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**POT CALCINATION PERFORMANCE
DURING FIRST RADIOACTIVE TESTS
IN WASTE SOLIDIFICATION
ENGINEERING PROTOTYPES: WASTE
SOLIDIFICATION PROGRAM, VOL. 4**

DECEMBER 1968

**AEC RESEARCH &
DEVELOPMENT REPORT**

J.P. Roberts 30976 325 AUG 5 1970

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UNITED STATES ATOMIC ENERGY COMMISSION UNDER CONTRACT AT(45-1)-1830

BNWL-814
UC-70, Waste Disposal
and Processing

POT CALCINATION PERFORMANCE DURING
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WASTE SOLIDIFICATION PROGRAM, VOL. 4

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DEC 26 '68

December 1968

BATTELLE MEMORIAL INSTITUTE
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RICHLAND, WASHINGTON

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

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ABSTRACT

Solidification of high level radioactive waste by the Oak Ridge National Laboratory pot calcination process was successfully demonstrated. Nearly 4 million curies of radioactivity were processed in six full scale tests at Pacific Northwest Laboratory. Radioactivity was increased from 85,000 curies in the first run to 1.3 million curies in the sixth run. The rate of heat generation within the pot increased from 600 to 5100 watts, respectively. The calcined waste in an 8 inch diameter pot represented 1.2 tonnes of power reactor fuel (20,000 MWd/tonne at 15 MW/tonne specific power) after 1 year out-of-reactor. Waste was processed at an overall rate from 12 to 14 liters/hr which was equivalent to processing wastes from 1 tonne/day of spent fuel. From 3 to 30% of the ruthenium in the waste volatilized from the pot; rework of the pot condensate in an evaporator and acid fractionator reduced radionuclides in the final liquid effluent to a concentration acceptable for low level treatment processes. Cumulative decontamination factors (curies in the waste before solidification/curies accumulated in final liquid condensate) were 10^6 and 10^8 for ruthenium and all other radionuclides, respectively. The calcined solids were stable and did not cause a significant pressure increase within the container after it was capped and welded.

WASTE SOLIDIFICATION PROGRAM REPORTS

This report is part of an on-going series of reports from the Waste Solidification Program at Battelle-Northwest. Other current reports in this series are:

K. J. Schneider, Editor, Waste Solidification Program, Volume I, Process Technology for the Pot, Spray, and Phosphate Glass Processes, in progress.

K. J. Schneider and V. P. Kelly, Waste Solidification Program, Volume 2, Design Features of the Waste Solidification Engineering Prototypes, in progress.

V. P. Kelly, Waste Solidification Program, Volume 3, Design Features of Facilities and Equipment for WSEP Product Evaluation Program, BNWL-832, in progress.

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1.0 INTRODUCTION

1.1 RADIOACTIVE WASTE PROBLEM

During chemical processing of spent nuclear fuels, essentially all of the fission products are accumulated as aqueous wastes. Traditionally these high level radioactive wastes have been stored in large, underground tanks. Since some of the radio-nuclides present in these wastes constitute a hazard for centuries; storage as mobile, corrosive liquids in tanks is considered a temporary or interim approach.⁽¹⁾ In the future, more permanent disposal methods must be used to better isolate hazardous radio-nuclides from our environment if the full benefits of nuclear power are to be realized.

Responsible authorities the world over generally agree that the best approach involves converting radioactive wastes to inert, refractory solids that are packaged in relatively small, high-integrity containers. The containers would then be isolated for long-term storage in concrete vaults with high integrity or in geologically remote locations such as salt mines.

Recent progress toward developing processes for high-level waste has been reported comprehensively in three international symposia.⁽²⁻⁴⁾

1.2 WASTE SOLIDIFICATION

Fluidized bed calcination developed at Argonne National Laboratory and at the National Reactor Testing Station was the first radioactive waste solidification process placed in routine operation. Currently, aluminum-bearing wastes derived from

enriched uranium fuels are solidified by this process at the Idaho Chemical Processing Plant (ICPP).⁽⁵⁾ Three other American processes in advanced stages of engineering are pot calcination [developed at Oak Ridge National Laboratory (ORNL)],⁽⁶⁾ a phosphate glass process [developed at Brookhaven National Laboratory (BNL)],⁽⁷⁾ and a spray solidification process [developed at Pacific Northwest Laboratory* (PNL)].⁽⁸⁾ Two waste solidification processes under development abroad include the United Kingdom FINGAL process⁽⁹⁾ and the French pot vitrification process.⁽¹⁰⁾

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

1.3 WASTE SOLIDIFICATION ENGINEERING PROTOTYPES (WSEP)

The WSEP were designed to provide information necessary for a technical, economic, and safety evaluation of the pot, spray and phosphate glass solidification processes. Information is now being obtained through full-activity-level demonstration of the three processes. Besides testing the basic processes for treating highly radioactive wastes on an engineering scale, the suitability of the processes and equipment for service as an integral part of a nuclear-power fuel processing complex will be assessed.⁽¹¹⁾

A pilot-plant demonstration of pot calcination with radioactive wastes was first planned at ICPP⁽¹²⁾ after promising developments at ORNL and a favorable economic evaluation.⁽¹³⁾

* Pacific Northwest Laboratory is operated by Battelle Northwest (BNW) for the United States Atomic Energy Commission.

In 1962, plans for testing the pot process at the ICPP were replaced by plans for a multipurpose pilot plant in which cooperative studies by ORNL, BNL, and PNL could be conducted using the newly conceived WSEP.

The WSEP were designed⁽¹⁴⁾ and constructed at PNL during 1962 through 1965. Radioactive testing started in November 1966. By the end of 1967, radioactive demonstration runs on all three processes had been conducted.

Prior to the radioactive testing of pot calcination in WSEP, several other tests were made. The pot calcination process was successfully operated in eight runs made at PNL using small-scale hot cell equipment and radioactive waste.⁽¹⁵⁾ Eight full-scale, nonradioactive design verification tests (DVT) were made in the WSEP equipment with simulated wastes. Chemical flowsheets were confirmed and equipment performance was verified.⁽¹⁶⁾

1.4 POT CALCINATION

In the pot calcination process, liquid waste is fed into a zone-heated pot where the waste is evaporated to dryness and calcined. The filled pot is cooled, removed from the furnace and sealed by remote welding. The pot serves as the shipping container and the final storage container.

Associated with pot calcination in WSEP were customary chemical processing plant operations: evaporating wastes, recovering nitric acid, and scrubbing and filtering effluent gases. In the basic operating mode (termed Mode C in this report), the condensate and noncondensable gases from the pot are routed to a close-coupled evaporator which operates in a closed loop to continuously recycle condensate, along with the concentrated feed, to the pot. Other operating modes (A and B in this report) involved the collection of condensates on a batch basis for subsequent recycle to fuel processing steps. In these modes, a close-coupled evaporator is not required. In the WSEP, all

condensate passes through an evaporator and condensate from the evaporator passes through an acid fractionator. Here dilute and concentrated nitric acid are produced.

Results and analyses of the first six radioactive runs in the WSEP are presented in this report. They are discussed under Pot Calcination Performance (Section 4.0) if they refer to the pot calciner and the first condenser. If the results refer to the evaporator, acid fractionator, feed makeup, etc., they are discussed under Auxiliaries Equipment Performance (Section 5.0). Where pertinent, the WSEP results are compared to previous non-radioactive results. Detailed results and descriptions of runs and equipment are given in the Appendix (Section 9.0).

2.0 SUMMARY

Solidification of liquid wastes containing nearly 4 million curies was successfully completed in six runs using the pot calcination process in WSEP. Accomplishments were as follows:

1. Heat generation from fission products produced temperatures in the calcine at the maximum contemplated for the process. Temperatures were easily controlled by proper timing of the heating-cooling cycle.
2. Radioactive wastes were solidified and encapsulated in stainless steel containers without significant pressurization, without corrosion and without distortion of the container.
3. Liquid effluents, acid and water after fractionation, were low enough in activity to permit recycle to a spent fuel processing plant or to permit treatment as low level wastes for disposal.
4. Gases from the process were quite low in activity and were directly released to the atmosphere.

2.1 CALCINATION PERFORMANCE

The principal variables investigated in the first six runs were fission product power, pot size and waste chemical composition.

Radioactivity levels were increased from about 85,000 curies (600 watts) in the first run to about 1,300,000 curies (5100 watts) in the sixth run. The 5100 watts of internal power in the last run was sufficient to maintain a pot centerline temperature of 940 °C, and a centerline-to-wall temperature difference of 700 °C with the pot suspended in air at ambient temperature.

Complete calcination of solids in the bottom of the pot occurred in some runs before feeding was terminated; however, temperature excursions above 940 °C in the solids were prevented during processing by using a three-step, manually controlled reduction of furnace temperatures, based on pot wall and internal calciner temperatures. As expected, the internal heat nearly completed calcination by the time the feed to a pot was shut off.

Since cooling was started before the feed was shut off, only 8 hours were required after the feed was shut off to cool the pot wall enough to permit removal of the pot from the furnace.

Radioactive wastes simulating PW-1 (Purex, low in sulfate but high in iron)* and PW-2 (Purex, high in sulfate but low in iron)* were processed at average overall rates of 12 to 14 liters/hr. This was equal to processing waste from 0.75 to 1 tonne/day of power-reactor fuel (20,000 MWd/tonne** at 15 MW/tonne). Average rates for 8- and 12-inch pots include time for feeding, calcining, and cooling the pots before removing them from the furnace, but do not include approximately 8 hours expected for changing a pot. There was no substantial difference in the overall processing rates for the two pot sizes (i.e., <10% greater for 12 inch pots than for 8 inch pots).

The radioactive wastes available for these tests did not permit preparation of feeds having exact PW-1 and PW-2 compositions. Feeds actually used to simulate PW-1 and PW-2 were similar in many respects. However, behavior of the two wastes during calcination was significantly different. The PW-1 waste had a tendency to foam out of the pot whereas PW-2 did not. Expulsions from the pot were prevented by reducing the liquid level during the initial high boil-off portion of the runs.

General conditions for each run are summarized on page 2.3.

The six-zone, induction-heated calciner furnace, which employs a temperature-controlled susceptor to transfer heat to or from the pot calciner wall, gave exceptionally good performance from the standpoints of reliability and safety. When all zones were being heated at control temperatures, each zone could be controlled to within ± 10 °C of the setpoint once the control

* For detailed chemical composition, see Appendix, Table 9.3.

** Tonne is used throughout this report to represent a metric ton (1000 kilogram) of U and Pu in a fuel.

POT CALCINATION RUNS IN WSEP

	<u>PC-1</u>	<u>PC-2</u>	<u>PC-3</u>	<u>PC-4</u>	<u>PC-5</u>	<u>PC-6</u>
Feed Type	PW-2	PW-2	PW-2	PW-1	PW-1	PW-2
Pot Diam, in.	12	12	8	12	8	8
Ci in Feed to Pot	85,000	430,000	375,000	650,000	1,150,000	1,300,000
Power in Pot, watts	600	1700	1800	2600	4300	5100
ΔT in Calcine to Wall, °C	70	235	220	312	495	700
Equivalent Tonnes in Pot*	2.2	2.3	1.4	2.8	1.25	1.2
Equivalent Age to Reduce Watts to Run Value, yr*	37	6.2	3.4	4.8	1.4	1.1

* Based on fuel irradiated to 20,000 MWd/tonne at 15 MW/tonne

temperature was reached. No gross influence from adjacent zones was noted except when heating one zone and cooling an adjacent zone; as expected, the setpoint in the heated zone could not always be maintained because of heat losses to the adjacent zone.

In WSEP, the vent line from the pot as well as the throat of the pot was kept free of solid deposits by a combination of washes. The vent line was cooled continuously so that refluxing condensate washed the interior of the vent line. Also, from 15 to 30 liters of water spray were added to the vent line prior to each run. Two liters were added after each run for further washing.

The feed rate to the pot was successfully controlled during most of the radioactive runs with a thermocouple-type level probe. However, during two runs, the probe lost sensitivity to the solution level in the pot. An alternate pneumatic probe, purged with steam and air, was used to continue operation by manually controlling the feed rate. During one of these runs, manual adjustments were not made soon enough after noting the indication of the pneumatic probe and the pot was filled above the normal operating level.

The effective thermal conductivity (defined in Section 6.0) of the calcine ranged from 0.32 to 0.37 W/(m²)(°C/m) [0.18 to 0.21 Btu/(hr)(ft²)(°F/ft)] at an average temperature of 350 °C and increased only slightly with increasing temperature.

Within the range of waste compositions and operating procedures used in these six runs, the amount of ruthenium volatilized from the pot calciner varied from 3 to 30% of the total amount fed to the pot; entrainment of nonvolatiles varied from 0.3 to 1.2%. Volatilized and entrained material was recycled or processed in the auxiliaries.

A method based on previous theoretical analyses was developed and confirmed for estimating the maximum power generation which can be present in a pot of calcined waste while maintaining internal and pot wall temperatures at adopted limits. Application of the method showed that power generation equal to 5000 to 6000 watts is attainable in 8- to 12-inch diameter pots of calcine without the temperatures rising above 900 °C when the pot is filled to 6 feet and cooled by natural convection in air.

2.2 AUXILIARY EQUIPMENT PERFORMANCE

The auxiliary equipment (i.e., condensers, evaporator, acid fractionator, scrubber and filters) decontaminate and separate nitric acid, water, and noncondensable effluents from the process. During these operations, mainline recycle of radioactive constituents is provided.

Feed-to-condensate cumulative decontamination factors (DF's) for ruthenium in the evaporator, (ratio of ruthenium in the evaporator at end of run to ruthenium evolved from the evaporator) ranged from 350 to 4700. DF's increased as the nitric acid concentration in the overheads was decreased. DF's were not significantly affected by the presence of sugar in the bottoms as a reductant. (From 25 to 55 g/hr was added to the evaporator bottoms.) When the acidity in the overheads was less than 0.6M, instantaneous ruthenium

DF's* approached 10^5 . They decreased to approximately 10^3 when the acidity increased to 0.8M. Instantaneous DF's for nonvolatiles across the evaporator and its high efficiency glass fiber mist eliminator varied from about 2×10^4 to 2×10^6 .

Cumulative ruthenium DF's in the fractionator (ratio of ruthenium in the fractionator at end of run to ruthenium evolved from the fractionator) varied from 420 to 6900. Values near 5000 were typical.

The cumulative DF's for ruthenium (ratio of ruthenium in the original pot feed to that accumulated in the condensate from the fractionator) averaged about 10^6 , while comparable DF's for nonvolatiles were about 10^8 .

Some contamination of samples of the acid fractionator condensate occurred because the samples were taken in a highly contaminated location. Procedures were improved later. The ratio of various radionuclides was used to assure that the calculated quantities were reliable.

Off-gases to the stack were consistently below discharge limits for both ruthenium and gross beta activity. Decontamination factors from feed to stack gas were consistently $>1 \times 10^9$ and $>1 \times 10^{12}$ for ruthenium and gross beta (less ruthenium), respectively.

Although PW-2 waste was very stable during calcination at a feed concentration of 378 liters/tonne, it contained sodium-rare-earth-sulfates as precipitates. These precipitates were relatively heavy and had a tendency to agglomerate and plug equipment if allowed to settle. As a consequence, it was necessary to reduce the sulfate concentration from 0.87M to approximately 0.6M to prevent plugs in equipment.

* Instantaneous decontamination factor is the ratio of the concentration in the boiling liquid to the concentration in the condensed vapor measured at the same time.

Although some minor malfunctions of auxiliary equipment occurred, no serious problems arose. The minor equipment problems which did occur can be eliminated by suitable design modifications. The malfunctions were (1) feed pumps failed, (2) the evaporator specific gravity dip tube plugged and the specific gravity indicator was somewhat sensitive to evaporator boilup rate, and (3) high efficiency filters in the feed tank vent system failed repeatedly because a larger heater was needed. (Moisture accumulated in the filters and caused high pressure drop.) The process filters which served the pot calciner evaporator and acid fractionator gave good performance.

2.3 FILLED POT PERFORMANCE

Although it is too early to evaluate the near-term (~5 year) performance of pots filled by the pot calcination process, current observations are encouraging. No excessive pressurization has occurred in any of the six pots and the pressure in at least three of the pots is remaining less than atmospheric. Good welds on the pots and negligible gas generation within the calcines are indicated. No corrosion (within the measurement accuracy of 10 mils) was detected in a test of the pot wall. Continued observation of pot behavior over an extended period is planned to evaluate long-term effects.

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

2.4 STATUS OF POT CALCINATION

Although the pot calcination demonstration runs are not all complete, the six runs made to date permit a projection of expected performance of the process. Total radioactivity content of the wastes for WSEP simulated that of wastes expected from the nuclear power economy in the early 1970's. However, some

individual nuclides (e.g., ruthenium) were not at the levels expected for a 20,000 MWd/tonne at 15 MW/tonne exposure. By applying the overall DF's experienced to date, several general statements can be made about the expected levels.

1. Wastes from fuels irradiated to 20,000 MWd/tonne at 15 MW/tonne can be calcined after a 1 year cooling period. At this level, a fission product power generation rate of 85 W/liter in the calcine is near the maximum (5000 watts total) capable of being handled in an 8 inch diameter container when 900 °C is considered the maximum allowable internal temperature for a pot cooled by natural convection in air.
2. Operation of the calciner, the evaporator loop and the fractionator with radioactive wastes can be expected to follow predictions based on nonradioactive tests. From 3 to 30% of the ruthenium will be volatilized out of the pot to the evaporator. Most of this can be recycled to the pot. Less than 0.2% of the total ruthenium will reach the fractionator. The ruthenium concentration in the condensate from the fractionator when calcining 1 year aged waste will be 7000 to 230,000 times higher than the discharge limits quoted in 10 CFR 20.* Ruthenium is the limiting nuclide followed by ^{90}Sr and $^{144}\text{Ce-Pr}$. Thus, in general, an additional decontamination of 10^3 to 10^4 is needed to reduce all nuclides in the final condensate to below 10 CFR 20 values. However, since less than 200 liters of total condensate is generated per equivalent tonne of fuel processed (from 380 liters/tonne waste), the condensate could easily be used in a fuel processing plant as an acid dilutant and/or dissolver wash during dissolution steps. Alternatively, the radioactivity level is acceptable for low level

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

treatment processes, such as distillation, preparatory to discharge of the water from the plant.

3. The concentrated nitric acid produced in the fractionator (10 to 12M; ~250 liters/tonne) will contain 30 to 600 $\mu\text{Ci/ml}$ (total $\beta\gamma$). Ruthenium, at 20 to 600 $\mu\text{Ci/ml}$, will be the principal contaminant. The acid would be acceptable for reuse in fuel processing. For example, fuel dissolution requires at least 1000 liters of 10M nitric acid per equivalent tonne, or four times that available from pot calcination of the wastes.
4. Calcined product from acidic wastes will have a volume of 1.4 to 2.0 ft^3 per tonne of spent fuel for the two types of Purex wastes. Calcine-filled pots can be sealed by welding. No significant internal pressurization of the pots is expected.

Demonstration runs in WSEP showed the pot calcination process, at capacities in the range of 1 to 3 tonnes/day of fuel, is ready for application as an industrial method. Remaining investigations suggested in WSEP include:

1. Runs at higher radioactivity content to determine the maximum acceptable power generation rate (i.e., the maximum exposure level of the fuel and the minimum age of the wastes).
2. Demonstration of the process on a continuous basis to establish the equilibrium level of recycled fission products within the system.
3. Demonstration of the performance of the close-coupled evaporator-calciner (Mode C) on wastes containing high sulfate concentrations.
4. Demonstration of automatic control.

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

3.0 PRIOR WORK, PROCESS DESCRIPTION AND WASTE COMPOSITIONS USED

3.1 PRIOR WORK

The pot calcination process is based on work performed principally at ORNL and supplemented with two series of tests at PNL. The work at ORNL consisted of both laboratory and engineering development performed with simulated Purex, TBP-25, Darex, and Thorex wastes.^(6,17) Laboratory work was devoted mainly to off-gas and solids characterization and was performed in glass and stainless-steel bench-scale equipment.⁽¹⁸⁾ Engineering development was performed in full-sized stainless steel equipment. Emphasis was on equipment operability and process control.^(19,20)

At PNL, eight tests (six of them with actual Purex waste) were made in bench-scale, hot-cell equipment to study fission product behavior as a function of feed additives and off-gas equipment.⁽¹⁵⁾ Eight runs were made with simulated Purex, Darex, and TBP-25 wastes in WSEP equipment for design verification tests (DVT)⁽¹⁶⁾ prior to the current radioactive test program.⁽¹¹⁾ Several modes for operating the auxiliary equipment (evaporator and fractionator) with the pot calciner were tested to evaluate optional requirements for specific individual processing plants.

3.2 PROCESS DESCRIPTION

In the pot calcination process, as developed at ORNL,⁽⁶⁾ waste is fed to a close coupled evaporator. Waste and recycle streams from the process are combined continuously in the evaporator and reduced in volume as much as possible before the mixture is pumped to the calciner (Figure 3.1). In the calciner pot, wastes are evaporated to dryness and then calcined at temperatures near 900 °C. Off-gases are decontaminated primarily in the calciner condenser. Additional decontamination of the condensate is obtained by evaporating it together with incoming wastes in the evaporator. The vapors are passed through a

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

de-entrainer to an acid fractionation column which produces (1) concentrated nitric acid and (2) an overhead condensate which is a dilute, low-activity nitric acid. About 75% of this condensate is recycled to the evaporator to strip nitric acid. This keeps the acidity of the evaporator bottoms low enough to minimize ruthenium volatilization.

A complete cycle of operations for pot calcination consists of four rather distinct periods. For convenience, they are referred to as the feeding, calcination, cooling, and pot change-out periods. During the feeding period, liquid waste is fed to the pot and some concentration occurs. This is followed by the calcination period; accumulated solids are dehydrated and decomposed by heating to a temperature near 900 °C. The third period consists of cooling the pot, usually with air under forced convection, to less than 425 °C. Pot changeout includes removing the pot from the furnace, sealing it, and placing an empty pot in the furnace.

While there are several possible methods of operating the pot, the preferred procedure, based on ORNL and PNL experience to date, is to keep the level of boiling waste constant at about 2 feet below the top of the pot. Initially, the pot is partially filled with water. Heating is started and waste is added to maintain the desired level. (In WSEP runs, the furnace was specifically set to produce a boil up rate approximately 20% above the maximum feed rate to the pot. This maintained a low liquid level in the pot during the high boiloff portion of the run.) As the waste is concentrated in the pot and the solubility of the salts is exceeded, solids deposit on the wall. As deposition occurs, the pot wall temperature increases to near the furnace operating temperature (900 °C). Decomposition occurs. The scale, or cake, grows radially inward, generally originating first in the lower zones and growing upward. When the cake thickens, the heat-transfer rate is reduced, the power which can be delivered by the furnace is reduced and boilup rates are

decreased. Finally, the feed rate drops 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 facility operating costs on the other.⁽²¹⁾ In the WSEP tests and in most previous development work, feeding was terminated at feed rates of about 5 liters/hr. Pots filled with solids to within about 90% of their working capacities were produced.

Even before feeding is stopped, calcine temperatures start to increase sharply. Internal power generation from radioactive decay accelerates the increase in temperature. Excessive temperatures in the calcine are prevented by cooling the furnace during the latter part of the feeding period. When this is done, only a few hours of additional cooling are required after the feed is shut off. The pot is then cool enough to remove from the furnace.

In 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 filled pot was welded to make the final seal.

3.3 WASTE COMPOSITIONS USED

Waste compositions adopted for WSEP tests have been documented for two waste types, PW-1 and PW-2.⁽¹¹⁾ Tables 7.1 and 7.2 list the compositions. PW-1 is a Purex acid waste containing high iron and no sulfate. PW-2 is similar, but contains sulfate and a lower iron concentration. In addition to the usual sodium, chromium, and iron, both waste types contain traces of mercury, fluorine, silicon, aluminum, uranium, plutonium and phosphorus. In WSEP runs, mercury, silicon, and fluorine were not added since unknown quantities already existed in the production plant waste. Combinations of production plant waste, inert chemicals, and selected fission products were used to produce wastes simulating

those expected from processing fuels irradiated to 20,000 MWd/tonne at 15 MW/tonne. Since some chemicals are prohibitively expensive, substitutions were made using cheaper but chemically similar elements. Most importantly, manganese was substituted for 80 to 90% of the ruthenium; molybdenum for technetium; potassium for cesium; cobalt for rhodium; nickel for palladium; and sulfur (as sulfate) for tellurium.

A complete spectrum of fission products from the production plant waste was enriched with specific radionuclides to increase the power generation in the waste. In all runs, feed was adjusted to the simulated chemical content of the 20,000 MWd/tonne at 15 MW/tonne nominal fission product concentration.

Radioactive cerium was used as the principal power generator to achieve the desired power in the waste. The concentration of any given radionuclide was not kept at any constant value for each run since it was neither necessary nor practical. Ruthenium, because of its volatility, was of primary interest. However, for economy, ruthenium concentrations were kept at 10% of the total ruthenium which would be expected in 20,000 MWd/tonne at 15 MW/tonne fuel (128 g/tonne versus 1286 g/tonne) in all runs except PC-6 where the concentration was increased to 20%. (As mentioned above, manganese was used as a stand-in for the remaining 80 to 90%.)

4.0 POT CALCINATION PERFORMANCE

Engineering scale performance of the pot calcination process with highly radioactive feed generally confirmed earlier development work. The predicted capacities of the process and the activity of the effluents were in the range indicated by nonradioactive work at ORNL and bench-scale hot cell tests at PNL. Calcination of wastes generating as much as 5000 watts of power in an 8 inch diameter pot followed theoretical predictions. Reasonable levels of radioactivity in the effluent acid and water confirmed the general suitability of pot calcination for industrial use.

Six radioactive runs have been completed in the WSEP to demonstrate the ORNL pot calcination process. A major objective was to increase the radionuclides in the waste stepwise to confirm the maximum allowable power generation in a pot. Other objectives were to determine the performance of the calcination process coupled with auxiliary equipment. Major variables of the runs are shown in Table 4.1.

TABLE 4.1. *Major Run Variables*

<u>Run</u>	<u>Pot Diam, in.</u>	<u>Waste Type</u>	<u>Curies Fed to Pot</u>	<u>Power, W/tonne</u>	<u>Equivalent^(a) Age, years</u>
PC-1	12	PW-2	85,000	270	37
PC-2	12	PW-2	430,000	740	6.2
PC-3	8	PW-2	375,000	1300	3.4
PC-4	12	PW-1	650,000	930	4.8
PC-5	8	PW-1	1,150,000	3400	1.4
PC-6	8	PW-2	1,300,000	4300	1.1

(a) Based on 20,000 MWd/tonne at 15 MW/tonne.

4.1 OVERALL PROCESSING RATES

Overall processing rates (including feeding, calcining and cooling times) for 12 inch pots ranged from 0.7 to 1.0 tonne/day;

for 8 inch diameter pots, from 0.7 to 0.8 tonne/day (13 to 15 liters/hr feed to 12 inch pots and 12 to 13 liters/hr feed to 8 inch pots). Processing rates increased as the internal power generation increased because less cooling time was required. Cooling began before feed to the pot was stopped.

Establishing the maximum overall processing rate for pot calcination was not a major objective of runs PC-1 through PC-6. 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 influenced the rates slightly. Approximately 1 kg/hr of steam was added to the pot to purge the pot-weight factor dip tube during the feeding period. Five to 10 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. A run was started with 15 to 30 liters of water accumulated in the pot from a vent line flush.

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 12 inch pots were limited to a maximum rate, at startup, of 50 liters/hr and the 8 inch pots to 25 liters/hr.

Table 4.2 summarizes the data on processing rates. Results were consistent except for PC-6. Final overall rates for PC-6 were not pertinent because of interruptions during the run. Examination of PC-6 data prior to the first interruption (at 16 hours of feeding) indicated a low rate. Two of the 8 inch diameter pot runs can be compared to run PC-6 for the feed delivered during the first 16 hours. This was 380 liters for PC-3, 400 liters for PC-5, and

TABLE 4.2. WSEP Pot Processing Rates

Run No.	Feed Type	Feed Volume, liters/ equivalent tonne	Pot Diameter, in.	Internal Power, W(a)	Total Feed, liters	Feed Time, hr	Calcination and Cooling Time, hr(b)	Total Run Time, hr	Average Feed Rate at Feed Off, liters/hr	Average Feed Rate, liters/hr(c)	Overall Processing Rate, Liters/hr(d)	Equivalent tonnes/day
1	PW-2	400	12	600	935(e)	43.7	27	70.7	2	21.4	13.2	0.73
2	PW-2	400	12	1700	1039(f)	42	28	70	5	24.7	14.8	0.79
4	PW-1	365(g)	12	2600	1060(h)	42	33	75	7	25.2	14.1	0.96
3	PW-2	420	8	1800	553	31	15.5	46.5	5	17.8	11.9	0.72
5	PW-1	410(g)	8	4300	515	28	11	39	3	18.4	13.2	0.78
6	PW-2	380	8	5100	460	43(i)	8	51(i)	2	10.7(i)	9.0	0.57(i)

(a) Total in pot at end of run.

(b) Time from feed off until pot cooled to where the pot steady state wall temperature in air would not exceed 425 °C.

(c) If the feed rates were 5 liters/hr at the time the feed was shut off, the average feed rate would be 27.5 for PC-1 and 20.2 for PC-2.

(d) Based on processing, calcination, and cooling. Actual overall rate will require inclusion of 8 hours for pot change-out.

(e) Includes 85 liters of additive.

(f) Includes 99 liters of water dilution.

(g) Mode C runs, concentration in evaporator averaged 270 and 485 liters/tonne in PC-4 and PC-5, respectively.

(h) Includes 60 liters expelled from pot.

(i) Feeding interrupted twice, so rates should not be compared to other runs.

365 liters for PC-6. Although this was within the normal variation for 8 inch pots, the instantaneous rate just prior to the first shutdown of PC-6 was 10.4 liters/hr (at 14 hours) compared to 18.2 and 19.3 liters/hr (at 14 hours) for PC-3 and PC-5, respectively. The lower rate in PC-6 indicates that the pot was prematurely full at the first shutdown. When the pot was filled later, only 1.2 equivalent tonnes of calcine could be placed in the pot. The boiling properties of the waste could have caused the low capacity of the pot and the low feed rate. Another possible explanation for the apparent loss in both rate and fill capacity is the high internal-power generation in the solids which may have caused a more porous solid deposition on the pot wall. The presence of porous solids was substantiated by an apparent decrease in the effective thermal conductivity of the final calcined solid for PC-6. Further runs are required to determine the effects of internal power on processing rates.

Figure 4.1 shows the feed rates and feed consumption curves for typical 8- and 12-inch pot runs. At the start of a run, the feed was set at the maximum rate. Net power to the furnace was set to boil off the feed at a slightly higher rate than the maximum input so that approximately four of the six pot zones became filled with boiling waste. When the waste in these four zones became concentrated, scaling and calcination began on the pot wall. This decreased the heat transfer through the wall. As a result, the boil-off rate decreased and the level in the pot increased to the normal operating level in Zone 1. The feed rate was then decreased to maintain the desired operating level. Generally, the feed was turned off when the average feed rate had decreased to approximately 5 liters/hr. As shown in Figure 4.1, the feed was turned off early for the 8 inch pot and was drawn out to 2 liters/hr for the 12 inch pot run.

In ORNL engineering development run, the initial feed rate was kept as high as the heat transfer would allow. Feed rates in DVT and WSEP runs were controlled to limit

FIGURE 4.1. Typical WSEP Pot Processing Rates

the vapor velocity in the pot to approximately 1.15 ft/sec. Although limits were placed on initial boil-off in WSEP runs, overall rates were similar to ORNL experience because the initial boil-off stayed high longer before calcine deposition occurred. Thus, overall rates in ORNL and WSEP runs were similar as shown in Table 4.3.

TABLE 4.3. Engineering Development and WSEP Rate Comparisons

	ORNL Laboratory Development	PNL Hot-Cell Experiments	ORNL Engineering Development	PNL Design Verification Tests, DVT	PNL WSEP
Pot size	4 in. diam by 1 1/2 ft long	5 in. diam by 13 in. long	8 in. diam by 8 ft long	8, 12 in. diam by 8 ft long	8, 12 in. diam by 8 ft long
Average feed rate, liters/hr	~4	2-5	~30	14-28	18-25
Calcining, cooling time, hr	~3	4-12	10-30	9-15	8-33
Overall processing rate, liters/hr	~3	1.5-2	12-15	11-16	12-14

During ORNL development of pot calcination, a deposit of solids was observed along the vertical walls of the pot. The deposit grew radially toward the center as the run progressed. A deposition model⁽²²⁾ showed that, in the absence of internal power generation, the average processing rate per unit length of vessel during the feeding period is independent of vessel radius. The fact that actual feed rates were largely independent of pot diameter confirmed that solids deposition was predominantly radial. Although there were differences in the Purex waste compositions, concentrations, and boiling characteristics, the processing rates were of the same magnitude in all large equipment.

Overall processing rates (i.e., feeding, calcining and cooling) are increased by internal power generation because cooling must begin before feeding stops. By reducing the pot wall temperatures to keep internal temperature ≤ 900 °C during feeding, the pot wall approaches its final out-of-furnace temperature while the center of the pot is calcining. Consequently, a higher average processing rate results. The maximum rate is achieved when the pot wall has

already been cooled sufficiently that the pot can be removed from the furnace (425 °C) by the time that calcination is completed in the center of the pot. If cooling is defined as the time from feed-off to pot-cooled, the actual hours for cooling in WSEP was reduced from greater than 15 hours to approximately 8 hours by the presence of internal power in an 8 inch diameter pot.

The effect of internal power on processing rates was not as large as expected. Analysis of the amount of waste fed to a pot at the time of wall scaling, as shown in Figure 4.2, revealed that the pot wall scaled earlier in runs with higher internal power. Scaling was determined by a rapid increase in the wall temperature at the two bottom zones of the pot. Normally, without internal power, scaling reduces the amount of heat which can be transferred from the furnace into the pot and the processing rate decreases. However, the processing rates were maintained by the presence of internal power to just offset the loss in rate by earlier scaling. Thus, there was essentially no effect on processing rates by internal heat other than the cooling period discussed above.

4.2 RADIONUCLIDE HEATING EFFECTS

Age and Temperature Maximums

Since high concentrations of radionuclides in solidified waste produce high internal temperatures even when the pot is cooled, the maximum allowable temperatures must be known. The temperatures are dependent on the concentration of fission products in the solid, the age of the waste, the container size, the thermal conductivity of the solids, and the environment in which the container is placed.

A set of maximum allowable temperatures has been chosen for WSEP to (1) limit the calcine temperature to 900 °C, and (2) limit the container wall to a maximum temperature of 425 °C. The 900 °C maximum center temperature prevents volatilization of material from the pot and reduces corrosion of the special well

FIGURE 4.2. Effect of Internal Power on Wall Scaling

used for internal thermocouples in the WSEP. (Presumably the well will not exist in production models of the pot.) The 425 °C wall temperature prevents excessive air oxidation of the container and allows normal remote handling of the pot without the need for special precautions.

The temperatures caused by internal power are listed in Table 4.4. During the series of six pot calcination runs in the WSEP, the temperature maximums were approached in steps by increasing the internal power in each run until, in Run PC-6, the power value was 85 W/liter of solids. Special control of the furnace was required.

TABLE 4.4. Temperatures Caused by Internal Power

Run	Pot Diam, in.	Waste	Total Power, W	Cake ΔT , ^(a) °C	Centerline Temperature, °C
1	12	PW-2	600	70	140
2	12	PW-2	1700	235	485 ^(b)
3	8	PW-2	1800	220	410 ^(c)
4	12	PW-1	2600	312	477
5	8	PW-1	4300	495	725
6	8	PW-2	5100	700	940

(a) Temperature difference taken for hottest zone (usually Zone 4). Pot cooled by natural convection and radiation in cell except Runs PC-2 and PC-3.

(b) Pot in receiver furnace at equilibrium.

(c) Pot in furnace with cooling air on. Furnace susceptor at 90 °C.

Furnace Control

In prior work, three separate mathematical analyses were made on the effects of radionuclide power generation on processing rate and the control of temperatures inside the pot. Perona⁽²²⁾ estimated that the time required to fill a 12 inch diameter pot with

solids from Purex waste would be decreased from 78 hours to 55 hours as the power generation in the final solids increased from 0 to 50 W/liter. However, he also pointed out that the temperature of the solids with 50 W/liter of internal power would subsequently exceed the 900 °C if some cooling of the pot was not done during calcination. Holmes⁽²³⁾ devised a program for cooling the pot wall to prevent excessive temperature rise during calcination. He showed that this might be done by holding the pot-wall temperature at 900 °C for about 1 hour, and then cooling the wall at rates dependent on the internal power-generation rate and average thermal conductivity.

Jury⁽²⁴⁾ proposed a more sophisticated program. The pot wall is kept at 900 °C until no further heat transfer through the pot wall to the calcine occurs. Then the pot is cooled in such a manner that a "thermal wave" moves through the cake with a temperature no greater than 900 °C.

In WSEP runs, a major objective was to calcine at a pre-determined temperature (900 °C for PW-1 and 850 °C for PW-2) and at the same time avoid excessive temperatures caused by internal heating. Temperatures greater than about 900 °C are known to cause excessive corrosion of containers and volatilization of sulfate and oxides of ruthenium, and cesium from the calcine. Melting of compositions high in sulfate can occur. The anticipated "heat wave" due to internal heating was noticeable in PC-2 and was distinctly evident in all other runs. In other words, at some point in the run, the internal pot temperature exceeded the pot wall temperature which, in turn, exceeded the furnace temperature. Temperature "overshoot" was controlled successfully by a manual reduction of furnace temperatures. The general procedure was as follows:

1. Partial reduction of furnace temperature in individual zones, when the pot wall temperature was nearly equal to the furnace temperature.

2. Partial reduction of furnace temperature when the "heat wave" reached intermediate thermocouples (in PC-6 run the zone was cut off completely).
3. Complete furnace shutdown in a zone when the centerline was dry (temperature ≥ 600 °C). (For small diameter pots, this step will be reached before Step 2. Step 2 is not needed if Step 3 is reached first.)
4. Turn on cooling air when centerline temperature reaches 800 °C.

The manual reduction of temperature in individual furnace zones was both practical and satisfactory but not totally optimized. It did not allow a direct comparison with the more automated approach by Holmes or Jury.^(23,24) Temperature transitions within the cake, or the thermal wave, were not as severe as predicted by their analyses (possibly because the heats of dehydration and decomposition of the salts were neglected in computing the power required to raise the temperature of the solids to 900 °C).

The Holmes analysis applied to PC-5 predicted a maximum cake temperature of 950 °C if the pot wall had been cooled from 900 to 650 °C in 1.1 hours. Actually, a 900 °C maximum temperature was maintained by cooling the wall from 900 to 700 °C in 1 hour.

The Jury program, applied to PC-5, indicated the wall temperature should be reduced to 600 °C within 3 hours after termination of feeding. Actually, in the bottom three zones, it was reduced to 700 °C, 13 hours before feeding was stopped. Perona's analysis⁽²²⁾ applied to PC-6 predicted a solids temperature at 1200 to 1400 °C if the furnace and pot wall temperatures were not reduced during the run.

In actual practice, when no thermocouples are present in the pot, the entire operation will require programming on the basis of the power content of the feed delivered to the pot and the general power requirements of each furnace zone. If programmed

properly, the calcining and cooling period may be shortened to where the pot will be ready for removal from the furnace very shortly after the feed is shut off.

Run PC-5 is an example of temperature control with a high internal power. Figure 4.3 is a schematic of pot thermocouples. Zone 4 temperatures during run PC-5 are shown in Figure 4.4. During the first 16 hours the furnace was on, 4 kilowatts of heat was used in Zone 4 and the furnace temperature controller was set at 900 °C. After 4 hours, the pot wall scaled and at 16 hours, the pot wall temperature increased to 875 °C. At this time, the furnace control point was reduced to 700 °C. Feed to the pot was shut off at 28 hours. About 3 hours later, the first indication of a "heat wave" was seen. The pot wall temperature was definitely greater than the furnace temperature and the intermediate calcine temperature started to rise. The furnace was turned off and the cooling air to all zones was turned on at 36 hours. But, the "heat wave" continued as expected and peaked 2 1/2 hours later at 910 °C. When all of the temperatures were below 900 °C (39 hours), the cooling air was shut off and the pot temperatures were allowed to come to steady state with the pot in the furnace. Maximum temperature inside the pot was 940 °C (briefly, Zone 2 at its peak). The relationship of furnace control changes and the response of the furnace and pot are illustrated on a multichannel plot in the Appendix, (Figure 9.2). The response of each zone was timely and orderly.

Temperature control for the maximum temperature and maximum internal power run (PC-6) was adequate but the limit of the furnace cooling system was reached while one blower rated at 275 scfm was being used. Natural cooling of the pot (natural convection in cell air) gave 50 °C lower pot wall temperatures than could be obtained by cooling the outside of the furnace susceptor with an air blast.*

* Air blasting inside the susceptor was available but was not used.

FIGURE 4.3. Pot Calciner Thermocouple Arrangement

FIGURE 4.4. Zone 4 Temperatures During PC-5

4.3 WASTE VOLUME REDUCTION AND POT CAPACITY

Volume Reduction

Because of large variations in the chemical composition of the waste processed during calcination, an approximation was used to predict the volume of feed required to fill a pot. The weight of oxides required to fill a pot was calculated from the volume of the pot and an assumed density of the calcine. The weight of oxides was used to calculate the volume of feed necessary to fill the pot since the quantity of oxides per unit volume was known from the feed composition and the amount of additives.

Actual numbers in WSEP runs gave reasonable agreement when a value of 1.4 g/ml was used for calcine density (see Table 4.5). Sixty and 120 liters of solid was assumed in 8 and 12 inch diameter pots, respectively. (All prior ORNL and PNL work produced calcine densities from 1.2 to 1.5 g/ml.) Estimates of the volume of waste that could be converted to a calcine were normally in good agreement with run observations. There was enough variation in the quantity of oxides and additives that a direct volume reduction factor had little significance even if volumes of waste were all corrected to 100 gal/tonne. (For example, volume reduction factors for the six runs varied from 7.7 to 9.0.)

Solids Capacity

The trend in the six WSEP runs (Table 4.6) for 12 inch diameter pots was a slight increase in equivalent tonnes with increasing internal heat and for 8 inch pots, a decrease in equivalent tonnes with increasing internal heat. However, these data represent two feed types with considerable variation in chemical composition. For example, feed for PC-1 contained a higher sulfate concentration than for the other three PW-2 runs. Consequently, it required more additives and had a 14% greater calculated oxide weight per liter of feed than for any other PW-2

TABLE 4.5. Calcine Densities and Waste Volumes

	Run	Waste Type	Calculated Oxide Weight, (a) g/ml	Expected Volume (a,b) of Feed, liters	Actual Volume (a) Feed, liters	Calculated Density, (c) g/ml
8 in. pot	PC-3	PW-2	0.145	580	553	1.43
	PC-5	PW-1	0.167	502	515	1.43
	PC-6 (d)	PW-2	0.159	528	460	1.33
12 in. pot	PC-1	PW-2	0.195	852	850	1.26
	PC-2 (e)	PW-2	0.148	1130	940	1.18
	PC-4	PW-1	0.167	1006	1060 (f)	1.38

(a) Based on feed concentrations used in each run.

(b) Calcine density of 1.4 g/ml assumed to calculate the volume of feed required at the feed concentration used.

(c) Based on actual net weight, a volume of 60 liters was used for 8 inch pots and 120 liters for 12 inch pots. Actual fill volume is somewhat less because of the conical crater at the top of the calcine surface.

(d) High thermal content and multiple startups may have produced lower density.

(e) Pot not completely filled. Feed source was depleted.

(f) 60 liters expelled from pot during processing.

TABLE 4.6. Capacity of a Pot

Run	Pot Size Diameter, in.	Total Internal Power, W	Product Weight, kg	Equivalent tonne/pot
PC-1	12	600	151	2.2
PC-2	12	1700	141	2.3
PC-3	8	1800	86.4	1.4
PC-4	12 (a)	2600	166	2.8
PC-5	8 (a)	4300	86	1.25
PC-6	8	5100	79.5	1.2

(a) PW-1 waste (all others were PW-2).

run. The calcined solids capacity of a pot was 1.4 to 1.8 cubic feet of pot volume per equivalent tonne of uranium for both PW-1 and PW-2.

4.4 VOLATILIZATION OF RUTHENIUM FROM THE POT

The six pot calciner runs were intended to characterize the behavior of ruthenium. Ruthenium, volatilized during calcination, must be totally recycled to the pot calciner or it must be treated for disposal in separate operations. The only other alternative is storage of effluents until the ruthenium decays to innocuous levels. Recycle results with ruthenium have been encouraging; but more definitive experiments are needed.

Early laboratory work indicated that from 5 to 30% of the ruthenium would volatilize from the pot during the calcination step.^(18,20) Bench-scale tests indicated volatilization of 20%.⁽¹⁵⁾ This was corroborated during the WSEP runs. As predicted, most of the ruthenium was evolved during the latter part of the feeding period and during the drying-calcination period when nitrate concentrations and temperatures were highest.

Ruthenium eluded a rigorous analysis of cause and effect in WSEP as expected. General trends were evident for volatilization from the pot; however, not enough runs have been completed at this time to delineate predominant effects nor to assess the behavior of recycle under continual operation. Less evolution of ruthenium was experienced for:

- Closed loop recycle to the evaporator
- PW-1 waste
- Earlier scaling of the pot wall.

Apparently, feed temperature and feed rate had no effect on ruthenium volatilization.

Because PW-1 waste, and closed loop recycle (Mode C) were involved in the same two runs (PC-4 and PC-5 as shown in Table 4.7)

TABLE 4.7. Ruthenium Volatilization from the Pot Calciner

Run	Pot Size, in.	Feed Type	Feed Temp, °C	Operating Mode ^(a)	Fraction of Feed Consumed at Wall Scaling	Feed Concentrations, M ^(b)					Total Ruthenium Volatilized, % ^(c)
						Fe ⁺⁺⁺	Al ⁺⁺⁺	SO ₄ ⁻⁻	NO ₃ ⁻	Ru	
PC-1	12	PW-2	30	A ^(d)	0.59	0.445	0.02	0.87	~5.4	0.0032	14
PC-2	12	PW-2	30	B	0.59	0.224	0.224	0.618	~5.4	0.0032	30
PC-3	8	PW-2	70	A-Mod ^(e)	0.43	0.074	0.388	0.623	~5.4	0.0032	31
PC-4	12	PW-1	<70	C	0.24	0.82	0.11	0.26	~6.5	0.0032	5
PC-5	8	PW-1	50-60	C	0.17	0.8	0.13	0.35	~6.5	0.0032	3
PC-6	8	PW-2	35	A	0.35 ^(f)	0.094	0.35	0.62	~5.4	0.0064	13 ^(f)

(a) See Operating Modes (Section 5.1) for definition.

(b) All molarities are at 378.5 liters/tonne. See Appendix for feed concentrations in the feed tank or evaporator.

(c) Percent of total ruthenium fed to the pot, which was found in the total condensate from the pot no matter where or how the condensate was handled.

(d) Reflux routed separately.

(e) Pot condensate caught in tank (not in evaporator) and noncondensable vapor passed through evaporator.

(f) Run was shutdown and restarted due to pump failures; Data is through first shutdown only including the calcining-cooling cycle.

individual effects cannot be adequately analyzed at this time. Notably, the net ruthenium volatilization was 5% or less for the combination of PW-1 and closed loop recycle. Table 4.7 lists ruthenium volatilization along with major variables that could affect its volatilization. Except for PC-6, better ruthenium retention occurred in runs with a high iron-to-ruthenium ratio in the feed. Conversely, a high sulfate to ruthenium ratio gave poor ruthenium retention except for PC-1. Also, except for PC-1, there was better ruthenium retention when early scaling of the pot wall occurred (Table 4.7). The low volatilization in PC-1 was probably due to deposition of ruthenium on process equipment (PC-1 was the first radioactive run in the WSEP).

Ruthenium concentration was monitored in the condensate from the self-cleaning vent line. In all runs, approximately 10% of the volume evaporated from the pot was refluxed and routed to a separate tank or to the evaporator. The condensate was drawn off at the base of the off-gas line just before it entered the pot. During run PC-1, in which the stream was isolated, it contained approximately 33% of the total ruthenium evolved from the pot during the entire run. Most of this evolution occurred late in the run when the overhead condensible vapor velocity to the condenser was low. For instance, after 60% of the feed was processed, only 5% of the total ruthenium evolved up to that time was in the reflux condensate.

Figure 4.5 shows ruthenium volatilization as a function of the quantity of feed added. It is similar to data obtained by Allemann.⁽¹⁵⁾ Generally, after feeding stopped and calcining continued, the accumulation of ruthenium was close to a straight line extrapolation on a semi-log graph.

Other general ruthenium observations were:

- The behavior of nonradioactive ruthenium was identical to the behavior of the radioactive species, ^{103}Ru and ^{106}Ru . Although the total amount of ruthenium in the runs was only 10 to 20% of a nominal 1 year old waste, it was sufficient to

FIGURE 4.5. Cumulative Ruthenium in the Pot Condensate

conclusively show that nonradioactive ruthenium can be used in combinations with radioactive ruthenium to represent actual ruthenium concentration in wastes from 20,000 MWd/tonne at 15 MW/tonne fuel.

- The mole ratio of ruthenium (volatilized plus entrained) to cerium in the pot condensate increased greatly after wall scaling occurred. However, the earlier this scaling occurred, the less total ruthenium was volatilized.
- The volatilization of ruthenium per unit time was nearly constant when operating with recycle from the evaporator and a PW-1 waste. For PW-2 and no recycle, the volatilization of ruthenium (grams of ruthenium volatilized per gram of ruthenium fed per unit time) continued to increase as the run progressed.

Multiple startups and shutdowns apparently did not adversely affect the volatilization of ruthenium. During the first shutdown of PC-6, 13.5% of the ruthenium delivered to the pot volatilized. After the third shutdown, when the pot was full, 12.1% of the total ruthenium delivered to the pot had volatilized.

4.5 ENTRAINMENT AND OFF-GAS RADIONUCLIDE CONTROL

Entrainment from the pot and from the evaporator during the WSEP runs was about the same as had been observed in previous work. Cumulative DF's from feed to pot condensate of 100 to 300 were typical. Entrainment from the pot is considered relatively unimportant as long as it does not markedly affect the overheads from the downstream evaporator, or create a potential for plugging the calciner vent line. Typically, cumulative DF's of 100 to 1000 were obtained in both ORNL engineering development and PNL hot cell experiments. The ORNL DF's were with initial maximum boilup rates of 60 liters/hr in 8 inch diameter pots. In the Design Verification Tests, DF's from 200 to 4000 were obtained by limiting initial rates to 25 liters/hr in 8 inch diameter pots.

Entrainment from the pot was between 0.29 and 1.2% of the total nonvolatile activity in the feed to the pot. The higher entrainment reflects pot operation with a high liquid level. Normally, values of approximately 0.3 and 0.5% can be expected for 8 and 12 inch pots, respectively, when the boiloff rates are limited to 25 and 50 liters/hr, respectively (superficial vapor velocity of 1.15 ft/sec in either size pot). In Figure 4.6, the effect of boiloff rate on entrainment from the pot is shown for all six pot runs. Although the data have considerable scatter, greater entrainment obviously occurred at higher boiloff rates. Figure 4.7 is a typical plot of the accumulation of radionuclides in the pot condensate during an 8 inch run (PC-3) and shows similar results for the isotopes $^{95}\text{Zr-Nb}$, ^{137}Cs , and ^{144}Ce .

Entrainment from the pot is more extensive if foaming or overfilling occurs. (A pot is overfull if the liquid or foam level is above the midpoint of the top furnace zone of the pot.) Rapid reductions in feed rates, when operating at a high liquid or foam level, can cause an excessive level. Normally the entering feed tends to suppress swelling of the liquid contents in the pot. During run PC-4, approximately 5% of the activity in the feed to the pot was expelled because of foaming. During run PC-6, 1.2% was expelled primarily because the liquid level became too high. Reductions in the pot feed rate were not made soon enough during manual control of the rate. If a waste is prone to foam, experience shows that expulsions from the pot can be prevented by maintaining a sufficient freeboard in the pot during the high boiloff portion of the run (approximately 4 feet in an 8 foot pot). More stable wastes can be operated near the normal fill level of 6 feet without difficulty.

Entrainment was not influenced by in-leakage of air since in-leakage did not add significantly to the vent line vapor velocity. A 1 liter/hr boilup rate is approximately 1 scfm of vapor. In-leakage of air into the WSEP process vent system during a pot run

FIGURE 4.6. *Entrainment from the Pot Calciner
Versus Vapor Velocity*

FIGURE 4.7. Cumulative Nonvolatile Radionuclides in Pot Condensate

was normally 1 to 2 scfm. In-leakage at the pot gasket was normally nil; however, as much as 10% of the system in-leakage could have occurred at the vent line sight glasses.

4.6 CONTROL OF OTHER VOLATILES - SULFATE AND TECHNETIUM

The technique of using alkalis* and alkaline earths* to suppress the volatility of sulfate during the calcination of sulfate-bearing waste was used during early laboratory development and during engineering demonstration.⁽²⁰⁾ In numerous tests, sulfate volatilization did not occur (i.e., amounts greater than entrainment of nonvolatiles) as long as the sulfate was balanced with alkali and alkaline earths. Ironically, the oxides of sodium and cesium were also found to be volatilized at calcination temperatures in the absence of a sufficient amount of nonvolatile anion. It was discovered^(18,20,25) that alkalis were not volatilized at 900 °C if the ratio

$$\frac{\text{chem. equiv. alkalis}}{\text{chem. equiv. } (\text{SO}_4^{-2} + \text{PO}_3^-)} \leq 1.0 \quad ,$$

and that sulfate was not volatilized if the ratio

$$\frac{\text{chem. equiv. (alkali + alkaline earths)}}{\text{chemical equivalents sulfate}} \geq 1.1^{**} \quad .$$

To satisfy these relationships, chemical additions were used in the processing of both PW-1 and PW-2. Sulfate was added in the PW-1 runs to suppress alkali metal volatilization, and sodium ions and/or calcium ions were added to the PW-2 high sulfate wastes. Sodium ions were used as the additive to suppress sulfate whenever permissible. However, to satisfy both of the above relationships, some alkaline earth addition was required. Calcium is preferable to magnesium as the alkaline earth additive.^(20,25,26)

* The term *alkalis* in this report is used to represent the presence of an alkali metal ion irrespective of the compound in which it exists. The term *alkaline earth* represents the presence of an alkaline earth ion irrespective of the compound in which it exists.

** The excess 0.1 should be as alkaline earths.

In DVT and radioactive runs, the additives for adjusting the waste to retain sulfate were sometimes successfully divided between sodium and calcium. Evolution of cesium from the calciner was also held to the same value as entrainment of nonvolatile species (Figure 4.7) by keeping the desired sulfate (or more properly the nonvolatile anions) to alkali metal ratio.

Since internal pot temperatures become high during the calcining period, this is a critical period for sulfate volatilization. At this time, the off-gas is generally not diluted by other vapors. Severe corrosion, especially of titanium, can occur as the vapors condense. For this reason, a 5 kg/hr steam spray was added to the titanium condenser to serve as a dilutant-sweep during all pot calcining periods.

Complete data were not taken on sulfate volatilization during WSEP tests because prior work was conclusive and no new information could be obtained relative to radioactive performance. The only indication of volatilization during the six WSEP runs was a visual indication of SO_3 (in PC-2) during the calcining period. A "white fog" was observed in the off-gas. (The same observation was made during the two DVT runs when sulfate volatilization occurred.) The volatilization was caused by a lower than desired sodium concentration in the waste feed, but the sulfate evolution was not great enough to produce significant corrosion. Less than 0.5% of the total sulfate was volatilized or entrained during this period.

The volatilization of technetium from the pot calciner was determined during one run (PC-6). Four percent of the total technetium in the feed to the pot was found in the pot condensate. Although this was 3.4 times greater than the percent of nonvolatiles entrained from the pot, it was a factor of 2.7 less than the percent of ruthenium volatilized. Technetium should pose no problems as long as its volatilization is in this range.

4.7 GENERAL PERFORMANCE

Performance of the processes and equipment was excellent. General items which influenced performance of the process and significant experiences with operation of the pot calciner equipment are discussed below.

Waste Composition Effects

During WSEP pot calcination of highly radioactive liquid wastes to solids, a minimum of processing problems occurred. Two runs with PW-1 and four runs with PW-2 demonstrated performance with acidic Purex type wastes. In the two PW-1 runs, foaming during feeding was found to be a potential problem. However, it is not considered serious since expulsions from the pot were prevented by maintaining approximately one half of the 8 foot pot for freeboard during the initial high boiloff portion of the runs. The PW-2 waste did not foam during feeding and, except for run PC-6 in which the pot was slightly overfilled, no difficulties were encountered in its concentration and calcination.

Waste feed compositions for the six runs, as well as other pertinent data on the feeds, are listed in the Appendix, Table 9.3 and are summarized in Table 4.8. Waste feeds were prepared using actual Purex 1WW and $^{144}\text{Ce-Pr}$ solutions, to provide the desired internal power in the calcine. However, because the stock solutions contained excess sodium and aluminum, the composition of PW-1 and PW-2 feeds varied from the desired composition. After necessary chemicals were added, the actual feed compositions of PW-1 and PW-2 were quite similar as shown in Table 4.8. Overall, the only significant operating differences between the two wastes was foaming in PW-1 and troublesome solids in PW-2.

The two PW-1 feeds contained 3 to 5 times more sodium than the desired 0.14M. Consequently, it was necessary to add sulfate and the intended sulfate-free PW-1 became 0.3 to 0.4M in sulfate. Feed compositions for PW-2 varied for two reasons: (1) the excess aluminum in the Purex 1WW was used as a partial substitute for

iron, and (2) the sulfate concentration was reduced from 0.87 to 0.62M to avoid caking and plugging problems caused by excess rare-earth solids in PW-2 feed.

TABLE 4.8. General Feed Composition Ranges^(a)

<u>Constituents</u>	<u>Nominal PW-1</u>	<u>Actual PW-1</u>	<u>Nominal PW-2</u>	<u>Actual PW-2</u>
H ⁺	3.7	2.6	3.9	4.2
Na ⁺	0.1	0.5 - 0.6	0.9	0.8 - 1.1
Fe ⁺⁺⁺ (b)	0.9	0.8	0.4	0.1 - 0.4
Al ⁺⁺⁺ (b)	0.001	0.1	0.001	0.2 - 0.4
SO ₄ ⁻⁻	0.00	---	0.9	0.6 - 0.9
NO ₃ ⁻	7.5	~6.5	5.4	~5.4
<u>Additives</u>				
Ca ⁺⁺	---	---	0.3	0.1 - 0.3
Na ⁺	---	---	0.3	0.1 - 0.3
SO ₄ ⁻⁻	0.1	0.3 - 0.4	---	---

(a) All values are quoted @ 378 liters/tonne and rounded to a significant digit. PW-1 was concentrated and fed from the evaporator to the pot. PW-2 was fed from feed tank.

(b) Fe and Al were always adjusted to maintain a constant Σ of Fe and Al.

Chemical additives were combined directly with the feed except in PC-1. In PC-1, the first PW-2 run, the additive was successfully added as a separate stream to the pot in proportion to the feed added. Addition as a separate stream is desirable when additives cause troublesome solids in the feed. Since laboratory tests showed that additives did not substantially change the type or amount of solids already in the feed, chemicals were added directly to the feed in all runs except PC-1.

Compilation of nearly all of the run data pertinent to the six pot runs is given along with definitions in the Appendix, Table 9.1.

Foaming

The composition of the wastes and the feed makeup procedures used in the six WSEP runs varied significantly; therefore, a preliminary boildown of each waste was completed in a beaker before any run was started. The objective was to learn if there was any qualitative measure which could be applied to predict the successful processing of a particular waste. A qualitative measurement of the tendency to foam was sought.

When unconcentrated feed solutions are boiled, the vapor bubbles break quickly. As the solutions become concentrated and the viscosity increases, the bubbles become more stable and the tendency to foam becomes greater. In laboratory batch boildowns of a series of different waste solutions, foaming was not observed in any waste until the boiling point reached 125 °C.

Swelling caused by foaming normally gave no operating problems during calcination if rapid decreases in feed rate were avoided. However, during DVT run CPC-2⁽¹⁶⁾ and WSEP run PC-4, foaming was encountered. It was so severe that expulsion of feed from the pot through the safety overflow system occurred. The reason for the severe foaming in these two runs is not precisely known. The feed solutions were quite different. CPC-2 feed was low in iron, high in aluminum and fission products, and did not contain sulfate. PC-4 feed was nominally PW-1, but it contained excess sodium, aluminum, and sulfate. Although the feed compositions were substantially different in the CPC-2 and PC-4 runs, the behavior during the severe foaming occurrences was very similar. In both, buildup of foam, almost amounting to an eruption, occurred at about the time calcine deposition or scaling began at the pot wall. Laboratory experiences suggest superheating was the cause of these eruptions.

Progressively more complex procedures were used in the laboratory to investigate the foaming problem. Initially, the foaming test used involved boiling waste in a 100 milliliter Pyrex breaker.

A preheated hot plate was used to boil the waste to dryness in 15 to 20 minutes. This technique showed that foaming tendency was definitely a function of waste composition. The waste composition used as feed in DVT run CPC-2, when simulated in the laboratory, foamed more severely than any of eight other compositions tested. General conclusions from the beaker foam tests were:

- The presence of sulfate tended to decrease foaming.
- Solutions initially containing 6.8M HNO_3 foamed more readily than solutions containing 3.7M HNO_3 .
- Aluminum concentrations above 0.5M tended to aggravate the foaming tendency.

Even though the boildown test indicated very little foaming tendency for PC-4, foaming occurred. Therefore, the laboratory foam test procedure was revised to duplicate more closely the physical conditions in the pot calcination process. Simulated PC-5 feed was evaporated to dryness in a long glass tube heated through the walls. Although sulfate was not added in the test, the results were informative. Boildown proceeded smoothly, with very little foam formation, except for two eruptions which occurred at concentration factors of 2 and 2.8. The two eruptions were associated with superheating and the familiar bumping phenomenon. In both cases, although heat input remained constant, there was a significant decrease in rate of condensate collection for 5 to 10 minutes prior to the eruptions. In a final foam test, simulated PC-5 feed was added continuously to the long glass tube during boildown. The steady state foam level in this test was much higher (roughly 2 inches in a 2 inch diameter tube) than in the previous test but no eruptions occurred.

To be most valid, pretesting techniques for pot calcination feed solutions must closely approximate process conditions. Simple batch boildowns can be misleading but severe foaming can be detected. For this reason, before each WSEP run, 20 milliliters of actual feed were boiled in a 50 milliliter crucible. The

crucible was placed in an aluminum heat distributor to give uniform heating and the sample was boiled to dryness on a laboratory hot plate. Boiloff rate in the crucible tests was about 0.07 ml/min/cm^2 of surface compared to 0.03 ml/min/cm^2 in an 8 inch pot. Qualitatively, if the waste boiled to dryness without expanding to more than twice the liquid volume, it was considered satisfactory for pot calcination.

Foaming occurred during PC-4 despite satisfactory boildown in a crucible before the run. The run was salvaged by reducing the feed rate to the pot. This allowed more freeboard for foaming. Since foaming was also possible in PC-5, close control of the feed rate was maintained. PC-5 was completed satisfactorily without severe foaming difficulties, although indications of foaming were evident during the run.

Foaming did not occur with PW-2 waste in any of the WSEP runs.

Liquid Level Control in the Pot

Keeping the liquid level in a pot at 6 feet is desirable but not always practical during the feeding period. Keeping the pot full of liquid effectively uses the maximum heat transfer surface. Two methods of liquid level detection and control were used (Figure 4.8). In one method, based on an ORNL development, a thermocouple probe detected liquid level by changes in temperature. The probe was heated radiantly by the hot walls of the pot, but the probe was cooled when contacted by boiling liquid (or foam). 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.

Both "weight factor" and "thermal" probes were used at ORNL and in WSEP. At ORNL, the thermal probe gave more satisfactory service and was particularly suitable for automatic control. The weight-factor probe plugged frequently. Blowing with air was only partly successful in unplugging the line.

FIGURE 4.8. Pot Liquid Level Control

Automatic control of most WSEP runs was successful with the thermal level probe. However, during two of the six runs, the probe became insensitive to changes in solution level and the "backup" weight factor probe was used to manually control the feed rate. Although the weight factor showed liquid level satisfactorily, manual adjustments were not made soon enough on one occasion and the pot was overfilled. The weight factor probe in WSEP runs operated satisfactorily and was reliable in the five runs where it was used. Plugs were mostly eliminated by using a continuous steam purge in addition to the normal air flow.

In the WSEP runs, the weight factor probe was normally the same length as the thermal probe but response did not indicate the same liquid level. Operation of the thermal probe at a minimum temperature of about 250 °C produced no indication of liquid on the weight factor probe. Whenever a weight factor indication existed, the thermal probe read the solution boiling temperature. During PC-2, the weight factor probe was extended 3 inches. The solution level was still below the weight factor probe during normal operation of the thermal probe. The weight factor probe was intended to serve only as a secondary indication of liquid level since it is rather insensitive to foam. Weight factor was particularly useful during the last 8 hours of operation when the thermal probe often became insensitive. Successful functioning of the weight factor probe during the last part of a run is partially attributable to the fact that it was not in the solution during most of the run. So far in WSEP, both devices were used to assure proper liquid level in the pot. It is possible that the performance of the thermal probe can be improved by positioning it such that it does not contact incoming feed.

Vent Line and Fill Head Assembly

The calcine pot fill head (Figures 4.9 and 9.3) is essentially a single manifold fitted with off-gas, feed, chemical addition, pot pressure, and vent connections for the pot head.⁽⁶⁾ When the pot

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. H₂O

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 ft²

FIGURE 4.9. Pot Calciner Self Cleaning Vent Line and Fill Head Assembly

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 connectors.

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 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 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 15 to 30 liters of water after a new pot was installed for the start of the next run. Visual inspection of the pot throats and detailed inspection of the equipment following the six runs disclosed no deposit of solids; the flushing procedure was apparently effective.

After the six 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; one of the sight glasses on the view-port in the upper section of the line was relatively clean; the other was coated with a dark film. The darkened glass had been in use during all six runs while the clear glass was used only during the final three runs.

As shown in Figure 4.9, the pot fill head contained sufficient nozzles for separate chemical addition to the pot and for monitoring either the pot pressure or level (weight factor).

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 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 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 line shortly after any occurrence of an excessive pot operating level. After run PC-6, the inlet to the pot calciner safety-relief seal pot was nearly plugged, presumably as a result of a high operating level during PC-6. Historically, the line was apparently clean, as evidenced by the pressure readings and by visual inspection before runs PC-2 and PC-4. Because of the expulsion in PC-4, the inlet to the seal pot was

inspected and mechanically cleaned and washed before PC-5. The exit line of the seal pot was always found to be clean.

Pot Furnace

The six zone induction-heated calciner furnace (See Appendix, Figure 9.7), 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. 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 4 and 8 net kilowatts for 8 and 12 inch pots, respectively.

Cooling by forced air around the outside of the susceptor was sufficient for the six 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). This was shown by PC-6 pot wall temperatures. They dropped approximately 50 degrees when the pot (containing 5100 watts of radioactive power) was transferred from the furnace (using cooling air) to the ambient air in the cell.

Most of the runs at ORNL were made using a six-zone electrical resistance furnace. However, three calcination tests were performed with an induction unit.⁽²⁷⁾ Considerable thermal and electrical coupling between zones was observed. No significant interzone heating has been detected in the WSEP induction furnace within the reliability of power consumption data.

The pot thermocouple connector (a 20 thermocouple, Cannon[®] KPTM 00F20-41P) functioned without difficulty. Excessive

[®] International Telephone and Telegraph Corporation.

temperatures, which caused connector failures in DVT runs, were avoided by using a heat shield and by cooling the connector with air.

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 inlet to the titanium condenser to prevent corrosion at this point. After the DVT and WSEP runs, the liner was found corroded where vapor condensation occurred on the bottom edge. Maximum penetration was estimated at 40 mils at a point where the condensate dripped off into the condenser. The liner had been in place for nine DVT runs and for two other WSEP runs in addition to the six "hot" pot calciner runs.

Four corrosion coupons had been installed inside the liner in the off-gas stream. These were made of A-55 titanium, 304-L SS, 316-L SS, and Nionel.[®] Although no corrosion was apparent, a black deposit (possibly ruthenium) about 1/16 inch thick was found on the upstream side of the coupons. This deposit was easily scraped off to reveal a clean unattacked surface similar to surfaces where there was no deposit.

5.0 AUXILIARY EQUIPMENT PERFORMANCE

An important objective of the WSEP runs was to determine the effectiveness of the auxiliary systems supporting the solidification processes. In the final design of a solidification plant, equipment must be selected to assure the production of effluents acceptable for reuse or for low-level waste treatment and release to the environment. For example, slightly contaminated acid can be recycled to the chemical processing plant. Integration of similar equipment functions in the processing plant and the waste solidification process should be considered to obtain overall economy.

Process auxiliaries consist of the equipment necessary for (1) preparing feed and feeding the pot, (2) treating the pot condensate for recycle, and (3) cleaning the off-gases and recovering the acid. Effluents directly from the pot calciner require recycle through auxiliaries since generally 3 to 30% of the ruthenium fed to the pot is volatilized and 0.3 to 1.2% of nonvolatile constituents is entrained. The need to demonstrate how the condensate and acid can be recycled or otherwise disposed prompted the selection of three different operating modes.

5.1 OPERATING MODES

Auxiliary equipment can either be a part of the fuel processing plant (e.g., a plant waste evaporator and acid recovery system) or it can be operated as a separate unit independent of the processing plant. In either case, the auxiliary equipment can be coupled to the pot calciner to produce three major modes of operation--Mode A, Mode B, and Mode C (Figure 5.1).

In Mode A operation, waste was fed directly to the pot without immediate preconcentration. The pot condensate was concentrated but not recycled to the calciner feed.

FIGURE 5.1. WSEP Operating Modes

In Mode B operation, the incoming raw waste is preconcentrated to reduce the evaporation load on the pot. In this operation, one batch of waste was concentrated in the evaporator simultaneously with pot condensate while a previously prepared batch of waste was fed to the pot from a hold tank.

In Mode C operation, the pot and evaporator were operated as an integral, close-coupled unit similar to the unit developed at ORNL. Feed entered the evaporator. Bottoms from the evaporator were pumped to the pot continuously during the feeding period.

In the evaporator, the incoming raw waste was mixed and concentrated continuously with condensate from the pot.

All three modes were tested in the WSEP to determine differences in radionuclide behavior. Arrangement of equipment used for each run is given in the Appendix.

Final applications of the modes are visualized as shown in Figure 5.2. Mode C provides the simplest equipment arrangement if no factors other than solidification are considered.

In WSEP, operation of the auxiliaries consisted of condensing the overhead vapors from the evaporator and routing them to a fractionator which was used to further decontaminate the process off-gas and to recover nitric acid (potentially for reuse in a fuel processing plant). The fractionator produced a slightly acidic condensate (largely water) as a low level waste. About 75% of this stream was recycled to the evaporator to strip nitric acid and to maintain the evaporator bottoms at low acidity. By maintaining a low acidity in the evaporator bottoms and overhead, the volatilization of ruthenium from the evaporator was minimized. Off-gases not condensed in the fractionator were filtered, scrubbed, and filtered again prior to release to the atmosphere.

Performance of the auxiliary system was assessed by determining the decontamination factors at each stage in the system while using one of the three modes. Data on operating modes are presented in Table 5.1 as typical of the observed data. Fractionator condensate during Mode A operation was lower in radioactivity than during the operation of Mode B or C by a factor of at least 10. This factor varied according to the fraction of ruthenium volatilized from the calciner and according to the concentration level in the evaporator bottoms. During Mode A operation, the evaporator bottoms is a side stream which must be recycled to the fuels processing plant. In Mode B and Mode C, the evaporator bottoms are mixed with incoming waste.

FIGURE 5.2. Operating Mode Applications

TABLE 5.1. Typical Effluents^(a) Produced During Operation of the Three Modes
(Based on the First Six Pot Calcination Runs)

Operating Mode	Stream	Volume, (b) liters/ liters waste	Gross Activity (less Ru), (c) Ci/Ci in Waste	Ru Activity, (c) Ci/Ci in Waste	Potential Disposal
A	Evaporator Bottoms	0.2	$4 \times 10^{-3}(d)$	1.3×10^{-1}	Recycle to fuel processing plant waste concentrator
A	Fractionator Bottoms 10M HNO ₃	0.6	0.1×10^{-6}	3.5×10^{-4}	Recycle to plant acid system
B	Fractionator Bottoms 10M HNO ₃	0.7	90×10^{-6}	14×10^{-4}	
C	Fractionator Bottoms 10M HNO ₃	0.6	7×10^{-6}	$10 \times 10^{-4}(e)$	
A	Fractionator Overhead 0.03M HNO ₃	0.6	$1.0 \times 10^{-9}(f)$	1.7×10^{-7}	Low level treatment
B	Fractionator Overhead 0.03M HNO ₃	1.5 ^(g)	40×10^{-9}	40×10^{-7}	
C	Fractionator Overhead 0.03M HNO ₃	0.6	10×10^{-9}	2.8×10^{-7}	
A, B or C	Off-Gas	~200	$<1 \times 10^{-12}$	$<2.3 \times 10^{-9}$	

- (a) Values are from actual run data unless otherwise noted. If specific run data were not used, the best weighted value was used. Detailed data are given in the Appendix, Table 9.1. Run PC-6 data were used as representative of Mode A; Run PC-2 data were used as representative of Mode B and Run PC-4 data were used as representative of Mode C.
- (b) Because actual data were used, fractions do not add to 1.0. Volumes include other additions to system (see the Appendix, Table 9.2).
- (c) Fraction of feed activity in listed streams.
- (d) Weighted result. Value for PC-6 was 0.012 with the operating liquid level high in the pot.
- (e) Average of data for runs PC-4 and PC-5.
- (f) Weighted, observed data were a factor of 10 lower.
- (g) Includes condensate from PC-3 feed concentration.

Activity levels of condensate during Mode B operation were up to 10 times higher than during Mode C operation. This was attributed partially to a larger evaporator throughput for the Mode B run. However, there is no well identified reason why Mode B operation should produce significantly different results than Mode C for waste at the same acid concentration. Volatilization of ruthenium from the pot in WSEP runs was considerably lower for the two Mode C runs. Both of these runs were made with PW-1 waste; hence, data are not presently available for PW-2 waste using Mode C operation. Data for PW-1 waste with Mode A or B will not be available until more runs are completed.

Although there were differences in the activity in the fractionator acid and fractionator condensate produced in the three modes, the activity was high enough that further treatment will be the same regardless of the operating mode.

5.2 RUTHENIUM CONTROL

The volatile form of ruthenium is the tetroxide (RuO_4). The fraction of the total ruthenium existing as RuO_4 in a boiling nitrate solution depends on the nitrate (both acid and salt) concentration of the solution.⁽²⁸⁾ By controlling the calculated overhead concentration of nitric acid from the evaporator at less than 1.0M, volatilization of ruthenium can be suppressed. The general relationships have been summarized previously.⁽²⁹⁾ Briefly, the following trends apply.

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

- Kinetics of oxidation and reduction of ruthenium influence volatilization. In general, conversion of ruthenium to volatile RuO_4 is faster than reduction of RuO_4 to nonvolatile species.

During all six pot runs, the evaporator was operated on 4 to 8M nitric acid or acidic waste to serve as a high efficiency decontamination stage between the pot and the nitric acid fractionator. Table 9.1 in the Appendix lists most of the average operating conditions for the evaporator as well as for the other auxiliaries. Part of the data for the evaporator is repeated in Table 5.2 to show the effects of evaporator contents, overheads acid concentration, and sugar (reductant) addition on the ruthenium DF. The ruthenium DF (cumulative for an entire run) across the evaporator varied from a low of 350 to a high of 4700 under a variety of operating conditions. Overall, the ruthenium volatilized from the WSEP evaporator was only about 0.1% of the ruthenium present. This was in good agreement with data observed in the ORNL evaporator where 0.2% of the ruthenium entering the evaporator was volatilized.⁽⁶⁾

Nearly all of the ruthenium DF's can be directly related to the overheads acid concentration. By controlling the evaporator overhead acidity below 0.8M, the instantaneous ruthenium DF was equal to or greater than 1000. Actual ruthenium DF in the evaporator varied considerably but exceeded expectations, as shown by data in Figure 5.3. The ruthenium DF was as high as data in References 28 and 29 in which reductants were used to obtain improved DF. In WSEP runs, ruthenium DF was as good during Mode C operation with PW-1 waste as for wastes with sugar reductant added.

Generally, the data followed the normal trend of increasing decontamination with decreasing overhead acid except when the evaporator operation was unstable or in a transition during sampling. The best fit of data during steady-state conditions

TABLE 5.2. Ruthenium and Cerium Decontamination Factors

PC Run	Mode	Solution in Evaporator	Additive	Evaporator			Instantaneous Cerium DF(c)	Fractionator			
				Average Overhead Acidity, (a) M	Cumulative Ruthenium DF(b)	Cumulative Cerium DF(b)		Acidity of Fractionator Bottoms, M	Tower Additive	Average Overhead Acidity, M	Cumulative Ruthenium DF(d)
1	A	Nitric Acid plus Pot Condensate ^(e)	Sugar and Strip Water	0.65 to 0.25	1.2×10^3	0.02×10^4	1.7×10^4	10	---	0.04	5.7×10^3
2	B	Batch Waste plus Pot Condensate	Sugar and Strip Water	0.7 to 0.3	0.56×10^3	0.77×10^4	31×10^4	7.5	---	0.03	0.42×10^3
3	A ^(f)	Nitric Acid plus Aged Pot Condensate	Sugar and Strip Water	0.5	2.6×10^3	$>5.9 \times 10^4$ ^(g)	6×10^4	9.5	---	0.02	6.9×10^3
4	C	Continuous Feed of Waste plus Pot Condensate	Strip Water	0.84 to 0.3	0.7×10^3	15.5×10^4	70×10^4	9.6	4M NaOH	0.03	6.0×10^3
5	C	Continuous Feed of Waste plus Pot Condensate	Strip Water	0.7 to 0.5	4.7×10^3	340×10^4	$\sim 185 \times 10^4$	10.4	---	0.07	$0.2 \times 10^{3(h)}$
6(i)	A	Nitric Acid plus Pot Condensate	Strip Water	0.8 to 0.3	0.35×10^3	12.7×10^4	---	7.8	---	0.02	2.1×10^3

(a) First value was during pot feeding period. Second value was during pot drying when the evaporator was allowed to become more dilute.

(b) Total curies in evaporator at end of run/total curies gained in the fractionator. (Not identical to Appendix, Table 9.1. Explanation given there.)

(c) Instantaneous concentration in evaporator/instantaneous concentration in overhead. See Figure 5.3 for instantaneous ruthenium DF versus acidity.

(d) Total Ru curies in fractionator at end of run/total Ru curies evolved to the fractionator condensate.

(e) Part of pot condensate (vent line reflux) was caught in separate tank.

(f) Modified Mode A. Aged batch of Ru in nitric acid was fed to evaporator and pot condensate from the run was caught in a separate tank so only noncondensibles from the pot were going to the evaporator.

(g) Value assumes gain in fractionator to be 0.1 Ci. No gain was detected.

(h) Apparently the entire batch of fractionator condensate became contaminated.

(i) Data through first shutdown period only, but includes a complete pot calcining and cooling cycle.

FIGURE 5.3. Ruthenium Volatilization from the WSEP Evaporator

(Figure 5.3) gives the following equation for bottoms to overheads DF.

$$\text{Instantaneous DF(Ru)} = 700 (\text{HNO}_3 \underline{\text{M}})^{-7}$$

where:

M = nitric acid molarity in the overhead over
an applicable range of 0.5 to 1.5M.

Ruthenium that escapes the evaporator to the overhead condensate is caught in the fractionator where an additional decontamination occurs. Figure 5.4 shows the accumulation of radioactivity in the evaporator condensate. The activity did not increase substantially after about 50 hours of running because (1) the evaporator was operated at a lower boiloff rate after the pot calciner feeding terminated [boilup rates were near 150 liters/hr during feeding versus 50 liter/hr during idling for the calcination period (Figure 5.4)] and (2) the evaporator overhead was maintained at a lower acid concentration during the calcination period. Figure 5.4 also shows the variation in strip water addition to the evaporator and the corresponding overhead acidity. For other runs, the addition rates for strip water to the evaporator are listed in the Appendix, Table 9.1.

In-leakage of air to the system (1 to 2 scfm) caused essentially no change in vapor velocities in the evaporator and the fractionator tower.

For the six runs, the cumulative DF across the fractionator (Table 5.2) varied from a low of 420 during a Mode B run where a large volume of condensate (~1600 liters) was accumulated to a high of 6900 during a modified Mode A run when a small volume (~600 liters) was accumulated. Based on the data in Table 5.2, one should expect a DF of about 5×10^3 under normal conditions.

FIGURE 5.4. Radionuclide Accumulation in the Evaporator Condensate

The very low DF obtained during run PC-5 is believed to be the result of contamination of the entire batch of fractionator condensate.

In one run (PC-4), NaOH solution (4M) was added to the fractionator tower (top plate) in an attempt to improve the ruthenium DF. As shown in Table 5.2, the DF was only as good as the better DF's achieved without the caustic addition. The 4M solution was added to the single sieve tray at 5 liters/hr and collected separately from the tray. Apparently the contact efficiency was poor since the collected solution was still basic. Fractionator overheads acidity was about the same as during other runs.

5.3 CONTROL OF OTHER RADIONUCLIDES

Cumulative decontamination factors for nonvolatiles in the WSEP evaporator ranged from 200 to 3.4×10^6 , but were typically between 10^4 and 10^5 . Instantaneous DF's for nonvolatiles across the evaporator were calculated from cerium concentrations and varied from 1.7×10^4 to 2.1×10^6 (Table 5.2). The data on nonvolatiles showed satisfactory operation, but also showed an improving trend which could lead to two conclusions. Better DF's were obtained when operating the evaporator with feed than with contaminated acid or a gradual increase in tower efficiency was obtained in successive runs. Further runs are required to be definitive. For comparison, the ORNL evaporator gave an instantaneous DF of about 10^4 when equipped with a two-stage impingement de-entrainer.⁽⁶⁾

The pot calcination process produces a relatively small quantity of off-gas that must be decontaminated before it is released to the environs. Noncondensable gases correspond to only about 5% of the nitrate present in the feed and consist of nitrogen oxides and oxygen. In the ORNL equipment, this stream averaged less than $0.01 \text{ ft}^3/\text{min}$. In the WSEP, with more and larger

auxiliary equipment, noncondensibles averaged about $2 \text{ ft}^3/\text{min}$ (including air in-leakage). Volumetric flow was acceptably small for effective decontamination in WSEP; however, it may have been sufficient to adversely affect the nitric acid stripping efficiency in the rectifying column. Design criteria called for 0.01M acid in the distillate from this column; concentrations from 0.02 to 0.07M were observed (Table 5.2 and Appendix). Noncondensable off-gases from the process were approximately 200 liters (STP) for each liter of aqueous feed. They were due almost entirely to in-leakage and instrument purge air. After off-gases left the fractionator, they were filtered, scrubbed, filtered again, and then discharged to the atmosphere. Their radioactive content was well below release limits. Activity discharged to the stack was measured continuously on a weekly basis. Although it included ventilation air from the high level waste-vault tanks, it was normally below the limit of detection for both ruthenium (4.7×10^{-5} curies/week calculated as ^{106}Ru) and gross beta (8.4×10^{-7} curies/week calculated as ^{90}Sr and ^{90}Y). Typical results were $<1 \times 10^{-12}$ and $<1 \times 10^{-9}$ for fractional losses of gross beta and ruthenium, respectively, to the stack. The gas-vapor stream within the WSEP complex was not sampled. Thus, the contamination level after the off-gas left the fractionator was not determined.

Generally, decontamination of the process off-gas in the WSEP runs was at least as good as that achieved in the PNL hot-cell tests where overall decontamination factors from feed to off-gas at the point of release to the atmosphere were 10^8 and 10^9 for ruthenium and particulates, respectively.⁽¹⁵⁾

5.4 PREPARATION AND HANDLING OF ACID PUREX WASTE

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

precipitates can plug pipes. Thus, a good knowledge of the precipitate characteristics is required for proper equipment design and operation.

The precipitate present in a given waste solution depends on the flowsheet used in the separations plant and the subsequent treatment of the waste. In general, the PW-1 and PW-2 solutions used in runs PC-1 through -6 were representative of any Purex plant waste. That is, they contained the full gamut of expected precipitate types although the comparative amounts of precipitate varied with each waste. The volume of solids observed in actual samples of the feed solutions used in the six WSEP pot calcination runs is shown in Table 5.3.

TABLE 5.3. Observed Solids Content in Actual Pot Feeds

	Waste	Waste Volume, liters/tonne	Major Constituents, M ^(a)					Settled Solids, vol%
			Fe	Al	Na	Ca	SO ₄	
PC-1	PW-2	400	0.4	---	1.2	0.3	0.9	12
PC-2	PW-2	400	0.2	0.2	0.8	0.2	0.6	3
PC-3	PW-2	420	0.1	0.4	0.8	0.2	0.6	11
PC-6	PW-2	390	0.1	0.4	1.1	0.1	0.6	17
PC-4	PW-1	370	0.8	0.1	0.5	---	0.3	6
PC-5	PW-1	410	0.8	0.1	0.6	---	0.3	13

(a) *Rounded values. The yttrium and rare earth concentration was 0.12M and the zirconium concentration was 0.065M in each run.*

Probably the variations in the observed volume of precipitate are not significant. In general, the volumes were about the same as those observed in laboratory tests with simulated waste solutions.

The solids in PW-2 are of two main types, namely, sulfates and zirconium phosphomolybdate compounds. Sulfate solids formed hard cakes on standing and were presumably the cause of several cases of plugged pipes. These occurred prior to the second pot calcination run (PC-2). The phosphomolybdate pounds were more amorphous and did not cake in laboratory tests.

Sulfate Solids in PW-2

A major portion of the sulfate precipitate in PW-2 is a double salt of sodium and rare earth elements. The rare earths form double salts of variable composition with the sulfates of the alkali metal elements, $x \text{ RE}_2(\text{SO}_4)_3 \cdot y \text{ M}_2\text{SO}_4 \cdot z \text{ H}_2\text{O}$, where RE is rare earths and M is an alkali metal. Values of x and y can vary depending upon the relative concentrations of RE and M in the solution. Solubilities of the rare earth double sulfates increase as the atomic number of the rare earth increases, i.e., from lanthanum to lutetium, and decrease with increasing temperature.⁽³⁰⁾ Precipitation of such double salts is used commercially to recover rare earths from some ore extract solutions and to effect rough separations into subgroups.⁽³¹⁾ Precipitation as sulfate salts has been proposed for separating radioactive cerium for shipment.⁽³²⁾

Laboratory experiments to determine the amount of sodium rare earth sulfate precipitate to be expected in PW-2 wastes were performed. The fission product rare earths in PW-2 were simulated for 20,000 MWd fuel by using 0.120M Lindsay 350 mixed rare earth nitrate (assumed molecular weight = 434; La_2O_3 -24%, CeO_2 -48%, Pr_6O_{11} -5%, Nd_2O_3 -17%, Sm_2O_3 -3%, Gd_2O_3 -0.2%, others, 0.8%). In experiments involving the Na-RE- SO_4 - HNO_3 only system at concentrations normally in PW-2 (0.93M Na, 0.12M RE, 0.87M SO_4 , and 4.0M HNO_3) about 8 volume percent settled precipitate was obtained at 25 °C. In the absence of sodium, there was no precipitate. The volume percent of precipitate decreased to 3.5 at 50 °C and to 3.1 at the boiling point. The volume decrease, presumably due to dehydration, was accompanied by a hardening of the precipitate. At 25 °C, the precipitate was somewhat amorphous and would stand several days without caking badly. When formed in situ at 50 °C and above, the precipitate formed a tenacious scale. When loosened, this precipitate was heavy, and very difficult to suspend by

agitation. Increasing the HNO_3 concentration increased the volume of precipitate. Also, the volume of precipitate increased with increased sulfate concentration. Below about 0.45M SO_4 , sodium rare earth double sulfate was soluble in the system $0.12\text{M RE}-0.98\text{M Na}-4.0\text{M HNO}_3$ at 25°C .

Other Solids in PW-2

The principal nonsulfate precipitate in PW-2 contains molybdenum, phosphorous, and zirconium, and is probably a zirconium phosphomolybdate compound. Only a small fraction of the molybdenum and zirconium in the WSEP feed solutions originated from fission. Most was introduced as solid sodium molybdate and zirconyl nitrate during makeup of solutions which were later added to the radioactive waste.

In laboratory-prepared PW-2 solutions, the zirconium phosphomolybdate precipitate formed very slowly at temperatures below the boiling point. Even at boiling temperature, 15 to 20 hours were required for equilibrium amounts to form. The solid is a hydrous, amorphous precipitate which has never been observed to cake in the laboratory even after standing several months. During boiling, thin films plated out on some surfaces in laboratory equipment. Dilution up to 400 gal/tonne did not prevent formation of phosphomolybdate solids in PW-2.

PW-2 nominally contains about 0.01M silicon. Thus, silicic acid is another contributor to the solids content. In laboratory tests, the silicic acid precipitate formed even more slowly than the zirconium precipitate. Several days at boiling temperature were required to approach equilibrium. The loose, flocculent precipitate of silicic acid did not cake but may have contributed to film formation. Silicon was not added to the WSEP pot calcination feed solutions; it was present in the Purex wastes used as feedstock.

Total Solids

Information on the total solids content of PW-2 is summarized in Table 5.4. Figure 5.5 shows the effects on solids content of diluting the waste up to 400 gal/tonne at constant 4.0M HNO_3 . Data on individual precipitates were obtained by studying PW-2 solutions in which components that would form interfering precipitates were omitted. In all cases, the solutions were refluxed 20 hours. After refluxing, the slurries were allowed to stand one week at room temperature. Settled volume of the solids was noted. The solids were then filtered, dried, and weighed.

TABLE 5.4. *Characterization of PW-2 Solids at 100 gal/tonne and 4.0M HNO_3*

<u>Type of Precipitate^(a)</u>	<u>Solids Present, g/liter of waste</u>	<u>Apparent As-Settled Density, g/cm³</u>
Zirconium phosphomolybdate	13	0.08
Silicic acid	2.2	0.1
Sulfates (~10 wt% Ba, 7 wt% Sr, and 83 wt% mixed Na-RE)	41	0.45

(a) *Solutions were refluxed 20 hours. Laboratory data are for simulated wastes after settling 1 week at 25 °C.*

Caking tendency of the sulfate precipitate is probably related to its density. This was found to be at least four times that of the noncaking precipitates.

Behavior of the sodium rare earth double sulfate in PW-2 at 4.0M HNO_3 was found to be very similar to that in 4.0M HNO_3 alone. Thus, dilution by a factor of less than two was sufficient to prevent precipitation of the double sulfate in PW-2. (Dilution was utilized to reduce caking tendency in runs PC-2, 3, and 6.)

FIGURE 5.5. Solids in PW-2 (Simulated High Sulfate Waste)

Laboratory data indicate caking of the precipitate in PW-2 can be avoided by adding phosphoric acid, but the minimum concentration which is satisfactory remains to be determined.

The presence of sulfate limits the volume reduction which can be done before the concentrated feed is pumped to a pot for solidification. Since this can directly affect the overall processing capacity, further investigation is needed to characterize the volume limits and the beneficial effect of additives such as phosphoric acid.

Effects of sulfate precipitation can be serious if the problem is not recognized. Stagnate areas in the equipment should be minimized. For example, although transfer lines that were plugged prior to run PC-2 were eventually opened, feed tank spargers and the feed tank airlift remained plugged after many attempts to free them.

Effect of Calcium Addition to PW-2 Waste

Calcium nitrate was added to the waste during PW-2 processing to prevent sulfate volatilization. In run PC-1, the $\text{Ca}(\text{NO}_3)_2$ was added to the pot as a separate stream. Laboratory tests indicated that neither the volume nor the character of the solids present was appreciably worsened by adding $\text{Ca}(\text{NO}_3)_2$ directly to the waste. It was added directly to the feed batch in runs PC-2, -3, and -6. Differences in volume of solids observed in laboratory studies at 0.87M sulfate are shown below.

<u>Simulated PW-2 Waste</u>	<u>Settled Solids, vol%</u>	
	<u>Without Calcium</u>	<u>0.25M Calcium</u>
PC-2	4.6	5.0
PC-3	7.3	8.2

Solids in PW-1

The solids in PW-1 are similar to those in PW-2 except that the concentration of added sulfate is nominally below that where caking would occur.

In the two PW-1 runs, PC-4 and PC-5, sulfate was added to suppress the volatilization of alkali metal oxides. Sulfate concentrations were not more than 0.45M in the evaporator. Although considerable solids were formed, the solids caused no appreciable transfer problems. However, during PC-4 and PC-5 the wastes were continuously boiled in the evaporator. The specific gravity dip tube and the air sparger became plugged during both runs.

Variations in Feed Composition

Purex feedstock solutions usually contained more sodium, aluminum, and sulfate than desired for the PW-1 and PW-2 nominal compositions. Fortunately sodium and sulfate were needed for pot calcination processing; therefore, when possible, the excess of these elements in the feedstock was used to represent the flowsheet additive.

Studies on the effects of aluminum were made. PW-2 nominally contains only 0.001M Al. Concentrations were as high as 0.4M in some of the pot calcination runs. When aluminum was present, a corresponding molar quantity of iron was omitted from the feed makeup. The presence of aluminum did not affect feed stability. Precipitation behavior of PW-2 containing 0.38M Al-0.06M Fe was similar to that of standard PW-2 with 0.44M Fe.

5.5 GENERAL PERFORMANCE OF AUXILIARIES

All auxiliary equipment functioned quite well in the six pot calciner runs except for some feed pump failures and for plugging of specific gravity dip tubes and other lines. All six runs were successfully completed; only the sixth run was interrupted during the operating period. Table 5.5 is a compilation of the general operating performance of the prototype equipment. The WSEP equipment flow diagram is shown in the Appendix, Figures 9.4 and 9.5.

Pumps

The feed pumps were canned-rotor inline pumps^(14,33) with boron carbide seals and boron carbide bearings which had graphite thrust faces. Water lubricant to the bearings was recirculated through a small reservoir and a jacketed cooler but was separated from the process fluid by a mechanical seal. Two pump failures were due to electrical shorts. Another failure occurred when the pump shaft became "bound" shortly after the boron carbide seals failed and seal water began mixing with the feed. A new type pump (uncanned and with a mechanical seal) is presently being used. Actual pump history is summarized in the Appendix, Table 9.5. Although it was not the intent in WSEP to develop pumps, the difficulty experienced emphasizes the need for serious attention to pumps to assure that standard production type pumps will perform satisfactorily for waste solidification.

Feed pumps were always somewhat of a problem at ORNL, also. Development and pump testing at ORNL resulted in the recommendation

TABLE 5.5. WSEP Operating Performance

Equipment Piece	Construction Material	Temp., °C	Press., in. H ₂ O	Chemical	Operating Time, hr	Remarks
Feed tanks	304L SS	60	-5	Darex, Purex, TBP-25 Type Waste	1786	Agitators used 1168 hr.
Condensate tanks	304L SS	25	-18	H ₂ O Dilute HNO ₃	1716	Submerged pump used 350 hr.
Caustic scrubber	304L SS	25 to 40	-20	Dilute NaOH	1716	Circulating pump used 1009 hr.
Evaporator	A-55 Titanium	110	-18	Boiling Feed	1586	Minor titanium corrosion caused by fluoride ion during early DVT runs.
Fractionator	A-55 Titanium	115	-18	8 to 12M HNO ₃	1566	
Pot Calciner Condenser	A-55 Titanium	100 to 200	-18	HNO ₃ Vapors	1716	Localized vapor entry corro- sion (up to 1/16 in.) during early DVT runs 3 and 4.
Feed Pumps	304L SS	60	---	Hot Feed	1193	Under radioactive service 4 pumps have failed either mechanically or electrically in 350 hr.
Induction Furnace	Hastelloy-X	900	---	Hot Calcine Pots	1652	Delaminated insulation was completely replaced with Ceraform ^(a) at 1025 hr just before radioactive service.
Calciner Pots	304L SS (not corrosion tested)	100 to 900	-18	Concentrated Wastes	1453	No warping, bending or detectable corrosion except during an experimental rising level glass run where severe corrosion was encountered.
Magnetic Flowmeters	Vitreous Enamel Liner. Platinum sealed elec- trodes. Inconel flow- tube.					
Feed		30 to 80	---	Concentrated Wastes	1193	Have experienced occasional deviation from calibration.
Condensate		25 to 40	---	Condensate	2302	
Filters Absolute	Glass-asbestos with aluminum separators in 304L SS housing.					
Process Vent		50 to 70	-20	Predominantly Air	375 Days	No filter changes; ΔP started to increase one month after pot runs.
Feed Tank Vent		50 to 70	-10	Predominantly Air	375 Days	Changed three times; 74 days was the shortest duration of any one filter.
Air Lift ^(b)						

(a) Product of Johns Mannville

(b) The airlift for feeding the evaporator worked satisfactorily during the runs. The airlift which served as an alternate feeding system to the pot plugged during the sulfate precipitation problem in PC-2.

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of a Chempump Model T(CFT-1-1/2-3/4S).⁽³⁴⁾ This pump is lubricated by water pumped through the bearings and into the process solution. To date, this model has not been run in WSEP.

Airlift

A two-stage airlift on the feed tank worked satisfactorily in a DVT run prior to radioactive operation but has not been usable since. The airlift was intended as a backup for the feed pump. However, the lower section of the first stage plugged with solids at the same time that solids caused plugging of several other feed tank lines (before the start of run PC-2).

Feed Control System

Operation of the recirculation feed control system over the range of 2 to 60 liters/hr was excellent. Lower operating pressure at the control valve, e.g., 15 psig versus 30 psig would give even better control. A 1/2 inch Hammel Dahl valve with a No. 5 spline trim was used for control of the feed to the pot. Control was not affected appreciably by the solids in the system since they readily passed through the valve. A special startup and shutdown procedure was used to prevent plugs in the feed line. Condensate was recycled through the feed line at the start of a run and again whenever the feed was shut off to the pot calciner. Flushing the line after the feed was shut off prevented calcination in the feed line at the pot neck.

Evaporator and Acid Fractionator

The evaporator and acid fractionator performed satisfactorily. Specific gravity was used as the primary control for maintaining the desired bottoms concentration. Temperature was used on some occasions. During both of the Mode C runs (feed in the evaporator), the specific gravity dip tube became plugged; therefore, while operating without specific gravity information, the average bottoms concentration varied by approximately 35% from the desired

385 liters/tonne. Although much closer control would be possible as more physical data and operating experience is obtained with any one waste type, it is desirable that specific gravity controls be usable for more reliable operation. Relocation of the dip tubes to a point external to the evaporator (a standard stilling chamber) may be required to prevent their plugging. Plugging of the weight factor dip tube also occurred but not as frequently. The present location of the specific gravity and weight factor tubes made them somewhat sensitive to the evaporator boiling rate and, in turn, made automatic control of steam flow impossible.

In Mode C operation, the WSEP evaporator had an average boilup rate during the feeding period of 125 liters/hr and had a holdup of about 150 liters. It was controlled manually. The control was based on the density and/or temperature of the boiling liquid. Conductivity of the evaporator overheads was used to maintain a low nitric acid concentration in the overheads. At ORNL, the evaporator was operated automatically at an average boilup rate of about 120 liters/hr and with a liquid holdup of 25 liters. Acidity of the overheads was controlled at $0.8\text{M H}^+ \pm 50\%$ in the WSEP Mode C runs, while the ORNL unit operated with overheads at $1\text{M H}^+ \pm 15\%$.

Filters

As shown in Table 5.5, the absolute filters in the process ventilation system performed well while those in the secondary feed tank vent system required several changeouts because of excessive (>10 inches water) pressure drops. The pressure drop across the process filters (original filters in place) was still less than one inch after completion of the six pot calciner runs. Inspection indicated that the secondary vent filter failures were the direct result of their becoming wet with acidic vapors. This was probably the result of having an inadequate preheater upstream of the filters. The air preheater to this filter was steam-heated

with only 2.6 square feet of heat transfer area. The preheater for the process vent system, where no filter problems occurred, was a tube bundle type exchanger with 8 square feet of tube area.

Sampling

Contamination of low level radioactive samples, primarily fractionator condensates and scrubber solution, within the hot cell was a problem during most of the six pot runs. These samples frequently became contaminated either by contaminated remote handling equipment by contacting contaminated objects or by picking up contamination from the "hot cell" atmosphere. In order to determine if "low level" samples were contaminated, the cerium-to-ruthenium ratio was checked since the ratio should not increase in downstream samples. For the fractionator condensate, it was assumed that the DF for cerium (from the fractionator to the fractionator condensate) should be better than, or as good as, the ruthenium DF. Therefore, the maximum amount of cerium and other fission products in the fractionator condensate could be determined by using the cerium content in the fractionator and applying the same DF as obtained for ruthenium by analyses. This correction was made to the fractionator condensate for runs PC-3 and PC-6. In the fractionator bottoms, the radioactivity was high enough that the contamination was not significant.

Material Balances

Material balances for the six pot calcination runs are shown in the Appendix, Table 9.2. Since samples were not taken of the calcine product, specific component balances were not made. For most purposes, it can be assumed that the percent of nonvolatile activity retained in the pot was the difference between 100 and the percent evolved from the pot. For volatile components, previous laboratory and development work^(18,19) has shown that 800 to 900 °C is sufficient to reduce the nitrate content of

the calcine to $\leq 0.1\%$ and that the specified chemical additives would prevent volatilization of cesium and sulfate (0 to 2% in the case of sulfate).

Percent recovery for the six pot runs is shown in Table 5.6.

TABLE 5.6. *Material Balances for Pot Runs*

<u>Run</u>	<u>Percent Recovery</u>	
	<u>vol%</u>	<u>wt%</u>
1	93.7	94.1
2	94.5	95.2
3	101	98.4
4	98.6	95.5
5	100	94
6 (a)	96	96

(a) *First part of run*

6.0 FILLED POT PERFORMANCE

An important part of the waste solidification program is the evaluation of the products (pot and calcine) to assess their suitability for storage on both an interim and a long-term basis. A Solids Storage Engineering Test Facility (SSETF) for storing, monitoring, and observing the products in likely environments has been constructed as part of the WSEP Program. Initial and near-term behavior of the products is under scrutiny.

Inasmuch as filled pots may be held in an interim storage facility until conditions (e.g., heat generation rate) are suitable for transferring them to a final storage site, it is very important to know what behavior to expect during the interim period. Of interest are the answers to such questions as: How much, if any, pressurization occurs? Is pot wall corrosion significant? Can a leak-tight seal be made and maintained? Is there a significant change in the distribution of heat generating isotopes in the sealed pot?

6.1 EVALUATIONS

Most of the pot performance characteristics of interest in the program are concerned with changes which are expected to occur slowly, if at all. In fact, the success of waste solidification hinges to a large extent on the absence of notable effects. Of course, if changes are to be detected, it is necessary to measure the base-line conditions for use in later comparisons.⁽³⁵⁾ Most of this section deals with the current progress and problems in determining baseline conditions.

Maximum Temperatures

The temperatures produced by heat generating nuclides in a pot is theoretically predictable from knowledge of the waste, its source and age. A major objective of WSEP runs was to determine the predictability of temperatures and the quantity of

radionuclides required to produce the maximum allowable temperatures in a pot. The accuracy of predicting temperatures produced by radionuclide decay depends on the accuracy to which system properties (such as thermal conductivity) are known. If these are known, the general capability to process a waste by pot calcination can be judged.

The temperature, T_c ($^{\circ}\text{C}$) at the centerline of a heat generating cylinder is given by:

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

where:

Q = power (watts) generated in the cylinder; radionuclides are assumed to be uniformly distributed

L = length of heat generating cylinder (meters)

K = thermal conductivity $\text{W}/(\text{m}^2)(^{\circ}\text{C}/\text{m})$

T_w = temperature at the cylinder wall ($^{\circ}\text{C}$)

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

Equation (1) may be rearranged to give:

$$\Delta T = \frac{Q}{4\pi K_e L} \quad (2)$$

where:

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

K_e = effective thermal conductivity.

Equation (2) shows that the temperature drop from the centerline of a pot to the outside wall is a function of the total internal power generated by radionuclide decay. For a given internal power, thermal conductivity and fill height, the temperature difference ΔT is the same for an 8 inch and a 12 inch diameter pot. Of course, the power density, W/liter for an 8 inch diameter pot is a factor of 2.0 greater than that for a 12 inch pot. Q in Equation (2) is equal to $\frac{\pi d^2 L}{4} q$ where d is diameter and q is the specific power (W/liter) generated in the solid. For a given specific power (W/liter) in the solid, the temperature difference ΔT is a function of the square of the diameter. However, for this report ΔT as a function of total power was the major interest.

Graphical solutions to Equation (2) for several different values of K_e are presented in Figure 6.1. Centerline temperature estimates can be obtained by adding the ΔT from Figure 6.1 to the pot wall temperature, T_w , from Figure 6.2. Pot wall temperatures are shown in Figure 6.2 for 8 and 12 inch diameter pots cooled by natural convection and radiation in 38 °C (100 °F) air. The curves are derived from standard methods for convective and radiative heat transfer as given by McAdams.⁽³⁶⁾ An emissivity of 0.8 is assumed for the pot wall at all temperatures.

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

FIGURE 6.1. *Temperature Drop (Centerline to Outside Wall) in Pots Containing Solidified Waste*

In both Figures 6.1 and 6.2, experimental results from filled pot temperature measurements are shown. The observed pot wall temperatures are shown for four of the runs in Figure 6.2 and ΔT is shown for five runs in Figure 6.1. Measured wall temperatures for 8 inch pots were slightly lower than would be predicted from

FIGURE 6.2. Pot Wall Temperature in Air

the curves. This difference may be due to the assumed value of emissivity or it may indicate that the surface thermocouple readings were in error. A slight error toward low readings can be expected for thermocouples welded to the surface of the pot. In Figure 6.1, the location of experimental points indicates that thermal maximum estimates for pot calcined material should be based on thermal conductivities of 0.3 to $0.4 \text{ W/(m}^2)(^\circ\text{C/m)}$, [0.17 to $0.23 \text{ Btu/(hr)(ft}^2)(^\circ\text{F/ft)}$] with PW-2 tending toward the lower end of the range, and PW-1 toward the higher end.

Effective Thermal Conductivity

The thermal conductivity for pot calcined waste derived from the experimental data is not necessarily the true value. It will be the true value only if heat generation is actually uniform and heat flow is radial. Earlier nonradioactive experiments have shown that pot calcination produces a cake which is not solid, but has a central cavity which may extend some distance toward the lower zones. Thus, heat generation is not uniform throughout the cylinder. Deviation from radial heat flow is to be expected. Experience has shown that the general shape and size of the cavity is more or less reproduced from run to run. Hence an effective value of K based on data from a particular run might be a reasonable approximation for making temperature predictions in later runs with the same feed. The data in Figure 6.1 support this conclusion; they show that reasonably accurate estimates of the power and temperature drop relationships can be made, based on an experimentally derived K_e .

In Figure 6.3, the relationship between K_e and the power is shown for maximum temperatures in 8 inch and 12 inch pots. Twelve inch pots filled to the 6 foot level, for example, would hold waste equivalent to 4.7 to 6 kilowatts at $K_e = 0.3$ and 0.4 , respectively, without causing centerline temperatures above 900°C or

FIGURE 6.3. Effect of Effective Thermal Conductivity on Total Power at Maximum Temperatures.

wall temperatures above 425 °C in air. For the range of K_e and pot diameters shown, the centerline temperature, rather than the wall temperature, was always the limiting temperature.

Thermal conductivities were calculated at different steady-state temperatures using heat-generation rates determined by calorimeter measurements. When these data were plotted against average calcine temperature, a correlation for PW-1 waste showing a linear increase with temperature was obtained (Figure 6.4). With the limited data available, K_e for PW-2 waste did not correlate with temperature.

The exact position of the data point shown for PC-1 in Figure 6.4 is uncertain. The high value of $0.37 \text{ W/(m}^2)(^\circ\text{C/m)}$ is based on feed heat content at the time of the run. This same value is obtained by backward extrapolation of the pot heat content measured by calorimetry three months after fill date. The low value is the three-month-old value. It is shown because it is nearly equal to the value calculated from the curies in the feed to the pot. The analytical expression for the PW-1 curve is:

$$K_e = 0.306 + 1.67 \times 10^{-4}t$$

where:

$$K_e = \text{W/(m}^2)(^\circ\text{C/m)} \text{ and,}$$
$$t = ^\circ\text{C}.$$

In prior work at ORNL, Godbee and Roberts⁽¹⁸⁾ showed that the thermal conductivity, K , of Purex 1WW waste calcine varied with temperature according to the expression, $K_e = 0.31 + 3.7 \times 10^{-4}t$. Since the waste types in ORNL runs and WSEP runs were not identical, a direct comparison cannot be made. The major difference between ORNL data and the K_e of radioactive calcine was a factor

FIGURE 6.4. Variation of Effective Thermal Conductivity with Temperature

of about 2 decrease in the slope, i.e., less increase with temperature. As a result, the total power permissible in an 8 inch pot for PW-2 waste was nearly 30% lower than expected [5000 watts at K_e of $0.36 \text{ W/(m}^2)(^\circ\text{C/m)}$ instead of 7000 watts at K_e of $0.52 \text{ W/(m}^2)(^\circ\text{C/m)}$] (See Figure 6.3). However, if K_e for PW-1 (Table 6.1 and Figure 6.4) is higher than K_e for PW-2, a pot filled with PW-1 waste could contain approximately 6500 watts [$K_e = 0.4 \text{ W/(m}^2)(^\circ\text{C/m)}$].

TABLE 6.1. *Variation in Effective Thermal Conductivity with Temperature*

<u>Waste Type</u>	<u>Run No.</u>	<u>Average Temperature, $^\circ\text{C}$</u>	<u>Effective Thermal Conductivity, $\text{W/(m}^2)(^\circ\text{C/m)}$</u>
PW-2	1	105	0.37
	2	368	0.32
	3	300	0.36
	6	450	0.26
		590	0.32
PW-1	4	200	0.35
		321	0.36
		485	0.39
	5	477	0.38
		675	0.42

The average air film coefficient, h , (PC-2 and 3 excluded because air surrounding them was not at room temperature) was $15.5 \text{ W/(m}^2)(^\circ\text{C)}$ with a $\pm 30\%$ range for the six runs (Table 6.2). Part of the scatter can be attributed to the known inaccuracy of measuring the wall temperature (Figure 6.2) plus normal thermocouple error. Nonuniform distribution of heat is probably a cause of the observed scatter in the value of h .

TABLE 6.2. *Convective Air Heat Transfer from Pot Wall*

Run	Pot Size, in.	Waste	Total Power, W	Cake ΔT , ^(a) °C	Wall Temperature, °C	h , ^(b,c) $W/(m^2)(^{\circ}C)$
1	12	PW-2	600	70	70	11.4
2	12	PW-2	1700	235	250 ^(d)	19.4
3	8	PW-2	1800	220	190 ^(e)	14.4
4	12	PW-1	2600	312	165	11.9
5	8	PW-1	4300	495	230	18.1
6	8	PW-2	5100	700	240	20.4

- (a) Temperature difference taken for hottest zone (usually Zone 4). Pot cooled by natural convection and radiation in cell except Runs PC-2 and PC-3. Ambient air temperature = 40 °C.
- (b) Calculated from $h = Q/A\Delta T$ where, Q = Total power watts; $A = 1.25$ and $1.75\ m^2$ for 8 and 12 inch pots, respectively; ΔT is taken between the pot wall and 40 °C, except in runs PC-2 and 3 where the furnace temperature replaces 40 °C.
- (c) $W/(m^2)(^{\circ}C) \times 0.176 = Btu/(hr)(ft^2)(^{\circ}F)$
- (d) Pot in receiver furnace, cooling air off, furnace susceptor at 200 °C.
- (e) Pot in receiver furnace, cooling air on, furnace susceptor at 90 °C.

Gamma Spectrum Analysis and Radiation Profiles

To get some idea of the solids deposition pattern, gross gamma profile scans were made on each of the filled pots. The results of several scans are shown in Figure 6.5. Gamma radiation profiles were obtained simply by positioning an ionization chamber at a distance of 6 inches from the pot and recording the radiation level at several points along the length of the pot. No collimation was attempted. In general, the profile was about what would be expected from the appearance of the contents of pots produced in earlier, nonradioactive runs.

The pot centerline temperature profile for the pot from Run PC-5 is also shown in Figure 6.5. As might be expected, the temperature and radiation profiles are quite similar; both reach a maximum in Zone 4.

FIGURE 6.5. *Radiation and Temperature Profiles of Calcine Filled Pots*

A gamma spectrometer and multichannel analyzer system was designed and installed for gamma energy analysis of process streams and a gamma energy spectrum profile of the filled pots. An indication was sought of the distribution of heat generating isotopes in the pot. However, the system was not easily

adaptable to use for determining the distribution of fission products in the pot. The two major problems were: (1) the sodium iodide crystal saturated in the high radiation field when using a 0.094 inch diameter collimation tube and (2) energy channels were not discernible due to distortion of the gamma energy spectrum by Compton scattering.

Pot Dimensions and Physical Data

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

Before a pot was filled, it was subjected to tests and measurements to assure its integrity and to establish a basis for detection of changes which might occur during filling. Pot gross dimensions (length, diameter) were measured, and a pot wall thickness scan was made. As soon as possible after the pot was filled, the gross dimensions were checked to see if any gross swelling or pot deformation had occurred. A pot wall thickness scan was made to detect corrosion.

Pot Corrosion

Typical corrosion data are presented in Figure 6.6 for Run PC-2. Pot wall thickness is shown at 97 points around the pot at each of several elevations before and after the pot was filled. The data shown in Figure 6.6 were selected from pot wall thickness scan output sheets such as the one illustrated in the Appendix, Figure 9.8. No corrosion of pots was detected in the WSEP runs. This confirmed the low rates obtained in laboratory tests.⁽³⁷⁾

The device⁽³⁸⁾ used to measure pot wall thickness was based on the ultrasonic pulse echo principle. A pot was submerged in water and an ultrasonic transducer was mounted normal to the pot wall and on a vertical track. As the pot was

FIGURE 6.6. PC-2 Pot Wall Corrosion Scans Obtained by Remote Ultrasonic Tests

rotated, information on radial position, vertical position, and the wall thickness was transmitted to a General Electric 412 digital computer. The computer averaged the thickness readings over each rotational increment and produced a punched paper tape which was processed to obtain the digital output map shown in Figure 9.8. Some difficulty was experienced in the remote operation of this equipment. Specifically, it was difficult to maintain the required degree of perpendicularity between the transducer and the pot wall.

Internal Pressure

Bourdon tube gages were installed on filled pots as soon as the pots were sealed. For the six runs reported here, the gages provided the only information as to how well the pots were sealed. The pressure readings that were taken, however, indicate that pressure in the sealed pots did not exceed 1 psig. The absence of pressure buildup in the sealed pots indicates that the residual level of nitrate and other unstable or volatile constituents is as low as had been predicted. In fact, some pots showed pressures below atmospheric. Cooling reduced the pressure when the pots were stored in water after welding (also cooling occurs due to aging of the heat generating nuclides). Pot pressures are summarized in Table 6.3.

Leak Testing

Helium leak testing of pots in-cell, by evacuating the pots while they were shrouded in helium, was tried without much success. Excessive outgassing of the pot contents occurred under vacuum, outgassing rates exceeded the pumping capacity of the system.

A mass spectrometer and vacuum system on the nonradioactive side of the cell wall was connected through stainless steel tubing to the in-cell pot. Under normal operation, a

TABLE 6.3. *Pot Pressure Data*

<u>Run No.</u>	<u>Time from Fill Date to Weld Date, days</u>	<u>Time from Weld Date to Date of Pressure Reading, days</u>	<u>Pressure, psig (Vacuum, in. Hg)</u>
PC-1	0	0	0
		3	0.5
		18	15 (a)
		103	7
		152	4
PC-2	13	13	0
		49	0
		146	8 (vac)
		240	10 (vac)
PC-3	2	13	0.5
		213	25 (vac)
		280	26 (vac)
		345	28 (vac)
PC-4	88	0	0
		194	12
PC-5	3	0	0
		250	2 (vac)
PC-6	30	28	5 (vac)
		180	11 (vac)

(a) *Pot pressurized artificially by addition of nitrogen.*

roughing pump was used to reduce system pressures to below 10 microns; a diffusion pump was used to maintain the system at that pressure. Helium was sprayed in the regions to be tested for leaks and the detection of helium by the mass spectrometer indicated a leak. With the radioactive pots, the lowest vacuum attained was 28 microns, using 425 liters/min roughing pump. While this indicated that no gross leaks existed, it could not be interpreted quantitatively with any degree of reliability. At this time, observation of pot vacuum or pressure is still the best indication of pot seal integrity.

Calorimetry

Heat generation in filled pots was measured by a flowing water calorimeter. The calorimeter was a water-filled, insulated cylinder, equipped with a cooling coil. Cooling water flow rate and temperature rise under steady-state conditions provided a measure of the rate of evolution of heat from a pot immersed in the water. Operation of the calorimeter was quite satisfactory.

6.2 POT HANDLING, CONTAMINATION CONTROL AND WELDING

Handling of pots filled with calcine was much less difficult than initially anticipated. The handling system⁽¹⁴⁾ provided containment of the pot in a hood during processing and until the pot was capped. The pot cap was placed on the pot before the hood was opened; the pot was then transferred to the welding station. Containment in this manner was designed to minimize the spread of contamination from an open pot. However, experience with the handling and containment system leads to two conclusions:

1. Handling of uncapped pots after filling did not result in any major contamination problem in the cell. Visual

observation revealed little or no dust around the weld joint at the top of the pot. Pots did not have a tendency to erupt or dust. Therefore, the design of the pot calciner furnace containment hood and the pot capping and handling procedures could be simplified.

2. Although difficulties in handling the screw-in cap were infrequent, the general consensus favors a press-in cap to achieve simplicity and reduction in pot costs.

The remote welding process began by chucking the pot in the turntable and cleaning the pot lip with a damp swab. The pot cap was then threaded in place and the pot head runout was checked by dial indicator. Diametrical misalignment in excess of 1/4 inch was corrected by rechucking. The arc-head and torch were then positioned above the pot head. A weld test specimen was placed under the torch, welding parameters were selected and set on the remote console, and a test weld was made to verify system operability. The torch was positioned over the weld joint at an angle of about 45 degrees to vertical and the automatic weld cycle was started. Welding arc and weld puddle were continuously monitored through a spotting scope and minor adjustments were made in torch position, as required, by operator control of the manipulator.

The resulting weld was inspected visually for cracks or other flaws and, finally, a helium leak check was made using a mass spectrometer leak tester.

Six pots have been welded remotely. A summary of the welds, welding parameters, and results is given in Table 6.4. Experience with welding pots can be summarized as follows:

1. The raised step weld joint gave good results. It is still recommended for remote welding of waste pots.

TABLE 6.4. Remote Pot Welding Experience

Run No.	Weld Joint Run Out, in.	Welding Current, A	Welding Voltage, V	Welding Speed, in./min	Comments
PC-1	0.125	170	10.0	4.5	The pot cap was slightly undersized, resulting in a poor fit-up. During welding, contamination from the weld joint produced erratic operation in the torch control; a porous weld was made and second pass was required for complete closure. Visually, the weld was acceptable.
PC-2	0.125	180	10.5	4.5	Prior to making the test weld, the seals in the torch failed and water ran down the electrode. New seals were installed remotely and a successful weld was made. Visually, the weld appeared good.
PC-3	0.375	170	11.0	4.5	Radial runout was excessive. The weld was made while attempting to compensate for the radial runout by moving the torch manually. A second pass was necessary for final closure. Visually, the weld, after the second pass, was acceptable.
PC-4	0.040	160	12	4.5	Weld was made without any mishaps. Visually, a good quality weld was produced.
PC-5	0.050	160	12	4.5	During the test weld, water started running into the operating gallery from the sleeve that houses the power leads (H-3-2L222). A check revealed that the 1/2 inch tubing that carries the welding conductor was broken. A shop-made, sealess, water cooled torch was modified to accept standard torch leads. This torch was installed in the arc head. Leads were brought in through a spare wall nozzle and connected remotely. The weld was completed successfully.
PC-6	0.250	160	12	4.5	Weld was made without incident. Excessive runout was compensated for by moving the arc head horizontally with the master slave manipulator. Visually, a good quality weld was produced.

2. Viewing of the weld was one of the major problems in remote welding. The electrode must be accurately positioned with respect to the weld joint and the weld operation must be observed. A good quality lead-glass window and a spotting scope was an acceptable system; binoculars and periscopes might be required in facilities with radiation damaged or otherwise imperfect windows.
3. Accurate remote chucking of a pot to avoid misalignment was difficult. This, in turn, made manipulator control difficult. Need for accurate chucking has been eliminated or minimized by using a self-centering jig⁽³³⁾ mounted on top of the pot. The jig fastens to the pot and maintains positive joint and torch alignment. Although the jig was not used on the first six pots, it has been used successfully on other WSEP pots.
4. Weld joint cleaning was not a significant problem in the pot calcination process, except as noted in Table 6.4 on Run PC-1.

7.0 PROJECTED FLOWSHEETS FOR PW-1 AND PW-2

While it is desirable for a waste solidification facility to have the capability of processing wastes differing widely in chemical and radiochemical compositions, demonstration of all possible waste variations in the WSEP program is impractical. Experience in fuel processing and projections of future fuel processing requirements led to the selection of two generalized types of Purex acid wastes (Table 7.1).

The program for WSEP demonstrations is based on fission product wastes from light water reactor fuels with integrated exposure of 20,000 MWd/tonne at a specific power of 15 MW/tonne. Concentrations of the more significant fission products are given in Table 7.2. Decrease in power generation by fission products as one metric ton equivalent of this waste decays is presented in Figure 7.1. Both the initial power levels of the waste and its later aged levels must be considered in filling a pot. Initially, of course, the maximum power which can be placed in any container is limited by the centerline and wall temperatures allowable. Since maximum power generation is not compatible with economical heat dissipation in a final storage environment such as a salt mine, an aging period is required. If aging (radionuclide decay) in an interim storage basin is used, the container can be loaded with a higher power level than the final storage environment would allow. Figure 7.2 places in perspective, the ages required to meet present temperature limitations for filling an 8 and a 12 inch diameter pot stored in either water or air. Storage of the pots in salt depends on an economic choice but is generally most economical after about six years out-of-reactor.

Data from WSEP have been used in projecting typical flowsheets for pot calcination. Although exact PW-1 and PW-2 flowsheets were not demonstrated during the six pot calciner

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

	Purex Waste-1 (PW-1)	Purex Waste-2 (PW-2)
H ⁺	3.6M	3.8M
Fe ⁺⁺⁺	0.93	0.445
Cr ⁺⁺⁺	0.012	0.024
Ni ⁺⁺	0.005	0.010
Al ⁺⁺⁺	0.001	0.001
Na ⁺	0.138	0.930
U ⁺⁶	0.010	0.010
Hg ⁺⁺	<0.001	<0.001
NO ₃ ⁻ + NO ₂ ⁻	7.5	5.37
SO ₄ ⁼	----	0.870
PO ₄ ⁼	0.003	0.006
SiO ₃ ⁼	0.010	0.010
F ⁻	<0.001	<0.001
FP's (a) as M _{FP} ⁺ (b)	0.91	0.91
M _T ⁺ (c)	3.95	3.33
Volume	100 gal/tonne (378.5 liter/tonne)	100 gal/tonne (378.5 liter/tonne)
Power Density (d) @ 1 yr	12.2 W/liter	12.2 W/liter
@ 6 yr	2 W/liter	2 W/liter
Activity (e) @ 1 yr	2550 Ci/liter	2550 Ci/liter
@ 6 hr	580 Ci/liter	580 Ci/liter

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

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

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

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

(e) Includes ¹⁴⁴Ce daughter, ¹⁴⁴Pr.

TABLE 7.2. Fission Products from a Power Reactor Fuel
(20,000 MWd/tonne at 15 MW/tonne)(a)

Element	Average Atomic Weight	g/tonne @ 1 yr	Ci/tonne @ 1 yr	g/tonne @ 6 yr	Ci/tonne @ 6 yr	At 6 yr, moles/tonne and moles/liter for 100 gal/tonne	
						Moles/tonne	Moles/liter
Rb	86	230	---	234	---	2.68	0.71 x 10 ⁻²
Cs	134	1871	1.2 x 10 ⁵	1755	6.7 x 10 ⁴	13.10	3.45 x 10 ⁻² M
Sr	88	550	5.0 x 10 ⁴	512	4.1 x 10 ⁴	5.82	1.55 x 10 ⁻²
Ba	138	908	---	1023	---	7.40	1.95 x 10 ⁻²
Y	91	287	5.4 x 10 ⁴	287	4.2 x 10 ⁴	3.15	11.85 x 10 ⁻²
La	139	766	---	766	---	5.50	
Ce	142	1483	4.6 x 10 ⁵ (b)	1400	5.6 x 10 ³ (b)	9.85	
Pr	141	706	---	706	---	5.0	
Nd	148	2403	---	2475	---	16.70	
Pm	147	102	9.5 x 10 ⁴	27	2.5 x 10 ⁴	0.18	
Sm	147	463	---	537	---	3.65	
Eu	153	86	---	85	---	0.55	
Gd	156	26	---	28	---	0.18	
Zr	93	2266	1.5 x 10 ⁴	2300	Neg	24.7	6.50 x 10 ⁻²
Nb	95	Neg	3.0 x 10 ⁴	Neg	Neg		
Mo	97	2135	---	2370	---	24.5	6.50 x 10 ⁻²
Tc	99	523	---	523	---	5.3	1.40 x 10 ⁻²
Ru	103	1286	1.2 x 10 ⁵	1252	3.7 x 10 ³	12.1	3.20 x 10 ⁻²
Rh	102	285	---	285	---	2.8	0.74 x 10 ⁻²
Pd	105	647	---	680	---	6.5	1.72 x 10 ⁻²
Ag	109	33	---	33	---	0.3	0.08 x 10 ⁻²
Cd	112	33	---	33	---	0.3	0.08 x 10 ⁻²
Te	128	301	---	300	---	2.4	0.64 x 10 ⁻²
Total Ci/tonne			9.7 x 10 ⁵ (c)		1.9 x 10 ⁵ (c)		

(a) Obtained from Computer Program Isogen - a Computer Code for Radioisotope Generation Calculations. Reference 39.

(b) Includes ¹⁴⁴Ce daughter ¹⁴⁴Pr.

(c) Small contributors not itemized but are included in total.

FIGURE 7.1. Variation of Fission-Product Power with Time for One Tonne of Reactor Fuel Irradiated to 20,000 MWd/tonne at 15 MW/tonne

Basis: Waste from fuel irradiated at 20,000 MWd/tonne, 15 MW/tonne
 Fill Height = 6 ft
 Thermal Conductivity: Calcline 0.35 W/(m²)(°C/m)
 Water Storage Assumes a Water Temperature of 100 °C
 Air Storage Assumes Emmissivity = 0.8;
 Temperature, Ambient = 38°C

FIGURE 7.2. Heat-Age Environment Relationships for High Level Radioactive Solids Showing Fission Product Power Limits for 8- and 12-Inch Diameter Containers

runs, sufficient confidence in radioactive operation has been reached to specify most of the necessary details. One possible exception to this is that the PW-1 compositions used during radioactive operation had a tendency to foam, whereas a feed composition more typical of PW-1 that was tested during cold operation was more stable. Figure 7.3 is a Mode C flowsheet for PW-1 waste using an 8 inch pot and Figure 7.4 is a Mode A flowsheet for PW-2 using a 12 inch pot.* These two illustrations were chosen as typical for a waste plant after considering the feed types, operating modes, and pot size. Precautions that must be observed are solids in PW-2 waste and solids formation in the evaporator during continuous boiling operation. At present, it is recommended that PW-2 not be concentrated to less than 500 liters/tonne unless flowsheet changes can be made to reduce solids and the additives are in a separate stream to the pot. PW-1 can be concentrated much further (~325 liters/tonne); the small amount of sulfate additive required can be added directly to the feed. If this method of addition to PW-1 causes any "heavy" precipitates, the sulfate can be added to the pot in a separate stream. For good control of a separate additive stream, the volume of the additive stream should be at least 10% of the feed stream volume.

Two key control requirements are: (1) the HNO_3 concentration in the evaporator overheads should not be in excess of about 0.8M if the ruthenium decontamination factors shown are to be achieved, and (2) the maximum feed rates (and boiloff rates) should not be more than about 30 and 60 liters/hr for 8 and 12 inch pots, respectively, to attain the decontamination factor shown for nonvolatiles from the pot calciner. As mentioned above, a higher degree of confidence is needed to assure that true PW-1 will not foam during calcination. If it does

* See Page 7.9 for Flow Sheet Code for Figures 7.3 and 7.4.

foam, then maximum feed rates of about 20 to 25 and 40 to 50 liters/hr should be used for 8 and 12 inch pots, respectively, in order to maintain a sufficient freeboard in the pots.

The activity level in the fractionator is of particular interest because both the water and the acid require reuse or further treatment. Although the chemical level in each WSEP run was representative of 20,000 MWd fuel, the fission product spectrum used was not. In order to project WSEP data to actual performance, the same fractional distribution of activities as given in the Appendix, Table 9.1 was used for each run to increase particular radionuclides to the appropriate curie level assuming the waste was processed after one year discharge of the fuel from the reactor. Results are given in Table 7.3.

TABLE 7.3. *Calculated Curies in Fractionator Acid per Tonne of Feed if Feed Were Actual 20,000 MWd/tonne at 15 MW/tonne Waste Aged for 1 Year(a,b)*

<u>Run</u>	<u>Mode</u>	<u>Cerium- Praseodymium</u>	<u>Strontium</u>	<u>Ruthenium</u>
1	A	0.5	0.05	9
2	B	40	4	170
3	A-Mod.	0.7	0.07	14
4	C	4	0.4	200
5	C	0.2	0.02	32
6	A	0.04	0.005	42

- (a) *Calculated using activity distribution fractions from run data in the Appendix, Table 9.1 with both cerium-praseodymium and strontium represented by the total less ruthenium (T-Ru) values. These fractions are applied to the product of the tonnes processed and the selected Ci/tonne values in Table 7.2.*
- (b) *The volume of acid that contains these curies depends on the operating technique, feed type, etc., but it will probably average 200 liters of 10M HNO_3 /tonne of fuel processed.*

The acid produced in WSEP was nominally 10M HNO_3 but it can be as high as 12 to 13M. In an actual solidification plant, this acid could be recycled to the processing plant for fuel dissolution.

The ratio of the final condensate activity to 10 CFR 20 release limits was obtained by projecting run data as shown in Table 7.4. If the effect of different operating modes is neglected, the ruthenium, cerium-praseodymium, and strontium could each average 1000 to 10,000 times the 10 CFR 20 release limits.

TABLE 7.4. Projected Radionuclides in Condensate from Acid Fractionator^(a)

Nuclide	Feed, Ci/tonne	10 CFR 20 ^(b) Limit, μ Ci/ml	Projected Condensate, ^(c) μ Ci/ml	Ratio, Projected Condensate ^(d) to 10 CFR 20 Limit
Ce- ¹⁴⁴ Pr	4.6×10^5	2×10^{-5}	6×10^{-3} to 90×10^{-3}	300 to 4400
⁹⁰ Sr	4.7×10^4	3.7×10^{-7}	6.1×10^{-4} to 92×10^{-4}	1800 to 26,000
¹⁰⁶ Ru	1.2×10^5	1×10^{-5}	6.3×10^{-2} to 240×10^{-2}	6300 to 240,000
Others	3.4×10^5	9×10^{-6}	5.4×10^{-3} to 68×10^{-3}	600 to 7500

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

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

(c) Using weighted activity distribution fractions from runs PC-2 through PC-4 and as they are listed in the Appendix with all nuclides except ruthenium represented by the total less ruthenium (T-Ru) values. A condensate volume of 200 liters is used but it depends on feed type, pot size, etc., and will actually vary between 150 to 400 liters/tonne.

(d) Another simple distillation of the condensate would, in general, bring all values below 10 CFR 20 limits. The bottoms would be recycled to the high level waste evaporator.

FLOW SHEET CODE FOR FIGURES 7.3 AND 7.4Stream

1. Incoming feed for processing.
2. Evaporator feed during Mode C. Evaporator bottoms during Mode A. The evaporator bottoms must be recycled to the feed or to another treatment process.
3. Recirculating feed.
4. Feed to pot: see text regarding boiloff rates.
5. Pot condensate and noncondensibles.
6. Pot vent line reflux: continuous and equivalent to about 10% of pot boiloff.
7. Evaporator overheads.
8. Additive to pot: proportional to instantaneous pot feed rate. Additives are $\text{Ca}(\text{NO}_3)_2$ for PW-2 and H_2SO_4 for PW-1. Can be added with feed if solids do not jeopardize operation.
9. Evaporator strip water.
10. Pump seal water: depending on pump selection this stream may not be necessary.
11. Fractionator bottoms: can be reused for fuel element dissolution.
12. Fractionator condensate.
13. Fractionator condensate: available for recycle or treatment as low level waste.
14. System offgas.
15. Vent line water spray: approximately 15 liters/tonne are also added to the pot by washing the vent line.
16. Calcine product: pot is welded and stored.
17. Scrubber solution, approximately 1M NaOH.
18. Pot weight factor steam purge. If used, this will be continuous at approximately 1 liter/hr.

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	G	L	S	L
Volume, liters/tonne	378	378	325	325	310	50	3100	33	2637	50	250	2850	163	8×10^4	2	38	0.1
Average Rate, liters/hr	Batch	21	1200	18	17.8	2.0	203	1.8	177	3	Batch	189	Batch	4200	Batch	Batch	Batch
Gross Activity, Ci/tonne	1.0×10^6	1.0×10^6	-	1.01×10^6	8000	1000	127	0	0.74	0.014	127	0.8	0.046	$\leq 3 \times 10^{-4}$	0	1.0×10^6	-
^{106}Ru , Ci/tonne	1.2×10^5	1.2×10^5	-	1.25×10^5	5000	700	120	0	0.58	0.011	120	0.63	0.036	$\leq 3 \times 10^{-4}$	0	1.2×10^5	-
^{90}Sr , Ci/tonne	5×10^4	5×10^4	-	5.00×10^4	150	20	0.35	0	0.008	1.5×10^{-4}	0.35	9×10^{-3}	0.0005	$\leq 5 \times 10^{-8}$	0	5×10^4	-
$\text{Ce-}^{144}\text{Pr}$, Ci/tonne	4.6×10^5	4.6×10^5	-	4.61×10^5	1380	200	3.2	0	0.08	1.5×10^{-3}	3.2	9×10^{-2}	0.005	$\leq 5 \times 10^{-7}$	0	4.6×10^5	-
Fission Product Power, W/tonne	3500	3500	-	3535	33	2	0.05	0	~ 0	~ 0	0.05	~ 0	~ 0	~ 0	0	3500	~ 0
Non-FP Oxides, kg/tonne	31.7	31.7	-	32.0	0.3	0.03	~ 0	0	~ 0	~ 0	~ 0	~ 0	~ 0	~ 0	0	31.7	0.06
FP Oxides, kg/tonne	19.3	19.3	-	19.5	0.2	0.02	~ 0	0	~ 0	~ 0	~ 0	~ 0	~ 0	~ 0	0	19.3	~ 0
Total Oxides and Sulfates, kg/tonne	51.0	51.0	-	51.5	0.5	0.05	~ 0	2.5	~ 0	~ 0	~ 0	~ 0	~ 0	~ 0	0	53.5	0.06
Nitrate, g-moles/tonne	2840	2840	-	2130	1870	260	2910	0	64	1.0	2837	68	3	~ 0	0	~ 0	~ 0

FIGURE 7.3. Typical Flowsheet for PW-1 Waste with Mode C Operation
(See Page 7.9 for Flow Sheet Code)

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	G	L	S	L
Volume, liters/tonne	500	100	500	500	550	50	2800	98	2300	50	211	2589	289	8×10^4	2	60	0.1
Average Rate, liters/hr	Batch	Batch	1200	18	20	2	101	3.5	83	2	Batch	93	Batch	2800	Batch	Batch	Batch
Gross Activity, Ci/tonne	8.3×10^5	2.3×10^4	-	8.3×10^5	2.1×10^4	2000	120	0	0.13	-	35	0.15	0.02	$\leq 3 \times 10^{-4}$	0	8.0×10^5	-
^{106}Ru , Ci/tonne	1.0×10^5	2.0×10^4	-	1.0×10^5	1.8×10^4	2000	35	0	0.13	-	35	0.15	0.02	$\leq 3 \times 10^{-4}$	0	8.00×10^4	-
^{90}Sr , Ci/tonne	5.0×10^4	200	-	5.0×10^4	200	20	0.005	0	4×10^{-4}	-	0.005	4×10^{-4}	5×10^{-5}	$\leq 5 \times 10^{-8}$	0	5.0×10^4	-
$\text{Ce-}^{144}\text{Pr}$, Ci/tonne	4.5×10^5	1.8×10^3	-	4.5×10^5	1.6×10^3	200	0.05	0	4×10^{-3}	-	0.05	4×10^{-3}	5×10^{-4}	$\leq 5 \times 10^{-7}$	0	4.5×10^5	-
Fission Product Power, W/tonne	2970	200	-	2970	180	20	~ 0	0	~ 0	~ 0	~ 0	~ 0	~ 0	~ 0	0	2800	~ 0
Non-FP Oxides, kg/tonne	49.5	0.20	-	49.5	0.18	0.02	~ 0	10.5	~ 0	~ 0	0	~ 0	0	~ 0	0	49.3	0.06
FP Oxides, kg/tonne	20.4	0.08	-	20.4	0.07	0.01	~ 0	0	~ 0	~ 0	0	~ 0	0	~ 0	0	20.3	~ 0
Total Oxides and Sulfates, kg/tonne	69.9	0.28	-	69.9	0.25	0.03	~ 0	10.5	~ 0	~ 0	0	~ 0	0	~ 0	0	80.1	0.06
Nitrate, g-moles/tonne	2700	550	-	2700	2764	310	2530	374	50	1	2470	60	6	~ 0	0	~ 0	~ 0

FIGURE 7.4. Typical Flowsheet for PW-2 Waste with Mode A Operation
(See Page 7.9 for Flow Sheet Code)

8.0 FUTURE WORK

Analysis of the data available from the first six runs indicates the need for further work on the pot calcination process in several areas.

8.1 CALCINATION

Conclusive data are needed to define the maximum permissible centerline temperature. The pot calciner data at a 940 °C centerline are somewhat questionable because the run was interrupted. Data are needed for higher temperatures at total fission product power between 5 and 10 kilowatts to confirm the maximum power which a container can safely handle. Present temperature limits (900 °C centerline and 425 °C wall) need both laboratory and engineering scale evaluation to determine how much higher temperatures can safely go. This is necessary to establish a safe margin in production pots where thermocouples may not be present. To test higher specific power (watts/liter) in the calcined solid, a way is needed to achieve cooling during a run which represents the maximum power in a container cooled by water. Data on fission product power for the water cooled case are required to firmly project the allowable power for 6 to 12 inch diameter containers. Ways to increase the thermal conductivity of the calcine would be beneficial. All this should lead to the demonstration of pot calcination of wastes originating from a 45,000 MWd/tonne at 30 MW/tonne fuel as soon after discharge from reactor as practical.

The ability of the pot calciner to retain volatile constituents such as ruthenium should be demonstrated further. The results from the first six runs were favorable but more definitive data are needed to identify the equilibrium level of concentrations under recycle conditions. The level is expected to be low enough that operations will not be affected appreciably.

8.2 WASTE TYPES

Additional performance data for PW-1 and PW-2 wastes are needed. Values for ruthenium volatilization vary and further demonstration runs are needed to define the differences due to waste type and operating mode. In addition, at least one more waste type should be demonstrated; one which is typical of a low salt, high fission product waste produced by a modified "clean" Purex process (i.e., low iron, low sodium and no sulfate).

8.3 AUXILIARIES

Clarification is needed on what concentration of Purex waste can be stored, transferred, evaporated, and solidified. Data are needed for wastes containing sulfate with or without agents to decrease solids formation. Demonstration of Mode C with PW-2 waste is desirable. Although effluent acid and condensate were at acceptable levels of activity, methods to improve the DF through the evaporator and acid fractionator are desirable and should be demonstrated. Additional performance data on de-entrainment and filters are desirable to determine if a caustic scrubber is needed.

8.4 POT PERFORMANCE

Observations so far are confirming the expectations that initial and short-term effects would be small in pots filled by the pot calcination process. Since the "oldest" pot is less than two years old, very little can be concluded about long-term effects. Future work in this area is outlined in the product evaluation program.⁽³⁵⁾

Under the product evaluation program, filled pots will be placed in controlled environments and will be examined at intervals to determine the effects of age, temperature, feed type, pot material, and radioactivity on product stability and pot

wall corrosion. Both destructive and nondestructive tests will be made. Some pots will be stored at temperatures corresponding to those which would be experienced in pots of high level radioactive waste due to radioactive decay rates expected for wastes from 20,000 MWd/tonne at 15 MW/tonne waste. Others will be stored at lower temperatures for use as control references.

In the near future, an assessment of the magnitude of hazards associated with the rupture of a pot in air or water is needed to assure a properly balanced emphasis on safeguard measurements.

9.0 APPENDIX

9.1 RUN CHRONOLOGY AND MODES

Each run is briefly described. A schematic of equipment arrangement for each run is given in Figure 9.1.

PC-1

The first conversion of highly radioactive liquid waste to solids by pot calcination was successfully completed November 7 through 11, 1966. A total of 850 liters of sulfate-bearing PW-2 waste containing 0.7 W/liter of radioactivity was fed to the pot calciner in 43.7 hours. This was equivalent to processing waste from 2.2 tonnes of 20,000 MWd/tonne at 15 MW/tonne power reactor fuel aged 37 years. Nearly 85,000 curies of activity were fed to a 12 inch diameter pot. An operational Mode A equipment arrangement was used. PC-1 was the only run in which calcium and sodium nitrates were fed to the pot through a separate feedline. These additions were made to minimize sulfate volatilization from the calciner, primarily during the pot calcining period of 19 hours. An initial combined feed and additive rate of nearly 60 liters/hr was maintained for approximately 8 hours before start of calcine deposition on the pot walls. Once deposition started, the boil-off rate decreased rapidly due to gradual growth of scale on the walls. Feeding, at rates which decreased to below 5 liters/hr, was maintained without interruption throughout the run. The thermal liquid level probe, which was used to control the feed rate to the pot, performed well with the exception that it maintained the pot liquid level an estimated 3 to 5 inches lower than desired. Internal heat generation in the lower two zones of the pot produced a temperature increase of 25 to 35 °C in the calcine above the furnace operating temperatures (850 °C).

Self-cleaning of the vent line and the pot neck was successful using internal reflux. Only a small deposit of scale was found in the pot neck following the run.

Eighty-six percent of the ruthenium fed to the pot calciner was retained in the pot. A low ruthenium DF of 1.2×10^3 across the evaporator tower was obtained even though continuous sugar (reductant) addition to the evaporator was made. However, the level of ruthenium activity in the final condensate stream from the nitric acid fractionator was near the 10 CFR 20* requirements for discharge.

PC-2

During PC-2, 940 liters of PW-2 waste containing 430,000 curies of radioactivity (including 35,000 curies of radioruthenium) were fed to a 12 inch diameter pot. Waste equivalent to 2.3 tonnes of 6.2 years old, 20,000 MWd/tonne at 15 MW/tonne power reactor fuel was calcined. The run was performed under Mode B operation on February 7 through 11, 1967. The pot was fed for 42 hours at an average feed rate of 22.4 liters/hr. (An additional 99 liters of water was used to dilute out the heel of feed in the bottom of the tank since there was insufficient feed to completely fill the pot. This water was not included in the calculated average feed rate.) The average rate was nearly equal to the combined feed and additive rate of 21.4 liters/hr for run PC-1. Average processing rate, including a 28 hour calcining and cooling period but not including pot changeout, was 13.4 liters/hr or equivalent to processing waste from 0.79 tonne/day of power reactor fuel.

Calcined solids with a self-generating power density of 16.5 W/liter were produced. The internal power (1700 watts total) produced a noticeable increase in the internal pot temperatures during processing. When the pot wall temperature reached the furnace operating temperature, 850 °C, the furnace temperature was reduced to prevent calcine temperatures in excess of 850 °C. This basis for maximum temperature was established for PW-2 waste since one of the calcine constituents, Na_2SO_4 , has a melting point

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

of 884 °C. After the feed was shut off, the pot contents were calcined and the pot was then cooled by forced air cooling of the furnace susceptor to where the equilibrium wall temperatures in air would not exceed 425 °C. At equilibrium, with the 12 inch diameter pot sitting in the cool furnace, the Δt from pot wall to centerline was 235 °C with a maximum centerline temperature of 485 °C.

Calcium and sodium nitrates were added directly to the feed before the start of the run to prevent sulfate volatilization. However, some sulfate volatilization from the pot was observed through the off-gas line sight glass during the drying period but no detrimental effects were observed.

Preparation for runs PC-2 and PC-3 was prolonged by problems encountered in making up and handling PW-2 waste. Numerous plugs in equipment were caused by solids in the feed. Sulfates, mostly sodium-rare-earth sulfates, caused plugging of the feed pump loop, feed tank sparger, and several feed transfer lines. To prevent further plugging, the solids content was lowered by reducing the sulfate in the feed from 0.87 to 0.62 M. Sulfate was omitted from the batch of wastes being concentrated in the evaporator during PC-2. This concentrated batch was used for PC-3 by chemically adjusting it to 0.62M in sulfate just before the start of PC-3.

Mode B was used and consisted of feeding the pot from a batch feed-tank and collecting the calciner condensate in the evaporator at the same time the evaporator received and concentrated feed for the next run (PC-3). Approximately 30% of the ruthenium was volatilized from the pot into the evaporator.

PC-3

Run PC-3 was successfully completed one week after PC-2. As in PC-2, the sulfate concentration in the PW-2 feed was reduced (0.62 versus 0.87M) to lower the quantity of solids. Also, as in PC-2, calcium and sodium nitrates were added to the feed and aluminum was used as a partial substitute for iron since it was in

excess in the radioactive waste feedstock. No significant operating problems developed, and no pumping or feeding problems occurred in the run. A Mode A modified equipment arrangement was used. This arrangement consisted of feeding the pot from a feed tank and collecting the calciner condensate separately in a catch tank. The evaporator and fractionator were operated to scrub off-gases. Contaminated acid from the fractionator bottoms of the previous run was fed to the evaporator to simulate recycle of process condensate.

In PC-3, a total of 553 liters of feed (prepared in PC-2) containing 375,000 curies of radioactivity (including 32,000 curies of radoruthenium) was fed to an 8 inch pot in 31 hours. By collecting all of the pot condensate separately, it was possible to determine the evolution of ruthenium and other radioactive species from the pot calciner as the run progressed. Nearly 31% of the radoruthenium and 0.3% of all other activity was collected in the condensate from the pot. This was twice the ruthenium that was evolved during PC-1 but was comparable to PC-1 for the other radioactive constituents.

Pot internal temperatures were controlled by reducing the furnace temperature when calcine temperatures in a zone reached approximately 800 °C. This technique gave a slight overshoot of approximately 25 °C above the maximum desired calcine temperature (850 °C).

The pot calcining and cooling periods required 15.5 hours. Thus, an average processing rate of 11.9 liters/hr or 0.72 tonne of power reactor fuel per day was achieved.

A self-generating power density of 30 W/liter in the calcine (1800 watts total) was achieved by processing waste equivalent to 1.4 tonne of 3.4 year old power reactor fuel (20,000 MWd/tonne at 15 MW/tonne). Equilibrium pot temperatures were similar to those for the 12 inch pot used in PC-2.

Equipment performance during both PC-2 and PC-3 was satisfactory. The pot vent line was washed by internal spraying prior to both runs and at the termination of the pot feeding periods. Because of this washing and the continual self-cleaning feature of partial reflux in the line, the pot throat was visually clean at the end of both runs. (The vent line was not inspected. Because the pot throat was clean, the vent line was also considered clean.) The thermal pot-liquid-level probe was used to control the feed rate to the pots and gave good results. Whereas in PC-1 and PC-2 the probe maintained the level from 3 to 8 inches lower than desired for the 12 inch pots, the operating level appeared to be normal in PC-3 where an 8 inch pot was used. In PC-1, the pot weight factor dip tube was the same length as the thermal level probe; in PC-2 it was 3 inches longer; in PC-3 it was shortened and used only as a pressure tap.

PC-4

Pot calcination run PC-4 was successfully completed June 26 through 30, 1967, with a modified PW-1 feed composition. Excessive sodium in the Purex Waste used for feed makeup required the addition of an equivalent amount of sulfate to prevent formation of volatile sodium and cesium oxides. Sodium and sulfate concentrations were 0.47 and 0.26M, respectively (vice flowsheet values of 0.14 and 0.10M).

A total of 650,000 curies, including 47,000 curies of Ruthenium-106 and a Strontium-90 spike of 30,000 curies, in 1060 liters was fed to the 12 inch pot in 42 hours at an average feed rate of 25 liters/hr. The high feed rate was partially due to some concentrating of the feed in the evaporator since a Mode C equipment arrangement was used; the pot was fed from the boiling waste evaporator. All of the pot condensate was returned to the evaporator for recycle with the feed, and the evaporator was continuously supplied with waste from a batch feed tank.

An objective of PC-4 was to observe the recycle effect on ruthenium since, with Mode C, a constituent which volatilizes from the pot will increase to some steady-state concentration in the evaporator. Analysis of pot condensate samples showed that only 5% of the ruthenium in the total feed to the pot was volatilized. Final samples of the feed remaining at the end of the run revealed no increase in ruthenium and confirmed the low volatilization. Although low volatilization from the pot was very encouraging, the quantity was so low that ruthenium recycle information was not definitive.

Additional removal of ruthenium from the gas stream was sought by adding sodium hydroxide solution to the top tray of the acid fractionator. It was found that the ruthenium decontamination factor (DF) was only as good as the better DF's (approximately 5000) during other runs where no caustic was used.

All equipment operation during the run was satisfactory except for expulsion of some feed from the pot and semi-continuous plugging of the waste-evaporator specific-gravity dip-tube. After the feed was concentrated to approximately 120 liters/tonne in the pot, a nearly instantaneous foaming condition was encountered and approximately 20 liters of concentrated feed was expelled through the safety-relief seal pot. After operating with water as feed to the pot for 1 hour, the relief system functioned normally and the run was continued. At the time of the expulsion, the feed rate to the pot was 57 liters/hr and the level was in Zone 3. Additional expulsions were avoided by operating at a reduced feed rate (35 liters/hr versus 50 to 60 liters/hr originally) and maintaining a lower operating level in the pot to allow more freeboard for foaming during the high boiloff portion of the run. (An approximate level can be inferred from the pot internal temperatures.) As in previous runs, refluxing condensate in the pot vent line resulted in a clean pot throat at the end of the run.

Completion of calcination and cooling of the pot contents after the feed was turned off required 33 hours to give an average

processing rate of 14.1 liters/hr. One hundred and sixty-six kilograms of calcine was produced; decay power was 2600 watts.

Pot temperatures were controlled at ≤ 900 °C by using step-wise temperature changes. The furnace temperature was reduced, from an initial 900 °C, in 200 °C steps when the pot wall temperature reached 875 °C and when the internal temperature in any zone reached 750 °C. After the pot was cooled and removed from the furnace, the steady state centerline temperature was 477 °C and the ΔT from centerline to pot wall was 312 °C with the pot hanging in 40 °C air.

PC-5

Run PC-5 employed a modified PW-1 feed composition. As in run PC-4, excess sodium in the Purex 1WW used for feed makeup required the addition of sulfate to prevent volatility of the alkali metal oxides. Sodium and sulfate concentrations were 0.64 and 0.35M, respectively, rather than the 0.14 and 0.10M nominal PW-1 composition.

A total of 1,150,000 curies, including 18,000 curies of radioruthenium, was fed in 515 liters to the 8 inch pot in 28 hours for an average feed rate of 18.4 liters/hr. Eleven hours were required for calcining and cooling. The overall average feed rate was 13.2 liters/hr. Wastes equivalent to 1.25 tonnes of 1.4 years old 20,000 MWd/tonne at 15 MW/tonne power reactor fuel were processed to a calcine containing 4300 watts. The calcine power density (approximately 80 W/liter) was sufficient to produce a maximum pot centerline temperature of 725 °C and a centerline to wall ΔT of 495 °C. Thus, although the power was approximately 15% below that planned, the ΔT was 5% greater than expected. This was because the effective thermal conductivity for the calcine was only $0.38 \text{ W}/(\text{m}^2)(^\circ\text{C}/\text{m})$ [$0.22 \text{ Btu}/(\text{hr})(\text{ft}^2)(^\circ\text{F}/\text{ft})$] versus the pre-run estimate of $0.52 \text{ W}/(\text{m}^2)(^\circ\text{C}/\text{m})$. This latter value was arrived at by applying the temperature coefficient found for K during PC-4 to observed K found for PW-2 waste during PC-3.

Pot temperatures were controlled so as not to exceed 950 °C using essentially the same temperature control scheme as during PC-4, except different temperature reduction points were used. With the furnace operating at 900 °C, the control scheme was: when a pot wall temperature rose to 875 °C, the furnace temperature in that zone was reduced to 700 °C; at a pot centerline temperature of 600 to 650 °C, the furnace zone was turned off; and at a pot centerline or intermediate temperature of 800 °C, cooling of the zone was started. This method of control was easily performed and satisfactorily assured denitration of the calcine while preventing excessive calcine temperatures.

Natural heat loss from the furnace was barely adequate to provide cooling for the 4300 watts in the pot. At steady state temperature, with the furnace off and without air cooling, Zone 4 centerline temperature was 900 °C and the furnace susceptor temperature was 385 °C.

Less than 5% of the ruthenium in the feed to the pot was volatilized to the pot condensate while using a Mode C operation. This confirmed the low volatility which was experienced during PC-4 using Mode C and PW-1 waste. Again, as in PC-4, the 5% volatilization was so low that ruthenium recycle information, as the run progressed, was not definitive.

Sample contamination problems due to in-cell handling appeared to be corrected during PC-4 but were again apparent during PC-5. Contamination of samples was apparent in the fractionator, fractionator condensate, and caustic scrubber. This was primarily due to unclean samplers. In addition, it was also concluded that the entire batch of fractionator condensate became contaminated by "foreign" radioactivity during the run. This too may have been due to an unclean sampler.

Foaming of the PW-1 feed was evident during the run; however, no feed was expelled from the pot as happened during PC-4. Although the pot operating level was not controlled lower than

normal for an 8 inch pot, a sufficient freeboard for foaming was maintained, especially during the high boil-off portion of the run, by limiting the maximum initial feed rate to 25 liters/hr. During PC-5, the first indication of foaming occurred at the time that calcine began depositing on the pot wall.

As during PC-4, the only problem encountered with the auxiliary equipment was plugging of the specific gravity dip tube in the waste evaporator. The dip tube plugged after 16 hours of running even though the evaporator feed was kept slightly dilute up to this time. Control was maintained by the boiling temperature which was less accurate than specific gravity. Plans to purge the dip tube with a continuous steam purge were foiled when the dip tube became completely plugged midway through the run. The evaporator sparger also became plugged during PC-4 and PC-5. Sparger and dip tube were both opened after PC-5. The evaporator liquid level dip tube only periodically plugged while boiling feed and was always cleared by steam purging.

PC-6

Pot calcination run PC-6 converted 460 liters of PW-2 waste containing 1.3 million curies into a calcined solid in an 8 inch pot. The 5100 watts of internal power in the calcine produced a maximum pot centerline temperature of 940 °C and a pot centerline to wall ΔT of 700 °C with the pot suspended in 40 °C air. The centerline temperature was sufficient to exceed the planned maximum internal temperature of 900 °C for cooling by natural air convection. Thus, a major objective in the series of pot runs was achieved. The effective thermal conductivity of the calcine product was $0.30 \text{ W/(m}^2)(^\circ\text{C/m)}$ [$0.18 \text{ Btu/(hr)(ft}^2)(^\circ\text{F/ft)}$]. This was considerably below the pre-run estimate and was basically the reason for achieving thermal maximum using only 74% of the originally intended internal power (5100 versus 7000 watts).

Because of two feed pump failures, the run was conducted in three parts. The first failure occurred after 360 liters of feed to the pot.

Since the pot was allowed to complete the entire calcination and cooling temperature cycle, all analytical data were evaluated only up to this point and are thus uninfluenced by the run restarts. Data on the calcine in the pot were probably influenced by some undeterminable amount, however.

The pot centerline temperature in the receiver furnace was held to a maximum of 960 °C by means of the forced convection cooling system operating at capacity. The temperature was 10 degrees higher than the desired maximum, and it showed that the maximum cooling rate of the susceptor, externally air cooled, was reached in this run using one blower rated at 275 scfm. (Forced air flow inside the susceptor was not used.) Pot temperatures dropped by approximately 50 degrees when the pot was transferred from the furnace cooling environment to cell ambient temperature. The maximum cooling rate in the furnace was not quite as high as cooling by natural convection and radiation (at a pot wall temperature of about 250 °C).

Multiple startups and shutdowns during PC-6 did not adversely affect the volatilization of ruthenium. After the first shutdown, 13.5% of the ruthenium delivered to the pot had volatilized. After the third shutdown when the pot was full, 12.1% of the total ruthenium delivered to the pot had volatilized.

In order to determine if ruthenium concentration in the feed would affect the amount of ruthenium volatilized from the pot, the ruthenium concentration in the PC-6 feed was made twice that of the three previous PW-2 runs (0.0064M versus 0.0032 M). Since the percent of ruthenium volatilized was near the same range as previous PW-2 runs (14 to 31%), the concentration of ruthenium apparently had little effect on the amount volatilized. The volatilization of technetium from the pot calciner was determined for the first time and 4% of the total technetium in the feed to the pot was found in the pot condensate. This was not significantly different from the 1.2% of nonvolatile radioactivity that was found in the pot condensate.

Beside the two pump failures, the only other significant operating difficulty was the unreliability of the thermal-type level probe. Although the probe operated satisfactorily during the first four pot runs, its reading was unreliable in both PC-5 and PC-6. The weight factor probe was used manually to continue operation during PC-6 while the accuracy of the liquid level reading was being checked, the pot was slightly overfilled because manual reductions in the feed rate were not made soon enough. The two feed pump failures that occurred at close intervals during the run were unrelated since the first pump failed mechanically and the second failed electrically.

Feed consumed (460 liters) was approximately 10% less than previously experienced for a similar run with PW-2 feed. The decrease in capacity was evident early in the run when it appeared that the pot was nearly filled to its solids capacity just before the first interruption by a pump failure.

9.2 CALCINER POTS

Two sizes of solidification pots were used. A 12 inch diameter pot is shown in Figure 9.6. Pots were made from 304-L SS with a 0.312 inch thick wall. Outside diameters were 8.625 and 12 inches. Height was 8 feet. These sizes were selected on the basis of (1) heat generation rates anticipated, (2) size limitations in the WSEP, and (3) a volumetric scaleup factor of 2.0 between the two sizes.

The calcine pots were made with a small head (5 inches OD) to take advantage of easier clamping and sealing, and to provide four process pipe connections in one connector.

The process connections included a 2 inch diameter off-gas vent and three 3/8 inch ID pipes for feed chemical addition, and pressure measurements. The chemical addition or pressure line may be used as a liquid level measuring dip tube if purged with steam. The pot head incorporated a special "vee" flange for clamping to the mating process head, and an integral raised lip for sealing by fusion welding.

Each calcine pot had two internal thermocouple wells made from 1/2 inch diameter 304-L SS schedule 40 pipe. Each well contained one thermocouple in each of the six furnace heating zones. One well was located along the axis of the pot, the other well was between the axis and the pot wall. The centerline thermocouples provided information during processing and were used to monitor maximum calcine temperatures during storage of the pot. The thermocouples near the pot wall provided information on wall scaling and trends of centerline temperature during processing.

One thermocouple pad was welded to the outside wall in each heating zone to provide more accurate wall temperatures during and after processing. The thermocouples were ungrounded chromel-alumel junctions with magnesia insulation, and were covered with 1/8 inch diameter 310 SS sheaths. Ungrounded junctions provided easy checking of continuity. All pot thermocouples terminated through short, high-temperature leads with braided stainless steel protection. A single sealed 20-thermocouple connector (Cannon KPTM 00f20-41P) was used. It was mounted on a light, rigid framework attached to the pot and was protected from excess temperatures during furnace operation by both a heat shield and forced air cooling.

The WSEP pots included many more thermocouples than would be needed for routine production control. Similarly, many special features and requirements were attached to gain information on performance during and after processing.

9.3 INDUCTION HEATED FURNACE

High temperature induction and resistance furnaces were used in WSEP. The induction furnace was selected for evaluation during pot calcination (See Table 9.4).

An artist's concept of a vertical section through the induction furnace (See Figure 9.7) illustrates four basic design elements: (1) the rack structure, (2) the furnace proper, with its heating and cooling systems, (3) the containment systems, and (4) the pot fill head.

The support rack is a 6 inch pipe frame designed to support loads up to 16 tons centered at the fill head. Upper and lower rack plugs, integral with the frame, hold the rack to the wall. The upper plug is a pipeway for furnace cooling lines. It is filled with lead for shielding. The lower plug acts as a guide tube for the smaller furnace electrical plug which moves back and forth with the furnace.

The furnace is supported by a four-wheel trolley which is moved manually from "load" to "fill" position by pushing or pulling on the service gallery end of the furnace plug. Furnace movement is perpendicular to the wall and furnace centerline distances from the inside cell wall are 48 and 78 inches at "load" and "fill", respectively.

The furnace consists of six identical sections with individual heating and cooling. Induction heating power supply consists of six heating stations powered in parallel by a one-kilocycle, single-phase, ac 175 kilowatt motor generator set. Temperature control is on-off with manual setting of individual zone power supply up to 30 kilowatts. Thermocouples inside the furnace susceptor are connected to suitable control devices which open and close main heating station contactors in response to thermocouple signals.

Thermocouples for temperature control of the furnace are in a removable cage positioned inside the furnace susceptor. This cage consists of 24 vertical 1/4 inch Hastelloy-X tubes arranged in a 13 inch diameter circle. Eighteen of these tubes are for thermocouples, three in each zone equally spaced radially. Three tubes are for auxiliary coolant supply (air, water, or steam), two for jet suction intake, and one for liquid level indication.

Cooling air to the furnace is supplied by two 35 psig blowers located in the service gallery and rated at 275 scfm each of dry air. Air flow is controlled by solenoid valves. Air flows through the upper plug into each of the six furnace zones via

flexible steel hose and discharges into the annulus between the insulation liner and the furnace susceptor. It then flows upward and outward to the plenum chamber between the shell and coil, and downward to exhaust into the cell.

Tables 9.1 through 9.5
and
Figures 9.1 through 9.8

TABLE 9.1. Run Data and Definitions

Solidifier Run Number	PC-1	PC-2	PC-3	PC-4	PC-5	PC-6
<u>Operational Data</u>						
Date of Run	11/66	2/67	2/67	6/67	7/67	9/67
Operating Mode	A	B	A-modified	C	C	A
Pot Diameter, in.	12	12	8	12	8	8
Pot Material	304-L	304-L	304-L	304-L	304-L	304-L
Feed Type	PW-2	PW-2	PW-2	PW-1	PW-1	PW-2
Feed, liters/tonne	400	400	420	370	410	390
Run Feed Time, hr	43.7	42	31	42	28	43 ^(a)
Average Feed Rate, liter/hr	19.5	22.4	18	25	18.4	10.7 ^(a)
Calcination + Cooling Time, hrs	27	28	15.5	33	11	8 ^(a)
Total Feed Volume, liters	850 ^(b)	940 ^(c)	553	1060 ^(d)	515	460 ^(a)
Average Processing Rate, liter/hr	12	13.4	11.9	14.1	13.2	8.5
Tonnes Equivalent in Total Feed	2.2	2.3	1.4	2.8	1.25	1.2 ^(a)
Feed Added Prior to Calcine Deposition, liters	500	550	240	250	88	125
Feed: Solid Vol. Ratio	8	9	9	9.1	9.4	7.7
Feed Temp. to Pot, °C	30	30	70	<70	50 to 60	35
<u>Off-Gas Line</u>						
Reflux Rate, liter/hr	1.8	2	2 to 4	2	2	2
Water Spray Addition, liters						
Prior to Run Start	--	50	23	30	15	15
Following Feed Shutoff	--	6	5	--	2	2
Max. Vent Line Vapor Velocity						
2 in. Section, $\frac{ft}{sec}$	38	34	19	38	17	18
<u>Process</u>						
Vacuum in Pot, in. H ₂ O	20	15	15	15	15	15
Off-gas Flow (inleakage), scfm	1.5	2	1.5	1 to 2	1 to 2	1 to 2
EVAPORATOR (TK-113)						
<u>Average Operating Conditions</u> ⁽ⁿ⁾						
Bottoms						
Feed	--	PC-3 (PW-2)	PC-2 5M acid	PC-4 (PW-1)	PC-5 (PW-1)	--
Liters/tonne (during pot feeding)	--	400	--	270	485	--
Molarity, M HNO ₃	4.5	--	5.5	--	--	7
Overheads, M HNO ₃						
1st half (during pot feeding)	0.65	0.7	0.5	0.84	0.7	0.8
2nd half (during pot drying & cooling)	0.25	0.3	0.5	0.3	0.5	0.3
Sugar Reductant Addition (@ 0.085M), g-moles ^(o)	5.53	5.18	7.48	--	--	--
Boiloff Rate, liters/hr	105	179	112	108	138	61
Strip Water Addition Rate, liters/hr	90	152	85	94	102	48
FRACTIONATOR (TK-115)						
<u>Average Operating Conditions</u> ⁽ⁿ⁾						
Bottoms, M HNO ₃	10	7.5	9.5	9.6	10.4	7.8
Overheads, M HNO ₃	0.04	0.03	0.02	0.03	0.07	0.02
Reflux ratio	0.1 to 0.2	0.1 to 0.2	0.1 to 0.2	0.1 to 0.2	0.1 to 0.2	0.1 to 0.2
Boiloff Rate, liters/hr	100	197	112	105	121	56
NaOH Addition to Fractionator Tower, liters	--	--	--	361 liters 4M @ 5 liter/hr	--	--
FRACTIONATOR Condensate (TK-116), M HNO ₃	0.04	0.03	0.02	0.03	0.07	0.02
SCRUBBER (TK-118)						
Recirculation Rate, liter/hr	40	40	40	20	20	20
Bottoms, M NaOH	1.5	0.9	1.15	0.9	1.5	1.1

TABLE 9.1. (contd)

Solidifier Run Number		PC-1	PC-2	PC-3	PC-4	PC-5	PC-6
<u>Fraction of Activity Distributed: Total Less Ru (T-Ru) and Ru^(f)</u>							
Thru 1st Cond., 10 ⁻⁵	(T-Ru)	4.0	~4.0	2.9	NA	NA	12 ^(e)
	(Ru)	140	~300	310	54	33	135
Thru Evap. Cond., 10 ⁻⁶	(T-Ru)	1.0	90	<1.5	7.0	0.32	0.1
	(Ru)	74	1420	120	1700	310	350
Thru Fract. Cond., 10 ⁻⁹	(T-Ru)	<1.6	40	3.2 ^(g)	9.6	25 ^(h)	<0.1 ^(g)
	(Ru)	<13	3950	120	280	17,000 ^(h)	170
Off-gas to Scrub, 10 ⁻⁹ (i)	(T-Ru)	1.6	1400	100	3.1	NA	10
	(Ru)	880	10,600	1700	51	NA	70
Off-gas to Stack, 10 ⁻¹² (i)	(T-Ru)	NA	1.1	<1.7	<1.3	<0.7	0.6
	(Ru)	NA	<2400	<2300	<1000	<1300	NA
Ratio Activity in Fract. Cond. to 10 CFR 20 Limits	(T-Ru)	NA	350	70 ^(g)	1800 ^(j)	2200 ^(h)	20 ^(g)
	(Ru)	<16	6400	350	1000	40,000 ^(h)	1600
<u>Filled Pot Data</u>							
Curies in Feed to Pot (Total 8γ)		85,000	430,000	375,000	650,000	1,150,000	1,300,000 ^(e)
Curies of Ru in Feed to Pot		9,200	35,000	32,000	47,000	18,000	36,000 ^(e)
Solid in Pot, liters (estimated)		105	105	60	110	55	60
Solid in Pot, kg		151	141	86.4	166	86	79.5
		(166 ca)	(139 ca)	(88.5 ca)	(167 ca)	(86 ca)	(73 ca)
Solid in Pot, liters/tonne equivalent waste		50	45	47	41	43	50
Power in Pot, watts		600	1700	1800	2700	4300	5100
		(420) ^(k,l)	(1500) ^(k)	(1800) ^(k)	(2600) ^(k)	(4300) ^(k)	(4850) ^(k)
Equivalent Aging Time, years		37	6.2	3.4	4.8	1.4	1.1
̄ Temp. in Air, °C		140	485 ^(m)	410 ^(m)	477	725	940
̄ Temp. in Water, °C		NA	NA	NA	370	NA	850
Δ Temp ̄ to Wall, °C		70	235	220	312	495	700
Total Corrosion, mm		none	NA	NA	NA	NA	NA
Pot Pressure, Initial Pressure		15 psig	8 in. Hgvac	-0.5psig	-	-	54 in. Hgvac
Later Pressure		7 psig	10 in. Hgvac	28 in. Hgvac	12 psig	2 in. Hgvac	11 in. Hgvac
Time Between Readings, months		3	8	11.5	6.5	8	6
Radiation Reading, R/hr @ 6 in.		2.5x10 ⁴	2.4x10 ⁴	3.9x10 ⁴	3.8x10 ⁴	4.9x10 ⁴	5.7x10 ⁴

(a) Feeding period extended to obtain maximum fill. Data for all three run parts.

(b) Does not include 85 liters of Ca(NO₃)₂ additive which was a separate stream to the pot.

(c) Does not include additional 99 liters of water added to pick up feed heel.

(d) Includes 60 liters which were expelled from the pot because of foaming.

(e) All DF data for PC-6 are through the first shutdown only and include a complete calcination and cooling cycle. 980,000 total curies including 28,000 curies of Ru were fed to the pot prior to the first shutdown.

(f) These values cannot be used for calculating individual equipment DF's.

(g) Corrected because of contamination to give DF approximately equal to that for Ru.

(h) Entire batch believed to be contaminated from foreign source.

(i) Activity from all sources in WSEP passing through this point during solidification runs.

(j) PC-4 was spiked with strontium; strontium is 80% of this value.

(k) Values in brackets are from pot calorimetry data.

(l) After 3 months aging.

(m) Values are with the pot sitting in the cool furnace.

(n) Through part 1 for PC-6. See Note (e).

(o) Added continuously during feeding, calcining and cooling periods.

*Definitions for TABLE 9.1*Operational Data

Feed type	PW-1, 2 = Purex waste - 1 or 2, See Appendix Table 9.3.
Feed, liters/tonne	Feed concentration. Liters of basic feed per metric ton (2205 lb) of uranium processed
Pot diameter, inches	8 = 8 in. Sch. 40 pipe; 12 = 12 in. OD with 5/16 in. wall thickness
Pot material	Type of steel. 304-L = 304-L Stainless Steel
Run feed time, hours	Total hours that feed was actually on
Average feed rate, liters/hour	Average rate during run feed time. Does not include drying, cooling or pot removal. Does not include separate additive streams.
Calcination + Cooling, hours	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 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.
Feed: Solid volume ratio	Concentration factor from liquid feed to estimated volume of solid in the pot.
Operating mode	WSEP equipment arrangement, see Section 5 and Figure 9.1

Process

Off-gas flow, scfm	Total vapor flow exiting the nitric acid fractionator as measured with a calibrated orifice.
Average operating conditions	Values are for entire run unless otherwise specified.

Fraction of Activity Distributed

Fraction in off-gas to stack	Fraction of total activity fed to the solidification unit which was accumulated in the condensate or off-gas. The presence of additional activity (other than that going to the process) in the tanks at the start of a run and from feed to the evaporator during a mode B or C run is not factored in but does influence the results. Cumulative decontamination factors given in Table S-2 allow for this additional activity. (T-Ru) = total activity less ruthenium.
Ratio activity/10 CFR 20	Fraction of activity fed to solidifier which appeared in stack during the operating week. Basis is all activity from 324 Building whether originating from WSEP or not.
	Ratio of specific activity gained in final condensate in as-produced volume to maximum permissible concentration limits based on AEC Code of Federal Regulations, Title 10, Part 20, Table II, Column II. For (T-Ru), cerium praseodymium is predominant unless otherwise noted.

Filled Pot Data

Solid in pot, liters	Liters of solid produced from processed wastes.
Solid in pot, kg	Weight of calcine as measured and as calculated from expected quantities of oxides and sulfates.
Power in pot, watts	Rate of self-heat generation in pot from radioactive decay, based on analysis and heating test of feed tanks and on pot calorimetry after filling.
Equivalent aging time, years	Out-of-reactor time of 20,000 MWd/tonne at 15 MW/tonne power reactor fuel waste required to produce the same amount of power as in WSEP pot (but not necessarily the same number of curies).
̄ Temperature in air, °C	Maximum pot centerline temperature (usually Zone 4) with the pot suspended in approximately 40 °C air.
̄ Temperature in water, °C	Maximum pot centerline temperature with the pot sitting in 30 °C water
Δ Temperature, ̄ to wall, °C	Temperature difference between the centerline and outside of the wall of the pot with the pot cooled to its steady-state temperature in air. Measurements are in the same zone.
Total Corrosion, mm	Corrosion as detected by ultrasonic probe. (Detection limit ±0.25 mm)
Pot Pressure	Pressure in sealed pot as detected by a pressure gage.
Radiation reading, R/hr	Maximum radiation dose from pot. Detected with unshielded ionization chamber in cell.

TABLE 9.2. Material Balance for Pot Calcination Runs PC-1 through PC-6

Pot Calciner Run No.	FEED					TK-113 EVAPORATOR				TK-115 FRACTIONATOR			
	To Pot		To Evaporator			Volume, liters		Net Change		Volume, liters		Net Change	
	liters	kg	Material	liters	kg	Initial	Final	liters	kg	Initial	Final	liters	kg
PC-1	850	1113	--	--	-	143	232	+ 89	+ 89	412	944	+ 532	+ 677
PC-2	1039	1275	PC-3 feed	968	1126	445	51 ^(a)	+ 70	+ 76	296	940	+ 644.4	+ 836
PC-3	553	667	HNO ₃	543	637	1307	156	-1151	-1172	454	551	+ 97	+ 123
PC-4	1060	1450	PC-4 feed	1307	1790	63	504	+ 441	+ 532	390	1000	+ 610	+ 761
PC-5	515	695	PC-5 feed	758	1022	54	215	+ 171	+ 226	419	644	+ 225	+ 274
PC-6 ^(d)	360	474	--	--	--	186	251	+ 65	+ 65	393	618	+ 225	+ 225

	TK-116 FRACTIONATOR CONDENSATE				TK-118 SCRUBBER				TK-117 POT COND. CATCH TANK			
	Volume, liters		Net Change		Volume, liters		Net Change		Volume, liters		Net Change	
	Initial	Final	liters	kg	Initial	Final	liters	kg	Initial	Final	liters	kg
PC-1	166	907	+ 741	+ 741	409	218	- 191	- 195	60	129	+ 79	+ 90
PC-2	180	1007 ^(b)	+1538	+1542	405	267	- 138	--	--	--	--	--
PC-3	197	931 ^(c)	+1717	+1717	489	398	- 91	- 91	56	761	+ 705	+777
PC-4	212	900	+ 688	+ 688	510	380	- 130	- 132	956	991	+ 35	+ 35
PC-5	194	786	+ 592	+ 592	482	453	- 29	- 31				
PC-6	212	424	+ 212	+ 212	491	401	- 90	- 90				

	Pot				Additives				Product			
	Vent Line		Weight		Fractionator		Process		Netted,		Net	
	Spray, liters(f)	Factor	Steam, liters	Additive Ca(NO ₃) ₂ , liters	Tower NaOH, liters	Condenser Steam, liters	Evaporator Sugar, liters kg	kg	kg	liters	kg	Recovery, % (e)
PC-1	70	71		85	---	205	65 65.5	151	-91.2	-103	93.7 94.1	
PC-2	56[6]	27		--	---	178.5	61 61	141	-127	-129	94.5 95.2	
PC-3	28[5]	18		--	---	123.4	88 91	86.4	-15.4	- 43.4	101 98.4	
PC-4	30	73		--	108	275	-- --	166	-19	-103	98.6 95.5	
PC-5	17[2]	35		--	---	151	-- --	86	+ 2	- 73	100 94	
PC-6	15	25		--	---	125	-- --	74 ^(g)	---	---	96 96	

(a) 464 liter of PC-3 feed was transferred to a hold tank prior to 51 liter heel.

(b) 711 liter was transferred to TK-117.

(c) Excess volume was transferred out before run start.

(d) Up to first run interruption

(e) TK-118 excluded from material balance.

(f) Value in brackets is portion added at end of run. Remainder was added prior to run to provide water for startup.

(g) Total after all three parts of run.

TABLE 9.3. Run Feed Compositions

Component	Feed Type→	PW-2				PW-1	
	Run No.→	PC-1	PC-2	PC-3	PC-6	PC-4	PC-5
Molarity M ^(a)							
H ⁺		4.19	----	----	3.55	----	2.59
Fe ⁺³		0.445	0.224	0.074	0.094	0.82	0.8
Cr ⁺³		0.024	0.02	0.02	0.024	0.012	0.012
Ni ⁺²		0.01	0.02	0.02	0.01	0.005	0.005
Al ⁺³		0.02	0.224 ^(b)	0.388 ^(b)	0.35 ^(b)	0.11 ^(b)	0.13 ^(b)
Na ⁺¹		0.93	0.78	0.82	1.08	0.474	0.64
(NO ₂ ⁻ + NO ₃ ⁻)		~5.4	~5.4	~5.4	~5.4	~6.5	~6.5
SO ₄ ⁻²		0.87	0.618	0.623	0.62	---- additive	----
PO ₄ ⁻³		0.004	0.01	0.01	0.006	0.003 below	0.003
U ⁺⁶		----	0.007	0.01	0.01	0.01	0.01
SiO ₃ ⁻²		~0.01	~0.01	~0.01	~0.01	~0.01	~0.01
Cs ⁺ (added K ⁺)			0.042			0.042	
Sr ⁺²			0.0155			0.0155	
Ba ⁺²			0.0195			0.0195	
(Y + Rare Earths) ⁺³			0.12			0.12	
ZrO ⁺⁴			0.065			0.065	
MoO ₄ ⁻² + Tc as MoO ₄ ⁻²			0.079			0.079	
Ru ⁺²			0.0032		0.0064	0.0032	
Ru ⁺² (added Mn ⁺²)			0.0288		0.0256	0.0288	
Rh ⁺² (added Co ⁺²)			0.0074			0.0074	
Pd ⁺² (added Ni ⁺²)			0.0172			0.0172	
Ag ⁺¹ + Cd ⁺² (added Cu ⁺²)			0.0016			0.0136	0.0016
Te (added SO ₄ ⁻²)			0.0064			0.0064	
<u>Additive to Feed</u>							
Ca ⁺²		0.25	0.19	0.175	0.087	----	----
Na ⁺¹		0.3	----		----	----	----
SO ₄ ⁻²		----	----	----	----	0.26	0.35
M _T ⁺ (components + additives) ^(c)		4.13	3.67	3.44	3.65	4.29	4.45
<u>Data (@ Final Vol)</u>							
Final Vol, liters/tonne		400	400	420	390	370	410
Oxide Weight/liter feed, kg		0.195	0.148	0.145	0.159	0.167	0.167
Sp. Gr. @ 25 °C		1.31	1.24	1.26	1.32	1.37	1.35
Solids, Volume%		12	2.8	11.4	17	~6.0	13
<u>Radioactivity</u>							
Total, Ci/liter		100	460	680	2830	610	2230
Ru, Ci/liter		10.8	37	58	78.5	44	35
Power, W/liter		0.7	1.85	3.2	11	2.4	8.3

(a) Molarities are at 378 liters/tonne

(b) Aluminum existing in feedstock was used as partial substitute for iron in feed makeups.

(c) M_T⁺ is the summation of chemical equivalents of metallic cations including fission product cations.

TABLE 9.4. Pot Calciner Induction Furnace Specifications

Item	Induction
1. Number of Zones	6
2. Zone Height, in.	13
3. Power/Zone, kW	30
4. Design Temperature, °C	1000
5. Zone Heating Element	20 turn, 18 in. ID, Insulated copper coil (1/2 in. OD x 0.088 in. wall)
6. Power Supply	1 kc, 200 V, single phase ac from 175 kW motor generator set
7. Insulation	1 in. thick built-up layer with Ceraform® blocks cemented with Tipersul to asbestos paper backing
8. Magnetic Shield	3 layered insulated, carbon steel laminations
9. Susceptor (liner)	14 1/2 in. OD x 3/8 in. wall Hastelloy X tube
10. Air Cooling Capacity per Zone	15,000 Btu/hr @ 100 scfm air supply

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TABLE 9.5 Feed Pump Experience

<u>Pump No.</u>	<u>Service (Runs)</u>	<u>Feed Type</u>	<u>Hours</u>	<u>Date</u>	<u>Remarks</u>
P-3	RLG-2	PW-1	29	8-22-66	Installed on feed tank
	PC-1	PW-2	44	2-03-67	Connector was corroded away.
	SS-1	PW-1	37		(Sampler leaked on connector clamp)
	CSCM10	PW-2	15		
	SS-2	PW-1	57	3-30-67	Reinstalled on feed tank
	PC-6<Part 1	PW-2	23	8-22-67	Pump shaft froze during PC-6.
		Total	205		
P-6	PC-2	PW-2	42	2-06-67	Installed on feed tank
	PC-3	PW-2	31	3-29-67	Pump failed electrically (not during run)
		Total	73		
P-2	PC-4	PW-1	42	8-1-66	Installed on evaporator
	PC-5	PW-1	28	7-12-67	Removed pump from evaporator due to suction nozzle leak
				7-14-67	Replaced gaskets and reinstalled on evaporator
	PC-6<Part 2	PW-2	5	8-24-67	Pump shorted out and failed during PC-6.
		Total	75		
P-4	PC-6<Part 3	PW-2	20	9-08-67	Installed on feed tank
		Total	20		(Bearing water temperature ran high approximately 80 °C during 20 hr of operation of PC-6)

RLG = Rising level glass (design verification test)

PC = Pot calcination (WSEP)

SS = Spray solidifier (WSEP)

CSCM = Cold spray calciner melter (design verification test)

9.22

BNWL-814

MODE A

Arrangement PC-1, 6

MODE A-Modified

Arrangement PC-3

MODE B

Arrangement PC-2

MODE C

Arrangement PC-4, 5

FIGURE 9.1. Equipment Arrangement for the Pot Calciner Runs

FIGURE 9.2. Run PC-5 Pot and Furnace Temperatures

9.25

BNWL-814

FIGURE 9.3. View Through Cell Window at the Pot Calcination Equipment in WSEP

FIGURE 9.4. WSEP Auxiliary Equipment Flow Diagram

FIGURE 9.5. WSEP Solidification Equipment Flow Diagram

FIGURE 9.6. Pot, 12 Inch Diameter, Before Assembly

FIGURE 9.7. WSEP Pot Calciner Induction Heated Furnace

FIGURE 9.8. Computer Printout of Pot Wall Thickness

ACKNOWLEDGEMENTS

Successful demonstrations of six radioactive Pot Calcination runs were possible only through the excellent cooperative efforts of the staff of Oak Ridge National Laboratory, the U.S. Atomic Energy Commission and the Pacific Northwest Laboratory. Preliminary work for the demonstrations was begun in 1962 and has involved the contribution of many people not acknowledged here. In particular, the efforts of the technicians and other staff members who conducted the work are sincerely appreciated. The principal participants who so generously contributed to the successful efforts were:

ORNL

R. E. Blanco
W. C. Clark
H. B. Godbee
C. W. Hancher
J. M. Holmes
M. E. Whatley

F. L. Mourich
T. J. Owen
A. M. Platt
M. O. Rankin
G. Rey
K. J. Schneider
E. L. Shimoda
D. H. Siemens
J. S. Wallner

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R. D. Dierks
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J. N. Hartley
B. O. Kahle
V. P. Kelly
C. E. King
L. Lust
J. D. Moore

AEC

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

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