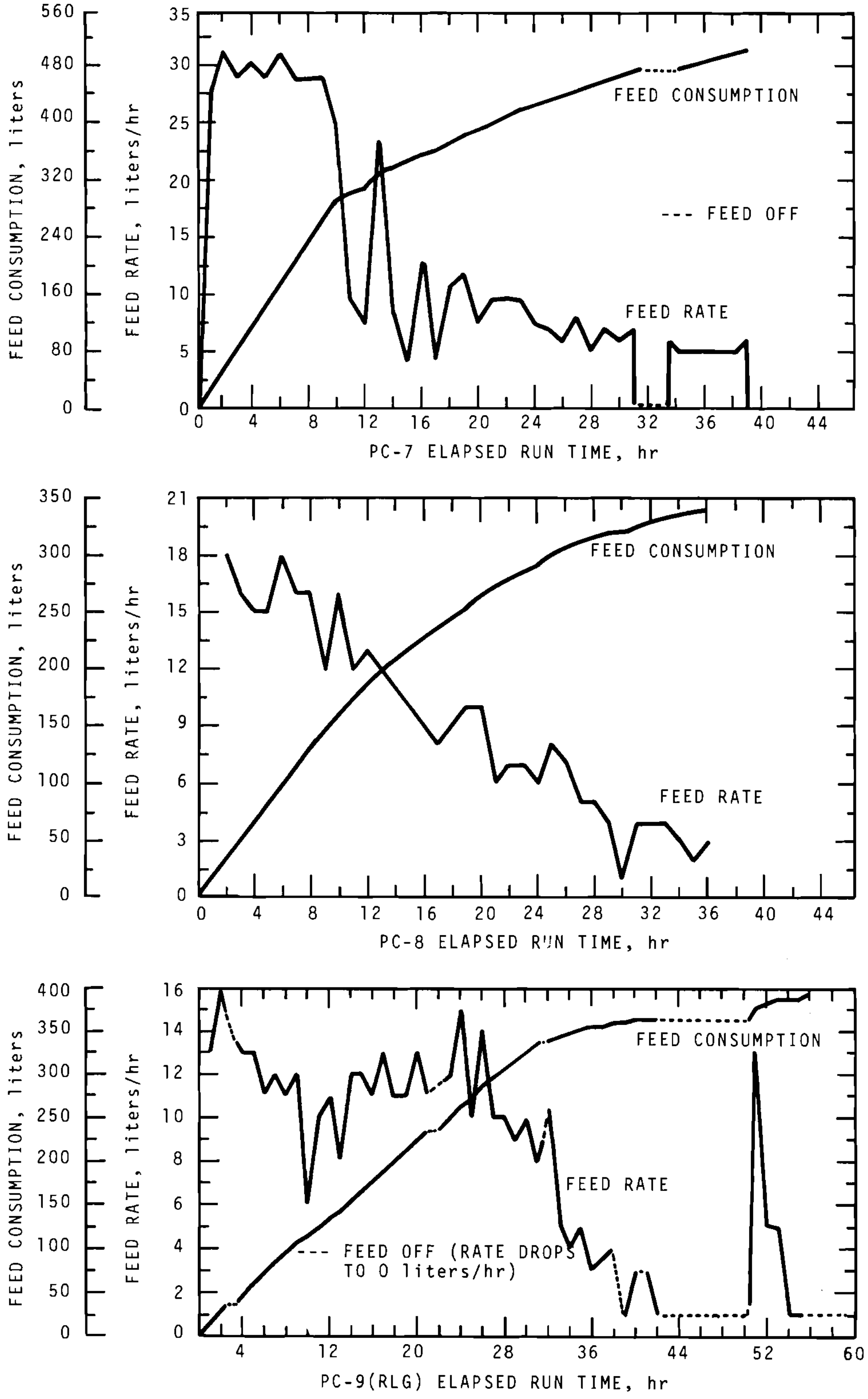


FIGURE 4.2. Feed Rate and Feed Consumption During Runs PC-7, PC-8, and PC-9(RLG)

feed shutoff was reduced as the heat generation rate was increased. However, sufficient data exists to show this only for 8-inch diameter pots. Only one 6-inch pot run was made and of the three 12-inch runs the highest heat generation rate was only 50% of the maximum allowable 5 kW. Therefore, the processing rate curve for 12-inch pots in Figure 4.2 may be adjusted upwards as much as 10 to 20% if the decreased calcining and cooling time occurs with 12-inch pots. No other effect of internal heat generation rate on processing rate was noted.

The average processing rate for the 6-inch RLG run was 0.31 tonnes/day (10 liters/hr); however, the run was terminated after it was approximately 65% completed due to feeding difficulties and a partial (75%) calcine blockage of the pot throat prior to the vent line. The expected boiloff rate from conventional 6 to 8-inch diameter RLG pots at 900 °C is 2 to 5 liters/hr.(2) Since the design of the WSEP feed system did not allow continuous operation at this low rate a method was devised to flow the feed, filmwise, down the RLG pot centerline thermowell(2,3) to improve the RLG capacity and to enable its operation in WSEP. By flowing the feed down the thermowell the effective heat transfer area for liquid boiloff was substantially increased (factor of about 8 for an empty pot) so that an initial feed rate of nearly 15 liters/hr was possible (Figure 4.2). This rate decreases as the pot is filled since the heat transfer area decreases as the thermowell becomes submerged in the rising glass.

During Run PC-9(RLG) the feed was started to the pot at 15 liters/hr without any difficulties; however, it was apparent shortly after the start of the run that, in addition to feed flowing down the centerline thermowell, the feed was being diverted and was wetting the intermediate thermowell as indicated by a substantial decrease in the recorded intermediate pot temperatures above the melt. Although the film feeding increased the capacity as expected, the diverted feed flow and calcine entrainment led to an eventual calcine blockage in the top of the pot; and the feed flow down the intermediate thermowell made it difficult to determine the glass, calcine, and liquid inventories in the pot.

4.2 RADIONUCLIDE HEATING EFFECTS

The high concentrations of radionuclides in high-level solidified wastes will produce high internal temperatures even when the receiver pot is cooled. The temperatures depend on the concentration of radionuclides in the solid product (the irradiation history of the fuel and the age of the waste), the receiver size, the thermal conductivity of the solid product, and the cooling environment in which the pot is placed.

The maximum allowable temperatures established for WSEP are a product temperature of 900 °C and/or a receiver pot wall temperature of 427 °C; if a molten core exists in the receiver pot, the radius of the molten core must not exceed one-half the receiver pot radius. The 900 °C temperature prevents excessive possible corrosion to the stainless steel thermowells used to house the thermocouples at the centerline of the pots. (The wells will probably not be used in production waste 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 to half the pot radius prevents molten waste from contacting the pot wall and thus reduces the corrosion potential.

The temperatures caused by the internal heat generation rate in the last 3 pot solidifier pots are listed in Table 4.3. During the first series of pot runs,(1) it was established that the maximum allowable heat-rate density in an 8-inch diameter pot was approximately 85 W/liter (5100 watts total). This was confirmed during Run PC-7 when a 93 W/liter heat-rate density (5600 watts total) produced a 1012 °C pot centerline temperature (1050 °C during processing) to exceed the desired 900 °C thermal maximum limit.

TABLE 4.3. Solidifier Pot Temperatures Caused by Internal Heat Generation

						Temperature, °C			
PC Run	Waste Type	Pot Diameter, in.	Pot Material	Total Heat Rate, W	Heat Rate Density, W/liter	Pot Furnace(a)	Steady-State Centerline in Furnace(b)	Steady-State Centerline in Air	Pot Wall(b)
7	PW-1	8	304L SS	5600	93	900	1025	1012	295
8	PW-4m	6	304L SS	4800	141	900	872	865	315
9(RLG)	PW-4m	6	310 SS	5600	310	950	740	NA	402

---

a. Furnace temperature during processing and prior to individual zone cooling.

b. Solidifier pot in the furnace with the furnace off and cooling air on. Average of Zone 4 and 5 temperatures except PC-9(RLG) is Zone 5 only.

During Run PC-8, a 141 W/liter heat-rate density (4800 watts total) produced an 865 °C centerline temperature in a 6-inch diameter pot. The data from Runs PC-7 and PC-8 indicate that maximum centerline temperatures of 900 °C would be produced with 4900 watts [$k_{eff} = 0.32$ W/(m^2)(°C/m)] and 5200 watts [$k_{eff} = 0.35$ W/(m^2)(°C/m)] with a 6-foot fill in 8 and 6-inch diameter pots, respectively. For these two conditions the pot wall temperatures would be 230 °C and 265 °C, respectively, based on an estimated pot wall emissivity of 0.8 and equations in McAdams(11) for calculating surface temperatures of cylinders.

During rising level glass Run PC-9(RLG) a 310 W/liter heat-rate density produced a 685 °C pot centerline temperature. Based on an average effective thermal conductivity of 1.3 W/(m^2)(°C/m) achieved with this pot (non-molten core conditions), a hypothetical 900 °C pot centerline temperature would be produced by a heat rate of 14 kW (a heat rate density of 410 W/liter) with a 6-foot fill in a 6-inch diameter pot. The pot wall temperature would be 425 °C ($\varepsilon = 0.8$). Since the melting point of the borosilicate glass is approximately 800 °C the molten core restriction is not attained; however, some softening of the product would probably prevent the 900 °C centerline temperature from being attained as predicted above.

Pot and furnace temperature control techniques were developed in the first series of pot runs.(1) The general procedure was as follows:

- Reduce furnace temperature about 200 °C in individual zones when the pot wall temperature was nearly equal to the furnace control temperature.
- Shut off furnace in a zone when the centerline or intermediate temperature of $\geq$600 °C indicated that the calcine was dry. In large diameter pots ($\geq$ 12 inches) a partial furnace temperature reduction may precede this step.
- Turn on cooling air when the pot centerline temperature reached 800 °C.

An example of pot and furnace temperature control is presented in Reference 1.

During Run PC-7 the pot temperature control was satisfactory as is shown in Figure 4.3. (The thermocouple locations for the calcine type pot are shown in Figure 4.4.) During PC-7 the pot centerline temperature exceeded the desired 900 °C due to the calcine internal heat generation rate and not the furnace control technique. The maximum pot centerline temperature of

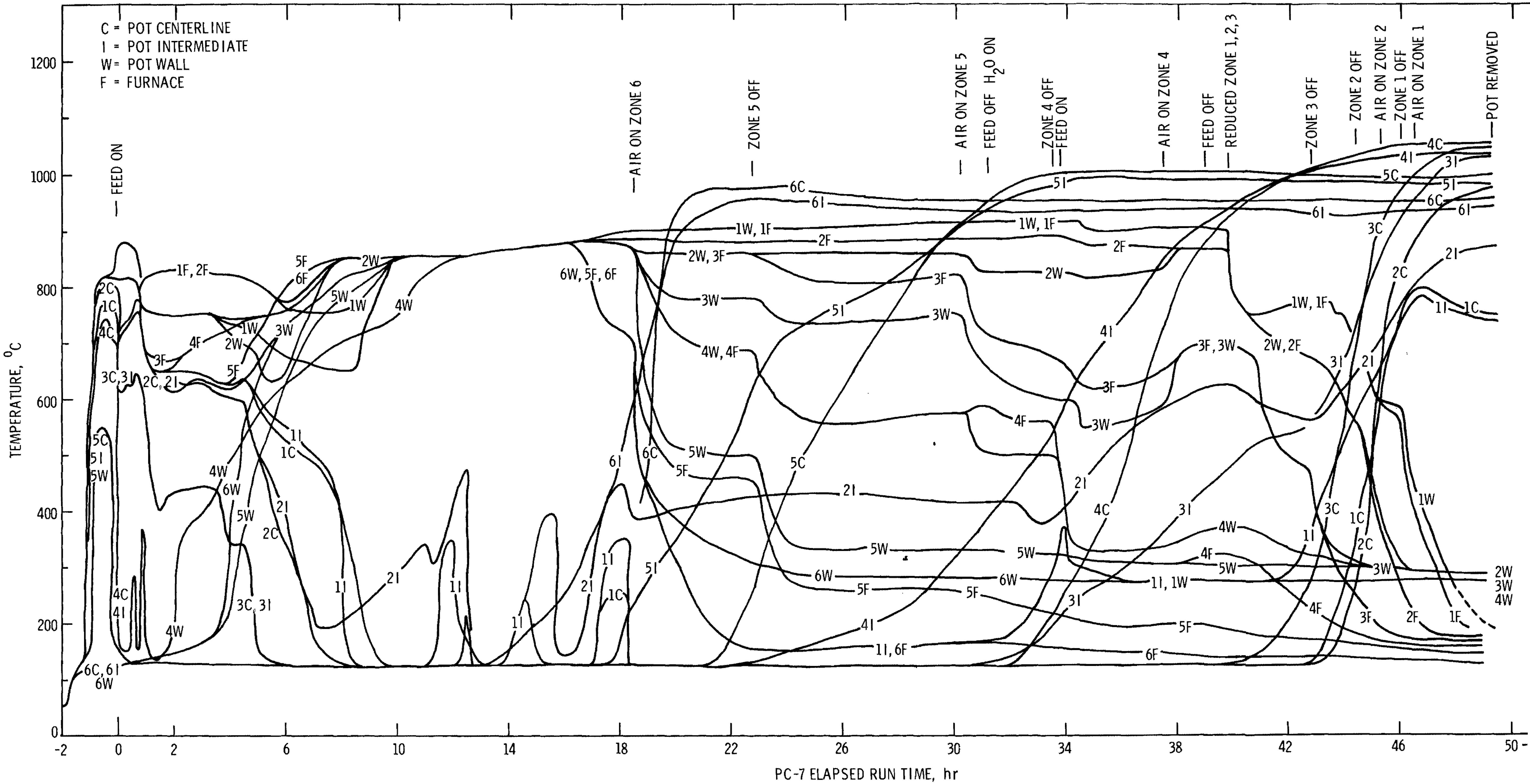


FIGURE 4.3. Pot Calciner Temperatures During Run PC-7

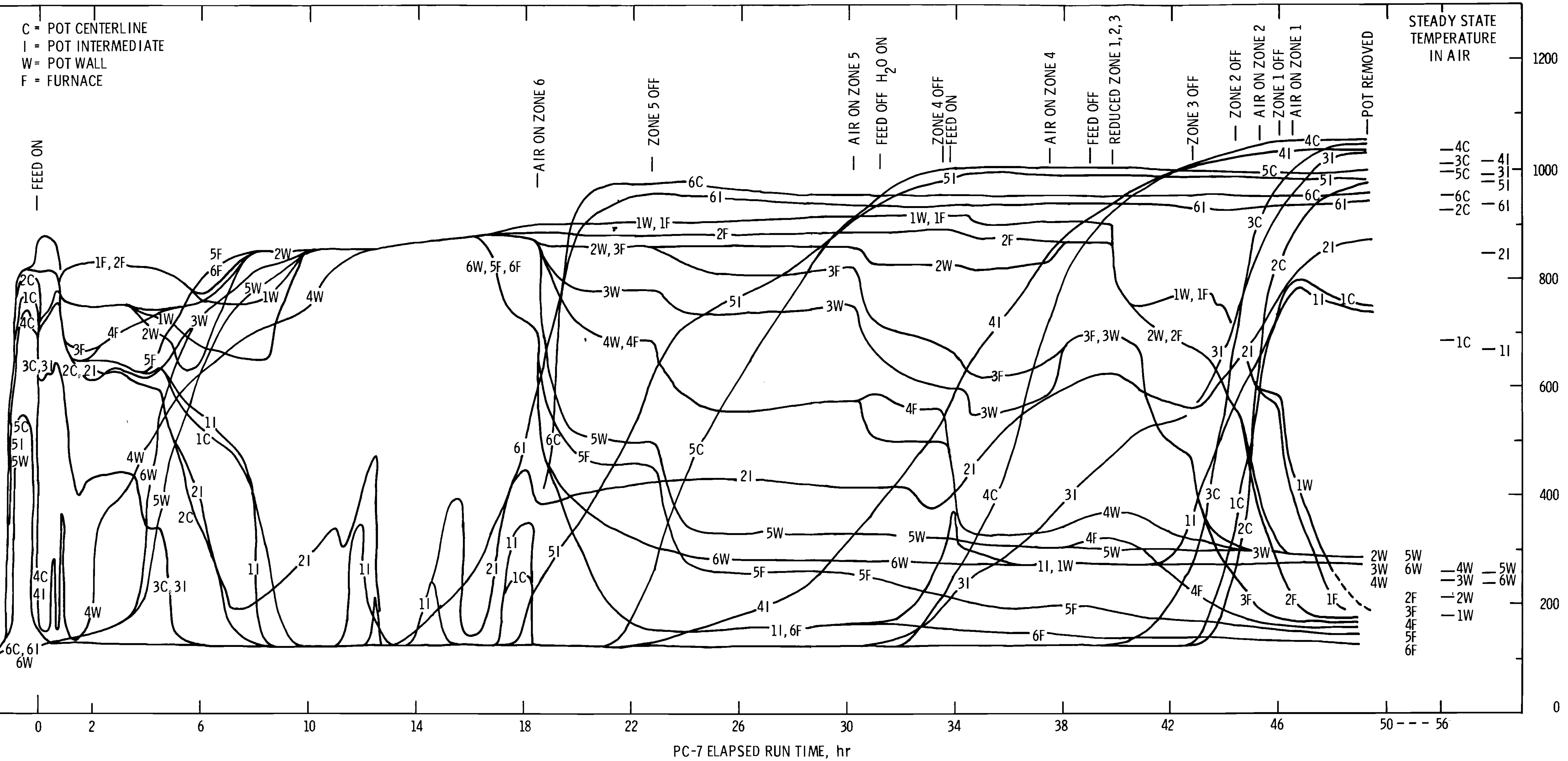
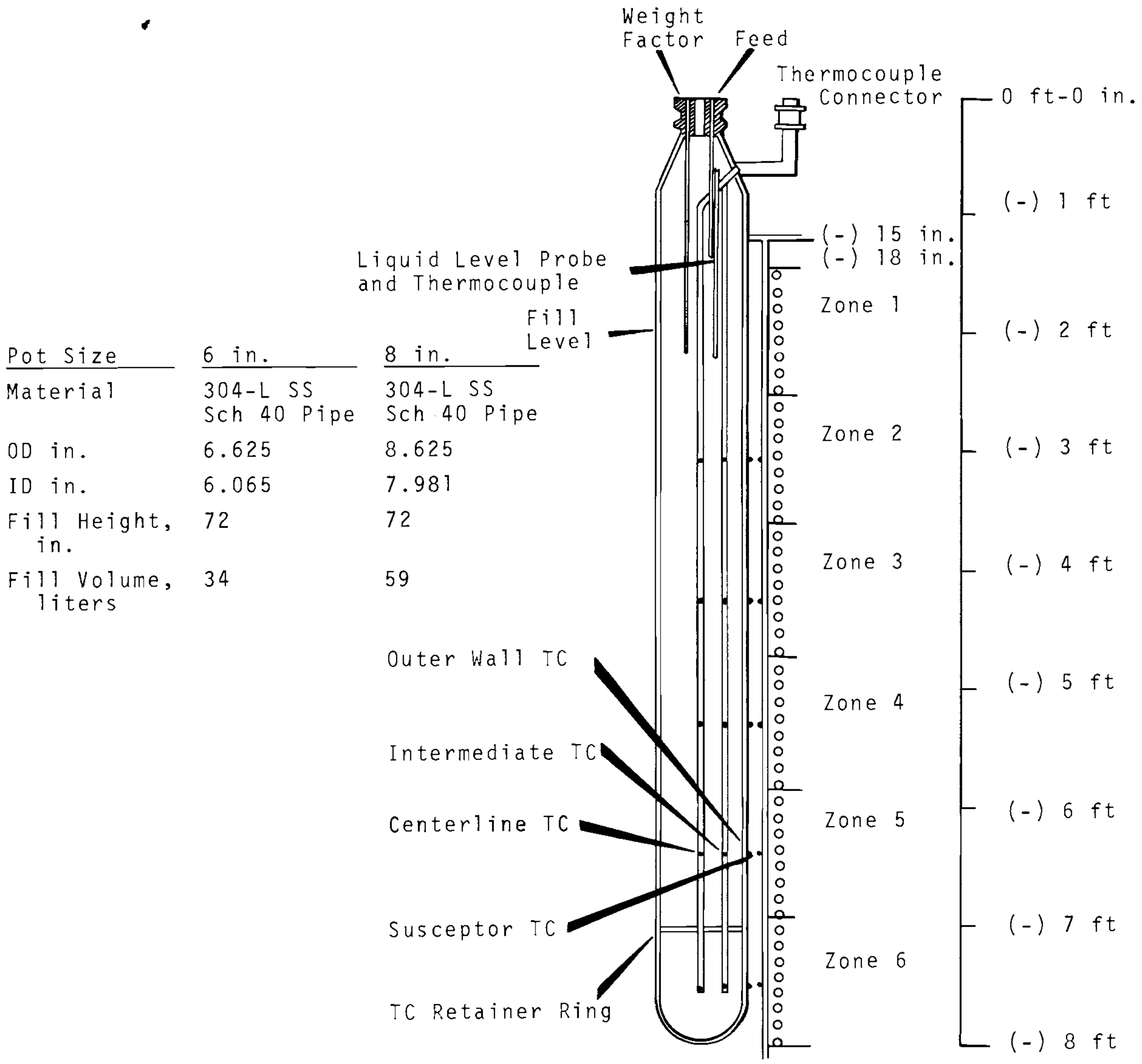


FIGURE 4.3. Pot Calciner Temperatures During Run PC-7



Pot Size	6 in.	8 in.
Material	304-L SS Sch 40 Pipe	304-L SS Sch 40 Pipe
OD in.	6.625	8.625
ID in.	6.065	7.981
Fill Height, in.	72	72
Fill Volume, liters	34	59

FIGURE 4.4. Pot Calciner Thermocouple Arrangement

1050 °C during processing was actually less than 50 °C above the maximum steady-state calcine temperature with the pot removed from the furnace and this is considered excellent control.

During Run PC-8 the temperature control was also adequate; however, the calcine temperatures did not increase smoothly in the 200 to 900 °C temperature range as did those for PC-7. As shown in Figure 4.5, the PC-8 calcine temperatures increased to 800 to 900 °C and then dropped to about 200 to 300 °C as though the calcine was being washed out by the liquid in the pot. The temperatures would then climb to about 900 °C and would either stabilize or make another smaller oscillation. This was the first 6-inch pot calciner run in WSEP and this was the first time this temperature pattern developed. It is partially attributed to the power input from the pot furnace being set sufficiently low that cooling air from adjacent zones would pull the temperature down in the zones with power still on. A higher initial net power than the 3 kW/zone (18 kW total) used with the 6-inch PC-8 pot is recommended; 4 kW/zone net would be more nearly optimum.

Temperature control during the rising level glass run was also adequate; however, because of the feed solution wetting both of the pot thermowells it was difficult to determine the level of liquid, calcine or glass in the pot. The temperature profiles for the lower zones of the RLG pot are presented in Figure 4.6. (See Figure 4.2 for feed history.) The pot centerline temperatures show the expected progression of melt rising to fill the pot. The intermediate temperatures start decreasing much earlier than expected (more evident in the top zones) due to the unwanted wetting by the entering feed. The pot thermocouple arrangement for the RLG pot is shown in Figure 4.7.

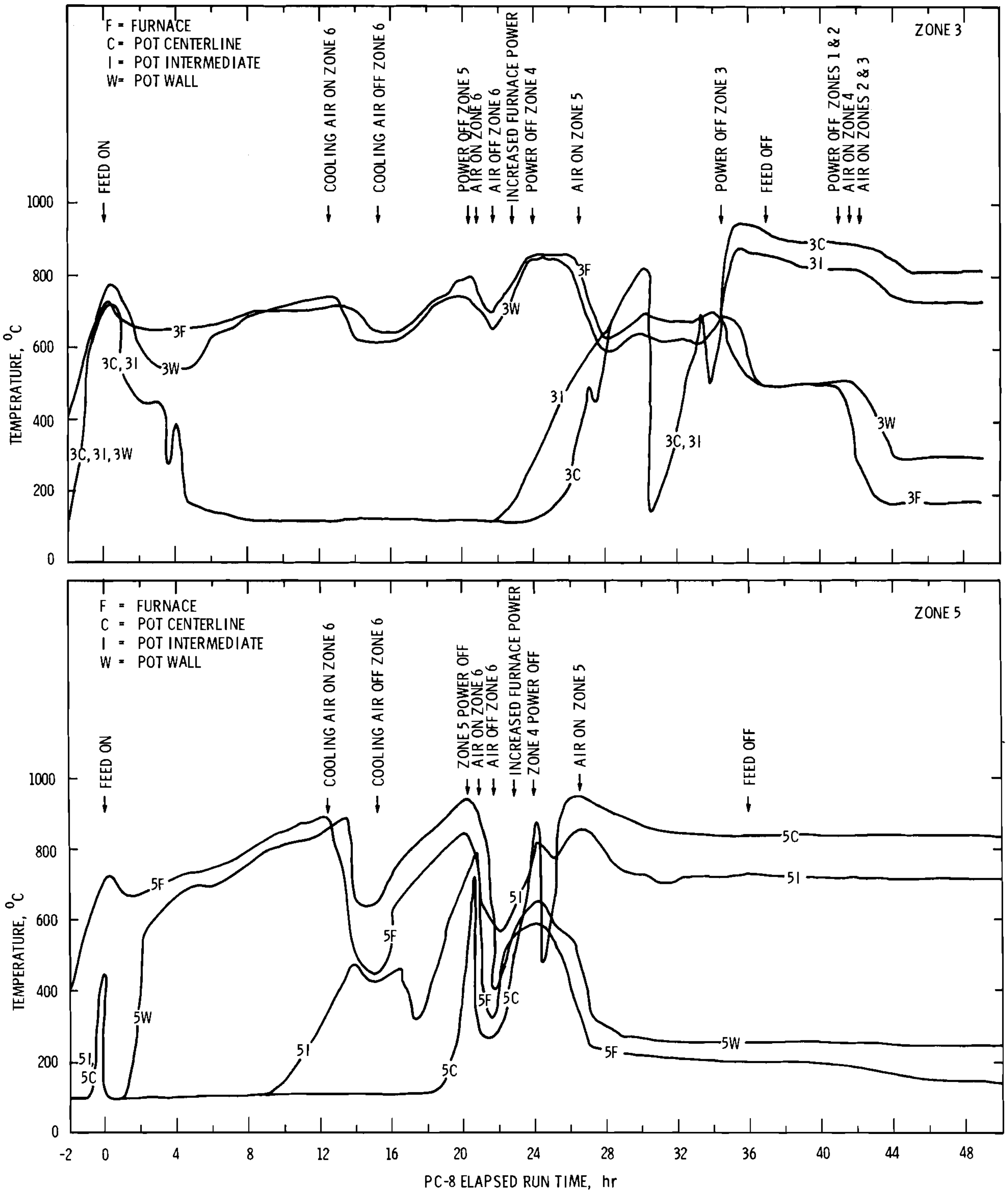


FIGURE 4.5. Pot Calciner Temperatures During Run PC-8

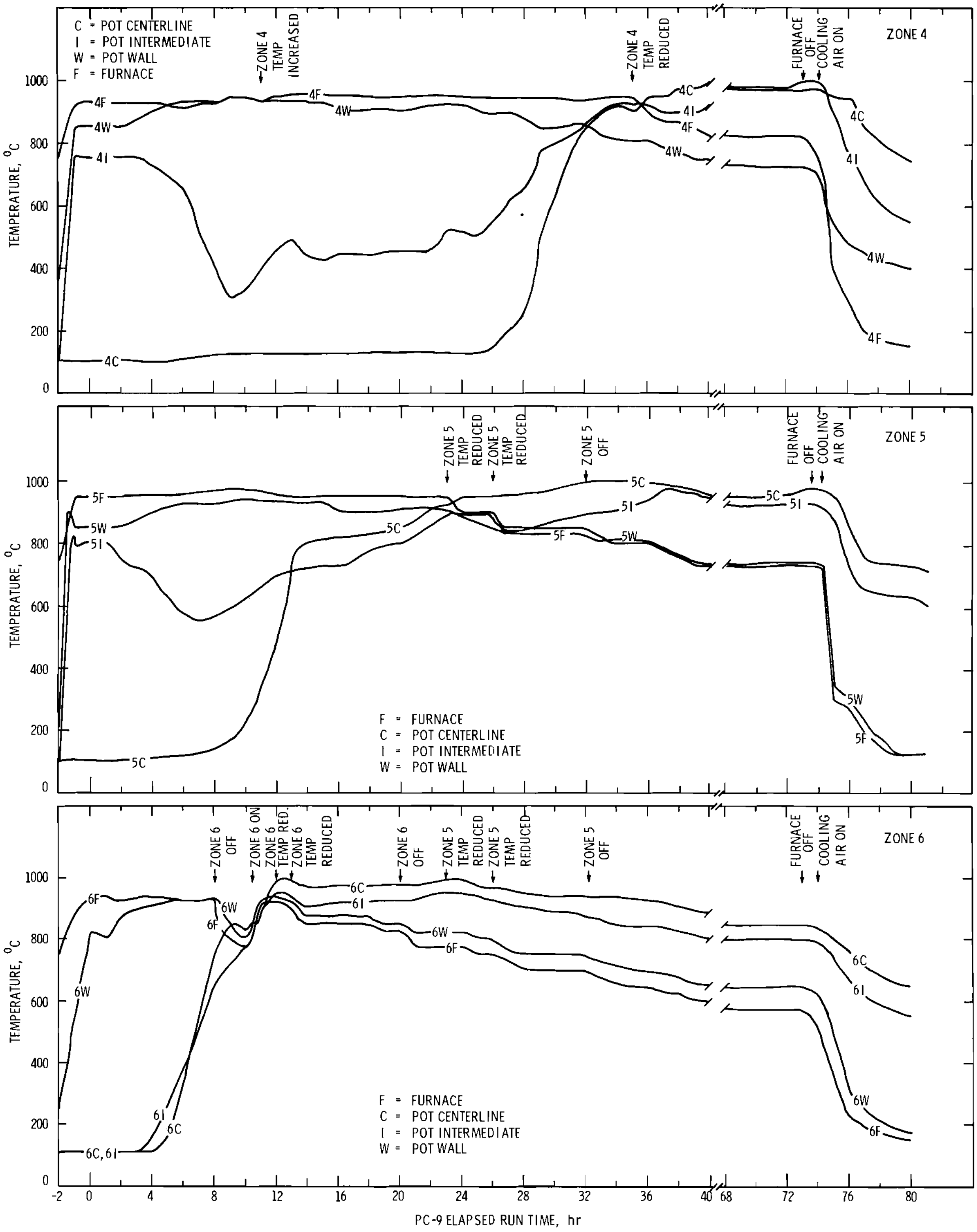
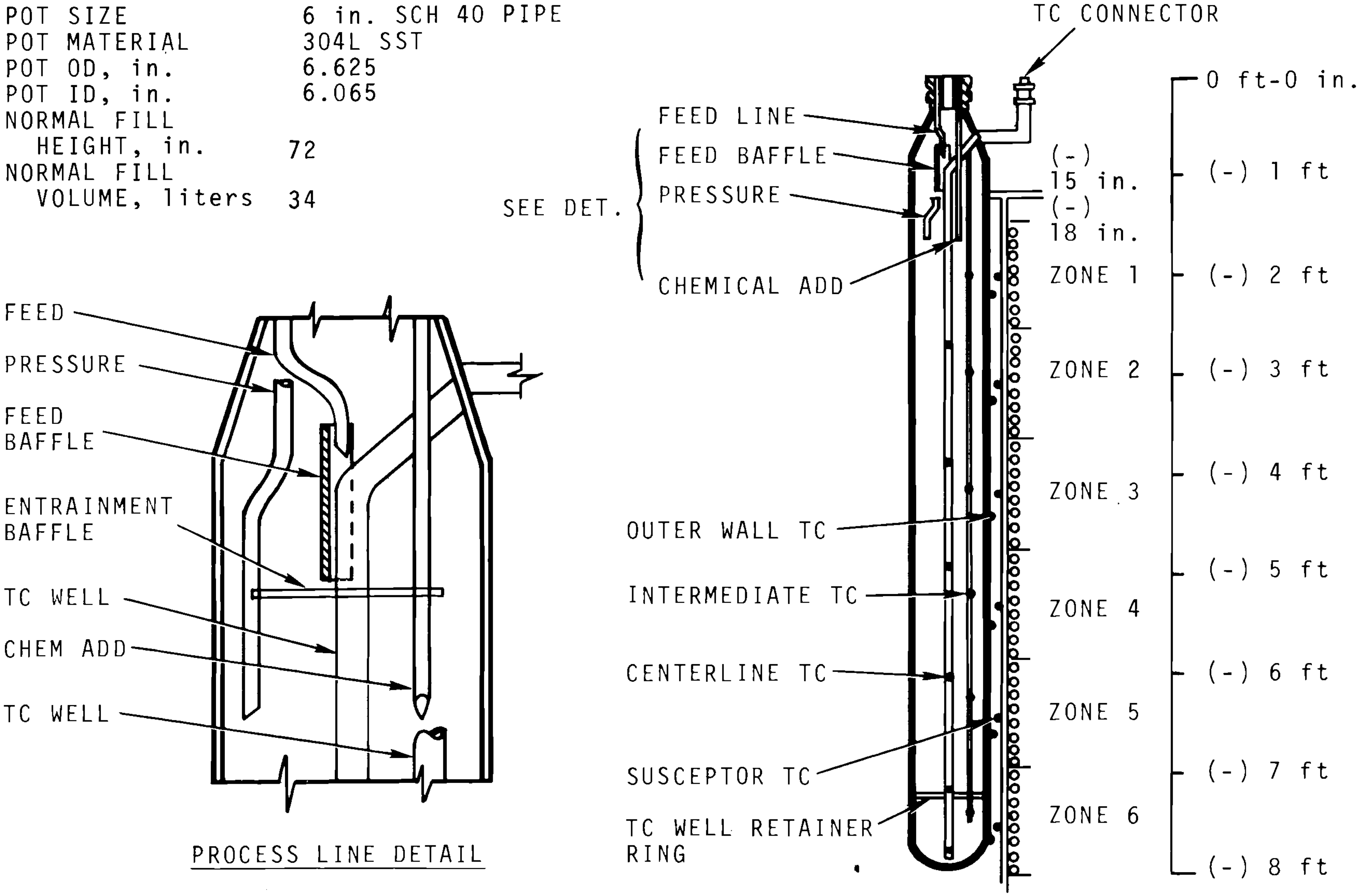


FIGURE 4.6. Pot Temperatures During Rising Level Glass Run PC-9(RLG)

POT SIZE	6 in. SCH 40 PIPE
POT MATERIAL	304L SST
POT OD, in.	6.625
POT ID, in.	6.065
NORMAL FILL HEIGHT, in.	72
NORMAL FILL VOLUME, liters	34



PROCESS LINE DETAIL

FIGURE 4.7. Rising Level Glass Process Line and Thermocouple Arrangement

Although the furnace temperature was maintained at 950 °C during processing, the maximum internal melt temperature attained was only 1015 °C despite the heat-rate density of 310 W/liter. This indicates the exceptionally high thermal conductivity [approximately 3 W/(m^2)(°C/m)] for the molten borosilicate product. Temperature and level control for a nonradioactive RLG run was described in Reference 3 and may be useful for showing how temperatures can be used to determine progress in a RLG pot.

4.3 WASTE VOLUME REDUCTION

Volume reduction data are shown in Table 4.4. The final waste solids concentration was 46 liters/tonne for the PW-1 and PW-4m calcines and 32 liters/tonne for the rising level borosilicate glass.

The density of the calcine products in Runs PC-7 and PC-8 for PW-1 and PW-4m waste were 1.22 and 1.34 kg/liter, respectively. The lower value for PW-1 waste falls near the lower end of the PW-1 and PW-2 data from the first series of runs(1) while the PW-4m value is near the average value of the first runs. The density of the RLG borosilicate product was 3.5 kg/liter. The volume reductions from liquid to solid ranged from 8.2 for the PW-1 and PW-4m calcines to 13.0 for the PW-4m borosilicate glass product, based on a liquid volume of 378 liters/tonne. These agreed reasonably well with expected volume reductions as shown in Table 4.4.

4.4 VOLATILIZATION AND ENTRAINMENT FROM THE POT SOLIDIFIER

An important objective during the pot solidifier runs was to characterize the path and behavior of volatile fission products. Ruthenium was volatilized from both the pot calcination and rising level glass runs and cesium was slightly volatilized during the RLG run.

TABLE 4.4. Volume Reductions

PC Run	Waste Type	Measured Weight of Product, kg	Estimated Volume of Product,[a] liters	Overall Volume Reduction Factor[b]	Estimated Volume Reduction Factor[c]	Calculated Density of Product,[d] g/ml	Volume of Product, liters/ tonne	Equivalent, tonne/ pot[e]
7	PW-1 (Calcine)	73.2	60	8.2	9.2	1.22	46	1.30
8	PW-4m (Calcine)	45.5	34	8.2	7.5	1.34	46	0.74
9(RLG)	PW-4m (Glass)	63.6	∿16 (plus ∿2 as calcine)	13.0	12.9	3.5	32	1.16

---

a. Estimated from pot temperatures.
b. Volume ratio of aqueous feed at 378 liters/tonne to the volume of the final solidified waste.
c. Based on the calculated density of the solidified product and the theoretical potential weight of oxides in the actual feed.
d. Density calculated from measured weight of product and estimated volume of product.
e. Based on a 100% fill volume of 6 feet.

During the final PW-1 and PW-4m calcine runs 6.1 and 11% of the ruthenium in the feed to the pot (based on ^{106}Ru) was volatilized. In comparing this data with that from the earlier runs,(1) the only correlation for ruthenium volatilization was:

- Less evolution of ruthenium occurred with low sulfate (PW-1 and PW-4m) waste.
- Less evolution of ruthenium occurred with earlier scaling of the pot wall.

The sulfate free PW-1 runs in the first series were made with a Mode C type of operation (feed from the boiling evaporator to the pot with solidifier condensate returned to the evaporator for recycle) and it was speculated at that time that the low ruthenium volatilization during these runs may have been due to the mode of operation. However, the PC-7 and PC-8 data indicate that Mode C operation was not a factor. For the conditions of low (or zero) sulfate in the feed and early scaling of the pot wall (before about 25% of the total feed is fed to the pot) the ruthenium volatility was generally less than 10%. Ruthenium volatility data for the last pot runs is presented in Table 4.5 and the accumulation of ruthenium in the pot calciner condensate is shown in Figure 4.8.

TABLE 4.5. Ruthenium Volatilization from the Pot Solidifier

PC Run	Mode(a)	Waste Type	Pot Size	Feed Volume, liters/tonne	Fraction of Feed Consumed at Wall Scaling	Feed Concentrations, M(b)					Percent Ruthenium Volatilized(c)
						Na^+	Al^{+3}	Fe^{+3}	NO_3^-	Ru	
7	A	PW-1	8	385	0.20	0.19	0.13	0.8	6.6	0.0032	6.1
8	A	PW-4m	6	460	0.06	0.20	0.10	0.04	4.9	0.0026	11
9(RLG)	A	PW-4m	6	705	--	0.73	0.09	0.04	4.2	0.0026	15(RLG)

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a. See Figure 5.2 for operating modes.

b. Actual concentrations in feed tank at time of processing.

c. Percent of the total ruthenium fed to the solidifier.

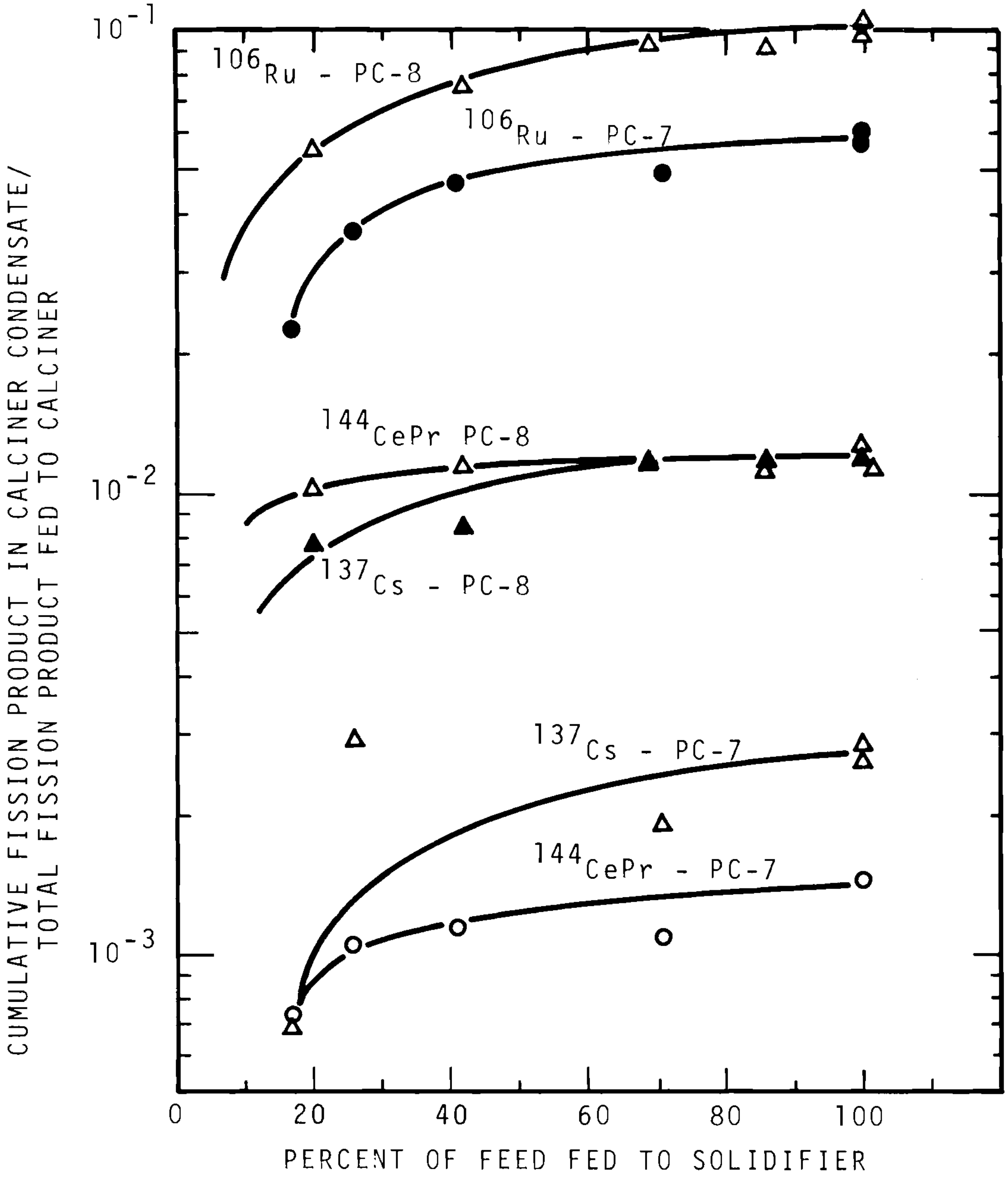

FIGURE 4.8. Accumulation of Fission Products in the Pot Calciner Condensate

Entrainment from the pot calciner based on the accumulation of ^{144}CePr in the pot condensate, was 1.2% or less during the last pot calcination runs as shown in Table 4.6. Data on the accumulation of ^{137}Cs in the pot condensate (Figure 4.8) were similar to the ^{144}CePr entrainment data, indicating that ^{137}Cs was not significantly volatilized.

Phosphoric acid was added to the calciner feed to prevent volatilization of the alkali metals (see Section 3.3.2) in place of the sulfate used during the first series of pot calcination runs(4,5) which caused undesirable solids precipitation problems in WSEP.(1) No sulfate containing waste was processed during the final runs.

During Rising Level Glass Run PC-9(RLG) 15% of the ruthenium and approximately 0.6% of the cesium (1.0% total cesium, including entrainment) in the feed to the pot was volatilized (based on ^{106}Ru and ^{137}Cs). Since this was the only RLG run made in WSEP there is no comparative data; however, for the similar FINGAL process approximately 30% of the ruthenium in the feed was volatilized.(6) (The FINGAL process was operated at 1050 °C compared to 950 °C for the PC-9(RLG) run.) The accumulation of ruthenium and cesium in the pot condensate during the RLG run is shown in Figure 4.9.

The amount of entrainment from the RLG pot (based on ^{144}CePr activity) is shown in Table 4.6 and Figure 4.9. Although only 0.38% of the feed was entrained from the pot, indications during the run (including partial plugging of the pot throat) indicated a much higher entrainment (see Section 4.6).

TABLE 4.6. Entrainment from the Pot Solidifier

PC Run	Waste Type	Pot Size	Boil Off Rate Range, liters/hr	Superficial Pot Vapor Velocity, ft/sec	Percent of ^{144}CePr in Feed Entrained From the Solidifier: Total Run[a]	Percent of ^{144}CePr in Feed Entrained From the Solidifier: Instantaneously[b]	Percent of ^{137}Cs in Feed Entrained from the Solidifier
7	PW-1	8	5 to 30	0.22 to 1.4	0.15	0.0002 to 0.075	0.27
8	PW-4m	6	3 to 18	0.22 to 1.3	1.2	0.008 to 0.4	1.1
9 (RLG)	PW-4m	6	3 to 14	0.22 to 1.0	0.38	0.0056 to 0.16	1.0[c]

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a. Based on the ^{144}CePr collected in the accumulated solidifier condensate for the total run.

b. Based on the ^{144}CePr concentration in periodic instantaneous condensate line samples as compared to that in the feed to the pot. Approximately 10 to 20% of the pot condensate is in a separate reflux stream and is not included here.

c. Of this 0.6% was due to volatilization.

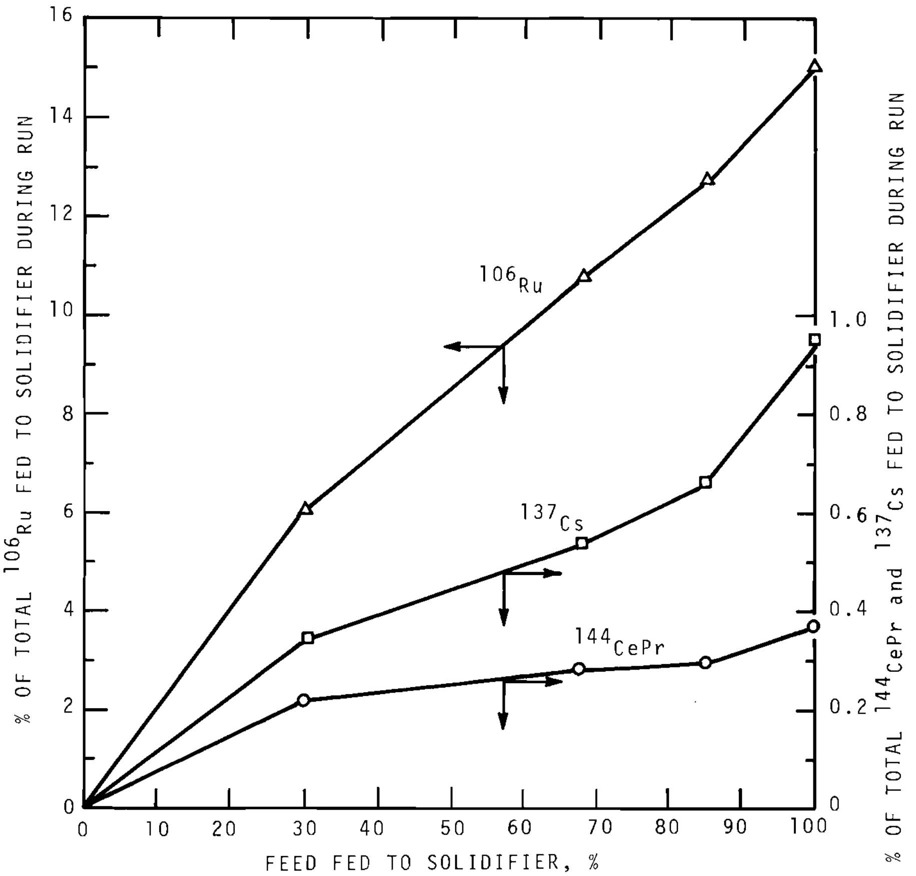


FIGURE 4.9. Accumulation of Fission Products in the Rising Level Glass Pot Condensate

4.5 PERFORMANCE OF POT CALCINATION PROCESS

Performance of the pot calcination process and equipment was generally satisfactory. Those items which influenced the performance of the process and equipment are discussed below.

4.5.1 Foaming

Foaming normally gave no serious operating problems during calcination if rapid decreases in feed rate were avoided. However, foaming was encountered during DVT Run CPC-2(7) and WSEP Run PC-4.(1) It was so severe that expulsion of feed from the pot through the safety overflow system occurred. Occasional mild foaming was also observed in other WSEP pot calcination runs. Although the cause of the severe foaming was not determined it was found during the radioactive phosphate glass runs in WSEP that the presence of small (ppm) quantities of dibutyl phosphate in the Purex 1WW waste used for feed makeup caused severe foaming in the denitrator evaporator when the wastes were concentrated.(8)

Because of the foaming experienced in previous pot calcination runs and in the phosphate glass denitrator evaporator, a silicone antifoam agent (Dow Corning Antifoam-B) was added continuously to the pot calciner during Runs PC-7 and PC-8. The antifoam was made up as an aqueous solution (6.75 g antifoam/liter) and added as a separate additive stream directly to the pot at 0.8 to 1 liter/hr. No indications of foaming were experienced during these runs. This was particularly noteworthy in view of the small diameter (6 inches) of the PC-8 pot.

Prior to each WSEP run, small scale batch boildowns were made with the actual feeds used in the runs to confirm their suitability for processing. The feeds were observed primarily for excessive foaming tendencies. The initial melting point of the RLG waste was determined to be slightly less than 950 °C in the small scale test.

4.5.2 Liquid Level Control in the Pot Calciner

Keeping the pot nearly full of liquid during the feeding period effectively uses the maximum heat transfer surface. Two methods of liquid level detection and control were used (Figure 4.10). In one method, based on an ORNL development, a thermocouple probe detects liquid level by changes in temperature. The probe was heated radiantly by the hot walls of the pot, and was cooled when contacted by boiling liquid (or foam).

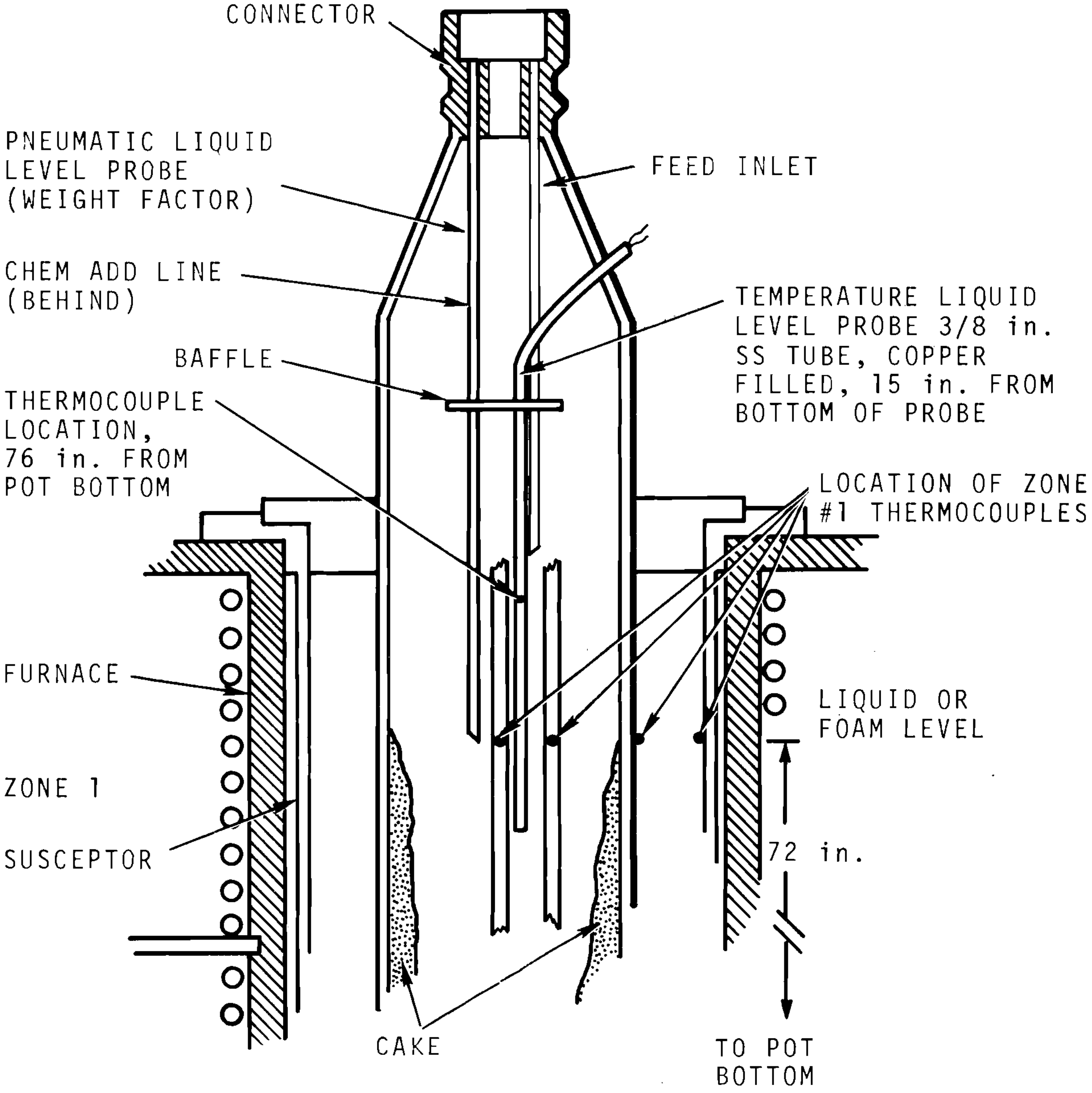


FIGURE 4.10. Pot Liquid Level Control

A cascade control system adjusted the feed rate to maintain constant liquid level. In the second method, a standard pneumatic-type bubbler dip-tube arrangement (weight factor) was used with a continuous air and steam purge.

During the first series of pot runs the thermal probe was not always reliable.(1) For the last series of runs the thermal probe was relocated in the top of the pot to insure that it was not affected by entering feed or the steam purge to the weight factor tube, and the thermocouple in the probe was moved 2 inches further down in the pot to place it in a hotter region. During Run PC-7 the weight factor tube was shortened to above the baffle and used for pressure indications only.

During Run PC-7, attempts to control the feed rate automatically were unsuccessful due to the poor response of the thermal probe. Although switching from steam to an increased air purge to the pot pressure tube (shortened weight factor tube) seemed to remedy the situation (condensate was thought to have been dropping on the thermal probe), this was only temporary. The feed was subsequently interrupted for 2.5 hours when the liquid level became too high, as indicated by the level reaching the pot pressure tube. In Run PC-8 attempts were again made to control the feed rate automatically with the thermal probe and were again unsuccessful. The steam purged weight factor tube provided reliable level information and served very well during the run.

Experience to date indicates that the thermal type level probe is not sufficiently reliable to indicate the level in the pot calciner or to control the feed rate. Although the steam purged liquid level tube (weight factor) was reliable it was not used for automatic control; partly because the level tube was not sensitive to foaming and because most effort was given to making the thermal probe work. With an antifoam addition to the pot calciner the steam purged liquid level tube should work satisfactorily for automatic level control. When using the weight factor system it is necessary to add the steam to the liquid level tube directly above and near the pot so that it doesn't affect the instrument signal.

4.5.3 Vent Line and Fill Head

The calcine pot fill head (Figure 4.11) is essentially a single manifold fitted with off-gas, feed, chemical addition, pot pressure (weight factor tube), and vent connections for the pot head.(9) When the pot is positioned for filling, the fill head connections are sealed to the gasketed pot head by a special vee-flange clamp. The pot is raised to mate with the fill head, and the clamp is closed to seal the joint. The fill head is adapted to WSEP piping by using a row of special semi-remote connectors.(9)

During calcination, volatile material leaves the pot via the vent line which is designed to reflux part of the condensate for self-cleaning. The reflux may be drained to several locations - a catch tank, an evaporator, or to the pot. Draining it to the pot washes the lower section of the vent line and the pot throat. A spray nozzle in the upper portion of the vent line is used for two purposes, i.e., to clean the line and to add water to the calcine pots prior to startup. (View ports are provided in the vent line at two locations for viewing the off-gas and the liquid reflux.)

In all WSEP pot runs, the process vent line from the pot was kept clean by condensing and refluxing approximately 10% of the pot condensate. This washed the line continuously and prevented the deposition of solids. Refluxing liquid was drawn off at the base of the vent line before it entered the pot. The remainder of the vent line between the reflux draw-off

CONSTRUCTION

Type	Welded or Flanged
Material	304-L SS
View Port	Quartz

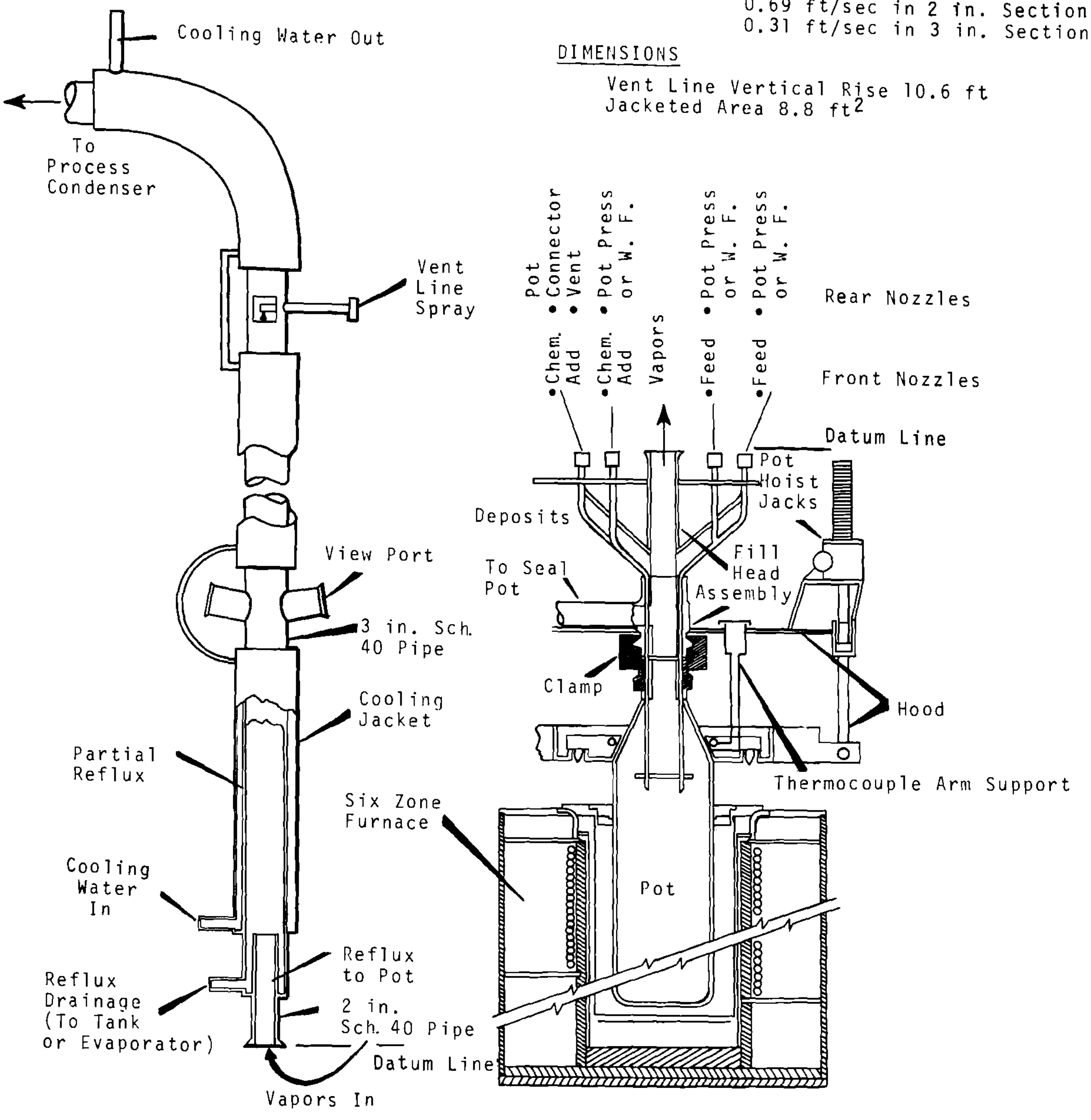
OPERATION

Reflux Rate	2 to 5 liter/hr
Temperature	100 to 300 °C
Pressure	-20 in. H_2O

Vapor Velocity at 1 liter/hr Boil-up at 100 °C;
0.69 ft/sec in 2 in. Section,
0.31 ft/sec in 3 in. Section

DIMENSIONS

Vent Line Vertical Rise 10.6 ft
Jacketed Area 8.8 ft^2



Vent Line

Fill Head Assembly and Pot

FIGURE 4.11. Pot Solidifier Self Cleaning Vent Line and Fill Head

point and the pot throat was washed by returning reflux to the pot once or twice during the run and also at the end of the pot feeding period.

A completely clean vent line was assured by spraying 2 to 5 liters of water from the top of the line into the pot after the feeding period of each run and by washing the line with 10 to 30 liters of water after a new pot was installed for the start of the next run. Visual inspection of the pot throats following each run disclosed no solid deposits.

After the pot runs, both the inlet and outlet and the visible portion of the interior of the vent line and fill head were found to be clean except for darkening of the metal. The reflux-drain sight glasses were clean but both of the vent line sight glasses were darkened by ruthenium deposition.

4.5.4 Seal Pot

A secondary vent line from the calciner was provided for relief of pressure if it increased to atmospheric level during operation. A water-seal pot in the line allowed the pot to vent and overflow directly to a catch tank. This water-seal pot was an 8-inch diameter by 36-inch long vertical section of pipe which was closed at each end and which contained a longitudinal baffle offset 1-inch from the axis. Normally, the seal pot was partially filled with water, such that maximum pressure differences of up to 24-inches of water were required to allow gas to flow from the calciner pot to the catch tank. The baffle was offset to prevent backward flow of water to the pot calciner during any unbalanced pressure condition.

The pot calciner safety-relief seal pot functioned normally during all runs and no instabilities in the calciner or seal pot pressure were observed. A means of flushing the inlet line between the vent line and seal pot was available but it was not used during or between runs. Flushing is apparently required to avoid calcine restrictions in the inlet line after a run with excessive entrainment or shortly after any occurrence of an excessive pot operating level. The inlet line became partially plugged with solids during Run PC-9(RLG) as discussed in Section 4.6.

4.6 PERFORMANCE OF THE RISING LEVEL GLASS PROCESS

Performance of the Rising Level Glass Process during Run PC-9(RLG) indicates that additional nonradioactive testing is necessary before the system can be used commercially. Although the run was not completed, the results were basically satisfactory, particularly in view of the fact that the Rising Level Glass Process had not received the high degree of development on a nonradioactive basis which had been accorded all other WSEP solidification techniques.

As discussed in Section 4.1, the feed to the RLG pot was directed to flow as a film down the centerline thermowell in order to substantially increase the process capacity. The feed system for the RLG pot consisted of in-line blending the feed solution, containing sodium nitrate and boric acid additives, with the silica additive in the fill head (Figure 4.11) directly above the pot. The feed was then dripped on the top of the centerline thermowell (Figure 4.7). Some of the feed was inadvertently diverted down the intermediate thermowell, possibly due to the restricted opening (0.2-inch clearance) where the center thermowell passed through the entrainment baffle. The clearance may have been insufficient for the feed film or the thermowell may have slipped off center. The wetting of the intermediate thermowell made temperature and liquid level control difficult, and the diverted feed stream (along with calcine entrainment from below) caused the calcine to bridge across the top of the pot.

With the similar FINGAL process, temperature control at the top of the pot was found to be critical in preventing solids deposition.(6) The FINGAL process was operated to keep the top of the pot below the 400 to 650 °C temperature range where maximum ruthenium dust deposition occurred. During PC-9(RLG), the upper furnace zones were not operated and the upper pot temperature was less than 400 °C when deposition started. The temperatures were subsequently increased to attempt melting part of the deposition; however, this did not work.

Inspection of the RLG pot after the run revealed a partial calcine plug in the pot neck (approximately 75% reduction in cross-sectional area) and considerable calcine (2 to 3 liters) above the pot baffle (the baffle is 4-inches in diameter and centered 13-inches down from the top of the pot). The calcine in the pot neck was most likely due to entrainment and a portion of that on the baffle was due to calcination of some of the entering feed. Indications of high entrainment were apparent early in the run as the absolute filter downstream of the solidifier condenser started to plug immediately after feed was started and it was subsequently bypassed. Also, approximately 20-hours into the run the outlet drain of the process condenser started plugging and had to be flushed. Inspection of the pot vent system after the run did not reveal any substantial deposits except in the emergency seal pot vent. Samples of calcine taken from the seal pot inlet were analyzed for silica and were thus identified as coming from the Rising Level Glass Run.

The Rising Level Glass pot did not contain any level indicating devices other than the pot thermocouples. The thermocouples were staggered as shown in Figure 4.7 to give a maximum of information about level; however, as discussed previously the wetting of both thermowells by entering feed severly limited this method of level detection. No other means of feed rate or level control has been attempted with the RLG process during the waste solidification program. (See Section 3.2.2 for other level methods that have been tested.)

4.7 GENERAL PERFORMANCE AND OPERATING HISTORY

4.7.1 Waste Composition Effects

During the last pot runs no processing problems resulted that were attributed to waste composition differences. Sulfate which caused solids precipitation problems during the first series of pot runs was not present in these last runs. During the two calcine runs phosphate was successfully used as an additive in place of sulfate for prevention of alkali metal volatilization (see Section 3.3.2). The phosphate produces a fine flocculant precipitate which does not cake or cause plugging difficulties.

Additives to the rising level glass pot required different handling procedures because of the presence of boric acid and silica. It was not possible to combine all of the additives with the waste because of solids precipitation and silica erosion of the feed pump, however, no problems resulted from combining the boron and sodium additives with the feed (actual feed conditions were 705 liters/tonne and >50 °C) and adding the silica as a separate stream (dilute colloidal silica) to the pot.

General waste compositions and additives for the three pot solidification runs are shown in Table 4.7. Feed compositions for the runs, as well as other pertinent data on the feeds are listed in Table 9.1 in the Appendix. Feeds to the pot process were prepared using actual concentrated Purex high level waste and radiorare-earth (mostly ^{144}CePr) solutions to provide the desired self-heat generation rate in the product.

TABLE 4.7. Summary of Waste Composition Ranges

		PW-4m Waste, $\underline{M}$(a)	
Constituents	PW-1 Waste, $\underline{M}$(a)	(Pot Calcine)	(RLG)
Na^+	0.19	0.25	0.53
Al^{+3}	0.13	0.12	0.17
Fe^{+3}	0.8(b)	0.05	0.083
$(Y+RE)^{+3}$	0.12	0.36	0.41
NO_3^-	6.6	6.0	7.8
Additive to Feed			
PO_4^{-3}	0.06	0.11	
B_2O_3			0.84
$NaNO_3$			0.84
Additive to Pot			
SiO_2 (as a 21.5 wt% colloidal suspension)			0.76

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

b. Analyses of feed showed 0.4$\underline{M}$ but is believed incorrect.

4.7.2 Related Equipment

Pot Furnace

The six zone induction-heated calciner furnace(1,9) which has a temperature controlled susceptor to transfer heat to or from the pot calciner wall, gave exceptionally good performance and was both reliable and safe. When sufficient power was applied each zone was controlled within ±10 °C of the set point (except during the first several hours of a run when all power was being used for boilup) without gross influence from adjacent zones while heating all zones. During heating and cooling of adjacent zones, the heated zone could not always be maintained at the maximum temperature (usually 700 °C at this point) because the available power was set to restrict each zone to 3 and 4 net kilowatts for 6 and 8-inch pots, respectively. When 3 net kilowatts/zone was used during PC-8 the furnace temperature in a heated zone was pulled down excessively when cooling air was on to an adjacent zone. Therefore, 4 net kilowatts/zone is the minimum recommended with this furnace for both 6 and 8-inch pots.

Cooling by forced air around the outside of the susceptor was sufficient for the pot runs. The maximum cooling rate for a pot in the furnace was slightly lower than the heat losses from a pot cooled by natural convection and radiation (at a pot wall temperature of about 250 °C). Pot wall temperatures decreased approximately 50 degrees when pots containing approximately 5000 watts were transferred from the furnace (using cooling air) to the ambient air in the cell.

During the entire WSEP program the furnace was operated at 600 to 950 °C for about 2600 hours without a significant problem. Prior to placing the furnace in radioactive service (at 1025 hours), delaminated Fiberfrax[R-1] insulation around the susceptor was replaced with Ceroform[R-2] insulation.

[R-1] Carborundum Corporation

[R-2] Johns-Manville Corporation

Process Condenser

Sulfate volatilization caused local corrosion at the inlet to the titanium condenser for the pot calciner during two DVT runs. A 304-L SS sleeve was installed at the condenser inlet to prevent corrosion at this point. This condenser was in service for about 3500 hours until it was replaced with a modified condenser prior to Run SS-11. The new condenser(10) contained Pall rings in the condenser tubes to improve the condenser scrubbing efficiency. This condenser was used for a total of 400 hours during the final spray and pot solidification runs.

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5.0 AUXILIARY PROCESS SYSTEMS PERFORMANCE

CONTENTS

5.0 AUXILIARY PROCESS SYSTEMS PERFORMANCE

The conversion of high-level aqueous wastes to solids results in liquid and gaseous effluent streams with a lower level of radioactivity. The radioactive content of these effluent streams must be reduced to a level which can be satisfactorily managed before the total benefits of solidification are truly realized. Therefore, important to any waste solidification system are the auxiliary systems (primarily decontamination equipment) located downstream of the solidification systems. Demonstration of effluent cleanup (decontamination) was a significant part of the WSEP program. This objective was established to investigate the parameters affecting the performance of the decontamination equipment and involves the following items:

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

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

Initial studies have indicated that the recovered nitric acid and water streams from the pot solidification process can be reasonably recycled to a fuel reprocessing plant.(1) The recovered nitric acid which is slightly contaminated with radionuclides, can be recycled for possible use in fuel element dissolution and/or for possible use in solvent extraction scrub streams. Effluent recycle is based upon having solidification processing capabilities integrated with each fuel reprocessing plant. If the solidification capabilities were remote from the fuel reprocessing plant, the solidification plant would need a complete but smaller capacity version of the effluent waste treatment and acid recovery facilities. Shipping of high-level aqueous waste and reusable effluents between the two plants would also be required. These conditions are believed to be impractical and unsafe.

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

In the WSEP auxiliary system, vapors from the solidification system, which are not acceptable for discharge without further treatment, are first routed through a condenser to the evaporator. The solidifier vapors are condensed and the resulting condensate is concentrated in the evaporator (along with incoming feed in some cases). The vapors from the evaporator are decontaminated from entrained aerosols in the evaporator tower by impingement plates, bubble caps, and a mist eliminator before being vented to the evaporator condenser. The evaporator condensate is concentrated in the acid fractionator where nitric acid is recovered. The vapors from the fractionator which are substantially decontaminated by evaporation in the fractionator are again condensed and about 90% of the fractionator distillate is recycled to the evaporator as acid stripwater. Then the remaining 10% is collected as an intermediate level waste stream. The remaining gases are treated by high efficiency filtration, scrubbing, and additional filtration before discharge to the atmosphere. Figure 5.1 illustrates the WSEP auxiliary process system.

The effluents resulting from the pot solidification process during the final series of runs can be generalized as follows:

1. The solidifier off-gases have been decontaminated from the ruthenium in the feed by factors of 6.7 to 16* so that the effluent remains as a high-level waste.
2. The decontamination of process off-gases by the WSEP auxiliary system was adequate for the final gaseous effluent stream but was inadequate for the final aqueous effluent stream (fractionator distillate) which contained radionuclide concentrations above 10CFR20,(2) concentrations by factors as high as 4×10^5.
3. The volumes of the evaporator bottoms and recovered acid are relatively small and can be recycled to the solidifier feed and to a fuel reprocessing plant, respectively. To be released to the environment, the fractionator distillate stream would require additional decontamination, but it may be suitable for recycle to a fuel reprocessing plant.

A summary of information on typical effluents resulting from the last three pot solidification process is presented in Table 5.1. During pot solidification Runs PC-7, PC-8, and PC-9(RLG), 6 to 15% of the radioruthenium fed to the solidifier

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* Defined as total curies in the feed divided by the total curies in the effluent stream over the entire run.

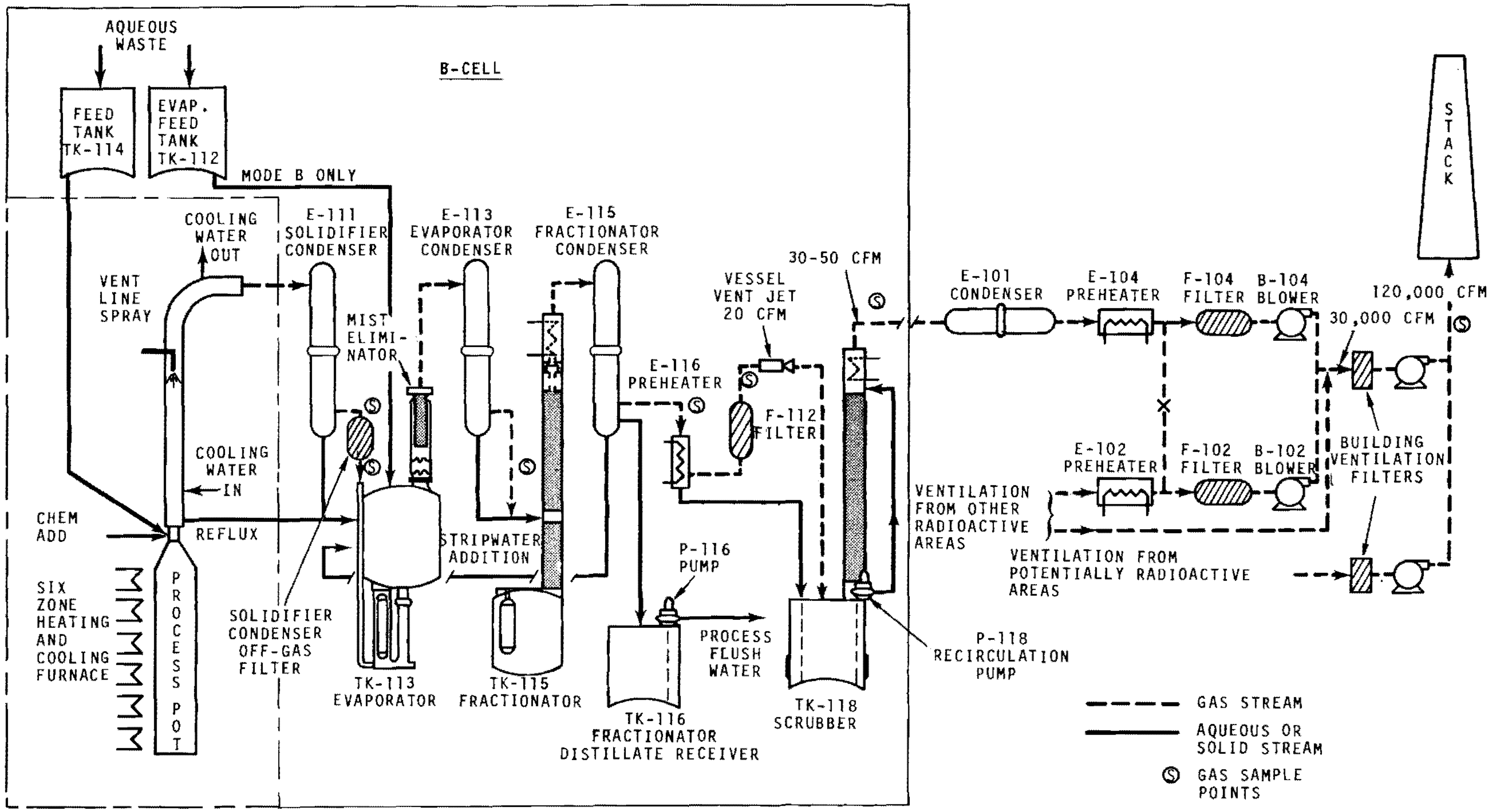

FIGURE 5.1. WSEP Auxiliary Process System

TABLE 5.1. Typical Effluents Resulting from the Operation of the Last Three Pot Solidification Runs[a]

Stream	Solution	Volume, liters/ liter feed	Radioactive Ruthenium, Ci/Ci in feed	Gross Radio-activity less Ruthenium, Ci/Ci in feed	Potential Disposal
Evaporator Bottoms	$5\underline{M}$ HNO_3	0.6 - 0.9[b]	10^{-1}	$<1 \times 10^{-2}$	Recycle to solidifier feed or to fuel reprocessing plant waste concentrator
Fractionator Bottoms	$9\underline{M}$ HNO_3	0.5 - 0.6	2×10^{-3}	2×10^{-6}	Reuse in fuel reprocessing plant
Accumulated Fractionator Distillate	$0.05\underline{M}$ HNO_3	0.7 - 0.9	4×10^{-4}	$<10^{-8}$	Reuse in fuel reprocessing plant
Scrubber Bottoms	$2\underline{M}$ NaOH	1.0 - 1.5[c]	2×10^{-5}[d]	NDG	Intermediate level waste treatment or combine with high level waste
Final Off-Gas from Scrubber	Air	—	10^{-7} - 10^{-9}	10^{-9} - 10^{-10}	To building ventilation filters
Final Off-Gas to Stack	Air	—	$<10^{-9}$[e]	$<10^{-12}$	To atmosphere

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a. Average of data taken from Pot Solidification Runs PC-7 through PC-9(RLG).
b. Assumes a working volume of 300 liters in the evaporator. This volume is present at the start of each run and must either be continuously recycled or batch recycled to the feed.
c. Assumes a working volume in the scrubber of 500 liters. This volume is present at the start of the run and must be recycled batchwise to the feed.
d. Based on data from PC-7 and PC-8.
e. Based on data from PC-7 and PC-9.

was volatilized from the solidifier and accumulated in the auxiliary evaporator. The highest volatilization of ruthenium occurred during the rising level glass Run PC-9(RLG). Nonvolatile entrainment represented by cerium was 0.15%, 1.2%, and 0.38%, for Runs PC-7, PC-8 and PC-9(RLG), respectively.

5.1 OPERATING MODES

The need to demonstrate how the treatment of effluents from solidification can be integrated into a fuel reporcessing plant prompted the selection of three different operating modes in WSEP. These are designated in WSEP as Modes A, B, and C and are described in References 3, 4, and 5. Figure 5.2 shows the three operating modes for WSEP. To date, all three modes have been tested with the pot solidification process, although only Mode A was demonstrated in the final series of runs.

Application of the modes in a fuel reprocessing plant are visualized as shown Figure 5.3. During Mode A operation, the evaporator bottoms is an additional effluent stream which must be recycled back to the solidifier feed or to the waste concentrator in a fuel reprocessing plant. In Mode B and C operation, the solidifier condensate is combined with incoming dilute waste in the high level waste evaporator. Typical effluent data for Mode A operation for the auxiliary system during Runs PC-7, PC-8, and PC-9(RLG), are summarized in Table 5.1.

5.2 RUTHENIUM CONTROL

Ruthenium, which can be volatilized during both solidification and evaporation, is the main contaminant in the process effluent. Several general relationships for minimizing the formation of volatiles of RuO_4 were summarized in References 3 to 7. These include:

- Maintaining a low concentration of nitric acid in the evaporator bottoms and resulting overheads.

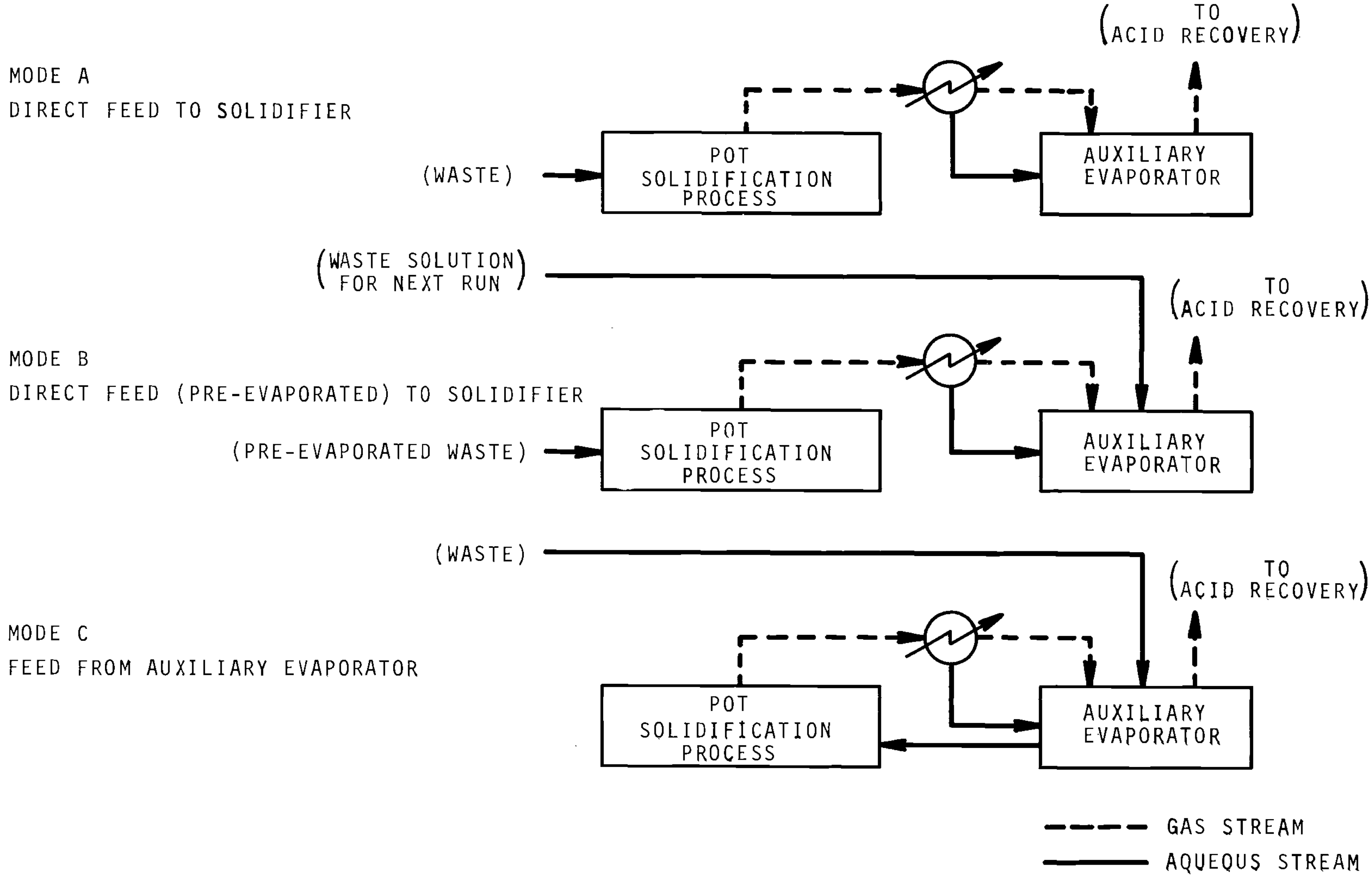

FIGURE 5.2. WSEP Process Mode Options

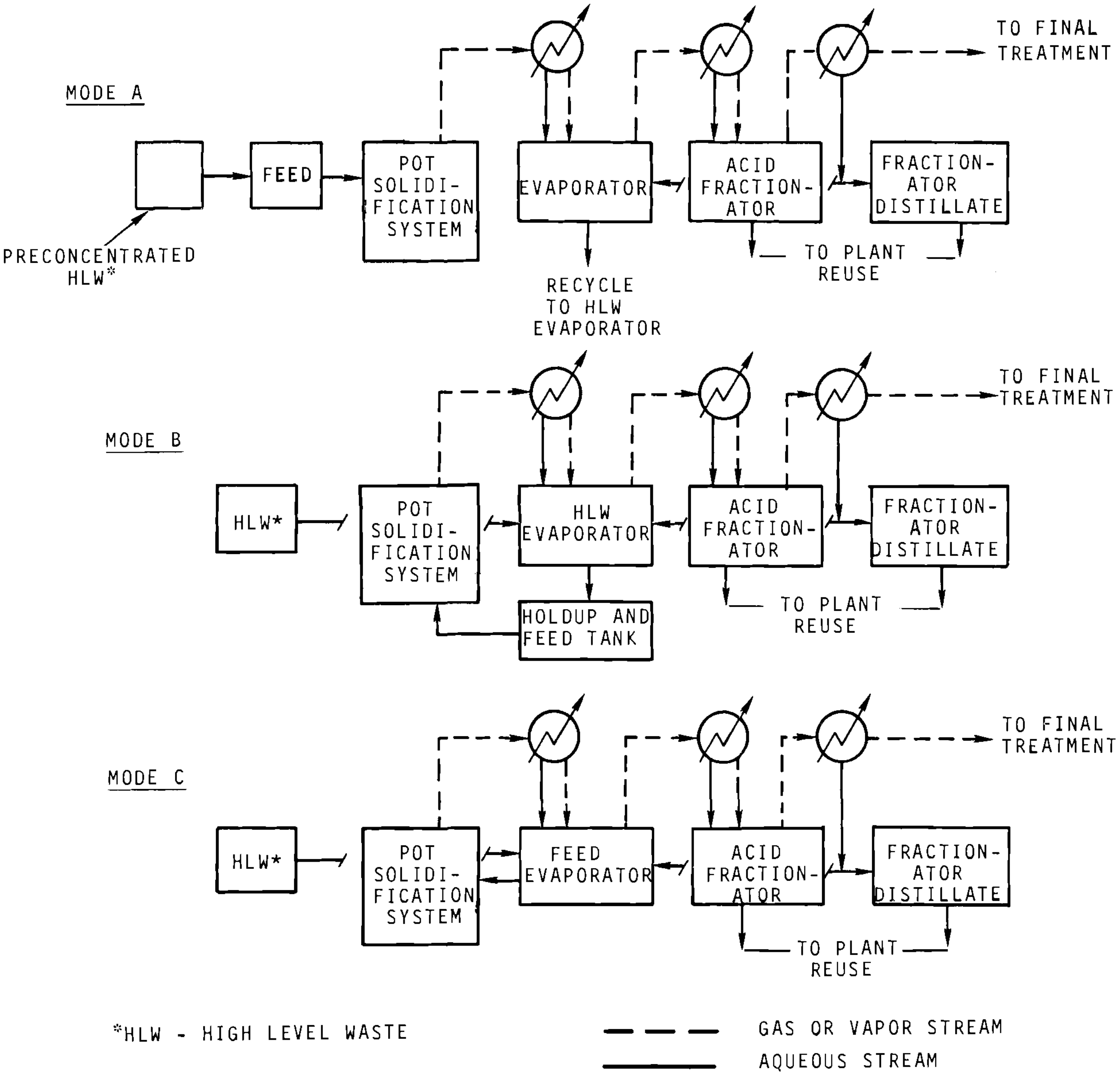

FIGURE 5.3. Operating Mode Applications in a Fuel Reprocessing Plant

- Addition of reducing agents (such as sugar and phosphite) into the solution.
- Lowering the distillation temperature by means of vacuum distillation.

A combination of these methods should prove advantageous.

The auxiliary evaporator which serves as a decontamination stage between the pot solidifier and nitric acid fractionator was operated in a Mode A arrangement as previously discussed. Most of the data presented in the following sections are from References 8 through 13. During Runs PC-7, PC-8, and PC-9(RLG), 6.1, 11, and 15%, respectively, of the ruthenium fed to the solidifier was volatilized from the solidifier, condensed, and accumulated in the evaporator. Figure 5.4 presents the accumulation of ruthenium (^{106}Ru) in the evaporator and the other auxiliary tanks as a function of percent of feed fed to the solidifier while Table 5.2 presents the radionuclide distribution in the auxiliaries.

The evaporator was operated with a bottoms acidity ranging from 3 to 6$\underline{M}$ HNO_3 and an overhead acidity of less than 1$\underline{M}$ HNO_3 by recycling a portion of the fractionator distillate as strip-water thus reducing the potential for ruthenium volatilization. Evaporator and fractionator operating parameter for Runs PC-7, PC-8, and PC-9(RLG) are presented on Figures 9.4 to 9.6 in the Appendix. Other operating data is presented in Table 9.3 in the Appendix. Typical operating volumes in the auxiliary tanks are shown on Figure 9.7 in the Appendix.

Reductants were not added to the evaporator during these runs, but even though the volatilization of the ruthenium was typically kept below 1% of that present in the evaporator bottoms, it would be desirable to decrease ruthenium volatilization by addition of reductants such as sugar or phosphite. These reductants have been shown to decrease ruthenium volatilization.(14,15)

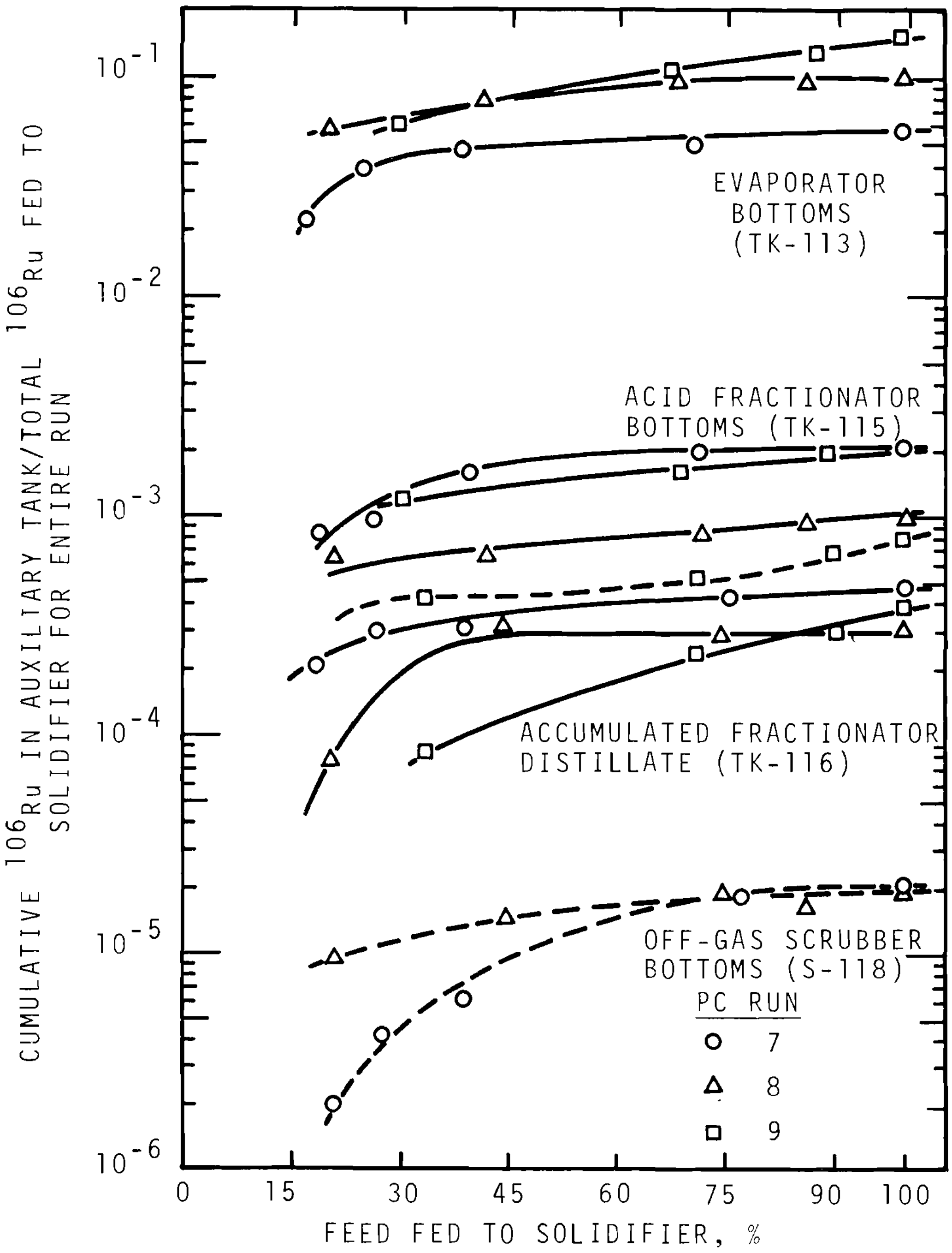

FIGURE 5.4. Accumulation of Ruthenium in WSEP Auxiliaries During Runs PC-7, PC-8, and PC-9(RLG)

TABLE 5.2. Radionuclide Distribution in WSEP Auxiliaries for Pot Calcination Runs PC-7 Through PC-9(RLG)

	Fraction of Equivalent Feed Radioactivity in Effluent Streams for Total Run[a]					
	^{106}Ru (Radioruthenium)			^{144}CePr (Radiocerium)		
PC Run	7	8	9(RLG)	7	8	9(RLG)
Mode	A	A	A	A	A	A
Evaporator Bottoms (TK-113)	6.1×10^{-2}	1.1×10^{-1}	1.5×10^{-1}	1.5×10^{-3}	1.2×10^{-2}	3.8×10^{-3}
Fractionator Bottoms (TK-115)	2.6×10^{-3}	1.4×10^{-3}	2.3×10^{-3}	4.6×10^{-7}	2.3×10^{-6}	4.1×10^{-6}
Fractionator Distillate Receiver (TK-116)	4.6×10^{-4}	3.0×10^{-4}	3.6×10^{-4}	NDG	4×10^{-10}	9.6×10^{-10}
Off-Gas Scrubber Bottoms (TK-118)	2.3×10^{-5}	2.0×10^{-5}	7.4×10^{-4}	NDG	NDG	NDG
Off-Gas from Scrubber[b,c]	1.2×10^{-9}	1.3×10^{-8}	1.7×10^{-7}	1.1×10^{-9}	7.5×10^{-11}	1.3×10^{-9}
Off-Gas to Stack[b]	$<6 \times 10^{-10}$	$<6.0 \times 10^{-7}$	1.0×10^{-9}	$<1.2 \times 10^{-12}$	9.0×10^{-13}	8.0×10^{-13}
Ratio (Fractionator Distillate Radioactivity to 10CFR20)	4.3×10^{5}	2.0×10^{5}	1.8×10^{5}	NDG	6.9×10^{3}	1.5×10^{2}
Ratio (Scrubber Off-Gas Radioactivity to 10CFR20)	22	3.9×10^{2}	2.6×10^{2}	94	4.3×10^{2}	2.4×10^{2}
Ratio (Stack Off-Gas Radioactivity to 10CFR20)	$<4 \times 10^{-4}$	2.2×10^{-2}	$<4.1 \times 10^{-4}$	1.7×10^{-3}	1.0×10^{-3}	1.0×10^{-3}

NDG - No detectable gain in radioactivity.

a. Total curies of component gained in auxiliary tank/total curies of component fed to solidifier for entire run.

b. Total curies of component in off-gas/total curies of component fed to solidifier for entire run.

c. Based on total noncondensible gas flow of 5 scfm.

Performance of the auxiliary system was assessed primarily by determining the fraction of solidifier feed radioactivity that accumulated in each auxiliary tank and by determining decontamination factors (DF's) at each stage in the system. Accumulation of radioruthenium in the auxiliaries is shown in Figure 5.4 and data on DF's across the evaporator and fractionator is presented in Table 5.3. Cumulative ruthenium DF's[a] across the evaporator, were 29, 82, and 59 for Runs PC-7, PC-8, and PC-9(RLG), respectively. These were lower than those obtained during the first series of pot solidification runs by factors of 10 to 100 but were typical of the later WSEP runs. This decrease in DF's is attributed to internal contamination (buildup of radioruthenium) in the WSEP.

The problem of ruthenium volatilization from the WSEP auxiliary evaporator was primarily investigated by defining instantaneous DF's (DF_i's)[b] across the evaporator. Generally, the DF_i's for the first series of pot solidification runs varied inversely with the nitric acid concentration in the evaporator bottoms and resulting distillate as shown in Figure 5.5.(3,4) This indicated that ruthenium volatility increases with increasing acidity in the evaporator bottoms. During solidification Runs PC-7, PC-8, and PC-9(RLG), there was considerable scatter in data points as shown in Figure 5.5 and a consistent correlation was not obtainable. The uncondensed flow of ruthenium had less effect on the DF_i's during these runs than in the previous pot solidification runs since the new modified solidifier condenser and condenser off-gas filtering system were used. A

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

[b] Instantaneous concentration of component in evaporator bottoms/instantaneous concentration of component in evaporator condensate.

TABLE 5.3. Decontamination Factors Across the WSEP Auxiliary Evaporator and Fractionator

				Evaporator					Fractionator				
				Average Acidity, M HNO_3					Average Acidity, M HNO_3				
PC Run	Mode	Solution in Evaporator	Additive	Bottoms	Distillate	Cumulative Ruthenium DF(a)	Cumulative Cerium DF(a)	Instantaneous Cerium DF(b)	Bottoms	Distillate	Cumulative Ruthenium DF(c)	Cumulative Cerium DF(c)	Instantaneous Cerium DF(d)
7	A	Nitric Acid Plus Solidifier Condensate	Stripwater (Fractionator Distillate)	5.0	0.35	29	3.5×10^3	$10^2 - 10^4$	9.6	0.04	7.8	NA	NA
8	A	Nitric Acid Plus Solidifier Condensate	Stripwater (Fractionator Distillate	5.5	0.30	82	5.4×10^3	$10^2 - 10^4$	8.3	0.06	10	3.2×10^2	$10^2 - 10^3$
9	A	Nitric Acid Plus Solidifier Condensate	Stripwater (Fractionator Distillate)	4.8	0.38	59	8.4×10^2	$10^2 - 10^4$	7.5	0.04	9.9	2.0×10^3	$10^3 - 10^4$

NA Not Available

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

b. Instantaneous concentration of component in evaporator/instantaneous concentration of component in evaporator distillate.

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

d. Instantaneous concentration of component in fractionator/instantaneous concentration of component in fractionator distillate.

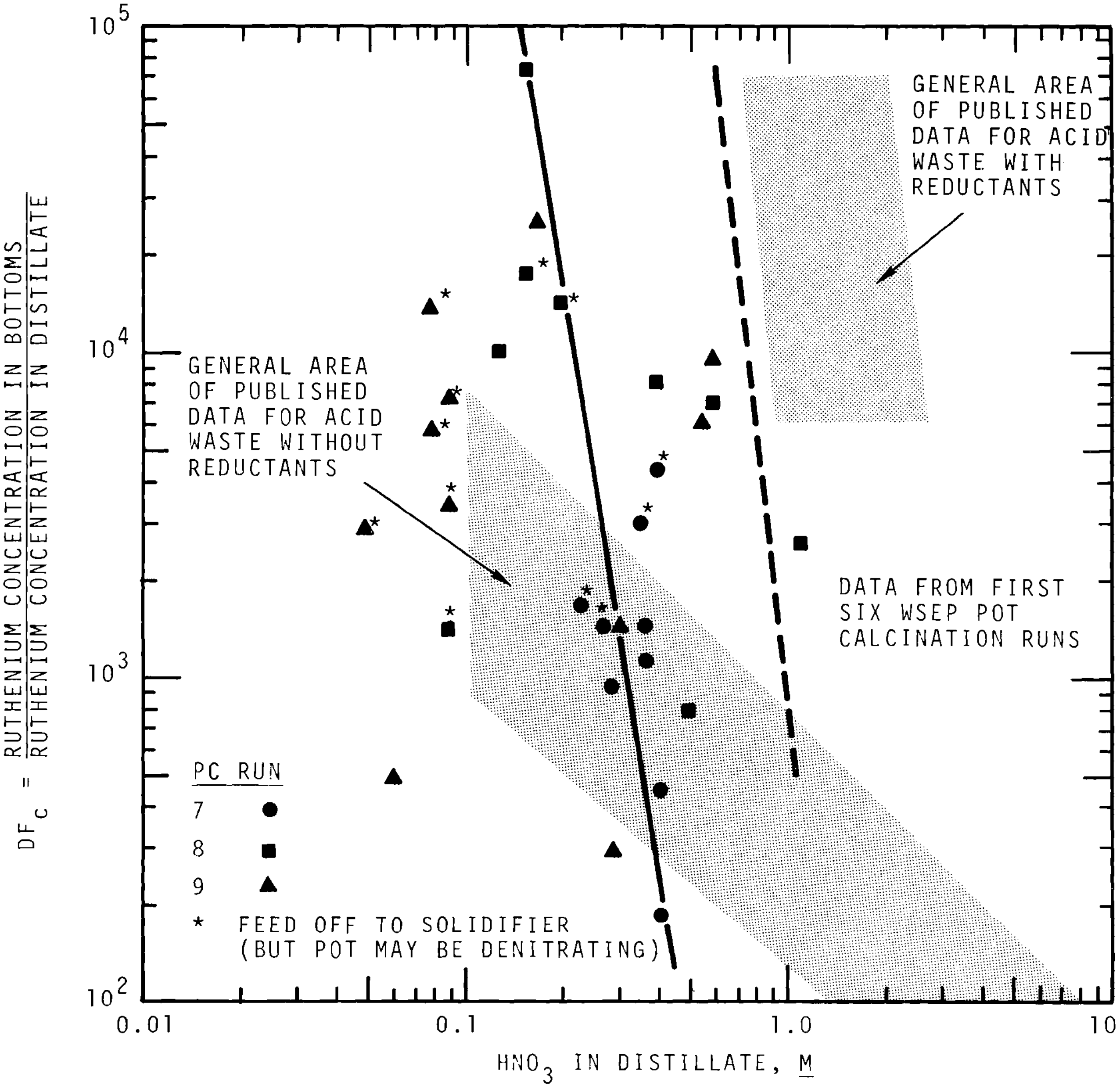

FIGURE 5.5. Volatilization of Ruthenium from the WSEP Auxiliary Evaporator

possible cause of the noncorrelation and lower DF_i's could be the contamination of the auxiliary system by continual buildup or adsorption of ruthenium from previous runs on the stainless steel piping and other auxiliary equipment.(15,16) Also, the presence of nitrogen oxides increases the evaporator distillate acidity resulting in no equilibrium between the evaporator bottoms acidity and the evaporator overhead acidity.

The solidifier condenser off-gas contained greater than 10^4 μCi/cm^3 of ^{106}Ru for all three runs. During Run PC-7, the condenser off-gas filter was bypassed to determine the effect on the auxiliary system. As can be seen in Table 5.4, there was a factor of 10 higher concentration of ruthenium in the evaporator condenser off-gas during PC-7 than during PC-8. This indicates that the carryover of ruthenium in the off-gas does effect the auxiliary system downstream of the condenser.

Gas sampling techniques were initiated and the modified solidifier condenser and condenser off-gas filtering system was installed prior to the last three pot solidification runs.(6) The average concentration of radionuclides in the process off-gas are summarized in Table 5.4 while cumulative DF's across the WSEP process condensers and process off-gas filters are summarized in Table 5.5. The cumulative ruthenium DF's across the solidifier condenser were 2.6×10^2, 6.8×10^2, and 1.1×10^3 for PC-7, PC-8, and PC-9(RLG), respectively. The ruthenium DF across the solidifier condenser off-gas filter for PC-8 was 1.8×10^2. Instantaneous DF's across the filter generally agreed with the cumulative DF's.

Most of the ruthenium that volatilizes from the evaporator is condensed by the evaporator condenser and accumulated in the fractionator. The average concentration of ^{106}Ru in the evaporator condenser off-gas was 1.2×10^{-5}, 2.5×10^{-6}, and

TABLE 5.4. Average Concentration of Radionuclides in the Process Off-Gas During Runs PC-7 Through PC-9(RLG)(a)

PC Run Number	Solidifier Condenser Off-Gas, μCi/cm^3		Off-Gas from Condenser Filter, μCi/cm^3		Evaporator Condenser Off-Gas, μCi/cm^3		Fractionator Condenser Off-Gas, μCi/cm^3	
	^{106}Ru	^{144}CePr	^{106}Ru	^{144}CePr	^{106}Ru	^{144}CePr	^{106}Ru	^{144}CePr
7					1.2×10^{-5}	2.8×10^{-5}	1.9×10^{-5}	3.6×10^{-8}
8	7.9×10^{-4}	6.1×10^{-3}	3.8×10^{-6}	8.8×10^{-5}	2.5×10^{-6}	1.6×10^{-5}	6.8×10^{-6}	4.6×10^{-8}
9	4.5×10^{-4}	7.7×10^{-4}	3.5×10^{-4}(b)	1.3×10^{-3}(b)	5.0×10^{-6}	1.5×10^{-5}	2.1×10^{-6}	1.4×10^{-7}

PC Run Number	Off-Gas from High Efficiency Filter, μCi/cm^3		Final Off-Gas from Scrubber μCi/cm^3		Final Off-Gas from Scrubber Ratio to 10CFR20	
	^{106}Ru	^{144}CePr	^{106}Ru	^{144}CePr	^{106}Ru	^{144}CePr
7	3.1×10^{-6}	2.7×10^{-5}	1.0×10^{-8}	3.7×10^{-8}	22	94
8	1.5×10^{-5}	1.2×10^{-5}	7.9×10^{-8}	1.1×10^{-7}	430	390
9	5.6×10^{-6}	3.9×10^{-6}	5.2×10^{-8}	9.5×10^{-8}	260	240

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a. Average values for entire run

b. The solidifier condenser off-gas filter was bypassed during Run PC-7 and PC-9(RLG)

TABLE 5.5. Decontamination Factors Across Process Condensers and Process Filters

	Average DF[(a)]					
	^{106}Ru			^{144}CePr		
PC Run	PC-7	PC-8	PC-9(RLG)	PC-7	PC-8	PC-9(RLG)
Solidifier Condenser (E-111)	2.6×10^2	6.8×10^2	1.1×10^3	4.3×10^3	5.0×10^3	1.2×10^4
Solidifier Condenser Off-Gas Filter	(c)	1.8×10^2	(c)	(c)	9.3×10^2	(c)
Evaporator Condenser (E-113)	1.3×10^2	2.6×10^3	2.2×10^3	4.6	3.8×10^2	6.35×10^2
Fractionator Condenser (E-115)	10	1.2×10^3	2.1×10^3	NA	5.6×10^3	4.7×10^1
High Efficiency Filter (F-112)[(b)]	NA	2.1×10^2	4.1×10^1	NA	3.3×10^2	4.1

NA Not Available

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

b. DF = Average concentration of component in the off-gas entering the filter/average concentration of component in the off-gas leaving the filter.

c. During Run PL-7 and PC-9(RLG) the solidifier condenser off-gas filter was bypassed.

5.0×10^{-6} μCi/cm^3 for PC-7, PC-8, and PC-9(RLG), respectively. Ruthenium DF's across the evaporator condenser ranged from 10^2 to 10^3. These were generally comparable to the solidifier condenser DF's.

Greater than 0.1% of the equivalent ruthenium fed to the solidifier accumulated in the fractionator. The fractionator nitric acid concentration was maintained at about 7 to 10$\underline{M}$, and the resulting fractionator overheads acidity ranged from about 0.02 to 0.06$\underline{M}$ HNO_3 using a tower internal reflux ratio varying from about 0.24 to 0.78. The ruthenium DF's across the fractionator averaged about 10. This was lower than expected by a factor of 10 to 100. The ruthenium DF_i's across the fractionator ranged from less than 100 to greater than 1000 and were typically greater than 100.

Ruthenium that escapes the WSEP acid fractionator is mostly condensed by the fractionator condenser and then either recycled back to the evaporator as stripwater or accumulated in a separate distillate receiver. Typically, 90% of the fractionator distillate was recycled back to the evaporator while the remaining 10% was accumulated in the fractionator distillate receiver. The amount recycled is inversely proportional to the evaporator overhead acidity. Average stripwater rates to and boil-off rates from the evaporator are listed in the Appendix Table 9.2. The distillate receiver accumulated generally about 0.01% of the equivalent ruthenium fed to the solidifier. This was an increase of about 100 times over that from previous runs and was probably caused by internal contamination of the system. The accumulated fractionator distillate (final aqueous process effluent) contained a concentration of radionuclides which was above 10CFR20 release limits by a factor as high as 4.3×10^5.

The off-gas leaving the fractionator condenser contained from 10^{-5} to 10^{-6} $\mu Ci/cm^3$ of ruthenium. Ruthenium DF's across the fractionator condenser were 10 for PC-7, 1.2×10^3 for PC-8, and 2.1×10^3 for PC-9(RLG).

Approximately 5 scfm of noncondensible gases leaving the fractionator condenser were filtered through a high efficiency filter before entering the off-gas scrubber. The filter DF's for radioruthenium based on gas samples were a low of 41 during Run PC-9(RLG) (attributed to contaminated sample lines and to the low level of radioactivity being measured) and 210 during PC-8. Most of the remaining radioruthenium in the process off-gas was removed in the off-gas scrubber where 2.3×10^{-3}, 2.0×10^{-3}, and 7.4×10^{-2}% of the equivalent radioruthenium fed to the solidifier accumulated in the scrubber bottoms. Accumulation of radioruthenium in the scrubber during Runs PC-7, PC-8 and PC-9(RLG) is shown in Figure 5.4.

The final process off-gas leaving the off-gas scrubber contained concentrations of radioruthenium that were factors of 22 to 430 above 10CFR20 release limits. However, the final process off-gases were filtered twice more and discharged into the main building ventilation system where they were mixed with about 120,000 scfm of air before entering the stack. This large dilution by the main building ventilation flow and the additional filtration reduced the ruthenium concentration to below detection limits for the available counting equipment (see Figure 9.8, Appendix). During the last pot solidification runs, the radioruthenium in the stack gases were more than 2500, 25, 2400 times less than the 2×10^{-10} $\mu Ci/cm^3$ 10CFR20 release limit (for Run PC-7, PC-8, and PC-9(RLG), respectively). The higher value during Run PC-8 could not be attributed completely to WSEP since the radioruthenium in the off-gas leaving the scrubber was typical of the other pot solidification runs. These values are conservative because they assume all radioruthenium emitted to the off-gas is from WSEP processing. Other sources of radionuclides in the facility are ventilation air from eight other high-level radioactivity cells and process vent effluents from other in-cell activities.

5.3 CONTROL OF OTHER RADIONUCLIDES

With pot solidification, a relatively small amount (less than 1%) of the nonvolatile constituents were entrained from the solidifier and accumulated in the auxiliary evaporator. Cumulative decontamination factors (DF_c) for nonvolatiles represented by ^{144}CePr across the WSEP evaporator were 3.5×10^3, 5.4×10^3, and 8.4×10^2 for Runs PC-7, PC-8, and PC-9(RLG), respectively. Instantaneous decontamination factors (DF_i's) for nonvolatiles across the auxiliary evaporator based on ^{144}CePr ranged from about 10^2 to 10^4. These data agree with data from the previous pot calcination runs.

Typical entrainment from the WSEP auxiliary evaporator was less than 1% of the nonvolatiles present in the evaporator. The overall DF's for nonvolatiles represented by ^{144}CePr from the original aqueous waste through the auxiliary system to the recovered acid in the fractionator ranged from about 10^6 to 10^7. Comparable DF's to the fractionator distillate were typically 10^{10}. Accumulation of nonvolatile radionuclides in the WSEP auxiliaries is shown in Figure 5.6.

The pot solidifier off-gases contained about 5 scfm of noncondensibles from inleakage. The presence of this noncondensable gas stream significantly affects decontamination, and efforts to keep air inleakage minimized should be applied to commercial applications. Overall, the nonvolatile constituents in the noncondensable gas flow were sufficiently removed by the auxiliary system to levels that were about 10^6 fold below radioruthenium levels.

Nonvolatile DF's across the process condenser and filter are presented in Table 5.5. The condenser DF's were typically above 10^3 but values as low as 4.6 and 47 were measured. The inconsistency and low DF's were probably caused by system contamination. The particulate DF across the solidifier condenser off-gas filter, based on ^{144}CePr was 930 for PC-8. The low DF for Run PC-9(RLG) resulted from bypassing the filter early in the run. The particulate DF's across the process filter prior to the off-gas scrubber were 330, and 4.1 for Runs PC-8 and PC-9, respectively. These represent filtering efficiencies of 99.7 and 76%, respectively. The low DF for Run PC-9(RLG) indicates that either the filter had failed or that the gas sample lines had become contaminated with radionuclides.

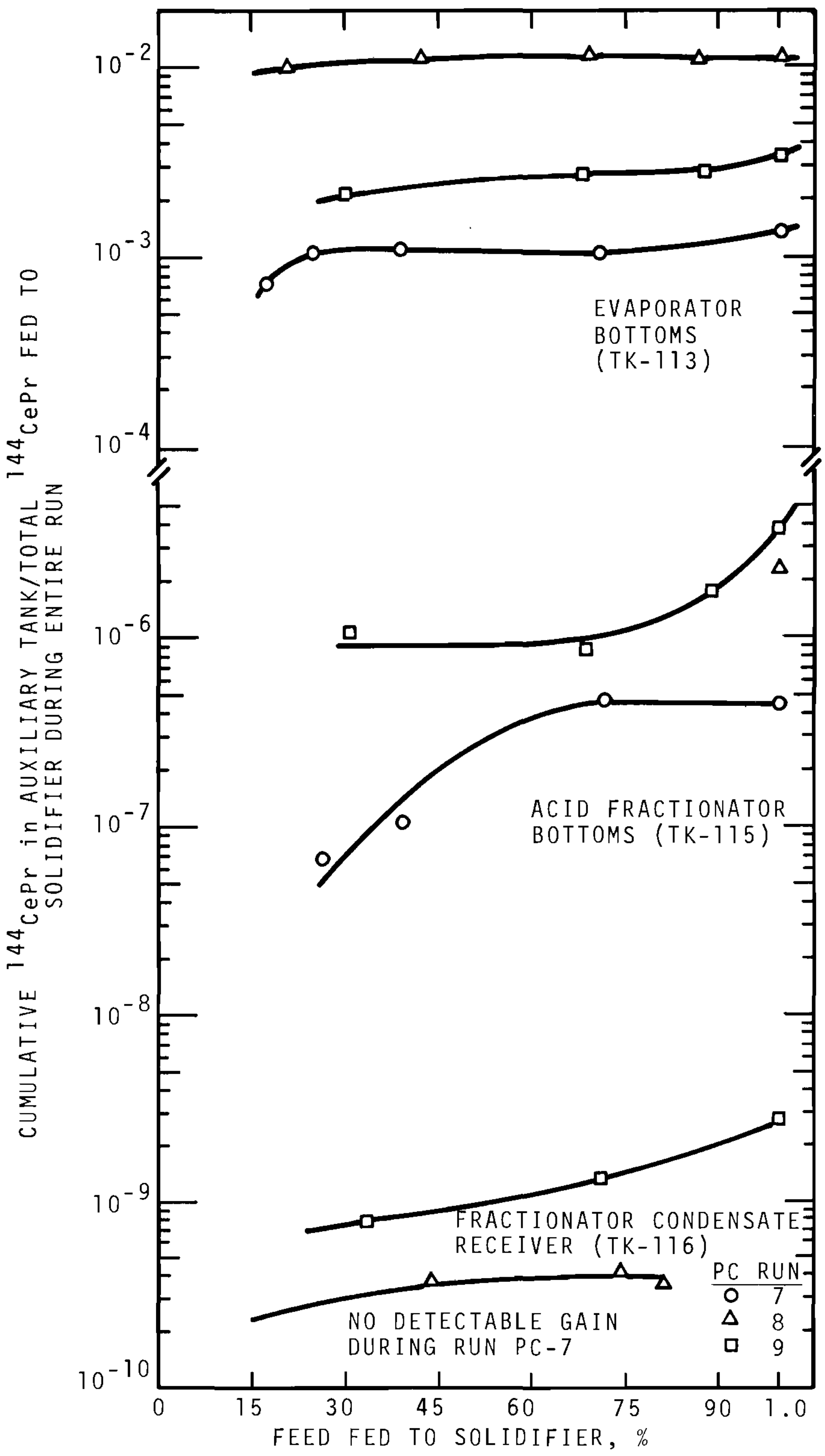

FIGURE 5.6. Accumulation of Nonvolatiles in WSEP Auxiliaries

The accumulation of nonvolatiles in the off-gas scrubber bottoms was nondetectable. The off-gas leaving the scrubber contained a concentration of radiocerium that was above 10CFR20 release limits by factors of 94, 430, and 240 for Runs PC-7, PC-8, and PC-9(RLG), respectively. However, the nonvolatile radioactive constituent concentration in the off-gas entering the atmosphere was well below 10CFR20 release limits after the scrubber off-gas was filtered twice more and diluted by other building and process air.

5.4 NITROGEN BALANCE

The modified solidifier condenser removed only 56, 50, and 39% of the nitrogen that volatilized from the solidifier during Runs PC-7, PC-8, and PC-9(RLG), respectively. The remaining 44, 50, and 61% was probably present as oxides of nitrogen which were carried through the condenser in the gas phase. The presence of nitrogen oxides in the solidifier condenser off-gas increased the acidity of the evaporator overheads and resulting distillate. This resulted in no equilibrium acidity between the evaporator bottoms and overheads.

The specific changes of nitrogen at various points in the auxiliary system are listed in Table 5.6. The off-gas scrubber which started with 3.6, 2.4 and 2.0M NaOH absorbed 8, 13, and 17% of the equivalent nitrogen fed to the solidifier during Runs PC-7, PC-8, and PC-9(RLG), respectively. As can be seen in Figure 5.7, which shows the scrubber operation during these runs, very little neutralization of the scrubber bottoms occurred. The neutralization that did occur is in direct proportion to the accumulation of nitrogen in the scrubber.

The only nitrogen losses from the WSEP system during this last series of runs occurred during PC-9(RLG) where only 79% of the equivalent feed nitrogen was recovered.

TABLE 5.6. Nitrogen Balance for Pot Solidification Runs PC-7, PC-8, and PC-9(RLG)

PC Run	Net Change, kg N PC-7	 PC-8	 PC-9
Feed to Solidifier (TK-114)	-47	-24	-23
Evaporator (TK-113)	-4.9	-6.4	-10
Acid Fractionator (TK-115)	+47	+28	+24
Accumulated Fractionator Distillate (TK-116)	+0.2	+0.2	+0.2
Scrubber (TK-118)	+3.6	+3.1	+4.0
Percent Equivalent Feed Nitrogen Recovered	98%	103%	79%
Percent Equivalent Feed Nitrogen in Scrubber	7.7%	13%	17%

5.5 PROCESS CONTROL OF WSEP AUXILIARY SYSTEM

During the last series of pot solidification runs, the operation of the evaporator and fractionator were controlled automatically by three interacting cascade control loops.(11) Six standard three-mode controllers were used in three cascade loops to control the auxiliary equipment as shown in Figure 5.8. The volume of the evaporator bottoms was maintained constant by one loop which regulated the steam flow to the evaporator tube bundle as a function of the weight factor. The evaporator acid concentration was maintained constant by a second loop which controlled the rate of recycle stripwater to the evaporator. When the overhead vapors from the evaporator were in equilibrium with the evaporator bottoms, the conductivity of the distillate was an indirect measure of

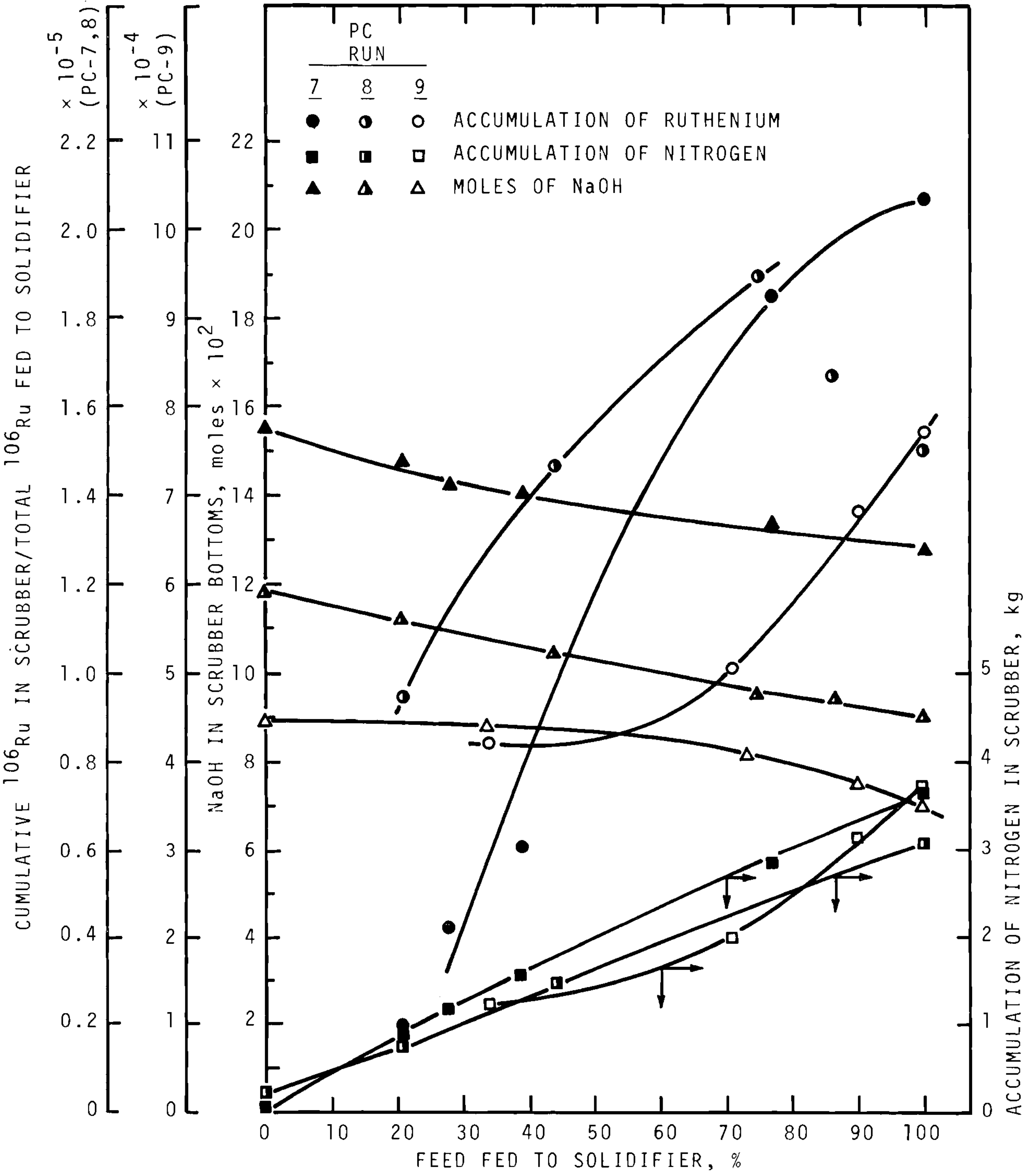

FIGURE 5.7. Off-Gas Scrubber Operation

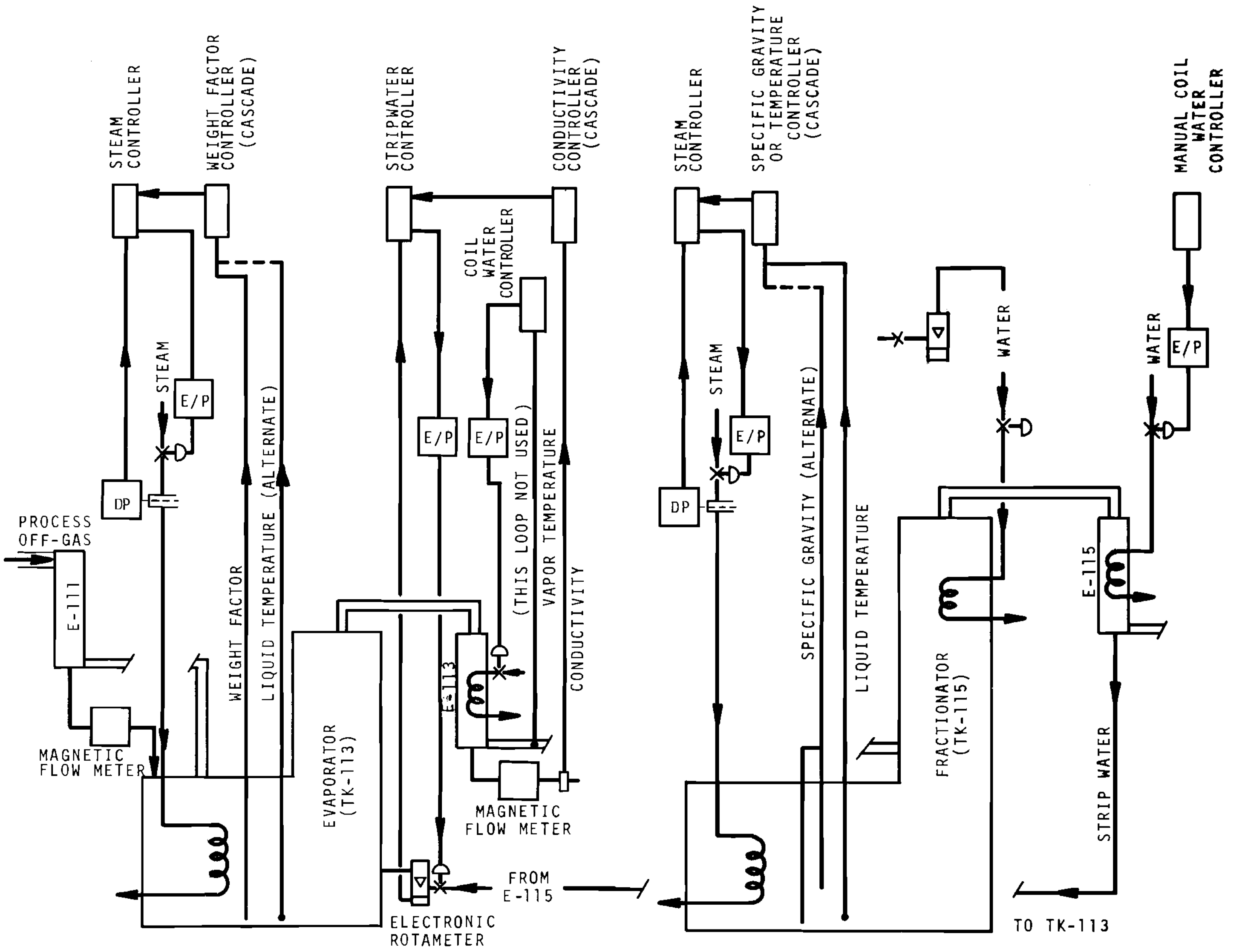

FIGURE 5.8. Basic Instrumentation for Automatic Control of WSEP Auxiliaries

the bottoms acidity. Boilup in the fractionator was controlled by a third loop which used the weight factor of the fractionator bottoms for control.

It had been shown in previous tests that to avoid overshoot in the steam control loops it would be necessary to operate the weight factor controllers with zero reset, but the reset could not be completely removed from the available three-mode controllers. Therefore the General Electric 412 process control computer, normally used for data logging, was programmed to obtain zero reset. The process computer established the set points for the two steam flow controllers as a function of the weight factor of the contents of the two tanks.

The operating parameters for both the evaporator and fractionator for the three runs are shown in Figures 9.4, 9.5, and 9.6 in the Appendix. During Run PC-7 two blown fuses in the computer output section prevented the control system from functioning prior to the start of the feed to the solidifier, accounting for part of the lack of control during the start up period. With the computer functioning properly, the volume of the evaporator bottoms was properly controlled along with the evaporator bottoms acidity. While the steam flow to the fractionator tube bundle was quite stable under weight factor control, it was necessary to periodically increase the weight factor set point to keep the acid concentration down as acid accumulated during the progress of the run.

Control of the evaporator bottoms acid concentration was compromised in the initial part of Run PC-8 by a faulty start up procedure, and by an unexplained partial failure of the overhead conductivity sensor during the remainder of the run. Therefore, the recycle flow control set point was manually adjusted rather than being cascaded from the conductivity measurement. The two steam flow control loops were quite stable and held the evaporator and fractionator volumes reasonably constant.

During most of Run PC-9(RLG) a partial failure of the overhead conductivity sensor compromised control, but when it was functioning all three of the cascade systems performed quite well. Weight factor control of the evaporator boilup was again very satisfactory. Specific gravity control of the fractionator worked quite well, producing only a mildly erratic boilup pattern. The failure of the conductivity sensor was attributed to the extremely low flow of condensate through the sensor well, resulting in the sensor being immersed in a non-representative sample. Conductivity measurements were roughly correlatable with the specific gravity of the bottoms as long as the evaporator boilup remained relatively high. As the recycle rate and the evaporator boilup decreased, conductivity values stabilized while specific gravity values continued to change.

5.6 AUXILIARY HANDLING OF PUREX WASTE

Fission product waste solutions contain precipitates which may interfere with liquid transfer, storage, or evaporation. While amorphous, noncaking precipitates can be handled at concentrations up to 50 vol% in WSEP, very small quantities of heavy, caking precipitates can plug pipes and equipment. Thus, proper design and operation requires a good knowledge of the precipitate characteristics. The precipitates present in a given waste solution depend to a large extent upon the chemical flowsheet used in the reprocessing plant and during the subsequent treatment of the waste. In general, the PW-1 and PW-4m solutions used in demonstration Tests PC-7, PC-8 and PC-9(RLG) were representative of typical Purex plant wastes. That is, they contained the full gamut of expected precipitate types, although the comparative amounts of precipitate varied with each waste.

The volume of settled solids in actual samples of the feed solutions used in the runs were not available for PC-7, 2% during PC-8, and 40% during PC-9(RLG). As discussed in Section 3.3.2, the use of phosphate as an additive during the pot solidification runs prevented sulfate type precipitates which are known to cake. During Run PC-9(RLG) special additive procedures were used for the borosilicate flowsheet (Section 3.3.3). The handling of pot solidification feeds in feed tanks, evaporators, and transfer lines was not considered to be a major problem during these final runs.

5.7 GENERAL PERFORMANCE OF AUXILIARY EQUIPMENT

The auxiliary equipment performed satisfactorily during Runs PC-7 through PC-9(RLG). All three runs were completed without an interruption. Table 5.7 is a compilation of the general operating experience of the WSEP auxiliary equipment.

5.7.1 Pumps

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

Feed pump operating experience is summarized in Table 9.5 (Appendix). No pump failures occurred during the last series

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TABLE 5.7. WSEP Auxiliary Equipment Operating Summary [Through Pot Solidification Run PC-9(RLG)]

Equipment	Construction Material	Temp., °C	Avg. Press., in. Water	Chemical	Operating Time, hr	Remarks
Feed Tanks	304L SS	25 to 60	-5	Darex, Purex, TBP-25 Type Waste	4475	Agitators used 3536 hr.
Condensate Tanks	304L SS	25	-10 to 20	H_2O, Dilute HNO_3	3902	Submerged pump used 1954 hr.
Caustic Scrubber	304L SS	25 to 40	-10 to 20	Dilute NaOH	3902	Circulation pump used 1954 hr.
Evaporator	A-55 Ti	110	-10 to 20	Boiling Waste	3654	Minor titanium corrosion caused by fluoride ion during early DVT runs.
Fractionator	A-55 Ti	115	-10 to 20	8 to 12M HNO_3	3654	
Solidifier Condenser	A-55 Ti	100 to 200	-10 to 20	HNO_3 Vapors	3850	Localized vapor entry corrosion caused by volatilized sulfate (up to 0.06 in.) during early DVT Runs 3 and 4.
Evaporator Condenser	A-55 Ti	100 to 110	-10 to 20	Dilute HNO_3	3654	
Fractionator Condenser	304L SS	100 to 110	-10 to 20	H_2O, Dilute HNO_3	3654	
Feed Pumps	304L SS	60		Adjusted Waste	2200	Changed from the original inline pump to conventional pump prior to Run PG-3.
					975	New pump jumper (see Appendix Table 9.5 for pump history).
Flowmeters:						
Feed, magnetic	Vitreous enamel liner. Platinum sealed electrodes. Inconel flowtubes.	30 to 80	$\sim$100	Concentrated Wastes	2840	Occasional intermittent readings due to lead wire failures. Also frequent shifts in calibration and loss of sensitivity, partially attributed to low WSEP flow rates.
Condensate, electronic rotameter		30 to 80	10 to 30	Dilute Acid, Water	3514	The meter was reliable for recycle flow measurement of stripwater.
Filters, Process Off-Gas						
Process Vent	Glass-asbestos with aluminum separators in 304L SS housing	50 to 70	-20	Predominantly Air, Nitrogen Oxides		

of runs. Pump life is decreased by start and stop operation and is substantially increased by a thorough water flushing after each run. In an extended pump operating test with non-radioactive feed, a similar pump was operated continuously for 553 hours before the seals failed.

5.7.2 Feed Control System and Flow Measurement

Operation of the feed control system over the range of about 5 to 30 liters/hr was only fair because this low feed flow rate was frequently below the range of the magnetic flowmeter. The automatic feed controller receives an input signal from the magnetic flowmeter and delivers an output signal to the feed control valve. A 1/2-inch Hammel Dahl® valve with a No. 5 spline trim was used to control the feed to the solidifier. Special flushing procedures were used prior to and after feeding to keep the feed line satisfactorily free of solids deposition. The pot solidifier liquid level control system is described in Section 4.5.2.

5.7.3 Modified Solidifier Condenser

The modified solidifier condenser and condenser off-gas filtering system was used during the last three solidification runs to improve decontamination of the solidifier off-gas. The bottom half of the condenser tubes was filled with Pall rings to improve the condenser performance. Filling the tubes completely with Pall rings would have substantially increased the pressure drop across the condenser to a point that vacuum requirements for the spray solidifier could not be met. The condenser was installed prior to the last series of spray solidification runs.

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5.7.4 Evaporator and Acid Fractionator

The WSEP evaporator and fractionator which are capable of boilup rates as high as 530 and 310 liters/hr, respectively, performed satisfactorily. Operating conditions for the evaporator are shown in Figures 9.4 through 9.6 and are discussed in Section 5.5.

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

Again as in previous WSEP runs, chemical complexants were added to the titanium evaporator and fractionator vessels to minimize fluoride-induced corrosion. Eight liters of 2.6$\underline{M}$ $AlNO_3 \cdot 9\ H_2O$ was added to the vessels during every run; however, when waste solutions are boiled in the evaporator, enough iron, zirconium, and aluminum ionic complexants are normally present in the waste solution to inhibit corrosion.

5.7.5 Filters

The high-efficiency process ventilation filters performed well as in previous WSEP runs.

5.7.6 Electrical and Instrument Wiring

During pot solidification Runs PC-7 through PC-9(RLG), less extensive deterioration of wiring insulation occurred than during earlier runs since most of the wiring that originally used linear polyethlene as insulation had been replaced with a more flexible and less expensive neoprene rubber-insulated wire.

5.7.7 Aqueous and Gas Sampling

Sampling techniques were considerably improved over those used in the first series of six pot solidification runs. Low-level radioactive aqueous samples (those of fractionator distillate and scrubber) were routed outside of B-Cell to a new sampling station. This reduced potential contamination by in-cell handling. Samples from the WSEP auxiliary evaporator and fractionator were obtained while the tanks were boiling to assure representative samples. Incorporation of the above improvements led to improved data from samples.

Gas sampling equipment was used to collect samples of process off-gas at various points in the auxiliary system. Gas samples taken during the last three pot solidification runs were believed to be representative of the process off-gases. Gas sampling techniques and equipment used are discussed in References 7 and 17.

5.7.8 Material Balances

Specific material balance data for pot solidification Runs PC-7, PC-8, and PC-9(RLG) are presented in Appendix Table 9.4. Samples of the product were not obtainable, therefore the total recovery of individual elements was not completely known. However, total material balances indicated fairly good recoveries. The overall material balances for pot solidification Runs PC-7 through PC-9(RLG) are shown in Table 5.8.

TABLE 5.8. Overall Material Balances for Pot Solidification Runs PC-7 Through PC-9(RLG)

	Percent Recovery[a]	
PC Run	Volume	Mass
7	100	98
8	101	100
9	97	99

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a. Based on total at end of run/total at start of run for all tanks added together.

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6.0 FILLED POT PERFORMANCE

CONTENTS

6.0 FILLED POT PERFORMANCE

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

Experimental measurements are made on each filled pot to aid in characterizing the suitability and compatibility of the pot and solidified wastes. This section presents a summary of the experimental measurements that have been made for the pots from pot solidification Runs PC-7 through PC-9(RLG). Data from Runs PC-1 through PC-6(2) are included where it is considered appropriate.

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

Table 6.1 is a summary of overall waste pot fill data. Waste type, pot diameter and material, and the product weight, volume, and bulk density for the last three pot solidification runs is given. The volume of product was estimated from pot internal temperatures since the small pot opening and entrainment baffle prevented obtaining a rodded depth of product. The pot design also makes it impossible to obtain product samples for laboratory measured density comparisons with the calculated bulk density shown in Table 6.1. Additional information on product volume reduction is presented in Section 4.3.

TABLE 6.1. Waste Pot Fill Data

PC Run	Waste Type	Pot Diam., in.	Pot Material	Volume of Product,[a] liters	Weight of Waste Product, kg	Bulk Density, kg/liter
7	PW-1	8	304L	60	73.2	1.22
8	PW-4m	6	304L	34	45.5	1.34
9(RLG)	PW-4m	6	310	∿16 (Plus ∿2 as Calcine)	63.6	∿3.5

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a. Product volume estimated from pot temperatures.

6.1 THERMAL CONDUCTIVITY

The effective thermal conductivity (k_{eff}) of the pot solidified waste as a function of average product temperature is presented in Figure 6.1. The data from all pot calcination runs indicates that k_{eff} is nearly constant at 0.35 W/(m^2)(°C/m) over the average calcine temperature range of 100 to 700 °C. Data from individual runs show a slight temperature dependence as k_{eff} increases with temperature. The calcine data do not indicate any k_{eff} difference resulting from waste type; however, there may be a dependence on calcine density. As seen in Figure 6.1, for the individual runs plotted as dashed lines, the higher density solids exhibit higher k_{eff}'s.

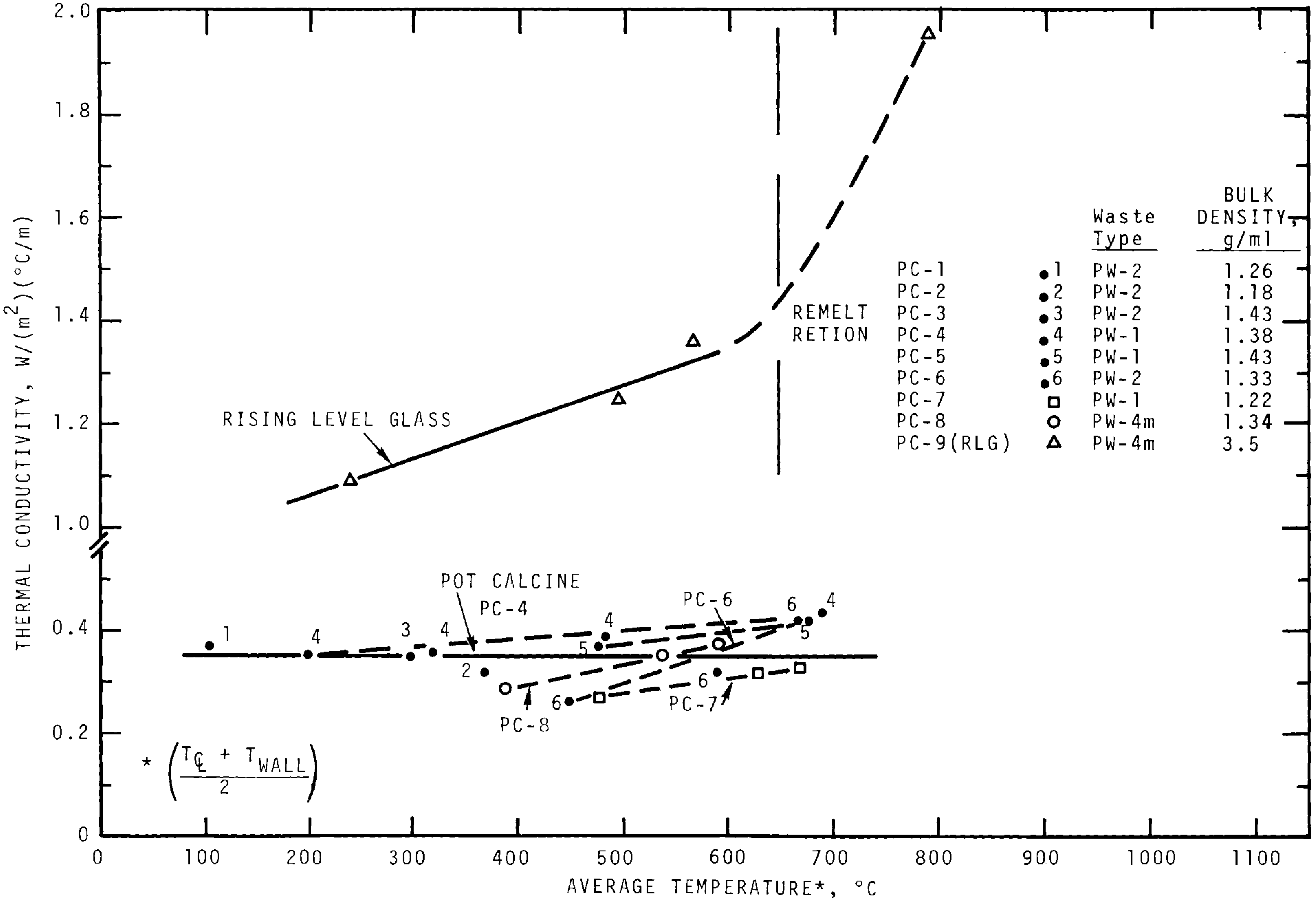

FIGURE 6.1. Effective Thermal Conductivity of Pot Calcine and Rising Level Borosilicate Glass

The k_{eff} of the borosilicate waste is more dependent on temperature and over the range of 200 to 600 °C the thermal conductivity fits the equation:

$$k_{eff}\ [\text{watts}/(\text{m}^2)(°\text{C}/\text{m})] = 0.00072\ (\bar{T},\ °\text{C}) + 0.92$$

Above approximately 650 °C the waste is in a softened or molten state and the thermal conductivity increases rapidly. Although only one RLG run was made, the RLG product is very similar to the spray solidified in-pot melting product,(3) and with some allowance for data scatter the k_{eff} for the two products are nearly identical.

6.2 GAMMA SPECTRUM ANALYSIS AND RADIATION PROFILES

Uniform heat generation rate is one of the basic assumptions used to determine the effective thermal conductivity of solidified waste.(2) Uniform heat generation rate is also important to safety considerations in that "hot spots" within a container could result in premature failure of the container. For these reasons, gross gamma scans of the phosphate glass waste containers were made after filling to look for any gross fission product migration or segregation. The temperature profiles from the pot internal and wall thermocouples were also studied for evidence of "hot spots." The data gathered in the pot solidification demonstration series indicates that fission product migration or segregation is not a problem.

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

Figure 6.2 shows the results of the gross gamma scans for pot solidification Runs PC-7 through PC-9(RLG). The dose rate measurements have been normalized to Zone 4 [except Zone 5 for PC-9(RLG)] which is located near the midplane of the filled portion of the pot. The purpose of normalization was to show the characteristic "banana shape" radiation profile that one would expect from a homogeneous, uniform distribution of fission products. Actual data from gross gamma dose rate measurements are presented in Table 6.2. Intermediate and wall thermocouple temperature measurements, also normalized to Zone 4 [except Zone 5 for PC-9(RLG)] are presented in Figure 6.3 for Zones 1 through 6 to further substantiate the product uniformity.

The fill height of solidified waste relative to the pot zones is shown for each waste receiver on Figures 6.2 and 6.3. Obviously, the amount of product in the receiver pot affects the shape of both the radiation and temperature profiles. For example, the radiation and temperature profiles for PC-9(RLG) fall off rapidly in the upper zones due to the relatively low fill height compared to the other runs.

Both radiation and temperature profiles indicate that the solidified waste in WSEP demonstration Runs PC-7 through PC-9(RLG) is uniformly distributed and that there are no "hot spots" within these waste containers that might lead to premature pot failure or invalidate assumptions for effective thermal conductivity calculations.

6.3 WASTE POT DIMENSIONS AND PHYSICAL DATA

Each waste pot is carefully examined prior to transfer to the hot cell. Prefill dimensions are taken of the pot wall thickness, length, and diameter at several locations in order to detect gross changes caused by waste solidification.

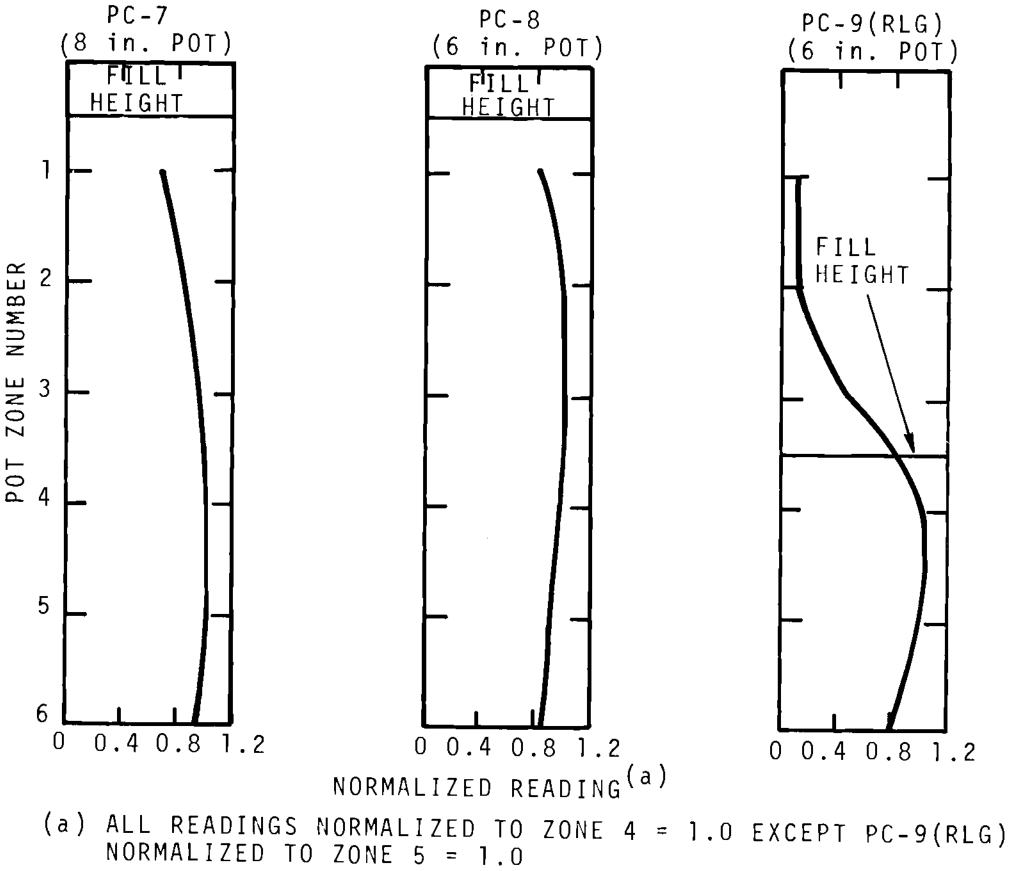

FIGURE 6.2. Normalized Gross Gamma Scan of Pot Solidifier Pots

TABLE 6.2. Gross Gamma Dose Rates for Pot Solidifier Pots

	R/hr Rates for		
Waste Container Zone	PC-7 Scanned 8/7/70	PC-8 Scanned 9/11/70	PC-9(RLG) Scanned 10/28/70
1 (Top)	2.1×10^4	4.4×10^4	0.5×10^4
2	2.6×10^4	5.5×10^4	0.6×10^4
3	3.0×10^4	5.4×10^4	2.2×10^4
4	3.1×10^4	5.2×10^4	5.1×10^4
5	3.2×10^4	4.6×10^4	4.9×10^4
6 (Bottom)	2.9×10^4	4.5×10^4	4.0×10^4

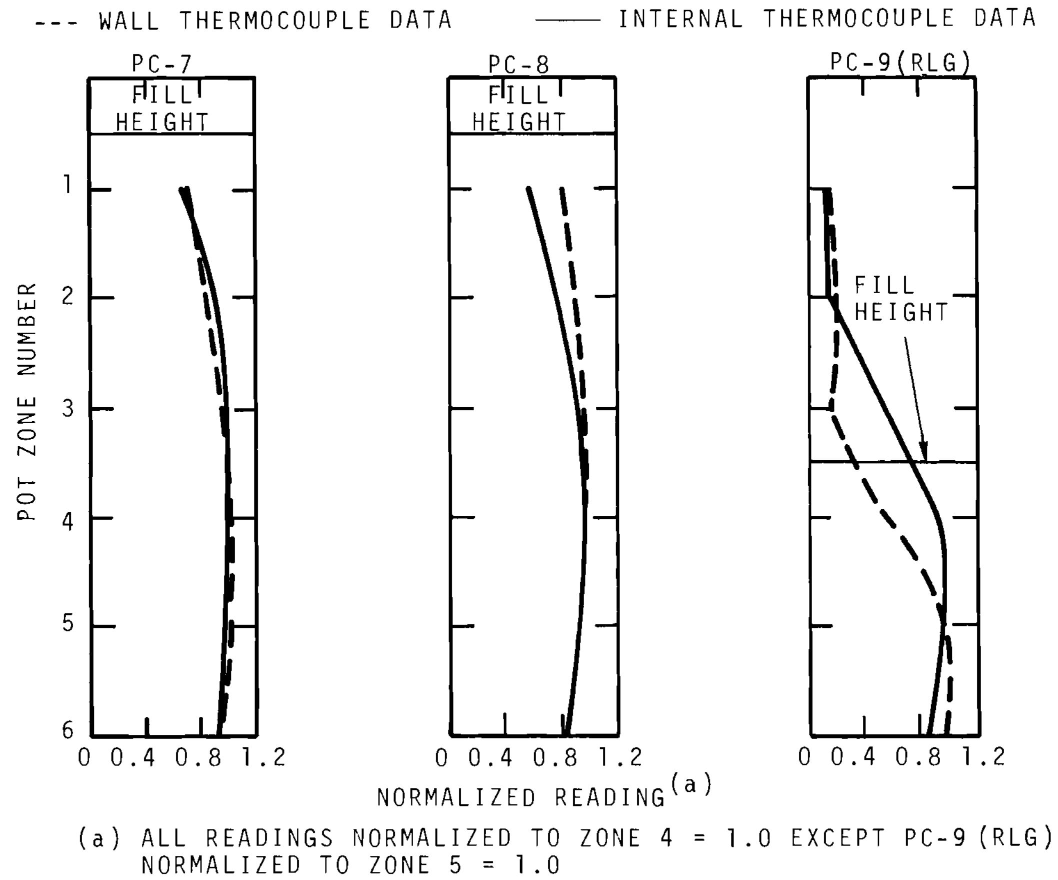

FIGURE 6.3. Normalized Temperature Data for Pot Solidifier Pots

Wall thickness measurements of the waste pots were made by an ultrasonic wall thickness scan system. Table 6.3 summarizes the data for all of the pot solidifier pots before and after filling. The pots have maintained their initial wall thickness through processing and various storage times. Table 6.4 summarizes the prefill and afterfill measurements of pot diameter and length for the last pot solidification runs. The diameter measurements were made using dial indicating micrometers which allow accuracies within 0.025 inches. No diameter changes of more than 0.1 inches occurred in any pot.

TABLE 6.3. Pot Solidifier Wall Thickness Scan
(All dimensions in inches.)

	PC-1		PC-2		PC-3		PC-4		PC-5		PC-6		PC-7		PC
Zone No.	Prefill 11/11/66	Afterfill 11/13/70	Prefill 2/10/67	Afterfill 11/13/70	Prefill 2/22/67	Afterfill 11/16/70	Prefill 6/22/67	Afterfill 11/18/70	Prefill 7/25/67	Afterfill 11/12/70	Prefill 8/21/67	Afterfill	Prefill 8/5/70	Afterfill 11/9/70	Prefill 9/10/70
1	0.340	0.335	NA	0.329	NA	0.315	0.330	0.336	0.320	0.323	0.320	NA	0.320	0.327	0.274
1-1/2	0.340	0.333	NA	0.328	NA	0.314	0.335	0.339	0.320	0.322	0.320	NA	0.318	0.327	0.273
2	0.330	0.336	0.320	0.330	0.310	0.312	0.335	0.340	0.320	0.320	0.320	NA	0.319	0.326	0.272
2-1/2	0.340	0.335	0.320	0.331	0.310	0.314	0.332	0.339	0.320	0.323	0.320	NA	0.318	0.325	0.271
3	0.330	0.338	0.330	0.333	0.310	0.312	0.330	0.336	0.320	0.320	0.320	NA	0.321	0.327	0.272
3-1/2	0.340	0.336	0.300	0.332	0.310	0.312	0.330	0.336	0.320	0.320	0.320	NA	0.318	0.328	0.271
4	0.340	0.326	0.330	0.334	0.310	0.310	0.325	0.331	0.320	0.318	0.320	NA	0.318	0.328	0.272
4-1/2	0.340	0.332	0.320	0.331	0.310	0.312	0.325	0.328	0.320	0.318	0.320	NA	0.320	0.328	0.271
5	0.340	0.327	0.320	0.332	0.310	0.310	0.325	0.330	0.320	0.322	0.320	NA	0.320	0.324	0.272
5-1/2	0.340	0.324	NA	0.324	0.310	0.310	0.320	0.326	0.320	0.321	0.320	NA	0.320	0.328	0.273
6	NA	0.327	NA	0.332	0.310	0.309	0.325	0.321	0.320	0.321	0.320	NA	0.316	0.322	0.272
6-1/2	NA	0.320	NA	0.325	NA	NA	0.325	NA	0.320	0.320	0.320	NA	0.317	0.323	0.271

NA Not Available

TABLE 6.3. Pot Solidifier Wall Thickness Scan
(All dimensions in inches.)

PC-2		PC-3		PC-4		PC-5		PC-6		PC-7		PC-8		PC-9	
Prefill 2/10/67	Afterfill 11/13/70	Prefill 2/22/67	Afterfill 11/16/70	Prefill 6/22/67	Afterfill 11/18/70	Prefill 7/25/67	Afterfill 11/12/70	Prefill 8/21/67	Afterfill	Prefill 8/5/70	Afterfill 11/9/70	Prefill 9/10/70	Afterfill 11/9/70	Prefill 9/15/70	Afterfill 11/6/70
NA	0.329	NA	0.315	0.330	0.336	0.320	0.323	0.320	NA	0.320	0.327	0.274	0.276	0.305	0.302
NA	0.328	NA	0.314	0.335	0.339	0.320	0.322	0.320	NA	0.318	0.327	0.273	0.273	0.305	0.302
0.320	0.330	0.310	0.312	0.335	0.340	0.320	0.320	0.320	NA	0.319	0.326	0.272	0.272	0.306	0.302
0.320	0.331	0.310	0.314	0.332	0.339	0.320	0.323	0.320	NA	0.318	0.325	0.271	0.271	0.304	0.300
0.330	0.333	0.310	0.312	0.330	0.336	0.320	0.320	0.320	NA	0.321	0.327	0.272	0.273	0.306	0.303
0.300	0.332	0.310	0.312	0.330	0.336	0.320	0.320	0.320	NA	0.318	0.328	0.271	0.272	0.305	0.303
0.330	0.334	0.310	0.310	0.325	0.331	0.320	0.318	0.320	NA	0.318	0.328	0.272	0.275	0.303	0.300
0.320	0.331	0.310	0.312	0.325	0.328	0.320	0.318	0.320	NA	0.320	0.328	0.271	0.274	0.306	0.303
0.320	0.332	0.310	0.310	0.325	0.330	0.320	0.322	0.320	NA	0.320	0.324	0.272	0.271	0.305	0.303
NA	0.324	0.310	0.310	0.320	0.326	0.320	0.321	0.320	NA	0.320	0.328	0.273	0.272	0.307	0.302
NA	0.332	0.310	0.309	0.325	0.321	0.320	0.321	0.320	NA	0.316	0.322	0.272	0.277	NA	0.302
NA	0.325	NA	NA	0.325	NA	0.320	0.320	0.320	NA	0.317	0.323	0.271	0.274	NA	0.302

TABLE 6.4. Pot Solidifier Waste Receiver Prefill and Postfill Dimensions

PC Run No.	Distance from Top of Pot, in.	Diameter, in. Prefill Maximum	Diameter, in. Prefill Minimum	Diameter, in. Afterfill Maximum	Diameter, in. Afterfill Minimum	Pot Length, in. Prefill	Pot Length, in. Afterfill
7	24	8.6	8.6	8.5	8.5		
	56	8.6	8.6	8.6	8.6	95 9/16	96
	80	8.6	8.6	8.6	8.6		
8	24	6.6	6.6	6.6	6.5		
	56	6.6	6.6	6.6	6.6	95 5/8	NA
	80	6.6	6.6	6.6	6.6		
9(RLG)	24	6.7	6.6	NA	NA		
	56	6.7	6.7	NA	NA	89 3/8	89 5/8
	80	6.7	6.6	NA	NA		

NA Data Not Available

Figure 6.4 is a photograph of the 8-inch diameter PC-7 pot prior to installation in the cell. The 6-inch diameter pots used in PC-8 and PC-9(RLG) are similar except the conical section near the top of the pot is steeper for the 6-inch pots. The pot wall thermocouples are readily visible in the figure. The interior thermocouples were inserted into the thermal wells through Conax glands (arrangement of the thermocouples is shown in Figures 4.4 and 4.7). Connection to the pot for thermocouple readout is through the L shaped thermocouple arm and Cannon connector. The intermediate and centerline thermocouples can and have been replaced remotely when thermocouples become inoperative.

6.4 WASTE POT WELDING AND LEAK CHECKING

The waste pots in this series have been welded. Leak checking of the pots by vacuum pumping after welding was generally not performed because it was found during the first

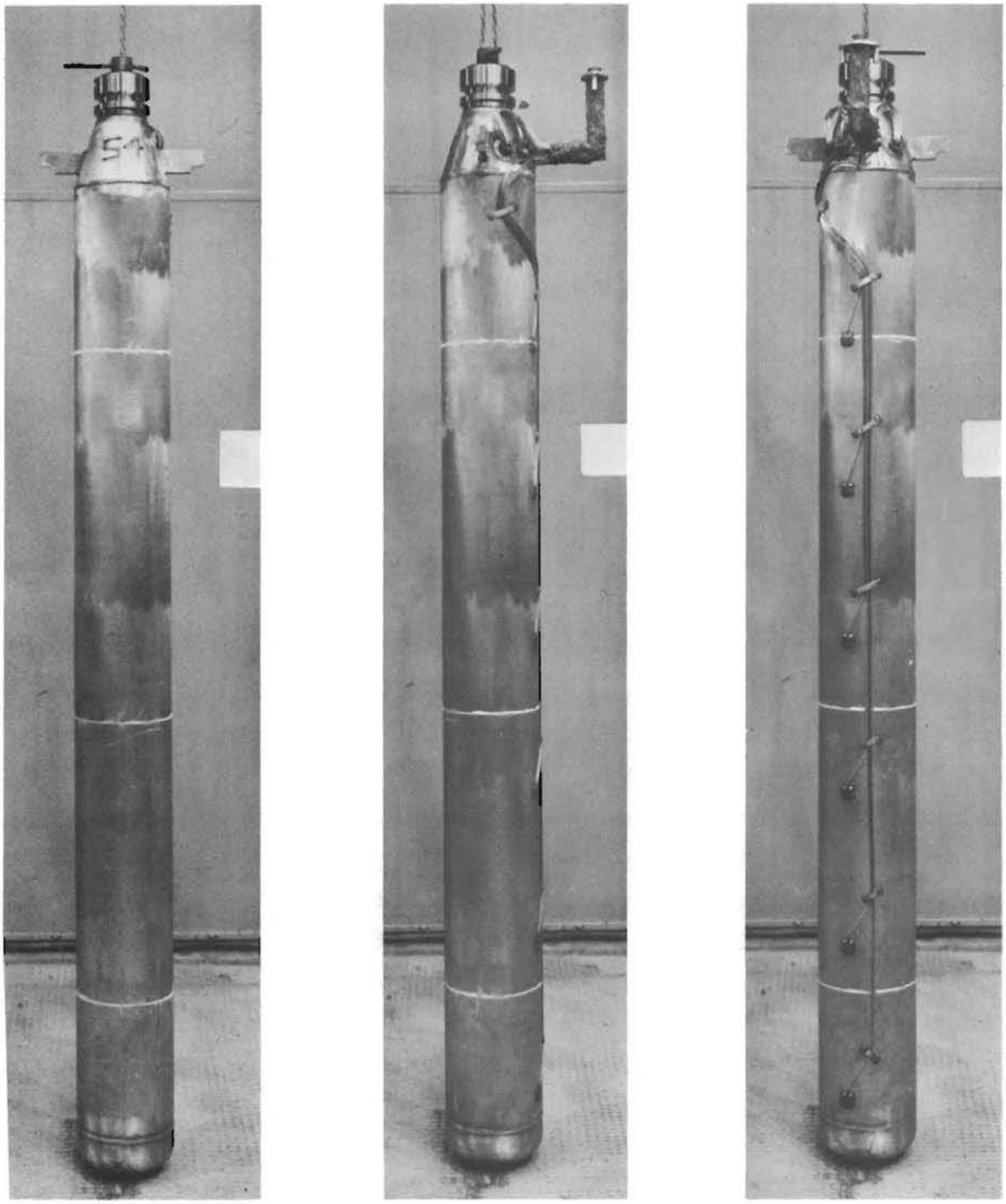

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FIGURE 6.4. Pot Solidification 8-inch Waste Container (PC-7)

series of pot runs that the calcine evolves gases (predominately nitrates) during the high vacuum testing. Prolonged vacuum pumping of the PC-6 Calcine pot for a semi-continuous 3 week period resulted in essentially complete off-gassing of the residual nitrate and a satisfactory leak rate of 5×10^{-8} atm/cc/sec. Vacuum pumping of the PC-8 calcine pot for two six hour periods reduced the pot vacuum from 150 to 120 microns during the first period and from 125 to 118 microns during the second. The vacuum pump cold trap contained nitric acid after each period.

The basic concepts and principles that have been applied to seal-welding the waste receivers have worked very well.(2) The Siaky weld unit was operated at 10 volts and 160 amperes with a turntable rotation set to give a weld speed of approximately 4.5 inches/minute.

6.5 POT INTERNAL PRESSURE

To date there has been no positive indications of pressurization of any WSEP pot. Internal pressures of this final series of pots were not measured. The bourdon pressure tube gage that was installed on the PC-7 pot has failed. The PC-8 pot did not have a pressure gauge attached to it (will be monitored during SSETF testing), and the PC-9 pot pressure cannot be monitored because a thermocouple well was drilled through while a product core sample was being obtained.

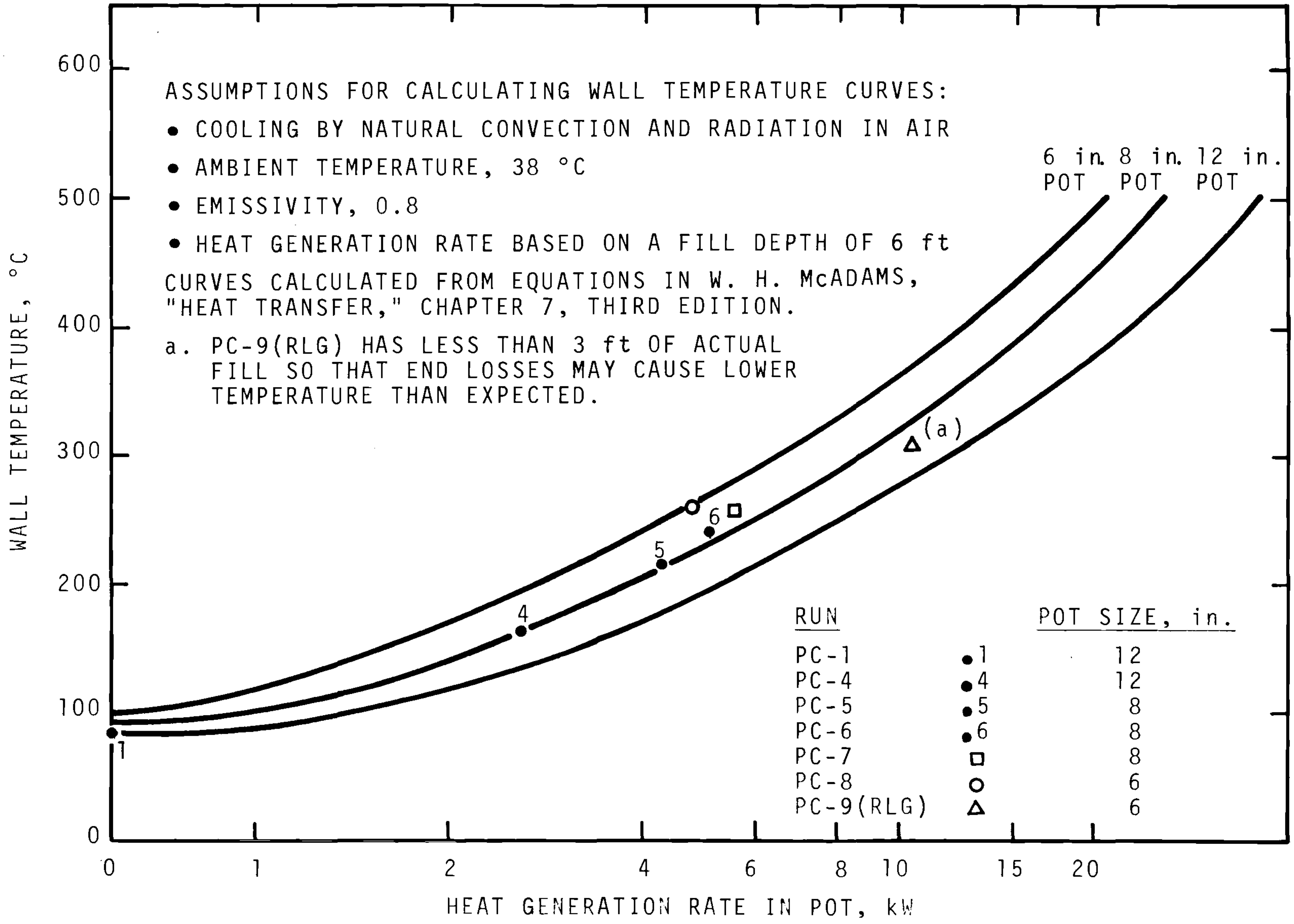
6.6 POT WALL TEMPERATURES

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

Figure 6.5 shows the calculated pot wall temperatures versus heat generation rates, and experimental pot wall temperatures obtained during air temperature profile measurements. Three pot sizes, 6, 8, and 12-inch diameter, and a 0.8 emissivity were used for the comparison. The surrounding media was assumed to be at 38 °C based on measured cell temperatures. All calculated wall temperatures are based on a 6 foot receiver fill height. The experimental data points are from a thermocouple positioned at the receiver midplane. The calculated and measured values compare favorably except for PC-4 and PC-9(RLG). A low emissivity (about 0.6) due to inadequate oxidation might explain the PC-4 value as the pot wall temperature only reached 825 to 845 °C during processing. Experience has shown that an apparent emissivity of 0.8 is attained if the pot wall temperature is at 900 °C for 8 hours. The low value for the PC-9(RLG) pot is probably due to the shallow (3 ft) fill depth of product.

6.7 ENVIRONMENTAL TESTING

This latter series of pot solidification runs is particularly important to the environmental test program. PC-8 and PC-9(RLG) waste pots are scheduled for further and more extensive evaluation.(4) These two waste receivers and PC-6 from the first series will be used to determine the product and container characteristics for up to 5 to 10 years after filling. The importance of this work lies in obtaining information about radiation, chemical, and thermal stability of the solidified waste. Equally as important are the corrosion resistance and environmental stability of the waste pot.



ASSUMPTIONS FOR CALCULATING WALL TEMPERATURE CURVES:

- COOLING BY NATURAL CONVECTION AND RADIATION IN AIR
- AMBIENT TEMPERATURE, 38 °C
- EMISSIVITY, 0.8
- HEAT GENERATION RATE BASED ON A FILL DEPTH OF 6 ft

CURVES CALCULATED FROM EQUATIONS IN W. H. McADAMS, "HEAT TRANSFER," CHAPTER 7, THIRD EDITION.

a. PC-9(RLG) HAS LESS THAN 3 ft OF ACTUAL FILL SO THAT END LOSSES MAY CAUSE LOWER TEMPERATURE THAN EXPECTED.

RUN		POT SIZE, in.
PC-1	● 1	12
PC-4	● 4	12
PC-5	● 5	8
PC-6	● 6	8
PC-7	□	8
PC-8	○	6
PC-9(RLG)	△	6

FIGURE 6.5. Pot Wall Temperatures in Air

REFERENCES FOR SECTION 6

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

3. W. R. Bond, J. L. McElroy, J. N. Hartley, J. E. Mendel and R. J. Thompson, Waste Solidification Program, Volume 8, Spray Solidification Performance During Final Radioactive Tests in Waste Solidification Engineering Prototypes, BNWL-1583, June 1971.

4. R. J. Thompson, J. E. Mendel and J. H. Kleinpeter, Waste Solidification Demonstration Program: Characterization of Nonradioactive Samples of Solidified High-Level Waste, BNWL-1393, Battelle-Northwest, Richland, Washington, June 1970.

7.0 PROJECTED FLOWSHEETS FOR PW-4m AND LMFBR WASTES

CONTENTS

7.0 PROJECTED FLOWSHEETS FOR PW-4m AND LMFBR WASTES

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

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

The fission product heat generation rate in waste from one tonne of the 45,000 MWd/tonne and LMFBR core fuels (100,000 MWd/tonne at 200 MW/tonne) are 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. The initial 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

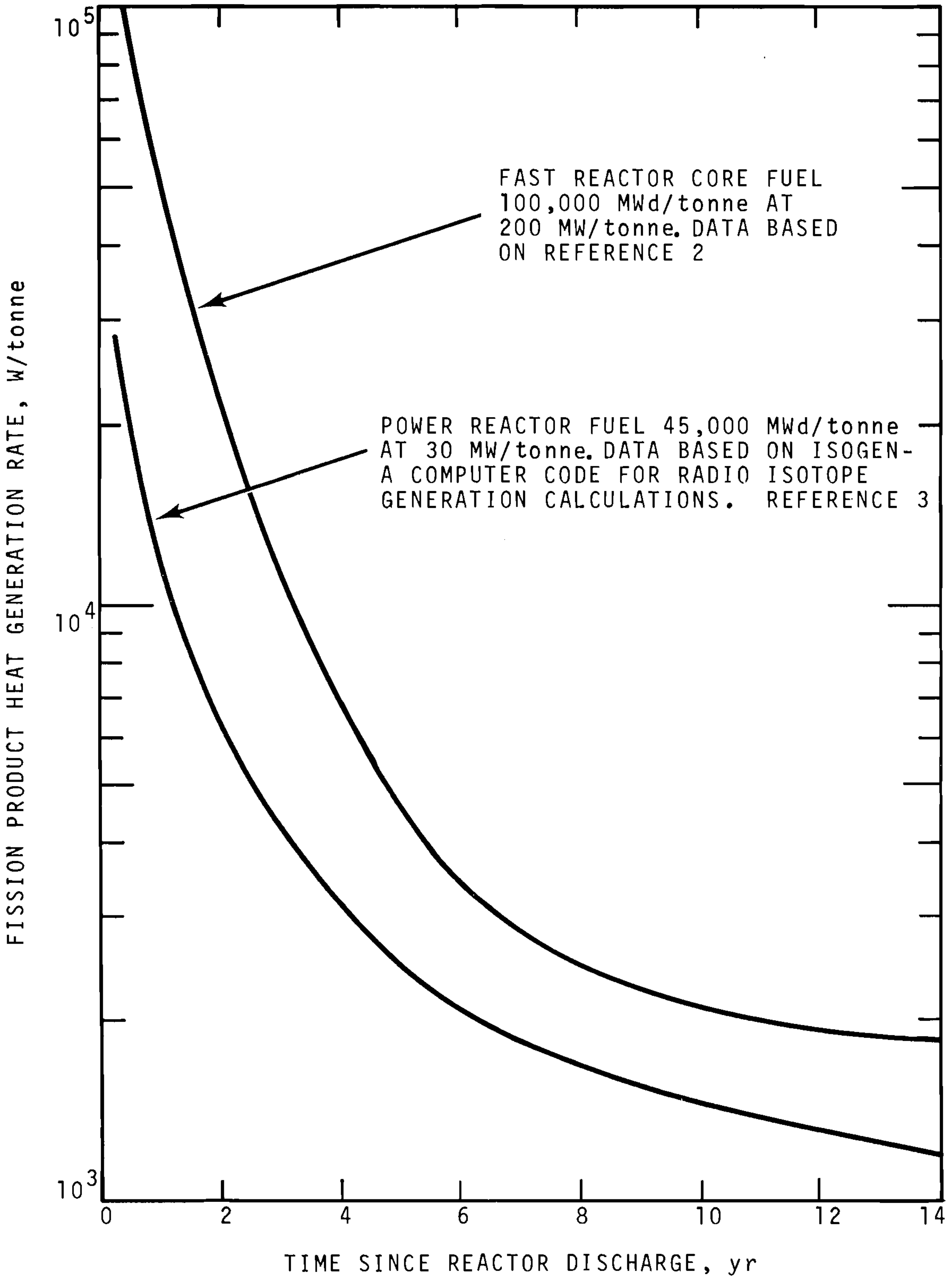

FIGURE 7.1. Fission Product Heat Generation Rate with Time for One Tonne of Reactor Fuel

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 rate density than the final storage environment may allow. The aging before storage of the pots in salt depends on economic choice. However, 10CFR50 requires that solidification of all high level wastes be completed before the fuel has been out of the reactor for five years.(4) Figure 7.2 shows the ages required to meet present temperature limitations for filling 6 and 8-inch diameter pots with pot solidified products for storage in either water or air. For the RLG process a solid waste composition containing 50 wt% waste oxides is used. Solidification can be performed at an earlier age out of reactor if a lower waste oxide percentage is used.

Conditions of a water cooled RLG pot are not shown in Figure 7.2 since it is not possible to fill a RLG pot while it is in water. Although the calcine pot also cannot be filled during water storage, the maximum centerline calcine temperatures of 1050 (6-inch pot) and 1100 °C (8-inch pot) that would be encountered during air cooling are probably not excessive for the short time of processing. The pot could then be placed in water.

Initially the maximum heat generation rate within any filled container is limited either by the maximum desired centerline or wall temperatures (which are 900 °C and 427 °C, respectively, in WSEP, based on corrosion considerations) or by other limits such as the WSEP limit for molten cores. If a molten core exists, the frozen wall thickness should not be less than one-half the pot radius. This is an arbitrarily established limit for WSEP for those waste products with remelt temperatures below 900 °C.*

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* These limits were selected for the WSEP waste containers and are used here in the absence of established limits to provide a preliminary basis from which to compare waste solidification and waste storage.

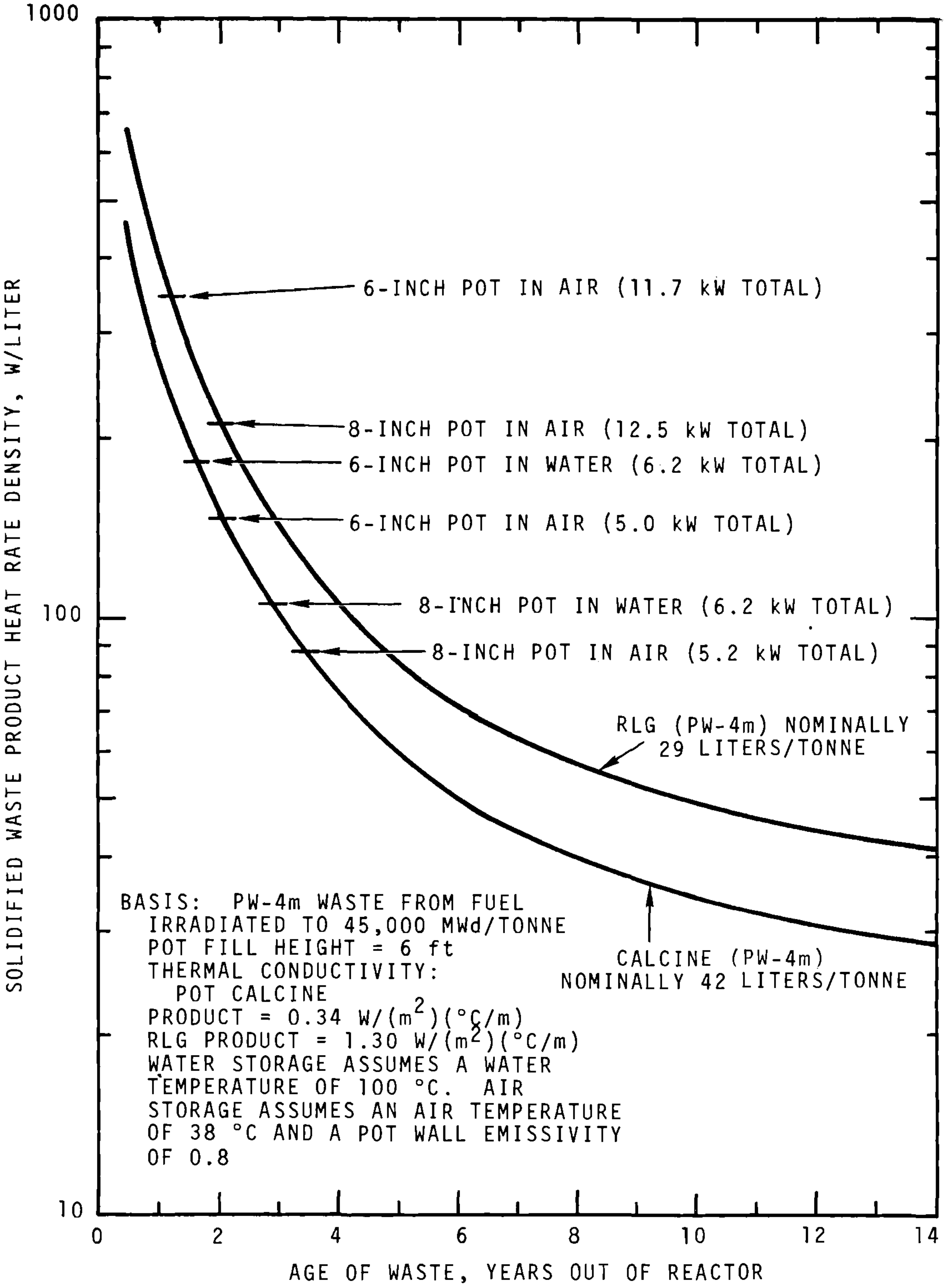
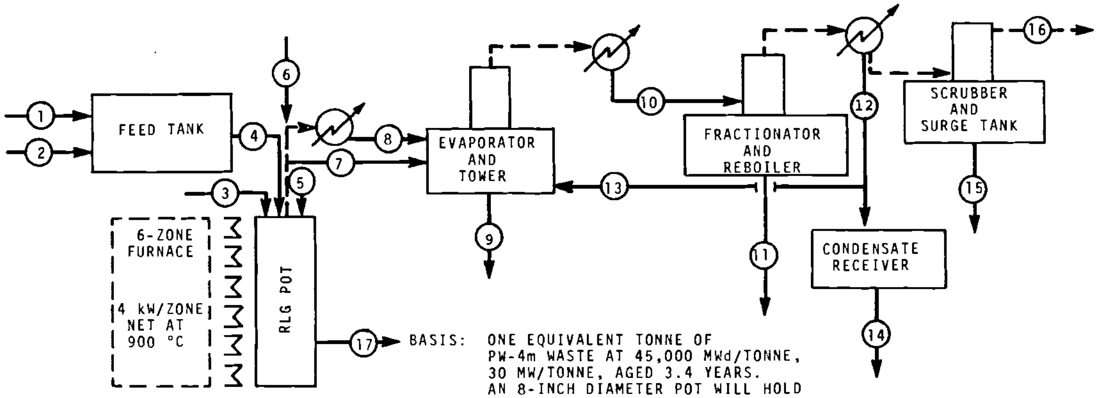


FIGURE 7.2. Heat Age Environment Relationships for High-Level Radioactive Pot Solidified Waste Showing Fission Product Heat Rate Density Limits

Since the pot calcination products have nominal melting temperatures above 900 °C, the centerline and wall temperature limits were used to determine the maximum heat rate density shown in Figure 7.2 for the 6-inch and 8-inch diameter pots such as were used in the WSEP program. Although the RLG solidified product has a nominal remelt temperature of approximately 800 °C, the hypothetical 900 °C centerline temperature limit is reached before the molten core limit is attained for the air storage condition.

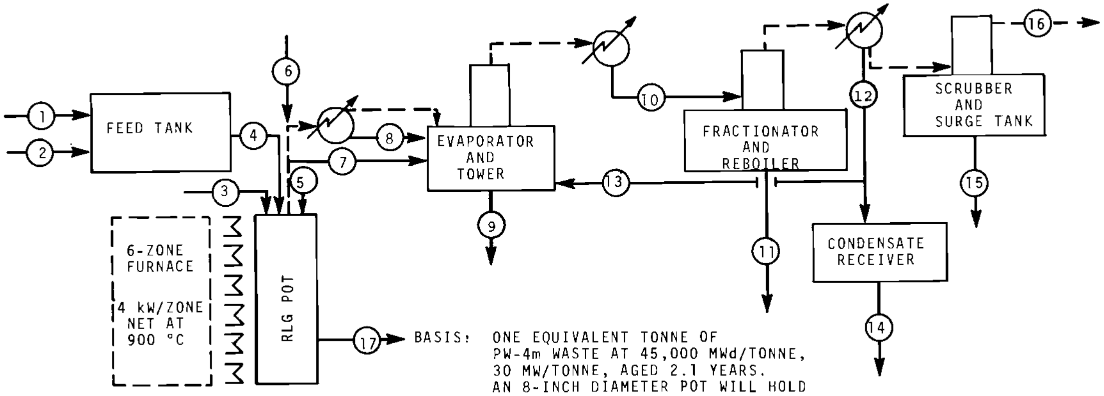
Data from radioactive WSEP demonstrations have been used in projecting typical chemical flowsheets for pot solidification. Sufficient confidence in radioactive demonstration has been reached to specify most of the necessary details for flowsheets with PW-4m waste using either pot calcination or the RLG scheme. (As mentioned in Section 4.6 the RLG process requires more development before it is ready for radioactive use.) Figure 7.3 shows a Mode A flowsheet for the solidification of one tonne of PW-4m waste aged 3.4 years (out of the reactor) using pot calcination and Figure 7.4 is a Mode A flowsheet for the solidification of one tonne of PW-4m waste aged 2.1 years and using the RLG technique. The aging time for each waste is the minimum out-of-reactor time prior to pot solidification for which the maximum allowable heat rate density is obtained for an 8-inch diameter waste container stored in air.



BASIS: ONE EQUIVALENT TONNE OF PW-4m WASTE AT 45,000 MWd/TONNE, 30 MW/TONNE, AGED 3.4 YEARS. AN 8-INCH DIAMETER POT WILL HOLD 1.4 TONNE. 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
Phase, L - Liquid G - Gas S - Solid	L	L	L	L	G	L	L	L	L	L	L	L	L	L	L	G	S
Volume, liters/tonne	397	3.4	Antifoam may be added continuously to the pot.	400	33.3	10	44	396	100	4600	220	4400	4160	230	500	2.8×10^5	42
Average Rate, liters/hr	Batch	Batch		12	1.0	Batch	1.3	11.9	Batch	138	6.6	132	125	6.9	BATCH	8500	1.3
Gross Activity, Ci/tonne	6.7×10^5	-		6.7×10^5	-	-	830	7.5×10^3	8.3×10^3	-	740	-	-	1	1	3×10^{-3}	6.6×10^5
^{106}Ru, Ci/tonne	5.3×10^4	-		5.3×10^4	-	-	530	4.8×10^3	5.3×10^3	-	740	-	-	1	1	3×10^{-3}	4.8×10^4
^{90}Sr, Ci/tonne	9.5×10^4	-		9.5×10^4	-	-	47	420	470	-	0.22	-	-	2×10^{-3}	1×10^{-4}	3×10^{-5}	9.5×10^4
^{144}CePr Ci/tonne	1.0×10^5	-		1.0×10^5	-	-	50	450	500	-	0.22	-	-	2×10^{-3}	1×10^{-4}	3×10^{-5}	1.0×10^5
Fission Product Heat Rate, W/tonne	3.6×10^3	-		3.6×10^3	-	-	5	50	55	-	7	-	-	0	0	0	3.5×10^3
Non-FP Oxides, kg/tonne	2.5	2.9		5.4	-	-	0.003	0.024	0.027	-	∿0	-	-	0	0	0	5.4
FP Oxides, kg/tonne	48.6	-		48.6	-	-	0.06	0.56	0.62	-	∿0	-	-	0	-	-	48.0
Total Oxides, kg/tonne	51.1	2.9		54.2	-	-	0.06	0.58	0.64	-	∿0	-	-	0	-	-	53.4
Nitrate, g-moles/tonne	2460	-		2460	-	-	220	1990	500	2300	2200	88	83	4.6	250	0	0
Density, kg/liter	-	1.58		1.34	1.0	1.0	1.18	1.18	1.16	1.0	1.3	1.0	1.0	1.0	-	-	1.3

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



BASIS: ONE EQUIVALENT TONNE OF PW-4m WASTE AT 45,000 MWd/TONNE, 30 MW/TONNE, AGED 2.1 YEARS. AN 8-INCH DIAMETER POT WILL HOLD 2.0 TONNE. 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
Phase L - Liquid G - Gas S - Solid	L	L	L	L		L	L	L	L	L	L	L	L	L	L	G	S
Volume, liters/tonne	400	300	70	700	-	10	86	754	100	3340	156	3170	2490	677	500	6.6 10^5	29.3
Average Rate, liters/hr	Batch	Batch	0.9	9	-	Batch	1.1	9.7	Batch	43	2.0	40.7	32	8.7	Batch	8500	0.38
Gross Activity, Ci/tonne	1.0×10^6	-	-	1.0×10^6	-	-	2.6×10^3	2.3×10^4	2.6×10^4	-	300	-	-	5	10	0.09	1.0×10^6
^{106}Ru, Ci/tonne	1.3×10^5	-	-	1.3×10^5	-	-	2.0×10^3	1.8×10^4	2.0×10^4	-	300	-	-	5	10	0.09	1.3×10^5
^{90}Sr, Ci/tonne	9.8×10^4	-	-	9.8×10^4	-	-	49	4.4×10^2	4.9×10^2	-	0.4	-	-	3×10^{-4}	3×10^{-4}	2×10^{-3}	9.8×10^4
^{144}CePr, Ci/tonne	3.3×10^5	-	-	3.3×10^5	-	-	160	1.4×10^3	1.6×10^3	-	1.3	-	-	1×10^{-4}	1×10^{-4}	5×10^{-4}	3.3×10^5
Fission Product Heat Rate, W/tonne	5.7×10^3	-	-	5.7×10^3	-	-	20	190	210	-	∿0	-	-	0	0	0	5.5×10^3
Non-FP Oxides, kg/tonne	2.5	41.0	10.2	53.7	-	-	0.03	0.29	0.32	-	∿0	-	-	0	0	0	53.4
FP Oxides, kg/tonne	48.6	-	-	48.6	-	-	0.08	0.75	0.83	-	∿0	-	-	0	0	0	47.8
Total Oxides, kg/tonne	51.2	41.0	10.2	102.4	-	-	0.11	1.1	1.2	-	∿0	-	-	0	0	0	101.2
Nitrate, g-moles/tonne	2460	-	-	2460	-	-	160	1440	500	1670	1590	63	50	13	370	490	0
Density, kg/liter	-	-	1.15	1.22	-	1.0	1.06	1.06	1.16	1.0	1.3	1.0	1.0	1.0	-	-	3.5

FIGURE 7.4. Typical Flowsheet for Processing One Tonne of PW-4m Waste with Mode A Operation Using Rising Level Glass

FLOWSHEET CODE FOR FIGURES 7.3 AND 7.4

STREAM

1. Incoming waste from processing one tonne of power reactor fuel with an integrated exposure of 45,000 MWd/tonne at a specific power of 30 MW/tonne. The computer program ISOGEN(3) was used to determine the fission product data for this reactor fuel. The total fission product values do not include the transuranium values. The ^{144}Ce values include its naturally occurring daughter ^{144}Pr.

2. Nonradioactive chemical additives to the raw waste. Additives to the PW-4m feed include 0.11$\underline{M}$ phosphoric acid (added as 75 wt% H_3PO_4) for pot calcination and 0.87$\underline{M}$ B_2O_3 and 0.86$\underline{M}$ NaOH or $NaNO_3$ for the RLG flowsheet and based on a feed concentration of 378 liters/tonne.

3. Nonradioactive chemical additives to the pot for the RLG process. 0.79$\underline{M}$ SiO_2 (added as a 21.5% colloidal silica solution) based on a 378 liter/tonne feed concentration. If antifoam is added to the pot, a 1 liter/hr flowrate containing about 7g of Dow Corning Antifoam-B should aid in preventing foaming.

4. Chemically adjusted waste feed to the pot solidifier.

5. Steam purge addition to the pot weight factor dip tube. (Continuous at about 1 kg/hr.)

6. Water (or acid) spray to the pot vent line added in 2 to 5 liter batches towards end of run.

7. Pot vent line reflux: continuous and equivalent to about 10% of pot boiloff.

8. Solidifier condensate.

9. Evaporator bottoms. The bottoms will be recycled and eventually returned to the solidifer. They may be recycled to the solidifier feed or to the high level liquid waste system of the reprocessing plant. A total of 100 liters of 5M HNO_3 was arbitrarily selected to represent the volume to be recycled for each tonne equivalent of waste processed. (Not included in balance.)

10. Evaporator overheads. A HNO_3 concentration of 0.05M is used here.

11. Fractionator bottoms. A HNO_3 concentration of 10M is used for calculations. This stream can be used for fuel element dissolution or possibly in solvent extraction scrub streams.

12. Fractionator distillate.

13. Evaporator strip water. A HNO_3 concentration of 0.02M is used here.

14. Fractionator distillate. This can be used as makeup water for fuel dissolution, solvent extraction scrub streams, or treated as intermediate level waste.

15. Scrubber solution, approximately 1 to 2M NaOH. Ten percent of the nitrate from the solidifier is removed by the scrubber during pot calcination and 15% during RLG (only one run on which to base).

16. System off-gas. Twenty percent of the total feed nitrate is present in this stream for the RLG process (only one run on which to base). The nitrate lost during pot calcination is negligible. An average noncondensible air flow of 5 scfm is assumed.

17. Solidified ceramic or glass product. Pot is welded and stored.

A flowsheet is not presented for LMFBR waste because the LMFBR waste was not demonstrated during the pot solidification runs. One possible LMFBR flowsheet formulation would consist of adding chemicals to make it nearly identical to PW-4m. Slight differences would include the different fission product spectrum and the presence of larger amounts of antimony and tin, and volatile selenium and tellurium in the LMFBR waste as discussed in WSEP volume 8.(5)

Although the chemical level of fission products in each WSEP demonstration run represented 45,000 MWd/tonne thermal fuel, the radioactive fission product spectrum used did not represent that value. In order to project WSEP data to expected 45,000 MWd/tonne exposure, the same fractional distribution of radionuclides to the auxiliaries as given in Table 5.3 was used for evaluation of each run. This exercise increased particular radionuclides to the appropriate curie level that would exist if the waste was solidified at the age shown in Table 7.1 where the fractionator results are shown. On this basis, approximately 70 curies of ruthenium and 0.2 curies each of ^{144}CePr and ^{90}Sr will be found in the fractionator bottoms per tonne of 45,000 MWd/tonne thermal fuel processed when using the pot calcination process. When the RLG process is used, these values are increased slightly as shown in Table 7.1. The gross $\beta + \gamma$ activity in the acid using waste from 45,000 MWd/tonne thermal fuel will range from about 400 μCi/ml for the pot calcination process to 1500 μCi/ml using the RLG process.

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

TABLE 7.1. Projected Radionuclides in Fractionator Acid Per Tonne of Equivalent Fuel Processed[a]

PC Run	Waste Type	Operating Mode	Age of Waste, yr[c]	Projected Fractionator Acid Radioactivity[b] ^{144}CePr, Ci	^{90}Sr, Ci	Ru(Total), Ci
7	PW-1	A	1.4	0.21	0.023	310
8	PW-4m	A	3.4	0.23	0.22	74
9(RLG)	PW-4m	A	2.1	1.3	0.40	300

---

a. Based on activity distribution data in Table 5.3, PW-4m waste from fuel irradiated to 45,000 MWd/tonne at 30 MW/tonne and PW-1 waste from fuel irradiated to 20,000 MWd/tonne at 15 MW/tonne.

b. Based on the production of 10M nitric acid, the nominal acid volume will range from 150 to 250 liters/tonne.

c. Age of waste is based on WSEP established maximum temperature limits in 8-inch diameter pots with air cooling.

The ratio of the radionuclide concentration in the final distillate to 10CFR20 concentrations was obtained by projecting run data as shown in Table 7.2. While ^{90}Sr and ^{144}CePr concentrations are approximately 10 to 100 times the 10CFR20 release limits(7) for the 45,000 MWd/tonne thermal fuel waste, ^{106}Ru is the controlling constituent at approximately 10^5 times its limit. Another careful distillation should bring all values, except possibly ^{106}Ru to below 10CFR20 release limits. The distillate could also be used as makeup water in the reprocessing plant.(6) If an additional distillation is made, the bottoms would be recycled to the waste evaporator or to the solidifier feed.

Alternative methods for treating the distillate have been studied.(8) These include adsorption, electrodialysis and electrodeionization, ion exchange, and oxidation and volatilization. Of these the most suitable method appeared to be two-stage electrodialysis followed by ion exchange.

The secondary effect of the recycle of ruthenium to the solidifier feed stream has not been demonstrated. However, for the continuous recycle of the evaporator bottoms (10 to 15% of the ruthenium in the raw waste volatilized from the solidifer), about a 15% increase in the total ruthenium concentration in the auxiliary process streams can be expected at steady state.

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

		PW-4m Waste(a)	
Nuclide	10CFR20(b) Concentration, μCi/ml	Projected Distillate,(c) μCi/ml	Ratio Projected Distillate to 10CFR20 Limit
^{144}CePr	2×10^{-5}	1.5×10^{-4}	7.5
		1.1×10^{-4} (RLG)	5.5 (RLG)
^{90}Sr	3×10^{-7}	1.3×10^{-4}	4.3×10^{2}
		3.1×10^{-5} (RLG)	1×10^{2} (RLG)
^{106}Ru(d)	1×10^{-5}	3.5×10^{-1}	3.5×10^{4}
		3.2 (RLG)	3.2×10^{5} (RLG)

---

a. PW-4m waste from fuel irradiated to 45,000 MWd/tonne at 30 MW/tonne and 3.4 years out of the reactor for the pot calcination runs and 2.1 years out of the reactor for the rising level glass runs.

b. USAEC code of federal regulations - Title 10, Part 20, Table II, Column 2.

c. A distillate volume of 300 liters is used but actual volumes depend on feed type, etc. and may vary from 200 to 400 liters/tonne of waste (may be as high as 700 liters/tonne for RLG).

d. Ruthenium projections are reduced by a factor of 10 from data in Runs PC-8 and PC-9(RLG).

REFERENCES FOR SECTION 7

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2. E. A. Coppinger, "Waste from Chemical Processing of Fast Reactor Fuels," Quarterly Progress Report, Research and Development Activities, Fixation of Radioactive Residues, May - July 1967, BNWL-889, A. M. Platt, Editor, Battelle-Northwest, Richland, Washington, August 1967.

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4. Code of Federal Regulations: Rules and Regulations, Title 10: Atomic Energy, Part 50: Licensing of Production and Utilization Facilities, Appendix F: Policy Relating to the Siting of Fuel Reprocessing Plants and Related Waste Management Facilities, United States Atomic Energy Commission, January 1, 1971.

5. W. R. Bond, J. L. McElroy, J. N. Hartley, J. E. Mendel and R. J. Thompson, Waste Solidification Program, Volume 8, Spray Solidification Performance During Final Radioactive Tests in Waste Solidification Engineering Prototypes, USAEC Report, BNWL-1583, June 1971.

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7. Code of Federal Regulations: Rules and Regulations, Title 10: Atomic Energy, Part 20: Standards for Protection Against Radiation: Appendix B, Table II, Columns 1 and 2. United States Atomic Energy Commission, August 9, 1966.

8. C. J. Touhill, B. W. Mercer and A. J. Shuckrow, Treatment of Waste Solidification Condensates, BNWL-723, Battelle-Northwest, Richland, Washington, July 1968.

8.0 FUTURE WORK

CONTENTS

8.0 FUTURE WORK

Although the WSEP solidification runs have been completed, work remains to evaluate the solidified products from these runs. Further development of the rising level glass version of pot solidification is also required. The pot calcination process is essentially ready for commercial use.

8.1 EQUIPMENT AND PROCESS REQUIREMENTS

Additional testing of the rising level glass process is required to develop process reliability. The areas of feed handling, pot feeding, entrainment, and level control require more development before the process should be considered for commercial use. The film feeding technique should be developed to provide an adequate processing capacity, otherwise the capacity is undesirably low due to the small heat transfer area.

Three of the waste containers from the pot solidification runs will undergo environmental testing in the Solid Storage Engineering Test Facility (SSETF).(1) Two of the waste containers, PC-6 and PC-9(RLG), have been transferred to environmental test pods and tests begun. The waste container from demonstration Run PC-8 is scheduled for test in the near future.

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

The controlled environment storage of the WSEP waste containers will provide data on the thermal, radiation, and chemical stability of the products as a function of time. The variables involved in the test plan[(2)] are:

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

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

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

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

Table 8.1 is a summary of SSETF environmental tests for pot solidifier filled waste containers.

TABLE 8.1. SSETF Environmental Tests of Pot Solidifier Receiving Pots

WSEP Demonstration Run Number	Feed Type	Container Material	Fill Date, month/year	Initial Heat Generation Rate, kW	SSETF Test Started, month/year	Storage Medium
PC-6	PW-2	304L SS	8/67	5.1	11/69	Air
PC-8	PW-4m	304L SS	9/70	4.8	8/71	Air
PC-9(RLG)	PW-4m	310 SS	10/70	5.6(a)	4/71	Air

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a. Pot only 50% filled.

REFERENCES FOR SECTION 8

1. V. P. Kelly, Waste Solidification Program, Volume 3, Design Features of the Facilities and Equipment for the WSEP Product Evaluation Program, BNWL-832, Battelle-Northwest, Richland, Washington, December 1968.

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

9.0 APPENDIX

CONTENTS

9.0 APPENDIX

WSEP radioactive Runs PC-7 through PC-9(RLG) are briefly described below. An operating procedure for the pot calcination process is presented in Section 9.2. General information for all runs on compositions, operating parameters and results, material balances, and feed pump experience are presented in Tables 9.1 to 9.5, respectively. A schematic diagram of the equipment arrangement for Mode A operation is shown in Figure 9.1. WSEP auxiliary and solidification equipment flow diagrams are shown in Figures 9.2 and 9.3, respectively. WSEP auxiliary evaporator operating parameters are shown on Figures 9.4 to 9.7. Figure 9.8 shows a schematic of the process off-gas ventilation system.

9.1 RUN DESCRIPTION

Pot Calcination Run PC-7

The thirty-first radioactive demonstration in WSEP was completed with pot calcination Run PC-7. Run PC-7 was the first in the second series of pot calcination runs and also the first pot calcination run made in nearly 3 years.

During Run PC-7, a total of 500 liters of simulated PW-4m waste at 385 liters/tonne were fed to the pot in 36.5 hours. Another 8 hours were required to dry and cool the pot. The 60 liters of calcine product contained approximately 1,400,000 curies of fission product radioactivity (including 3800 curies of radioruthenium) to give an internal heat generation rate of approximately 5600 watts in the 8-inch diameter, stainless steel pot.

The feed was started to the pot initially at approximately 30 liters/hr and averaged 25 liters/hr during the first 12 hours of the run. During PC-7, as the liquid level reached the top of the pot (50 to 60 liter level), difficulties were encountered with the pot liquid level (thermal probe) indicator. Attempts to control the feed rate automatically were unsuccessful due to the poor response of the level indicator. Although switching from a steam purge to an increased air purge of the pot pressure tube seemed to remedy the situation, (condensate was thought to have been dropping on the level probe) this was only temporary. The feed was interrupted for 2.5 hours when the liquid level became too high as indicated by the level reaching the pot pressure tube. Feed was terminated when at a rate of 4 to 5 liters/hr the liquid level again became excessive. Only 78% of the originally planned feed was consumed, indicating a much lower volume than anticipated (calculated calcine density of 1.22 versus an expected 1.4 kg/liter). The addition of Dow Corning antifoam-B to the pot at the rate of 5.4 g/hr (0.8 liters/hr of solution) was effective in preventing foaming.

The calcine centerline temperature of 1012 °C in air and 925 °C in water exceeded the WSEP thermal maximum (900 °C centerline) for both air and water cooling. These temperatures indicated a 0.27 to 0.33 $W/(m^2)(°C/m)$ effective thermal conductivity for the calcine. The lower than anticipated values for volume reduction and thermal conductivity indicated that the calcine was very porous. This decrease can possibly be attributed to not having sulfate or a higher sodium concentration present in the feed. All previous WSEP radioactive pot calciner runs contained considerable amounts of these two constituents.

Approximately 6% of the ruthenium in the feed to the pot was volatilized to the pot condensate using a Mode A type operation (Figure 9.1). This agrees with the approximately 5% volatilization that occurred during the earlier PW-1 runs (excess sulfate and sodium was present in the early runs) with

Waste Component	WSEP Subs.	PW-1 Nominal, $\underline{M}$	PW-1 Actual, $\underline{M}$[b] Run PC-7	PW-4m Nominal, $\underline{M}$	PW-4m Actual, $\underline{M}$[b] Run PC-8	Run PC-9(RLG)
H^+		3.7	2.2	4.5	3.2	2.2
FE^{+3}	(c)	0.93	0.4[e]	0.05	0.05	0.083
Cr^{+3}		0.012		0.012		
Ni^{+2}		0.005		0.008		
Al^{+3}	(c)	0.001	0.13	0.001	0.12	0.17
Na^{+1}		0.138	0.19	0.01	0.25	1.37
UO_2^{+2}		0.01		0.01		
NO_2, NO_3^-		6.5	6.6	6.5	6.0	7.8
PO_4^{-3}		0.003		0.003		
SiO_3^{-2}		0.01		0.01		
$Cs^+ + Rb^+$	K^+	0.042		0.0924		
Sr^{+2}		0.0155		0.0356		
Ba^{+2}		0.0195		0.041		
$(Y + RE)^{+3}$	RE^{+3}	0.12		0.274	0.36	0.41
Zr^{+4}		0.065		0.143		
$MoO_4^{-2} + TcO_4^{-1}$	MoO_4^{-2}	0.079		0.161		
Ru^{+4}		0.0032		0.0032		0.0048
Ru^{+4}	Fe^{+3}	0.0288		0.0784		
Rh^{+2}	Co^{+2}	0.0074		0.0133		
Pd^{+2}	Ni^{+2}	0.017		0.0425		
$Ag^{+1} + Cd^{+2}$	Cu^{+2}	0.0016		0.0041		
Additive to Feed						
PO_4^{-3}		0.06[d]		0.11 (Calcine Only)[d]		
B_2O_3				0.84 (RLG Only)		
$NaNO_2$				0.84 (RLG Only)		
Additive to Pot						
SiO_2 (as a 21.5 wt% Colloidal Suspension)				0.76 (RLG Only)		
Final Feed						
Total Volume, liters			500		340	393
Concentration, liters/tonne			385		460	705
Specific Gravity at 25 °C			1.30		1.28	1.23
Solids, Volume %			-		2	40
Total Radioactivity, Ci/liter			2800		3530	3560
Radioruthenium, Ci/liter			7.6		6.8	4.6
Total Heat Rate Density, W/liter			11.2		14.2	14.3

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a. Values are reported on a 378 liter/tonne basis.
b. Values reported are total concentrations including additives (if any) as determined by chemical analysis of the feed. All other chemical compositions are added quantitatively as given by nominal values.
c. Excess aluminum in Purex 1WW waste was substituted for part of the total nominal iron including the iron substituted for the ruthenium in the waste.
d. Added to suppress volatilization of alkali metal oxides.
e. Analysis believed incorrect as iron was added to the feed to give 0.8$\underline{M}$.

TABLE 9.1. Nominal and Actual Feed Compositions Used in Pot Solidification Runs PC-7, PC-8, and PC-9(RLG)[a]

e. Analysis believed incorrect as iron was added to the feed to give 0.8$\underline{M}$.

TABLE 9.1. Nominal and Actual Feed Compositions Used in Pot Solidification Runs PC-7, PC-8, and PC-9(RLG)[a]

SOLIDIFIER DATA (Definitions are on following page)			
Pot Solidification Run Number	PC-7	PC-8	PC-9(RLG)
Date of Run	8/3/70 - 8/5/70	9/8/70 - 9/10/70	10/12/70 - 10/15/70
Operating Mode(a)	A	A	A
Feed			
Type	PW-1	PW-4m	PW-4m
Concentration, liters/tonne	385	460	705
Temperature, °C	35	NA	65
Total Feed Consumed, liters	500	340	393
Additive to Pot, liters	—	—	40
Total Feed Time, hr	36.5	36	43.2(b)
Total Down Time, hr	2.5	0	15
Total Drying and Cooling Time, hr	8	7	—
Average Feed Rate, liters/hr	12.8(h)	9.4	9.1(c)
Average Processing Rate, liters/hr	10.7(d)	7.9(d)	9.0
Feed Added Prior to Calcine Deposition, liters	∿100	∿20	—
Antifoam Addition Rate, liters/hr(i)	0.8	1.0	—
Off-Gas Line			
Reflux Rate, liters/hr	∿2	∿2	∿2
Water Spray Addition, liters			
Prior to Run Start	15	10	—
Following Feed Shutoff	2	4	—
Max. Vent Line Vapor Velocity in 2 in. Section, ft/sec	1.4	1.3	1.0
Pot Data			
WSEP Pot Number	54	57	58
Pot Material (Stainless Steel)	304L	304L	310
Pot Diameter (Sch. 40 Pipe)	8	6	6
Pot Furnace Temperature, °C	900	900	950
Leakage After Sealing, atm-cm^3/cc(e)	NA	NA	NA
Solidified Product			
Weight, kg	73.2	45.5	63.6
Volume, liters(f)	60	34	∿16 (Plus ∿2 as Calcine)
Bulk Density, kg/liter	1.22	1.34	∿3.5
Feed to Solid Volume Ratio	8.3	10	22
Adjusted Feed to Solid Volume Ratio (Feed at 378 liters/tonne)	8.2	8.2	12
Equivalent Waste, tonne	1.3	0.74	0.56
Average Processing Rate, tonne/day	0.64(d)	0.4(d)	0.3
Unit Volume, liters/tonne	46	46	32
Fission Product Heat in Pot, W	5600	4800	5600
Heat Generation Rate Density, W/liter	93	141	310
Total Radioactivity in Feed to Pot, Ci	1,400,000	1,200,000	1,400,000
Total Radioruthenium in Feed to Pot, Ci	3800	2300	1800
Equivalent Age of Waste, years	3.0	2.0	1.2
Centerline Temperature,(g) °C			
In Air-Cooled Furnace	1025	872	740
In Air at ∿40 °C	1012	865	685
In Water at 30 to 60 °C	925	780	454
Centerline-to-Wall ΔT,(g) °C			
In Air-Cooled Furnace	730	557	338
In Air	753	604	370
In Water	895	750	424
Effective Thermal Conductivity, ke, W/(m^2)(°C/m)			
In Air-Cooled Furnace	0.33	0.37	1.36
In Air	0.32	0.35	1.25
In Water	0.27	0.28	1.09
Radiation Reading at 6 inches, R/hr	32,000	55,000	51,000

NA Not Available

a. Equipment arrangement for Mode A is shown in Figure 9.1.

b. Actual time feed was on. Due to eight interruptions in feed during the run, 58.2 hours actually elapsed between initial feed on and final feed off.

c. Based on actual feed time.

d. Includes feed time, down time, and drying and cooling time.

e. See Section 6.4.

f. Product volume estimated from pot temperatures.

g. Based on Zone 4 and 5 temperatures except PC-9(RLG) is Zone 5 only.

h. Includes down time.

i. 6.75 g/liter Dow Corning Antifoam-B

TABLE 9.2. Operating Parameters and Results of Pot Solidification Demonstration Runs PC-7 Through PC-9(RLG)

TABLE 9.2. Operating Parameters and Results of Pot Solidification Demonstration Runs PC-7 Through PC-9(RLG)

DEFINITIONS FOR TABLE 9.2

Operating Mode - WSEP equipment arrangement, see Section 5 and Figure 9.1.

Feed

Concentration, liters/tonne - liters of feed per metric ton (2205 lb) of uranium processed.

Total Feed Time - Total hours that feed was actually on.

Average Feed Rate, liters - Average rate during run feed time. Does not include drying, cooling or pot removal. Does not include separate additive streams.

Calcination + Cooling - Calcining time from feed off until pot cooled to where the pot steady state wall temperature in air would not exceed 425 °C.

Total Feed, liters - Does not include separate additive streams where used.

Total Feed, tonnes - Equivalent tonnes of uranium fuel from which the waste processed would be derived.

Feed Added Prior to Calcine Deposition, liters - Feed in pot at time of sharp increase in Zones 5 and 6 wall temperature.

Off-Gas Line

Reflux Rate, liters/hr - Manually adjusted to equal about 10% of pot boilup rate (estimated from drip rate in sight glass).

Solidified Product

Weight, kg - Weight obtained by weighing pot before and after run.

Volume, liters - Product volume estimated from pot temperatures.

Bulk Density, kg/liter - Net weight of solidified product divided by product volume.

Feed to Solid Volume Ratio - Concentration factor from liquid feed to volume of solidified product.

Equivalent Waste, tonne - Equivalent metric tons (tonnes) of 20,000 MWd/tonne at 15MW/tonne (PW-1) or 45,000 MWd/tonne at 30 MW/tonne (PW-4m) power reactor fuel from which the solidified waste would be derived.

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

Fission Product Heat in Pot, W - Rate of internal heat generation in receiver from radioactive decay, based on feed analyses (curies/liter converted to W/liter) and total feed processed.

Total Radioactivity in Feed to Pot, Ci - Based on feed analysis.

Equivalent Age of Waste, yr - Age of waste from 20,000 MWd/tonne at 15 MW/tonne power reactor fuel (PW-1) or 45,000 MWd/tonne at 30 MW/tonne (PW-4m) to produce the same fission product heat (watts) as in the WSEP receiver (but not necessarily the same number of curies.

Centerline Temperature, °C - Average steady-state receiver centerline temperature (usually average for Zones 3, 4, and 5).

Centerline-to-Wall ΔT, °C - Average 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.

Effective Thermal Conductivity, K_e, $W/(m^2)(°C/m)$ - Based on average pot calorimetry measurements. Values were obtained using the equation $\Delta T = Q/4\pi LK_e$ discussed in Section 6.0 of WSEP Report Volume 4.

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

TABLE 9.3. WSEP Auxiliary Operating Parameters and Results During Pot Solidification Runs PC-7 Through PC-9(RLG)

Pot Solidification Run	PC-7	PC-8	PC-9(RLG)
Operating Mode	A	A	A
Evaporator (TK-113) Average Operating Conditions			
Bottoms, M HNO_3	5.0	5.7	4.8
Distillate, M HNO_3	0.34	0.38	0.29
Boiloff Rate, liter/hr	122	42	39
Strip Water Addition Rate, liter/hr	105	30	23
Volume, liters - Start	504	232	432
- End	287	198	280
Fractionator (TK-115) Average Operating Conditions			
Bottoms, M HNO_3	9.3	8.20	7.5
Distillate, M HNO_3	0.04	0.06	0.04
Boiloff Rate, liters/hr	116	36	33
Reflux Ratio	0.24	0.71	0.78
Volume, liters - Start	342	434	416
- End	589	625	621
Fractionator Distillate Receiver (TK-116)			
Bottoms, M HNO_3 - Start	0.02	0.02	0.29
- End	0.03	0.02	0.16
Volume, liters - Start	284	540	384
- End	692	768	751
Off-Gas Scrubber (TK-118)			
Recirculation Rate, liters/hr	20.0	20.0	20.0
Bottoms, M NaOH - Start	3.6	2.4	2.0
- End	3.1	2.0	1.8
Volume, liters - Start	425	475	450
- End	417	438	388

TABLE 9.4. Overall Material Balance for Pot Solidification Runs PC-7, PC-8 and PC-9(RLG)

		PC-7	PC-8	PC-9(RLG)
Feed to Solidifier (TK-114)	Initial, liters	735	502	807
	Final, liters	235	162	414
	Net Change,			
	liters	-500	-340	-393
	kg	-634	-411	-452
	N, kg	-47	-24	-23
Antifoam Addition	liters	31.2	36	0
	kg	31.2	36	0
	g antifoam	211	243	0
Silica Additive	liters	0	0	40
	kg	0	0	45.6
Auxiliary Evaporator (TK-113)	Initial, liters	504	232	432
	Final, liters	287	198	279
	Net Change,			
	liters	-217	-34	-153
	kg	-210	-41	-163
	N, kg	-4.9	-6.4	-10
Fractionator (TK-115)	Initial, liters	342	434	416
	Final, liters	589	625	621
	Net Change,			
	liters	+247	+191	+205
	kg	+304	+217	+223
	N, kg	+47	+28	+24
Fractionator Condenser (E-115)	Initial, liters	6	23	33.8
	Final, liters	49	44	93.8
	Net Change,			
	liters	+43	+21	+60
	kg	+43	+21	+60
	N, kg	Neg	Neg	Neg
Fractionator Distillate Receiver (TK-116)	Initial, liters	284	540	384
	Final, liters	692	768	751
	Net Change,			
	liters	+408	+228	+367
	kg	+408	+228	+367
	N, kg	+0.2	+0.2	+0.2
Off-Gas Scrubber (TK-118)	Initial, liters	425	475	450
	Final, liters	417	438	318
	Net Change,			
	liters	-8	-37	-132
	kg	-10	-35	-132
	N, kg	+3.1	+3.1	+4.0
Product	Initial, liters	10	6	0
	Final, liters	60	34	18
	Net Change,			
	liters	+50	+28	+18
	kg	+62	+38.2	+58.6
	N, kg	Neg	Neg	Neg
Net Change	Volume, liters	+26	+57	-34
	Mass, kg	-37	+17	-79
	N, kg	-1	+1	-5.4
Percent Recovery[a]	Volume, liters	100	101	97
	Mass, kg	98	100	99
	N, kg	103	97	95

Neg Negligible

a. Based on total at end of run/total at start of run for all tanks added together.

TABLE 9.5. Feed Pump Experience During WSEP Pot Solidification Runs

Pump No.[a]	Service, Runs	Feed Type	Hours	Run Date	Remarks
P-18	—	—	Previous Run Time = 36 hr	—	
P-18	PC-7 PC-8	PW-1 PW-4m	43 40	8/3/70 9/8/70	Pump did not fail but was replaced for PC-9(RLG)
			119 Total		
P-19	PC-9(RLG)	PW-4m (borosilicate)	60	10/12/70	

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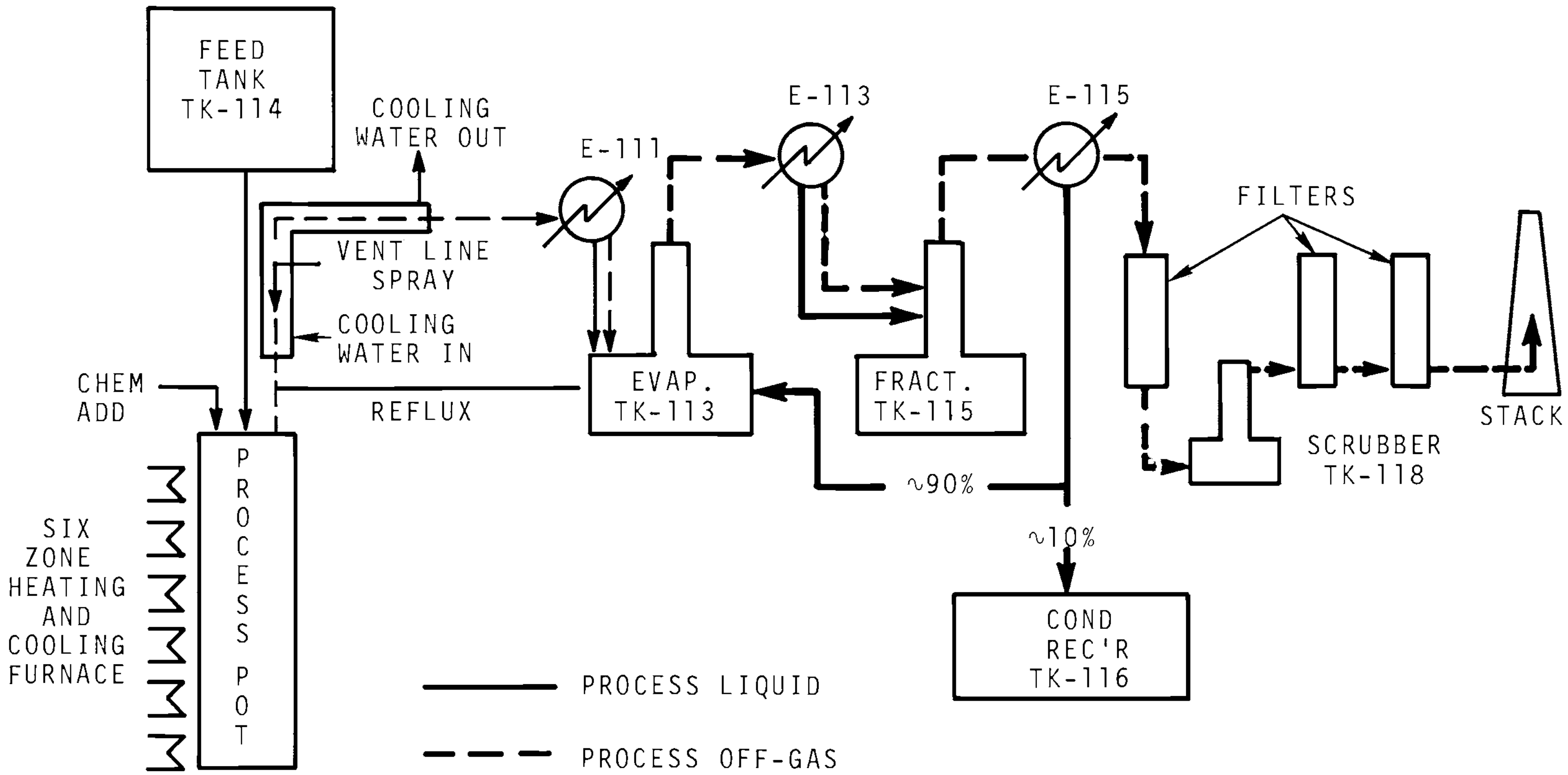
[a] Deanline Centrifugal Pump, Type 3/4 DL, Deanalloy Class 50, 316 SST Construction. 5 gpm at 130 ft head.



MODE A ARRANGEMENT FOR RUNS PC-7, PC-8, AND PC-9(RLG)

FIGURE 9.1. Equipment Arrangement for Mode A Pot Solidification Runs

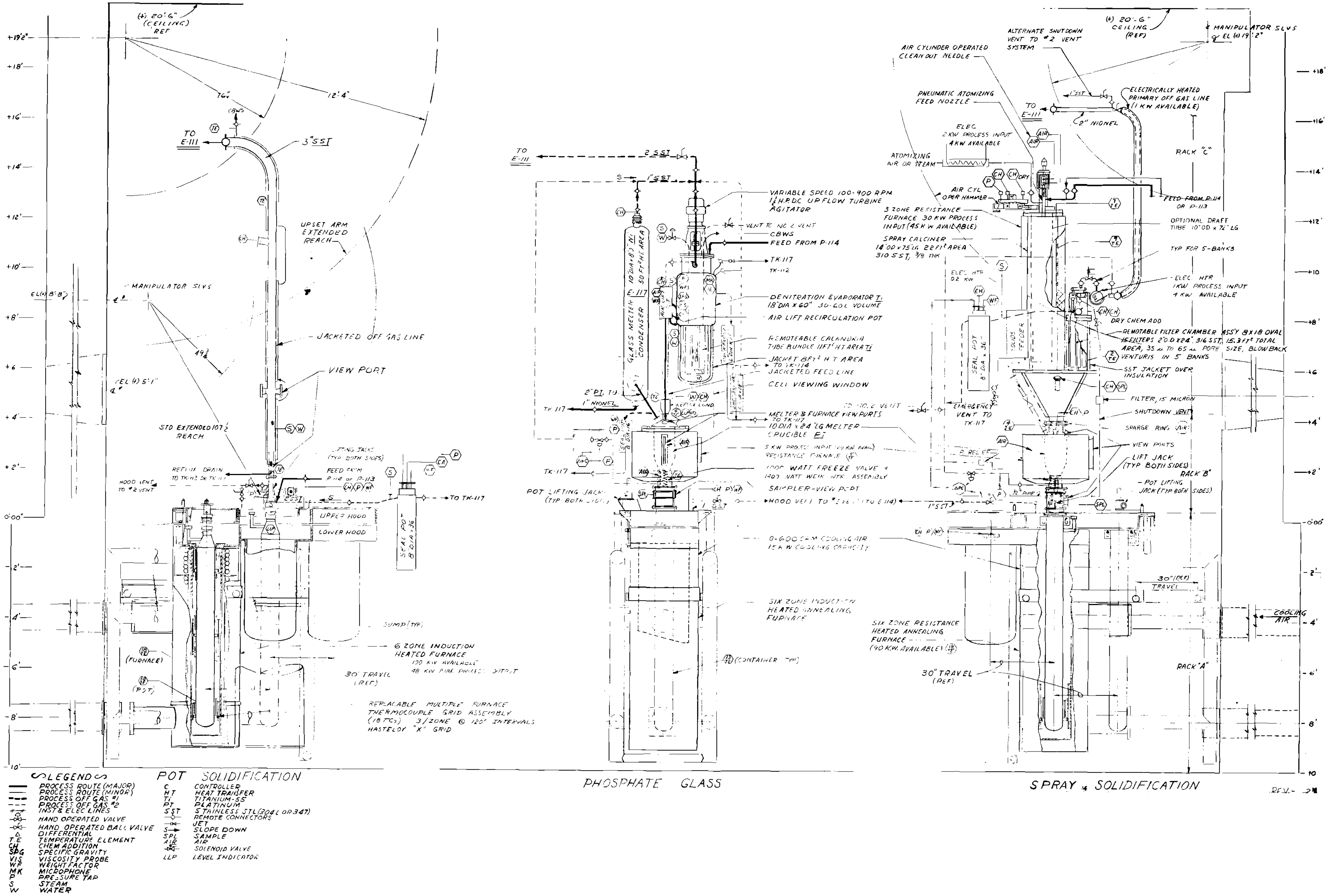


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FIGURE 9.2. WSEP Solidification Equipment Flow Diagram

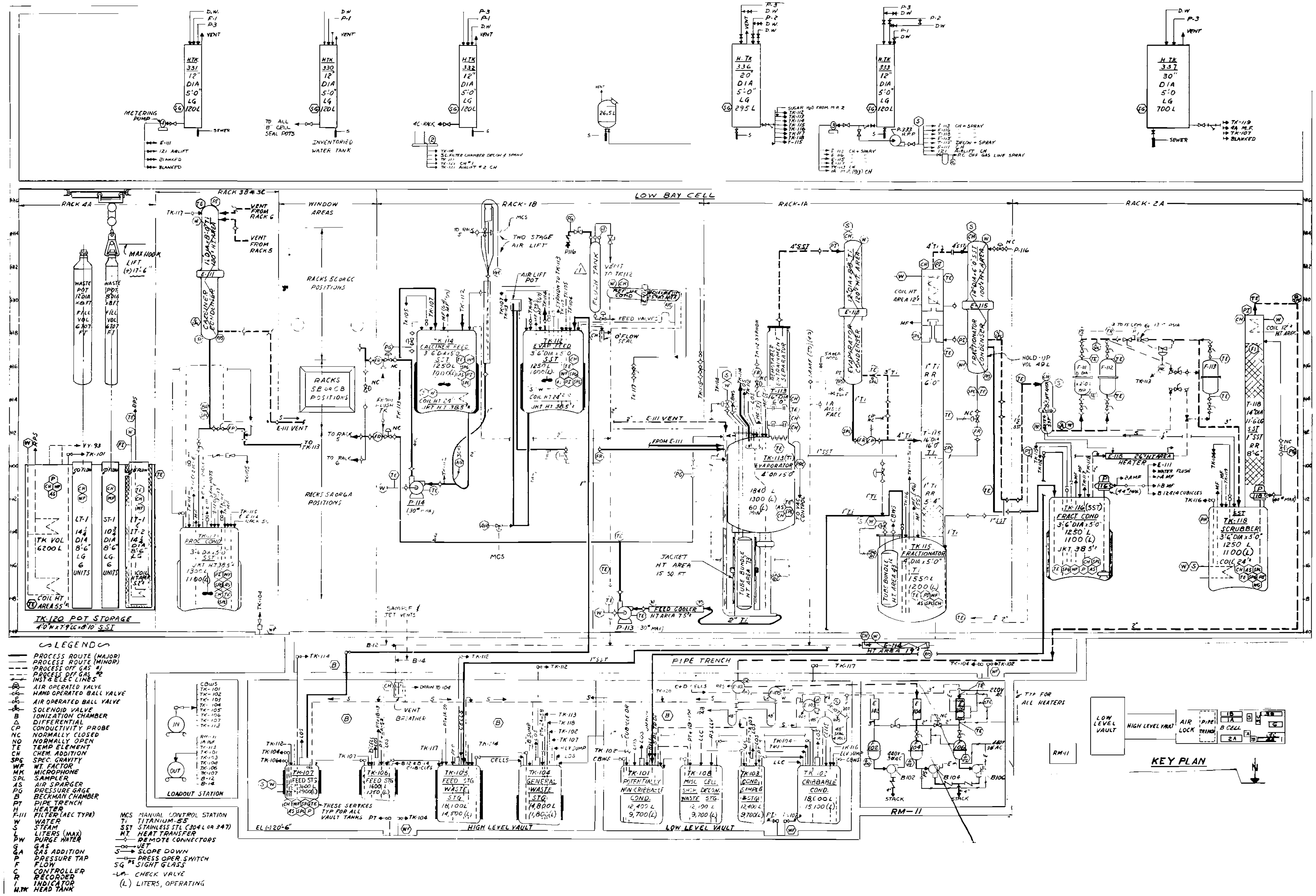

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FIGURE 9.3. WSEP Auxiliary Equipment Flow Diagram

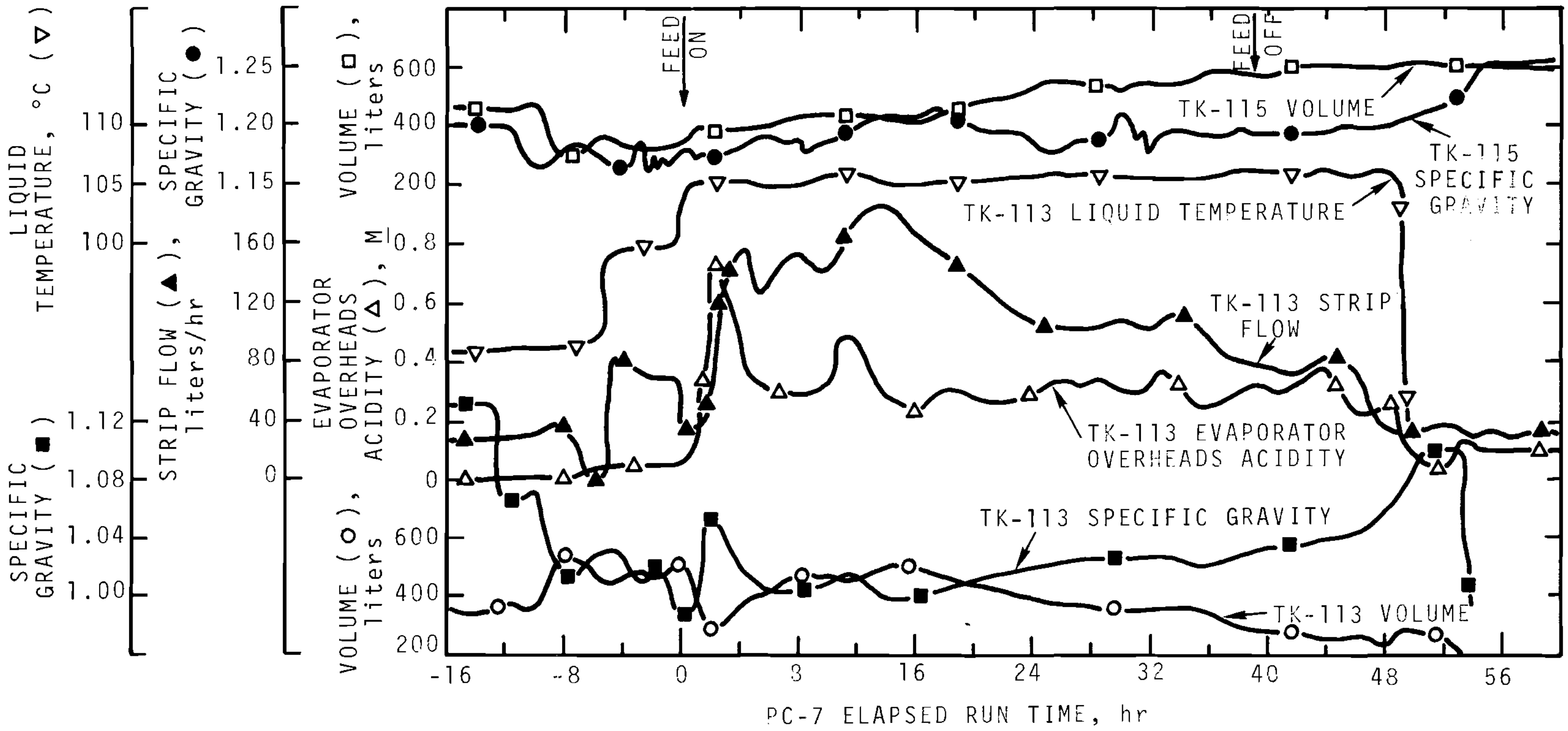


FIGURE 9.4. Auxiliary Evaporator and Fractionator Operating Parameters During Run PC-7

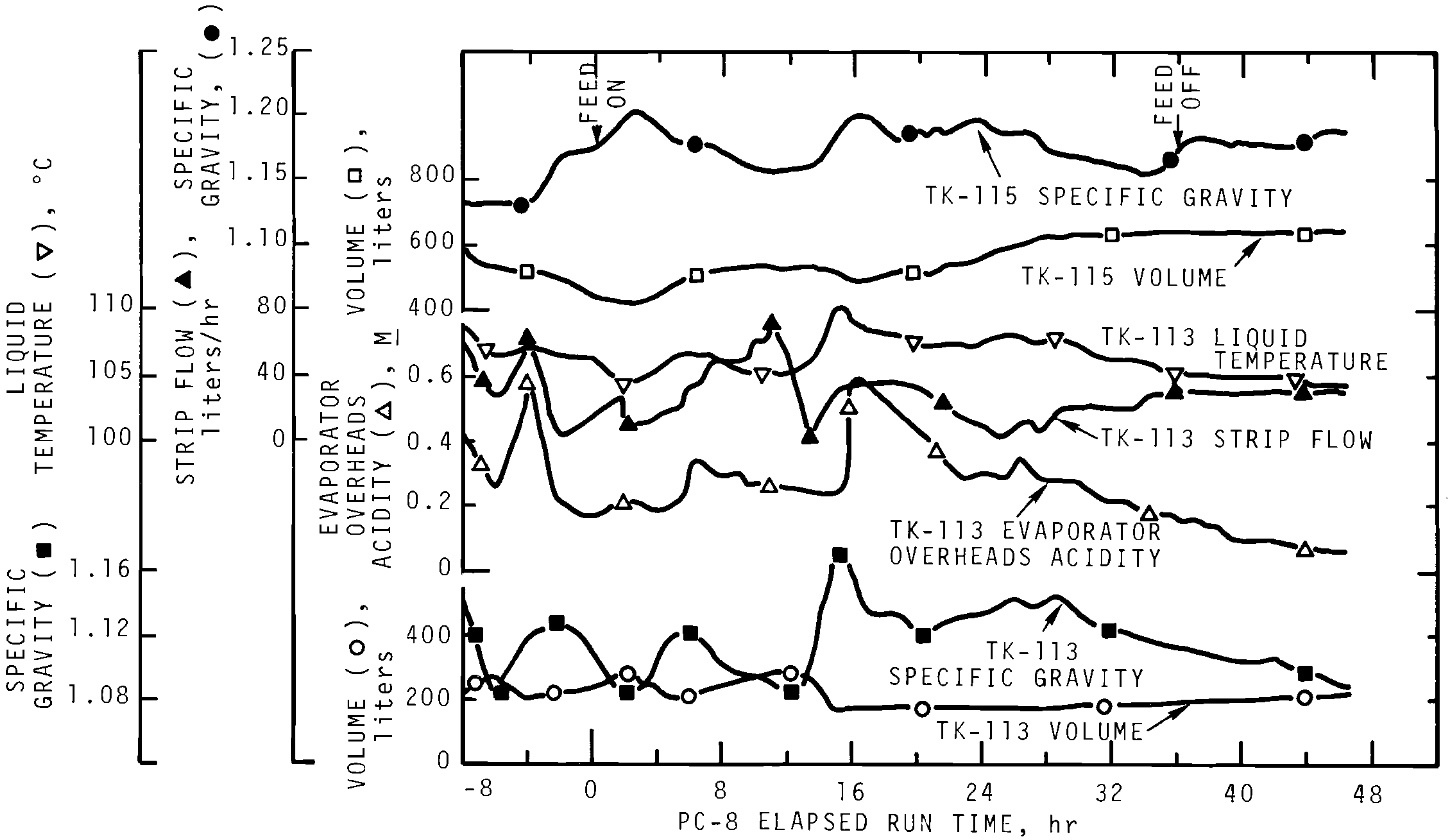


FIGURE 9.5. Auxiliary Evaporator and Fractionator Operating Parameters During Run PC-8

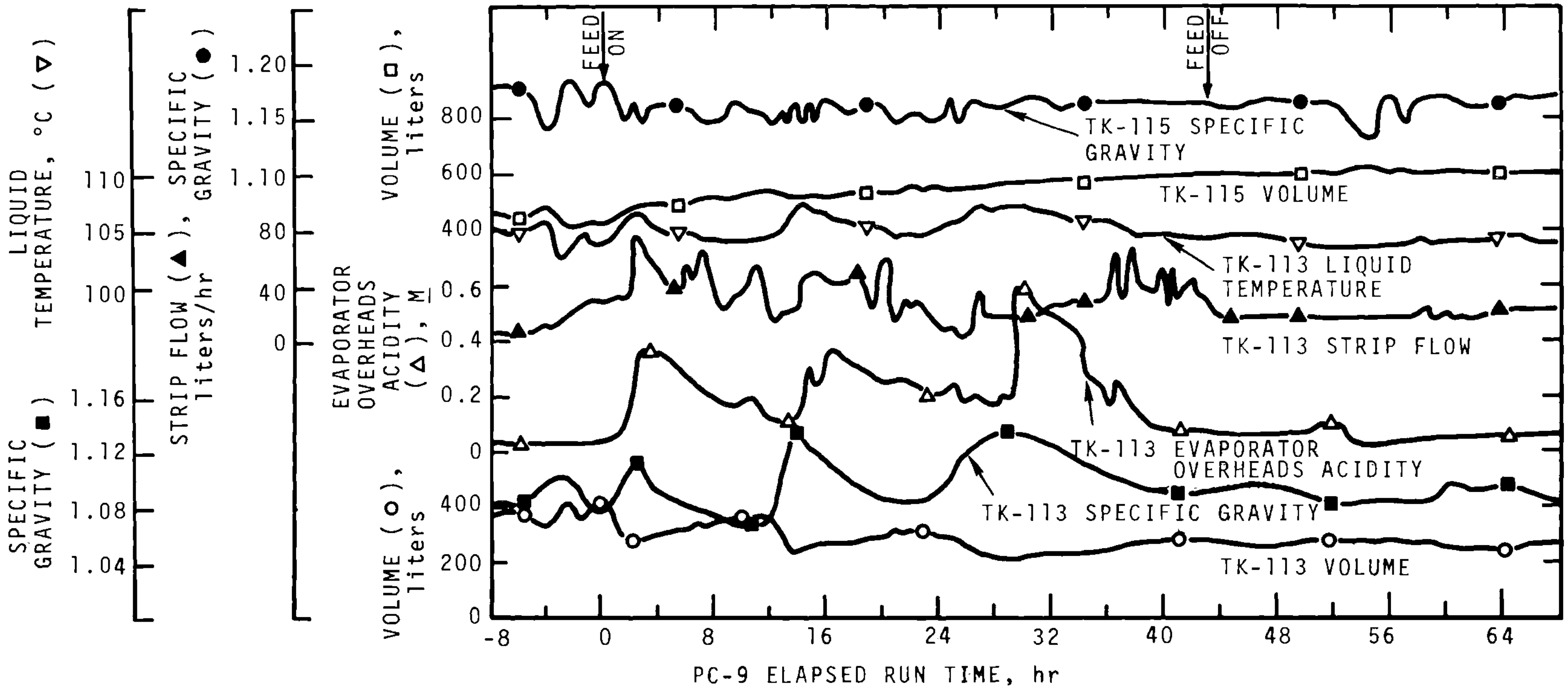


FIGURE 9.6. Auxiliary Evaporator and Fractionator Operating Parameters During Run PC-9(RLG)

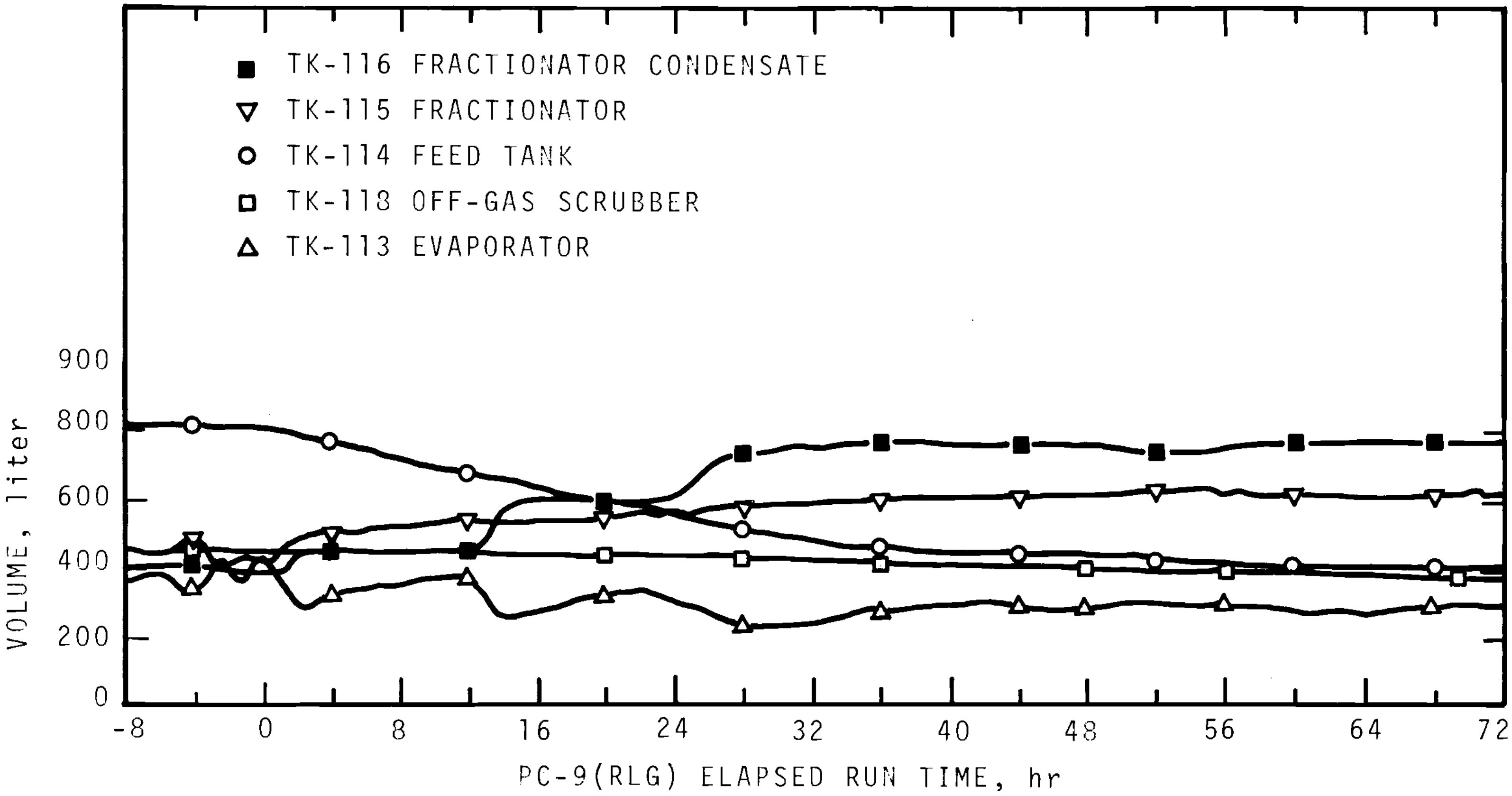
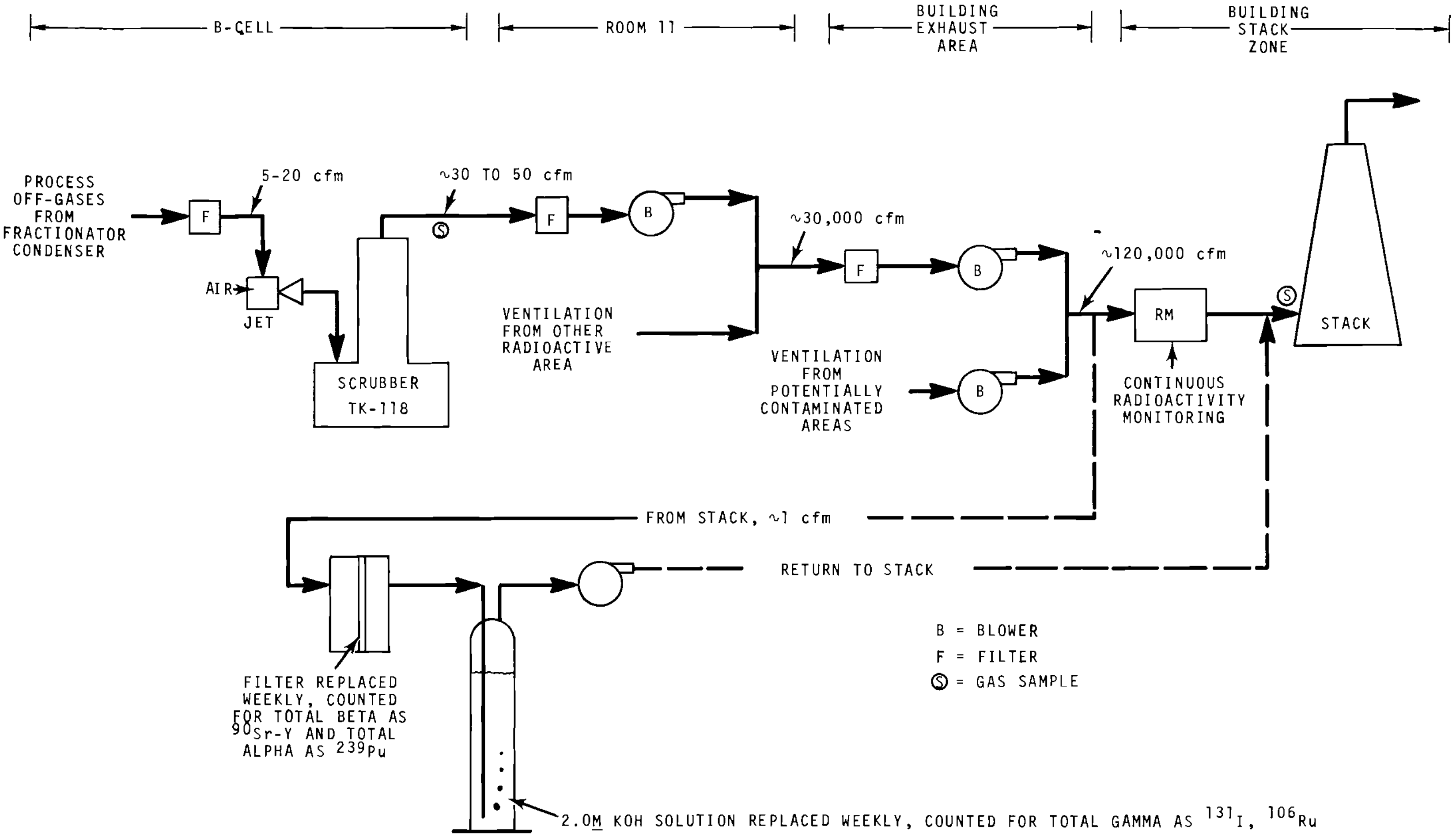


FIGURE 9.7. Typical WSEP Tank Volumes



LIMIT OF DETECTION OF $2\sqrt{\text{BACKGROUND}}$ FOR RADIATION COUNTING EQUIPMENT. NOMINAL RADIATION BACKGROUND IS 15 TO 25 COUNTS/MINUTE FOR COUNTING ROOM

FIGURE 9.8. Schematic Diagram of Ventilation System for Process Off-Gases (Also see Figure 5.1.)

a Mode C type of operation (feed from the evaporator to the pot with condensate returned to the evaporator for recycle). It was speculated at that time that the low volatilization may have been due to the mode of operation.

The evaporator and fractionator were controlled automatically using the GE412 process control computer. Two blown fuses in the computer output section prevented the control system from functioning prior to start of the feed to the pot, accounting for part of the lack of control during the start-up period. With the computer functioning, the volume of the evaporator was reduced to the proper level and the control of the evaporator bottoms acidity was quite effective.

The overall accumulation of radionuclides in the auxiliaries was generally typical of previous WSEP runs. Only 6.1% of the ruthenium (^{106}Ru) and 0.15% of the nonvolatiles represented by ^{144}CePr in the feed to the pot accumulated in the WSEP auxiliary evaporator.

Decontamination factors (DF's) across the solidifier condenser were 2.6×10^2 for ^{106}Ru and 4.3×10^3 for ^{144}CePr based on the average concentration of radionuclides in the solidifier condenser off-gas. During Run PC-7 the solidifier condenser off-gas filter was bypassed to determine if the filter was needed with the pot calcination process. Since there was low volatilization of ruthenium, very little ruthenium carried through the off-gas system in the gas phase and did not result in any significant contamination of the auxiliary system.

The auxiliary evaporator operated on about 5<u>M</u> HNO_3 in the bottoms. Instantaneous DF's across the evaporator from bottoms to condensed overheads varied from about 10^2 to 10^3 for ^{106}Ru and from 10^3 to 10^4 for ^{144}CePr. The fraction of equivalent feed radioactivity that accumulated in the fractionator was 2.6×10^{-3} for ^{106}Ru and 4.6×10^{-7} for ^{144}CePr which indicated cumulative DF's across the evaporator of 29 for ^{106}Ru and 3.5×10^{3} for ^{144}CePr. The DF's across the evaporator condenser were 1.3×10^{2} for ^{106}Ru and 4.6 for ^{144}CePr.

The instantaneous ruthenium DF's across the fractionator varied from less than 10^{2} to greater than 10^{3}. No ^{144}CePr was detectable in the fractionator distillate. The concentration of ^{106}Ru in the accumulated fractionator distillate was above the 10CFR20 release limits by a factor of 4.3×10^{5}. The ruthenium DF across the fractionator condenser was 10.

The fraction of equivalent ruthenium that accumulated in the off-gas scrubber was 2.3×10^{-5} while 4.8×10^{-9} escaped in the scrubber off-gas. The concentration of radionuclides in the scrubber off-gas was above 10CFR20 release limits by factors of 22 for ^{106}Ru and 94 for ^{144}CePr. After the scrubber off-gas was filtered twice more and diluted by the building ventilation air, the radionuclide concentrations in the off-gas to the stack were less than 0.2% of the 10CFR20 release limits.

Pot Calcination Run PC-8

The thirty-second radioactive demonstration in WSEP was successfully completed with pot calcination Run PC-8. A total of 340 liters of simulated PW-4m waste at 460 liters/tonne were fed to the pot in 36 hours. Another 7 hours were required to dry and cool the pot. The 34 liters of calcine product contained approximately 1,200,000 curies of fission product radioactivity (including 2300 curies of radioruthenium) to give an internal heat generation rate of approximately 4800 watts (141 W/liter) in the 6-inch diameter, stainless steel receiver pot.

The feed was started to the pot at 18 liters/hr and was terminated at a feed rate of 3 liters/hr. The average feed rate was 9.4 liters/hr. When the pot liquid level reached the upper portion of the pot, attempts were made to control the feed rate automatically with the thermal-probe liquid-level indicator; however, as in Run PC-7, this was unsuccessful due to the poor response of the control system. For this run, the steam-purged pressure tube was extended down to the pot fill level (34 liters) and served very well during the latter portion of the run as a level indicator. No difficulties with foaming were experienced during the run indicating that the addition of antifoam was effective. This was particularly noteworthy in view of the small diameter of the pot. The volume reduction of the PW-4m feed was similar to that of the PW-1 feed in PC-7 (a factor of 8.2 based on a feed concentration of 378 liters/tonne) with an apparent calcine density of 1.3 kg/liter being attained.

The average calcine centerline and wall temperatures of 865 and 260 °C, respectively, under the condition of free-air cooling indicated an effective thermal conductivity of 0.35 $W/(m^2)(°C/m)$.

Again as in Run PC-7 the auxiliaries were operated in a Mode A arrangement.

Control of the evaporator bottoms acid concentration was compromised in the initial part of Run PC-8 by a faulty start-up procedure and by an unexplained failure of the overhead conductivity sensor (for HNO_3 detection) during the remainder of the run. The recycle flow control set point was then manually adjusted based on the evaporator bottoms specific gravity as a measure of evaporator acidity rather than being cascaded from the conductivity measurement. The two steam flow control loops for evaporator and fractionator boilup were quite stable and held their respective volumes reasonably constant.

Eleven percent of the ruthenium fed to the pot volatilized and accumulated in the auxiliary evaporator while 1.2% of the nonvolatiles represented by ^{144}CePr were entrained. This entrainment was a factor of 7 greater than that occurring during Run PC-7. The entrainment from the pot calciner occurred mainly during the initial part of the run for both Runs PC-7 and PC-8. The DF's across the solidifier condenser were 6.8×10^2 for ^{106}Ru and 5.0×10^3 for ^{144}CePr while DF's across the condenser off-gas filter were 1.8×10^2 for ^{106}Ru and 9.3×10^2 for ^{144}CePr.

The auxiliary evaporator operated with an average bottoms acidity of 6$\underline{M}$ HNO_3 and ranged from 4 to 8$\underline{M}$ HNO_3. Instantaneous DF's across the evaporator varied from less than 10 to greater than 10^4 and were typically greater than 10^3 for ^{106}Ru. Instantaneous DF's across the evaporator were typically greater than 10^4 for ^{144}CePr. The fraction feed radioactivity that accumulated in the acid fractionator was 1.4×10^{-3} for ^{106}Ru and 2.3×10^{-6} for ^{144}CePr. These values were in general agreement with those of Run PC-7 except that the fraction of ^{144}CePr that accumulated in the fractionator during Run PC-8 was a factor of 5 greater than that during Run PC-7. These values indicated cumulative DF's across the evaporator of 82 for ^{106}Ru and 5.4×10^3 for ^{144}CePr. DF's across the evaporator condenser were 2.7×10^3 for ^{106}Ru and 3.8×10^2 for ^{144}CePr.

Instantaneous DF's across the fractionator ranged from approximately 10 to greater than 10^2 for ^{106}Ru and were typically 10^2 for ^{144}CePr. The concentration of radionuclides in the final aqueous effluent (fractionator distillate) was above 10CFR20 release limits by factors of 2.0×10^5 for ^{106}Ru and 6.9×10^3 for ^{144}CePr. DF's across the fractionator condenser were 1.2×10^3 for ^{106}Ru and 5.6×10^3 for ^{144}CePr.

The fraction of equivalent ruthenium that accumulated in the off-gas scrubber was 2.0×10^{-5} while 5.2×10^{-8} escaped in the scrubber off-gas. There was no accumulation of ^{144}CePr in the off-gas scrubber. The concentration of radionuclides in the scrubber off-gas was above 10CFR20 release limits by factors of 3.9×10^{2} for ^{106}Ru and 4.3×10^{2} for ^{144}CePr. The radionuclide concentration in the final off-gas to the stack was less than 2% of the 10CFR20 release limits. This was a factor of 10 higher than previous runs but can not necessarily be attributed to the WSEP run since other cells in the building are vented to the stack.

Rising Level Glass Run PC-9(RLG)

The thirty-third and final radioactive demonstration in WSEP was completed with rising level glass Run PC-9(RLG). During Run PC-9(RLG), 393 liters of simulated PW-4m waste at 705 liters/tonne were fed to the pot where it was continuously concentrated, calcined, and fused to a borosilicate glass product (50 wt% waste oxides). Sodium and boron additives necessary for fusion were added directly to the feed tank while the required silica additive was blended in-line with the feed as an aqueous suspension just prior to entry into the pot. To increase the processing rate of the 6-inch diameter pot from the 3 liter/hr rate which would be otherwise attained, the feed was added filmwise down the pot centerline thermowell. The intermediate thermowell in the pot was to be used as an indicator of the level within the pot.

The feed was started to the pot at 15 liters/hr without any difficulties; however, it was apparent shortly after the start of the run that, in addition to feed flowing down the centerline thermowell, the feed was also wetting the intermediate thermowell as indicated by a decrease in the top intermediate pot temperatures. After 2.5 hours of feeding, the pot feed was switched from waste to water due to the progressive decrease in the top intermediate pot temperatures. While feeding water for 40 minutes the intermediate temperatures increased to where they were initially but started decreasing once waste feed was again started to the pot. The intermediate temperatures eventually leveled out and feeding progressed smoothly; however, it was noted that with the exception of the bottom zone of the pot, the intermediate temperatures were not responding to the rising pot level as in early nonradioactive runs. This made it difficult to determine the pot liquid inventory. The intermediate temperatures only responded when it was apparent that melt had formed.

After approximately 25 hours of feeding, oscillations in the pot pressure indicated that liquid was contacting the pot pressure tube (located 18 inches down from the top of the pot), and a reduction in feed rate (13 to 10 liters/hr) was necessary to correct the situation. However, 5 hours later it was necessary to terminate feeding for approximately 30 minutes as the result of high liquid level indications. During the next 26 hours, feeding to the pot was interrupted five times due to high liquid level in the pot, and as a result only 55 liters of feed were fed to the pot in 12 hours of actual feeding during this period. During one of these interruptions the pot was allowed to bake for approximately 7 hours so that any calcine deposits or bridges in the upper portion of the pot might be melted down, but no improvement in operating was noted. The run was terminated following the last interruption in feed.

Inspection of the pot after the run revealed a partial calcine plug in the pot neck (approximately 75% reduction in cross-sectional area) and considerable calcine (2 to 3 liters) above the pot baffle (the baffle is 4 inches in diameter and centered 13 inches down from the top of the pot). The calcine in the pot neck and a portion of that on the baffle was most likely due to calcine entrainment. Indications of high entrainment were apparent early in the run as the absolute filter downstream of the solidifier condenser started to plug immediately after feed was started and had to be bypassed. Also approximately 20 hours into the run the vent system downstream of the condenser started plugging and had to be flushed. However, analysis of the accumulated condensate indicated that only 0.38% of the radioactivity fed to the pot during the run was entrained from it which was not any higher than in previous pot calciner runs.

The 393 liters of feed added to the pot during the run was only 65% of the total planned. The feed contained 1,400,000 curies of fission product radioactivity (including 1800 curies of radioruthenium) and had a heat generation rate of approximately 5600 watts. The feed rate averaged 9 liters/hr for the 43 hours of actual feeding. The glass level in the pot was estimated at 34 inches or 16 liters based on pot temperatures. This was only 86% of the product volume anticipated from the volume of feed added, indicating that the remaining 14% of the material was lodged in the upper regions of the pot.

The average glass centerline and wall temperatures of 740 and 402 °C, respectively, in the air-cooled furnace indicated an effective thermal conductivity of 1.36 $W/(m^2)(°C/m)$ based on a heat rate density of 310 W/liter in the glass. This thermoconductivity is in the same range as that of the WSEP phosphate glass and the in-pot melting borosilicate glass products. During processing, the rising level glass product behaved as the other products in that the effective thermoconductivity increased significantly when it became molten. At an average product temperature of 900 °C the rising level glass product had an effective thermoconductivity of approximately 2.0 W/(m^2)(°C/m). This is approximately 40% lower than that observed for the in-pot melting borosilicate glass product at the same temperature and may be due to the higher viscosity (poorer mixing) of the rising level glass product because of its higher waste oxide content.

Although the planned volume of feed was not processed, the performance during the run was basically satisfactory, particularly in view of the fact that the rising level glass process had not received the high degree of development on a nonradioactive basis which had been accorded all other WSEP solidification techniques. High points of the run were (1) a borosilicate glass product having a relatively high thermoconductivity was produced using the rising level glass concept, (2) film-feeding down the pot centerline thermowell gave an approximately three-fold increase in capacity; however, it must be assured that the feed does not wet other internal pot surfaces other than the centerline well, and (3) the boric acid was added to the feed tank without causing any solution precipitation problems by maintaining the solution temperature above 60 °C.

The auxiliaries were operated in a Mode A arrangement. A total of 15% of the ruthenium fed to the pot volatilized and accumulated in the auxiliary evaporator. As reported previously, 0.38% of the nonvolatiles represented by ^{144}CePr were entrained from the pot and accumulated with the condensate (evaporator bottoms). The cesium leaving the pot and accumulating in the evaporator was higher than could be attributed entirely to entrainment, and indicated that cesium volatilization was probably about 0.6% (1.0% total accumulated).

The overall accumulation of radionuclides in the auxiliaries was generally typical of previous WSEP runs.

The solidifier condenser off-gas filter was bypassed, and the average concentration of radionuclides in the off-gas was 3.5×10^{-4} μCi/cm^3 for ^{106}Ru and 1.3×10^{-3} μCi/cm^3 for ^{144}CePr. Again, as in the previous two pot calciner runs, there was very little ruthenium carried through the off-gas system in the gas phase. DF's across the solidifier condenser were 1.1×10^3 for ^{106}Ru and 1.2×10^4 for ^{144}CePr.

The auxiliary evaporator and acid fractionator were successfully operated automatically using the GE-412 process computer. The run was again compromised by a failure of the overhead conductivity sensor during most of the run; however, when it was functioning all three of the cascade systems performed quite well. Weight factor control of the evaporator boilup was again very satisfactory. Specific gravity control of the fractionator worked quite well, producing only a mildly erratic boilup pattern. The failure of the conductivity sensor was attributed to the extremely low flow of condensate through the sensor well, resulting in the sensor being immersed in a nonrepresentative sample. Conductivity measurements were roughly correlatable with the specific gravity of the bottoms as long as the evaporator boilup remained relatively high. As the stripwater recycle rate and the evaporator boilup decreased, conductivity values stabilized while specific gravity values continued to change. In general Run PC-9(RLG) demonstrated the feasibility of completely automatic interrelated control of the auxiliary acid recovery system.

The auxiliary evaporator operated with an average bottoms acidity of 5$\underline{M}$ HNO_3 and ranged from 4 to 6$\underline{M}$ HNO_3. Instantaneous DF's across the evaporator varied from less than 10^2 to greater than 10^4 and were typically greater than 10^3 for ^{106}Ru and 10^3 to 10^4 for ^{144}CePr. Again there was no apparent correlation between instantaneous ruthenium DF's and the evaporator overhead acidity. This is primarily attributed to internal contamination of the auxiliary system. The fraction of equivalent feed radioactivity that accumulated in the acid fractionator was 2.3×10^{-3} for ^{106}Ru, 4.2×10^{-4} for ^{137}Cs, and 4.1×10^{-6} for ^{144}CePr. These values were in general agreement with those of Run PC-8, except that the fraction of equivalent ^{137}Cs that accumulated in the fractionator during Run PC-9(RLG) indicated that some cesium volatilization occurred. These values indicated cumulative DF's across the evaporator of 59 for ^{106}Ru, 24 for ^{137}Cs, and 8.4×10^{2} for ^{144}CePr. DF's across the evaporator condenser were 2.2×10^{3} for ^{106}Ru and 6.4×10^{2} for ^{144}CePr.

Instantaneous DF's across the fractionator ranged from less than 10 to greater than 10^{2} for ^{106}Ru and from 10^{3} to 10^{4} for ^{144}CePr. The concentration of radionuclides in the final aqueous effluent (fractionator distillate) was above 10CFR20 release limits by factors of 9×10^{4} for ^{106}Ru, and 1.9×10^{2} for ^{144}CePr. DF's across the fractionator condenser were 2.1×10^{3} for ^{106}Ru and 47 for ^{144}CePr.

The fraction of equivalent ruthenium that accumulated in the off-gas scrubber was 7.4×10^{-4}, while 6.8×10^{-7} escaped in the scrubber off-gas. There was no detectable accumulation of ^{144}CePr in the off-gas scrubber; however, an equivalent fraction of 1.7×10^{-10} escaped in the scrubber off-gas. The concentration of radionuclides in the scrubber off-gas was above 10CFR20 release limits by factors of 2.6×10^{2} for ^{106}Ru, 1.2 for ^{137}Cs, and 2.4×10^{2} for ^{144}CePr. The radionuclide concentration in the final off-gas to the stack after being filtered twice more and combined with the building ventilation air was only 0.1% of 10CFR20 release limits.

9.2 OPERATING PROCEDURE FOR THE POT CALCINATION PROCESS

The calciner pot is placed in the calciner furnace and then raised into position to seal the pot to the off-gas line, fill-head assembly. The existence of normal vacuum in the pot is evidence that the pot is sealed. The pot thermocouples are plugged into a common connector and an air purge is directed on to the connector to prevent it from overheating during furnace operation.

Water is sprayed into the top of the refluxing off-gas line to provide washing of the line (cleanup for the preceeding run) and to fill the pot about 20 to 30% full with water for startup.

The six zone pot furnace is then started and the total power input is set to provide about 30% more power than is required to boiloff the maximum pre-established feed rate to the pot if the liquid level was at the maximum fill level. The upper and lower furnace zones should have a higher power input because of furnace end losses. The zone temperature controllers are set at the maximum desired operating temperature for the run (approximately 900 °C). In WSEP the control temperatures were the furnace susceptor temperatures. The actual furnace temperatures will increase to some temperature that is dependent on the furnace net power input to the pot and the feed rate (or boiloff rate) to the pot.

When the water in the pot begins to boil (about 1 hour after heating is started), the pot and vent line temperatures are checked for proper operation and the vent line reflux rate is adjusted to a minimum rate of about 1 liter/hr (as the pot liquid level increases the reflux rate will increase due to less off-gas superheat and a higher boiloff rate). A small steam condensate purge is initiated to the pot weight factor dip tube. Antifoam, if used, is also started to the pot.

Water is started to the pot at about 10 to 15 liters/hr to flush the feed lines and cool the feed entry line in the pot. Assuming all systems are satisfactory, feed is then gradually blended with the water (over a period of about 1 minute) until the switchover to feed is completed. The feed rate is then smoothly increased to the maximum pre-established rate. (This maximum rate corresponds to about a 1 to 1.5 ft/sec superficial gas velocity inside the calcine pot to minimize entrainment and instability.)

During the first few hours of feeding the feed level in the pot will increase to where the available furnace power input will maintain a constant boiloff rate (equal to feed rate) and liquid level. Optimized, this level will be approximately 75% of the normal operating level. This provides additional freeboard during the more unstable period of the run (during the maximum boiloff rate period and the time when a tendency to foam or swell occurs due to the initial calcination on the pot wall). The furnace temperature at this point will be between approximately 600 and 800 °C and the outer wall temperature will be about 150 °C in the zones having liquid.

When the waste in the pot reaches a high concentration it will begin to scale and denitrate at the hot pot wall. (Scaling and denitration are dependent on the solubility limits of the salts in solution, the temperature of the solution, and the decomposition temperature of the nitrates that form. Thus, the time the feed can be maintained at the maximum rate can vary considerably.) The scale generally forms first in the lower zones of the pot.

After scaling occurs in a given zone, the pot wall and the furnace temperatures begin to increase as the transfer of heat through the wall is reduced by the scale. At this time the boiloff rate from the pot starts to decrease; resulting in an increase in liquid level in the pot. The weight factor tube and upper pot temperatures will indicate the liquid level as it comes to the desired operating level near the middle of the top zone. It is then necessary to begin reducing the feed rate in order to maintain the desired level. The feed rate will continue to decrease as the boiloff rate is further reduced due to the thickening scale on the pot wall.

After the wall is covered with scale the furnace temperature increases to the 900 °C set point and the pot wall temperature increases to near this temperature. The wall temperature will continue to slowly increase as the calcine scale insulates the wall from the internals of the pot and as the calcine provides a buildup of internal heat due to fission product decay. When the pot wall temperature in a zone is almost at the furnace set point ($\leq$ 25 °C ΔT) the furnace zone temperature is reduced by as much as 200 °C so that the temperature set point in the calcine near the wall does not become significantly in excess of 900 °C due to the fission product decay heating.

During the run, periodic reductions are made in the flow rate of the off-gas line cooling water to maintain the reflux rate at 10 to 20% of the pot boiloff rate. (If the line is properly designed, this reduction may not be necessary if the reflux can be performed without it spilling back into the pot. The reflux is normally routed to the same location as the remainder of the pot condensate.) Approximately every 12 hours some reflux should be returned to the pot for about 15 minutes to wash the section of vent line that is not washed by the normal reflux. Caution must be exercised when returning the reflux to the pot to prevent overfilling the pot, especially when the pot is at reduced boiloff rates.

As the run continues, the scale growth in the bottom of the pot will have progressed to where the center of the pot becomes dry and the temperature rises beyond that of the liquid range. The temperature will continue to climb and would become excessive (>900 °C) if further reductions were not made in the furnace and pot wall temperature. Consequently, when the centerline temperature reaches approximately 600 °C in a given furnace zone, heat to that zone is turned off. When the centerline reaches 800 °C, forced air cooling of the furnace susceptor is started to aid in cooling the pot wall. For large pots of 12-inches or more diameter, these steps must be performed earlier due to the time lag inherent in transferring heat through the thick layer of calcine.

While the lower zones of the pot are going through the calcining cycle and are being cooled to prevent excessive temperatures, the upper zones of the pot are boiling off liquid at a continually reducing rate. When this rate gets to approximately 5 liters/hr, the feed is normally terminated by gradually blending in water to the feed line over a period of about 1 minute and then feeding water to the pot for about 15 minutes.

After the pot feed and water flows are turned off and most of the liquid is boiled off, the vent line should be sprayed with one or two 2-liter additions of water to provide final washing of the vent line and pot throat prior to disconnect. The antifoam stream (if used) and the steam condensate purge to the pot weight factor should be turned off after all additions have been made to the pot, to allow the calcine to completely dry.

Each zone will undergo the drying, calcining, and cooling sequence as described above. The presence of the internal fission product heat in the calcine aids in the drying of the calcine by heating it through the desired temperature range while the pot wall temperature is being cooled to prevent the temperature cycle from being excessive. Thus, ty the time the pot centerline temperature reaches 900 °C, the wall temperature has cooled to about 400 °C or less so that the pot is ready for removal from the furnace. The calcine in the upper zone will not normally heat beyond approximately 750 °C due to heat losses; however, it can be assumed that adequate calcining and denitration have occurred after all the calcine has been at $\geq$700 °C for 2 hours. With the cooling air on to all zones the pot is ready for removal.

The pot thermocouples are disconnected and the pot is removed by releasing the pot head to vent line clamp and lowering the pot. When the pot is removed from the furnace a lid is placed on it and then seal welded. The pot is then placed in interim storage.

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