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Richland, Washington 99352

AEC Research and Development Report

WASTE SOLIDIFICATION PROGRAM
VOLUME 8
SPRAY SOLIDIFICATION PERFORMANCE
DURING FINAL RADIOACTIVE
TESTS IN WASTE SOLIDIFICATION
ENGINEERING PROTOTYPES

June 1971

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WASTE SOLIDIFICATION PROGRAM
VOLUME 8
SPRAY SOLIDIFICATION PERFORMANCE
DURING FINAL RADIOACTIVE TESTS IN WASTE
SOLIDIFICATION ENGINEERING PROTOTYPES

By

W. R. Bond, J. N. Hartley, J. E. Mendel
J. L. McElroy, and R. J. Thompson

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June 1971

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PACIFIC NORTHWEST LABORATORIES
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ERRATA

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BNWL-1583, June 1971

Table 2.1, page 2.4: Values of Heat Generation Rate in Receiver Pot should be 204, 120, 107, 132, 175, 90, and 200 W/liter for Runs SS-7 through SS-13(IPM)

Table 3.1, page 3.10: $\Sigma_{M_{fp}}^{+}$ for 45,000 MWd/tonne at 30 MW/tonne should be 2.10.

Table 5.3, page 5.15: ^{106}Ru (Radioruthenium) Ratio (Stack Off-Gas Radioactivity to 10CFR20) should be $<4 \times 10^{-4}$ for Runs SS-8, SS-9 and SS-10. Ratio (Scrubber Off-Gas Radioactivity to 10CFR20) should be 50 for ^{106}Ru and 3.2 for $^{144}\text{CePr}$ for Run SS-9.

Section 5.6, page 5.35: Pall rings used in the process condenser were made of 304 stainless steel.

Table 9.1, page 9.2, Footnote d: Waste was titrated to pH-7.

Page 9.30, second paragraph: Ratio for ruthenium to 10CFR20 release limits was $<4 \times 10^{-4}$ for Run SS-9.

Page 9.47, third paragraph: Fraction of ^{106}Ru equivalent feed radioactivity accumulated in the off-gas scrubber was 3.1×10^{-5} .

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ABSTRACT

Testing of high-level radioactive waste solidification by the spray solidification process has been successfully completed by Battelle-Northwest. More than 17 million curies of radionuclides were processed and collected in 8-inch diameter containers during the final seven engineering-scale demonstration runs in WSEP at the Pacific Northwest Laboratory. Radioactivity processed ranged from 1.4 to 3.6 million curies during the seven runs. A maximum self-generating heat-rate of 12.7 kilowatts (204 W/liter) was attained in an 8-inch diameter pot. The solidified waste within a full 8-inch diameter pot represented 0.90 tonnes of PW-4m waste representative of power reactor fuel (irradiated at 45,000 MWd/tonne at a power level of 30 MW/tonne) and 0.54 tonnes for a waste representative of LMFBR core fuel irradiated to 100,000 MWd/tonne at 200 MW/tonne. An in-pot melting modification of the spray solidification process (spray calcined waste fused directly in the final storage container without need for separate melter) was successfully demonstrated. High-level aqueous radioactive waste was processed at overall rates of 11 to 18 liters/hr. The equivalent processing rates ranged from 0.50 to 1.1 tonnes/day of original fuel. From 35 to 75% of the total ruthenium fed to the solidifier was volatilized from the solidifier while processing waste

solutions containing phosphoric acid as a melt forming additive and less than 2% of the ruthenium was volatilized with wastes not containing phosphoric acid when the in-pot melting modification was used. Entrainment of nonvolatiles from the solidifier was routinely less than 0.1%. Volatilized and entrained material from the solidifier was further treated in the WSEP auxiliary process equipment. The auxiliary process equipment consisting of an evaporator, an acid fractionator, mist eliminator, filters, condensers, and a caustic scrubber reduced the radionuclide concentration in the stack gas to well below 10CFR20 release limits. The radionuclide content in the final aqueous liquid effluent was decontaminated by a factor of 10^9 for nonvolatiles and 10^5 to 10^6 for radioruthenium to concentrations that initial studies indicate are acceptable for recycle to a fuel reprocessing plant or for low-level treatment processes. The spray solidifier product caused no significant changes to the solidified waste containers or no pressure increases within the containers after they were capped and welded.

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

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

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

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1.0 INTRODUCTION

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1.0 INTRODUCTION

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

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

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

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

in the USA to the point of radioactive demonstrations on an engineering scale. The four processes are pot calcination, spray solidification, phosphate glass solidification, and fluidized bed calcination. Two waste solidification methods under development abroad include the FINGAL process in the United Kingdom and a pot vitrification process in France.

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

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

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

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

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

REFERENCES FOR INTRODUCTION

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3. W. R. Bond, J. N. Hartley, J. E. Mendel, J. L. McElroy, K. J. Schneider, and M. R. Schwab. Waste Solidification Program, Volume 6, Spray Solidification Performance During First Radioactive Tests in Waste Solidification Engineering Prototypes, BNWL-1391, Battelle-Northwest, Richland, Washington, August 1970.
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5. J. L. McElroy, J. N. Hartley, K. J. Schneider, and R. F. Drager (BNL). Waste Solidification Program, Volume 5, Phosphate Glass Solidification Performance During the First Radioactive Tests in the Waste Solidification Engineering Prototypes, BNWL-1185. Battelle-Northwest, Richland, Washington, November 1969.
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2.0 SUMMARY

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2.0 SUMMARY

Solidification of high-level aqueous radioactive wastes containing approximately 17.3 million curies was successfully completed in seven demonstration runs using the spray solidification process in the WSEP. Major accomplishments in the demonstrations were as follows:

- Heat generation from fission products produced temperatures in the solidified waste at the maximum contemplated for the process as prescribed in WSEP. Adequate heating and cooling control of the pots was demonstrated during filling to promote uniform filling and prevent excessive temperatures.
- Aqueous radioactive wastes were solidified and encapsulated in the mild steel and stainless steel containers without pressurization or distortion of the container.
- The in-pot melting modification of the spray solidifier (wherein the spray calcined waste was fused directly in the final storage containers without the need of a separate melter) was successfully demonstrated.
- Less than 2% of the ruthenium in the feed to the solidifier during in-pot melting runs was volatilized as compared to the 35 to 75% volatilized during standard spray solidifier runs. The decrease in ruthenium volatility was attributed to the absence of phosphoric acid in the feed during in-pot melting runs since all of the melt forming flux was added directly to the pot.
- Gases passing off from the auxiliary effluent treatment equipment and the facility to the atmosphere contained sufficiently low quantities of radionuclides to easily meet government regulations.

- Aqueous effluents (the fractionator distillate and bottoms) from the auxiliary effluent treatment equipment contained sufficiently low quantities of radionuclides to permit recycle to a fuel reprocessing plant; however, improved cleanup of these streams is desirable to improve the efficiency of their reuse.

2.1 SPRAY SOLIDIFIER PERFORMANCE

The prime objectives for the last seven runs were to determine the maximum allowable heat generation rate in a receiver pot and demonstrate the standard and in-pot melting modifications of the spray solidification process with several waste compositions.

The quantities of fission products which were solidified and encapsulated in storage containers ranged from 1.4 to 3.6 million curies. In the latter case the corresponding heat generation rate of 12.7 kilowatts (204 W/liter) represented the maximum heat generation rate in an 8-inch diameter pot as prescribed for WSEP since it produced pot centerline and wall temperatures of 900 and 425 °C, respectively with the pot stored in air.

Three aqueous waste compositions simulating those which would result from the Purex reprocessing of spent power reactor fuels were fed to the solidifier at rates of 11 to 18 liters/hr. The waste compositions were denoted as PW-1* (a high iron containing waste from thermal reactor fuels irradiated to 20,000 MWd/tonne** at 15 MW/tonne), PW-4m* (a "clean" waste from thermal reactor fuels irradiated to 45,000 MWd/tonne

* For detailed chemical compositions see Table 3.1 and Appendix Table 9.1.

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

at 30 MW/tonne) and LMFBR* (a "clean" waste from a liquid metal fast breeder reactor core fuel irradiated to 100,000 MWd/tonne at 200 MW/tonne).

The overall processing rates ranged from 0.74 to 0.94 tonne/day for PW-1 wastes, from 0.46 to 0.58 tonne/day for PW-4m wastes, and 0.29 tonne/day for LMFBR waste. During demonstration of the in-pot melting modification of the spray solidification process the overall processing rates ranged from 0.46 to 1.05 tonne/day for PW-4m wastes.

The radioactive waste used for these demonstration runs did not always permit preparation of feeds having exact PW-1, PW-4m, and LMFBR compositions. Because of the modest variations in chemical compositions of the feeds, the overall volume reduction factors varied from 10.8 to 11.3 for PW-1 waste, from 7.0 to 7.2 for PW-4m waste (standard process), 3.8 to 6.7 for PW-4m waste (in-pot melting modification), and was 3.4 for the one run with LMFBR waste, based on aqueous waste at 378 liters/tonne.

Although the design of the spray solidification system in WSEP is certainly not optimized, its performance was quite satisfactory. General conditions for each run are summarized in Table 2.1.

In general the internal-mix atomizing feed nozzle performed satisfactorially in atomizing the feed and solids deposition in the calciner was not a problem. However, on one occasion significant deposition of partially dried calcine in the calciner did occur when the atomizing air and feed flow rates were not adequately controlled.

The batch discharge of melt from the melter made possible the filling of unheated receiver pots with PW-1, PW-4m, and

* For detailed chemical compositions see Table 3.1 and Appendix Table 9.1.

TABLE 2.1. Spray Solidification Runs in WSEP

Run	Waste Type	Receiver Pot		Radioactivity Processed, MCi	Heat Generation Rate in Receiver Pot		Equivalent Tonnes to Receiver Pot		Equivalent Age ^(b) of Waste, years
		Diam., in.	Material		Total, kW	Density, W/liter	Actual	100% Fill ^(a)	
7	PW-1	8	304L SS	3.6	12.7	11.3	1.9	1.8	0.7 ^(c)
8	PW-1	8	304L SS	1.8	6.7	18.3	1.7	1.7	1.2 ^(c)
9	PW-4m	8	310 SS	2.0	7.2	8.0	1.3	1.1	2.3 ^(d)
10	PW-4m	8	Mild Steel	2.6	7.4	11.1	1.1	1.2	1.9 ^(d)
11	LMFBR	8	304L SS	3.1	10.6	16.4	0.54	0.54	2.2 ^(e)
12 (IPM)	PW-4m	8	304L SS	1.4	4.9	16.2	0.54	0.6	1.3 ^(d)
13 (IPM)	PW-4m	8	304L SS	2.8	10.0	33.8	0.88	1.1	1.0 ^(d)

a. The equivalent tonnes of waste actually collected normalized to a fill height of 6 feet in the receiver pot.

b. Out-of-reactor time for fuel with the same heat generation rate.

c. Based on fuel exposed to 20,000 MWd/tonne at 15 MW/tonne.

d. Based on fuel exposed to 45,000 MWd/tonne at 30 MW/tonne.

e. Based on fuel exposed to 100,000 MWd/tonne at 200 MW/tonne.

LMFBR solidified waste without stalagmite formation. This technique also permits the use of mild steel receiver pots for either waste.

The in-pot melting modification of the spray solidification process was successfully demonstrated when spray calcined PW-4m waste was fused with a borosilicate glass frit directly in the final storage container. The overall processing and melt formation rates for PW-4m waste with the in-pot melting modification were nearly twice that obtained for the waste with the standard spray solidification process.

The amount of ruthenium that volatilized from the standard spray solidification process ranged from 35 to 75% of the total amount fed to the solidifier. The low value of 35% was attained after extensive acid stripping of the phosphoric acid containing feed. Control of ruthenium volatilization from the standard spray solidification process to consistently low values remains to be demonstrated. The amount of ruthenium volatilized from the in-pot melting modification of the spray solidification process ranged from 0.5 to 1.9% of the total processed. The decrease in ruthenium volatility for the in-pot melting modification from that of the standard spray solidification process was attributed to the absence of phosphoric acid in the feed during in-pot melting runs since all of the melt forming flux was added directly to the pot. The mechanism by which phosphoric acid enhances ruthenium volatility was not determined. Cesium and tellurium were the only other volatile fission products noted and they were only volatilized to the extent of 0.002 to 0.3% and 0.1%, respectively. In all cases the sintered stainless steel off-gas filters decontaminated the spray solidifier off-gas of particulates to less than 0.1% of the nonvolatile radioactivity in the feed.

2.2 AUXILIARY PROCESS SYSTEMS PERFORMANCE

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

To evaluate the performance of the auxiliary system, decontamination factors (DF's) were determined at each stage of the system and from the original aqueous waste through each stage (overall DF's). The overall DF's from the original aqueous waste through the auxiliary system to the recovered nitric acid in the fractionator were typically 10^2 to 10^3 for radioruthenium and 10^4 to 10^6 for radiocerium. Comparable DF's to the recovered water (accumulated fractionator distillate) were greater than 10^5 for radioruthenium and greater than 10^9 for radiocerium. The overall DF's to the off-gas scrubber were greater than 10^4 for radioruthenium and ranged from 10^7 to 10^9 for radiocerium. Comparable DF's to the off-gas leaving the scrubber were 10^7 to 10^9 for radioruthenium and 10^{10} to 10^{11} for radiocerium. Comparable DF's for the final off-gas to the stack were typically 10^9 to 10^{10} for radioruthenium and 10^{11} to 10^{13} for gross beta less radioruthenium.

During spray solidification Runs SS-7 through SS-13(IPM), there was no apparent correlation between the instantaneous ruthenium DF's across the evaporator and the evaporator overhead acidity. However, an apparent correlation did exist between the ruthenium DF's and overhead acidity during Runs SS-8 and SS-10 acid stripping and waste concentration operations. The generally low DF's that occurred during the runs and the noncorrelation are primarily attributed to vapor phase flow of ruthenium from the solidifier which was only

partially scrubbed in the solidifier condenser. The presence of nitrogen oxides from the solidifier condenser also increased the evaporator overhead acidity resulting in no equilibrium between the evaporator bottoms acidity and the evaporator overhead acidity. The solidifier condenser only removed from 33 to 73% of the nitrogen that volatilized from the solidifier while the remaining 67 to 27%, probably present as nitrogen oxide, were carried through the condenser in the gas phase. Also, the low DF's could somewhat be attributed to contamination of the auxiliary system.

The installation of a modified solidifier condenser and condenser off-gas filtering system prior to Run SS-11 reduced the carryover of ruthenium in the noncondensable gas stream.

Indications were that water spray into the solidifier condenser during Runs SS-8 and SS-12 decreased the ruthenium concentration in the solidifier condenser off-gas by a factor of about 10. However, it did not substantially reduce (about 10% reduction) the carryover of nitrogen oxides with the noncondensables.

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

During the spray solidification runs, the nitrogen oxides entering the scrubber neutralized the scrubber solution at a fairly constant rate. When the solution (2M NaOH) became completely neutralized, no more nitrogen would accumulate in the

scrubber. From 8 to 39% of the equivalent feed nitrogen accumulated in the scrubber while approximately 15% of the nitrogen was lost to the stack.

Gas sampling techniques were initiated during Run SS-9 to provide engineering-scale data to help better define the type and extent of radioactivity present in the process off-gas. Gaseous effluents from the solidifier condenser, evaporator condenser, fractionator condenser, high efficiency filter, and off-gas scrubber were sampled for both particulate and volatile forms of radioactivity by routing a side stream through a glass fiber filter and KOH scrubber.

Ruthenium DF's based on data from Runs SS-11, SS-12, and SS-13 across the process condensers ranged from a low of 58 (fractionator condenser) to a high of 6.5×10^4 (evaporator condenser) while cerium DF's ranged from a low of 48 (fractionator condenser) to a high of 2.1×10^4 (solidifier condenser).

The process off-gas leaving the scrubber contained a concentration of radionuclides above 10CFR20 discharge limits by approximately 500 for ruthenium and 50 for nonvolatiles. The radioruthenium in the final stack gas is less than detectable in all cases after the off-gas leaving the scrubber is filtered twice more and combined with building ventilation air. All remaining beta radioactivity in the building stack gas is assumed to be Sr-90 and as with the radioruthenium is well below 10CFR20 release limits.

During Run SS-13(IPM), automatic control of the auxiliaries was demonstrated. The General Electric 412 process control computer that has been used as a data logging device was programmed to set the set point on the controllers for the steam flow to the evaporator and fractionator tube bundles.

2.3 FILLED POT PERFORMANCE

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

Both stainless and mild steel receiver pots have proven to be satisfactory for filling with spray solid. Both materials have been seal-welded remotely using WSEP-developed techniques with existing equipment and leak checked to 1×10^{-7} atm cm³/sec or better using a helium mass spectrometer.

Temperature profile measurements and calorimetrically determined heat generation have provided the basis for the effective thermal conductivity. The effective thermal conductivity for spray solid has been shown to be 1.2 W/(m)^2 (°C/m) over a temperature range of 0 to 650 °C.

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

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

2.4 STATUS OF SPRAY SOLIDIFICATION

The spray solidification demonstration runs in WSEP have been completed. Wastes from power reactor fuels irradiated up to 45,000 MWd/tonne and an LMFBR core fuel have been demonstrated. A fission product heat generation rate of 220 to 250 W/liter is the maximum for solidified PW-1, PW-4m, and LMFBR waste in an 8-inch diameter receiver pot (when stored in 38 °C air) when the WSEP restriction of limiting the product temperature to 900 °C is considered. Therefore, PW-4m wastes from light water reactor fuels irradiated to 45,000 MWd/tonne at a power level of 30 MW/tonne can be solidified within 0.8 years (standard process) and 1.5 years (in-pot melting modification with 50 wt% waste oxides in solid) out of the reactor. Also LMFBR wastes from fast reactor fuels irradiated to 100,000 MWd/tonne at a power level of 200 MW/tonne can be solidified within 1.6 years (standard process) and 2.4 years (in-pot melting modification with 50 wt% waste oxides in solid) out of the reactor.

Some individual nuclides (e.g., ruthenium) were not at the levels expected for the fuel exposures tested. However, data from these radioactive runs can be used to project results for full levels of all nuclides. By applying the overall decontamination factors experienced to date, several general conclusions can be made about the expected operation of the solidifier, the auxiliary evaporator, and the fractionator during processing of full level radioactive wastes:

- From 35 to 75% of the ruthenium will be volatilized from the solidifier to the evaporator during processing of PW-1, PW-4m, and LMFBR wastes containing phosphoric acid as a melt forming flux. Less than 2% of the ruthenium will be volatilized from the solidifier to the evaporator if these wastes are low in acidity and do not contain phosphoric

acid as is the case for the in-pot melting modification (all the melt forming flux is added directly to the pot as a solid). The evaporator bottoms can be recycled back to the fuel reprocessing plant high-level waste system.

- Less than 1% of the total ruthenium fed to the solidifier will reach the acid fractionator and the nitric acid produced in the acid fractionator (approximately 200 to 400 liters/tonne of 8 to 12M acid) will contain 1000 to 10,000 $\mu\text{Ci}/\text{m}\ell$ of total β radioactivity. Radioruthenium will be the principal contaminant.
- The ruthenium DF from solidifier feed to the fractionator distillate can be expected to be 10^5 to 10^6 with the ruthenium concentration in the fractionator distillate 100,000 to 3,000,000 times higher than the discharge limits quoted in 10CFR20* when solidifying actual wastes. There will be about 200 to 600 liters of distillate per tonne of 378 liters/tonne fuel processed. Ruthenium-106 is the dionuclide in the final aqueous effluent with the highest concentration ratio to the limits in 10CFR20, followed by ^{90}Sr and $^{144}\text{CePr}$. In general, an additional decontamination of 10^5 to 10^6 is needed to reduce all radionuclides in the fractionator distillate to below 10CFR20 values.
- The recovered acid and water are sufficiently low in volume and radioactivity that they can be reasonably recycled for use in fuel element dissolution and/or for use in solvent extraction scrub streams. Effluent recycle is based upon having solidification processing capabilities with each fuel reprocessing plant.

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

- As an alternative to recycling, the radioactivity level of the fractionator distillate is acceptable for additional low-level treatment such as by distillation to 10CFR20 concentration limits for discharge of the water to the environment.
- Solidifier product from acidic wastes will have a volume of 34 to 53 liters/tonne of spent fuel for the types of thermal reactor wastes demonstrated. These volumes represent 2.0 to 5.0 liters/1000 MWd_e for fuel irradiated to 45,000 MWd/tonne at 30 MW/tonne.

Runs in WSEP demonstrated the spray solidification process at capacities in the range of 0.5 to 1.1 tonnes of fuel per day. The in-pot melting modification of the spray solidification process is essentially ready for application as an industrial method of solidifying wastes. The standard spray solidification process is ready for application; however, a different melter material is desirable as the platinum melter used is an expensive and weak structural link with poor heat transfer characteristics. It would also be desirable to reduce the volatilization of ruthenium from the spray solidifier when processing the phosphate containing wastes.

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

3.0 BACKGROUND, PROCESS DESCRIPTION AND PROCESS TECHNOLOGY

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3.0 BACKGROUND, PROCESS DESCRIPTION AND PROCESS TECHNOLOGY

3.1 BACKGROUND

The WSEP spray solidification process evolved directly from the initial tests of radiant-heat spray calcination for radioactive waste solidification which started at Hanford in 1958.⁽¹⁾ The tests were part of a comprehensive program sponsored by the U.S. Atomic Energy Commission to develop safer methods for perpetual storage of highly radioactive wastes. Other solidification processes investigated in the United States as part of this program included the agitated trough calciner,⁽²⁾ the ceramic sponge process,⁽³⁾ the rotary ball kiln calciner,⁽⁴⁾ the fluidized bed calciner,⁽⁵⁾ the pot calciner,⁽⁶⁾ and the phosphate glass process.⁽⁷⁾ The latter three processes have been developed until they are essentially ready for some commercial applications.^(8,9,10) With the successful completion of the WSEP demonstration runs described in this report, the spray solidification process is also essentially ready for commercial application. The first six high-level radioactive WSEP demonstration runs of the spray solidification process (SS-1 through SS-6) were reported in August 1970.⁽¹¹⁾ The final high-level runs (SS-7 through SS-13[IPM]) are reported herein. Five of the seven final runs utilized the standard spray solidification process; the last two runs utilized an in-pot melting process modification.

In the early developmental period, a platinum melter was close-coupled to the radiant heat spray calciner.⁽¹²⁾ The resulting spray calciner-melter, or spray solidifier as it is called, produced melts which solidified to a coherent micro-crystalline solid rather than the granular particles or friable calcines produced in the rotary ball kiln, agitated trough, fluidized bed and pot calcination processes. Thus the spray solidifier process joined other melt-forming high-level waste

solidification processes, such as the phosphate glass process of Brookhaven National Laboratory, the English FINGAL Process,⁽¹³⁾ and the French pot vitrification process.⁽¹⁴⁾

Another technique, called in-pot melting, was also developed for producing melts from spray calcined powder. The in-pot melting modification of the spray solidifier process does not use a platinum melter; the calcine powder is dropped directly into a stainless steel receiver, which becomes the final storage vessel. The melt is formed by fusion with a fluxing agent which is metered into the pot concurrently with the calcine. The calcine dissolves in the melt to varying degrees dependent upon factors such as temperature, time and composition of the fluxing agent.

The spray solidifier was tested exhaustively in small hot cells,⁽¹⁵⁾ in a cold pilot plant,⁽¹⁶⁾ and in design verification tests⁽¹⁷⁾ before the WSEP runs were started. In-pot melting was tested in the laboratory and the cold pilot plant^(18,19,20) prior to the high-level runs.

Spray calcination of radioactive wastes is also being investigated in other countries. A 10-inch diameter unit has been constructed in India.⁽²¹⁾ A 24-inch diameter spray calciner coupler to an Inconel melter will be used for the first pilot-plant studies of waste solidification in Germany.⁽²²⁾ Spray calcination of radioactive wastes has also been described by Russian workers.⁽²³⁾

3.2 PROCESS DESCRIPTION

The basic operations accomplished in spray solidification are; (1) conversion of aqueous waste solution to finely divided oxide powder by spray calcination, and (2) formation of a melt which solidifies to a coherent mass that is physically stable

and chemically inert. The melt can be formed in a continuous melter and batch dumped into a receiver pot for final storage (standard spray solidification process) or the melt can be formed directly in the receiver pot (in-pot melting modification of the spray solidification process).

Spray solidification can be described conveniently as a series of more or less discrete steps, shown schematically in Figure 3.1. The differences between standard operation and the in-pot melting modification will be included in the process description that follows.

Calcine Formation - The liquid is fed through a pneumatic atomizing nozzle into the top of the spray calciner. In the standard process, chemical additions are made to the liquid waste before calcination; in the in-pot melting modification chemical additions are not usually required at this point. The atomized waste is sequentially evaporated, dried, and calcined to a powder as it falls through the cylindrical calciner barrel. Type 310 stainless steel is a satisfactory construction material for the calciner because of its generally superior resistance to process corrosion and to high temperature air oxidation. The maximum operating temperature for the walls of the calciner barrel is limited by the tendency of the calcine to sinter and stick to the walls at higher temperatures. Typically, the wall temperature is held at or near 700 °C during operation.

Effective operation of the spray calciner depends upon good atomization.⁽²⁴⁾ The atomizing nozzle must break up the feed solution into small enough droplets (on the order of 50 to 100 micrometers diameter) to permit drying and calcining of the feed during its short time (about 10 seconds) in the calciner barrel. Commercial internal-mix nozzles, wherein the

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FIGURE 3.1. Spray Solidification Processes

atomizing gas and the feed solution are mixed inside the nozzle before being discharged, have proven superior to external-mix nozzles. Air has generally been used as the atomizing gas. Superheated steam has also been used but has not consistently provided adequate atomization.

Entrained Powder Filtration - The product from the spray calciner is a fine powder (particles range from less than one micrometer to 100 micrometers in diameter). About half of the calcine powder tends to be entrained with the off-gases. Separation from the off-gases is effected by porous stainless steel filters with an average pore size of 65 micrometers. A total filter area of about $1 \text{ ft}^2/(\text{liter})(\text{hr})$ of feed to the calciner is required to keep the filter pressure drop at the reasonable maximum level of 10 inches of water. Periodic pulsed blowbacks (every 1 to 5 minutes) with superheated steam or air at 30 to 60 psig pressure in the reverse direction through venturis into the filters removes the powder collected on the filters.

Melting (Standard Process) - The continuous melter is positioned below the calciner to collect the powder as it falls from the calciner. Here the powder from the calciner and filter blow-back is combined and melted. The small amount of residual nitrate and water remaining in the calcine are driven off during melting and combined with the calciner off-gases in the calciner. Platinum is presently the only known reliable construction material for processing phosphate type melts. (Because of certain desirable properties, described in Section 3.3, most of the solidified waste formulations for the standard spray solidification process, as developed by Battelle-Northwest, are phosphate melts.) A chromium-alumina cermet was found to have good corrosion resistance to phosphate melts

at temperatures up to 1100 °C, but failed in a long-term test due to the stress of thermal cycling. A special alloy of 50% chromium-50% nickel was generally satisfactory at temperatures up to 1000 °C. High chromium-nickel stainless steel and some high-nickel alloys were satisfactory up to 900 °C.⁽²⁵⁾ Platinum has been used extensively at temperatures up to 1250 °C. Platinum has a low radiant emissivity which requires increased melter surface area or increased furnace temperature to obtain a given melting capacity.

The molten waste in the melter can be discharged continuously via an overflow weir, or batchwise using straight-tube freeze valves wherein a plug of melt about 2 inches long is melted or frozen to provide on-off control. Both techniques have been demonstrated in WSEP. The latter technique has the advantage of permitting encapsulation of more radioactive waste with decreased corrosion of the receiving vessel, and was used during Runs 7 through 11 described in this report. Minor upsets in process vacuum can occur during the drain period.

In WSEP, the pot into which the molten waste is cast is a steel cylinder, 6 to 12 inches in diameter and 8 feet long. The diameter of the pot is usually determined by the radioactive heat generation rate in the solidified waste. The pots may be constructed of mild or stainless steel, the choice depending upon the method used to fill the pot or the melting characteristics of the waste. Pots of mild steel may be used if the pot is filled by large, rapid, batchwise dumps from the melter, or if the melt has a melting point less than about 700 °C. Solidified waste products with melting points up to about 950 °C can be collected in stainless steel receiving pots with either filling technique. Level measurements are required in the pot and may be accomplished by direct viewing

or approximated by temperature measurement. The pot is located in a 6-zone heating and cooling furnace so that the top of the melt may be heated to assure complete filling without formation of stalagmites or voids. Because of the significant amount of heat generation from radioactive decay, it is frequently necessary to begin forced air cooling of the lower regions of a pot while the upper regions are being heated for their filling. In WSEP, the pots are filled until about 2 feet of freeboard remains, at which time the filled pot is removed for final sealing by a welded closure and for post-fill tests.

Melting (In-pot Melting Modification) - A melt containing the waste can be formed directly in the receiving pot, if the spray calcined waste powder is mixed with a suitable fluxing agent. The in-pot melting process has the favorable feature that the high-cost continuous melter is eliminated from the system. In addition, higher throughput capacity can be achieved with the same size spray calciner. The process is somewhat temperature limited because of potential corrosion of the stainless steel pot.

In the WSEP in-pot melting process, the fluxing agent was a -6+10 mesh borosilicate enamel frit, which was added via an air lock on a spool piece that was installed between the calciner and the receiving pot, in the space normally occupied by the continuous melter in the standard spray solidification process. Frit additions were made batchwise every ten minutes. Continuous addition of a smaller frit particle size would have been more desirable, as discussed in Section 3.3. However, in the WSEP tests existing in-cell equipment was utilized as much as possible in making the conversion from the standard spray solidification process to the in-pot melting

modification and it was not possible to provide for continuous addition of fine frit. Good results were achieved with batch-wise addition of large particle frit.

Eight-inch diameter 304L stainless steel pots were used in the WSEP in-pot melting program. These were temperature limited due to corrosion from the calcine-frit melt to an operating temperature of about 950 °C, with temperature excursions to 1000 °C allowable. Use of more expensive higher nickel-chromium content stainless steels, such as Type 310, would allow operating temperatures to 1050 °C. As in the standard spray solidification process the receiving pot was located in a 6-zone heating and cooling furnace. Cooling was not required. The thermal conductivity of the molten borosilicate melt was in excess of $3 \text{ W/(m}^2)(^{\circ}\text{C/m)}$ (versus approximately $1.1 \text{ W/(m}^2)(^{\circ}\text{C/m)}$ when solidified). The high thermal conductivity of the molten melt prevented an excessive centerline temperature at any time during filling of the pot, or during the one hour heat soak which followed the last calcine-frit addition to the pots.

3.3 PROCESS TECHNOLOGY

The following section on Process Technology will discuss the effect of waste composition upon the spray solidifier process, and the chemical adjustments required for best processing of different waste compositions. Process operability, product quality, and effluent quality will be considered.

3.3.1 Composition of High-Level Radioactive Wastes

High-level radioactive wastes from aqueous reprocessing plants are primarily mixtures of fission products and various

nonradioactive constituents, in the nitrate form. The composition of high-level radioactive wastes can be highly variable, depending upon such factors as fuel exposure and the flowsheet used in the separations plant. In order to properly consider the possible variations, several different waste compositions were studied in the WSEP program.

The three nominal waste compositions defined for use in the final series of spray solidifier runs described in this report are shown in Table 3.1. The waste compositions encompass three different fuel exposures and two different modes of separations plant operation. Fuel exposures of 20,000, 45,000 and 100,000 MWd/MT are included. The first two fuel exposures are representative of light water power reactors; the latter of liquid metal cooled fast breeder reactors. The waste denoted PW-1 represents a Purex waste solution containing a large amount of iron such as would result when an iron canister is used to transfer chopped fuel elements from the mechanical head-end to the dissolver, and the canister is co-dissolved with the fuel. PW-4m and LMFBR represent wastes from a Purex process optimized to produce a "clean" waste, that is, a waste containing a minimum quantity of nonfission product material.

The actual waste solutions used for the WSEP runs were prepared by blending high-level waste (IWW) from the Hanford Purex plant, concentrated fission product solutions (mainly rare earths with Cerium-144) from the Hanford Fission Products Processing Plant, and inert chemicals, to approximate nominal PW-1, PW-4m, and LMFBR compositions as closely as possible. Except for a significant amount of aluminum that was unavoidably introduced at the Purex plant, the actual waste compositions used in the WSEP runs were quite close to

TABLE 3.1. Chemical Compositions of High-Level Liquid Wastes for WSEP Demonstration

Constituent	Concentration, Molarity at 378 liters/tonne(a)		
	PW-1	PW-4m	LMFBR
<u>General Chemical Composition of Inert Materials</u>			
Na	low	low	low
Fe	high	low	low
SO ₄	0	0	0
<u>Actual Chemical Composition of Inert Materials</u>			
H	3.70	4.30	0.50
Fe	0.93	0.050	0.16
Cr	0.012	0.012	0.046
Ni	0.005	0.008	0.023
Al	0.001	0.001	--
Na	0.14	0.10	0.10
U	0.010	0.010	0.010
Hg	<0.001	<0.001	--
NO ₃	7.5	6.5	4.7
SO ₄	--	--	--
PO ₄	0.003	0.003	0.060
SiO ₃	0.010	0.010	--
F	<0.001	<0.001	--
ΣM^{+} (b)			
chem	3.03	0.37	0.83
kg oxide/ tonne	31.7	4.6	9.7
<u>Chemical Composition of Major Materials from Nuclear Fission</u>			
Constituent	Fuel Exposure in Thermal Reactors	Core Fuel	
	20,000 MWd/tonne at 15 MW/tonne	45,000 MWd/tonne at 30 MW/tonne	Exposure in LMFBR 100,000 MWd/tonne at 200 MW/tonne
Mo	0.065	0.130	0.24
Tc	0.014	0.031	0.060
Sr	0.015	0.036	0.040
Ba	0.019	0.041	0.068
Cs	0.035	0.078	0.21
Rb	0.007	0.014	0.019
Y+RE (c)	0.12	0.27	0.53
Zr	0.065	0.14	0.22
Ru	0.032	0.082	0.22
Rh	0.007	0.013	0.060
Pd	0.017	0.043	0.16
Ag	0.0008	0.0016	0.019
Cd	0.0008	0.0025	0.010
Te	0.006	0.014	0.034
Sn	0.0007	0.0016	0.010
Sb	0.0002	0.0004	0.003
ΣM^{+} (b)			
fp	0.91	1.73	4.10
kg oxide/ tonne	22.0	49.0	101.1

a. Tonne is a metric tonne, 1000 kg or 2205 lb.

b. M⁺ is metal equivalents, or normality of metal ions (does not include acid).

c. RE is rare earth elements.

the compositions desired. The aluminum contaminant, which is not expected to be present in significant amounts in commercial reprocessing wastes, was treated as if it were iron, that is $Fe_{\text{actual}} + Al_{\text{contaminant}} = Fe_{\text{nominal}}$. For the standard spray solidification process it was found that if the aluminum concentration was over about 25% that of the iron, the temperature at which the melt fused was increased. (26)

Chemical substitutions were used for several of the fission products which were too expensive, or impossible to obtain in the amounts required. Molybdenum was substituted for technetium, nickel for palladium, cobalt for rhodium, copper for silver and cadmium, and potassium for cesium and rubidium. Although the process behavior of ruthenium is of extreme importance, it was impractical to use the full amount present in the nominal waste compositions. Approximately 10% of the nominal concentration was added as inert $Ru(NO_3)_3$; iron was substituted for the remainder of the ruthenium.

3.3.2 Aspects of Melt Formation

In order to form a stable solid for long-term storage, the soluble and relatively volatile nitrate ions must be completely removed and a melt-forming matrix substituted which is stable at high temperatures and insoluble. In the spray solidification processes developed at Battelle-Northwest, phosphate is used as the melt-former in the standard process and borosilicate in the in-pot melting modification. The two melt-forming systems have essential differences. Therefore the process technology of the standard process and the in-pot melting modification will be discussed separately.

3.3.3 Melt Formation in the Standard Spray Solidification Process

The phosphate system is particularly well adapted to the standard process, wherein the melt-former is added to the waste solution prior to calcination. When phosphate is added to the radioactive waste solution, a soft, flocculent, readily-suspended precipitate is formed which can be easily pumped. The precipitates formed by borate and silica are more difficult to keep homogeneously suspended in the feed solution and, in the case of silica, cause severe wear of pumps, meters, and valves. In general, phosphate melts have a larger latitude of chemical composition than borate or silicate melts. For instance, sulfate can be incorporated in homogeneous phosphate melts; in borate or silicate melts, sulfate separates as a lighter phase. The primary disadvantages of phosphate melts is that they are more corrosive than borate or silicate melts.

The spray solidifier concept requires that the sintering point of the calcined feed be higher than the temperature of the calciner walls. Otherwise, the calcine can stick on the calciner walls and reduce heat transfer efficiency. In practice, the sintering temperature, or "stick point," of the calcine should be above about 700 °C to permit reasonable operating rates. In addition, it is desirable that the melting point of the final product be below about 950 °C to permit flexibility in techniques of filling the steel receiving vessel without excessive corrosion.

The required temperature limits between stick point and melting point for the spray solidifier product can be readily obtained using phosphate flux with an overall cation-to-phosphate ratio corresponding to the compositional range between pyro and ortho phosphate, i.e., with an M^+/P ratio

of 2 to 3, when the proper cation mixture is present. (Methods for obtaining the proper cation mixture are described below.) The M^+/P ratio is the method adopted in the WSEP program by Battelle-Northwest to express the relationship of total metal ion equivalents to phosphorus in a given solution or product. In this relationship, M^+ is the total metal ion equivalent present, and is obtained by multiplying the total moles of each metallic element by its assumed valence in the system. Molybdenum and silicon are arbitrarily assumed to exist as the anions MoO_4^{-2} and SiO_3^{-2} . Their equivalent value is therefore subtracted from the total metal ion equivalents. The value for P is the total molarity of phosphorus present.

As the M^+/P ratio is lowered, the product becomes more glass-like. (The phosphate glass process developed by Brookhaven National Laboratory operates at an M^+/P ratio of one and produces a true glass as product.) Early operating experience indicated that the more glass-like melts were difficult to handle in the spray calciner due to a tendency to form sticky deposits on the calciner walls and glazes on the stainless steel off-gas filters. Equipment improvements have helped alleviate these problems. Feed solutions with M^+/P ratios as low as 1.8 have been processed successfully, and it may be possible to process solutions with even lower M^+/P ratios. In the opposite direction, an M^+/P ratio of about 3.0 may be considered the upper limit. Melts with M^+/P ratios much above 3.0 are usually undesirably nonhomogeneous.

For practical purposes, "clean" wastes such as PW-4m and LMFBR, may be considered to consist only of fission products. The nonfission product content is less than 10 wt% (Table 3.1). Phosphate melts of PW-4m and LMFBR with M^+/P ratios between 2 and 3 melt above 1200 °C. Cationic additives are needed to lower the melting point. Sodium and lithium,

are most effective for this purpose. However, product quality suffers when excessive amounts of alkali metals are added to the melt formulations. Leachability and inhomogeneity are increased. Tests made during the WSEP program indicate satisfactory melt characteristics (melting point and viscosity) and product characteristics (durability and homogeneity) can be obtained by adding a limited amount of alkali metal, plus a multivalent metal, to the waste solution. A comparison of the effectiveness of several multivalent cations is shown in Table 3.2. Of the multivalent cations which satisfactorily lowered the melting point, iron was selected for use in the WSEP since iron is comparatively inexpensive to use as an additive, and since iron was already present as a major constituent in one of the WSEP waste compositions.

TABLE 3.2. Effect of Various Multivalent Cations Upon the Fusion Properties of Spray Solidified LMFBW Wastes

Additives (a)				
Multivalent Cation	Na	H ₃ PO ₄ (b)	Stick Point, °C	Melting Point, °C
-----	2.80	2.87	1000	>1200
2.17 Al	↓	5.47	1150	>1200
2.17 Cr		↓	1050	>1200
3.26 Ni			1125	>1200
3.26 Mn			675	800
3.26 Cu			650	875
2.17 Fe			700	975
3.26 Zn			750	975
3.26 Cd			750	950

a. Concentration in moles/liter at 100 gallons/tonne.

b. To make a M/P ratio of 2.5 in the feed solution.

The chemical additives used in processing the wastes, PW-1, PW-4m, and LMFBR, in the WSEP spray solidifier runs are shown in Table 3.3.

It is very important in waste solidification to know how the unavoidable variations in melt composition which must be expected will effect process operation and product characteristics. The most vital processing characteristic, when operating with a continuous melter, is melting point, while leachability is an important product characteristic. The data in Figures 3.2-3.7 show that both remain acceptable when the melt composition varies widely from the standard flowsheets.

In Figures 3.2-3.7 the spray solidifier melts are treated as four-component systems even though the melts in actuality are complex mixtures of twenty or more elements. By considering the fission products (FP) as an entity which will always have about the same composition a significant simplification is achieved. Most of the spray solidifier melts can then be treated as variations of the FP-Na-Fe-PO₄ system.

TABLE 3.3. Chemical Additives Used in the Spray Solidifier Process

Additives	Waste Type		
	Moles per Liter of Waste at 100 gal/tonne		
	PW-1	PW-4m	LMFBR
NaOH	0.5	0.75	2.90
LiOH	0.5	0.75	----
Fe(NO ₃) ₃	----	1.1	2.17
H ₃ PO ₄	1.74	2.80	5.60
	(M/P = 2.75)	(M/P = 2.50)	(M/P = 2.50)
Product Composition, Oxide wt%			
Fission Products	18	25	28
Waste Inerts	30	4	4
Melt Forming Additives	52	71	68

FIGURE 3.2. Melting Point (°C) of Spray Solidifier Product at M/P Ratio of 2.50

FIGURE 3.3. Leachability (% Weight Loss) of Spray Solidifier Product at M/P Ratio of 2.50

FIGURE 3.4. Melting Point (°C) of Spray Solidifier Product at M/P Ratio of 2.75

FIGURE 3.5. Leachability (% Weight Loss) of Spray Solidifier Product at M/P Ratio of 2.75

FIGURE 3.6. Effect of M/P Ratio upon Melting Point of Spray Solidifier Product

FIGURE 3.7. Effect of M/P Ratio upon Leachability of Spray Solidifier Product

For purposes of plotting in the ternary diagrams the chemical equivalents of fission products in PW-4m was taken as 1.683. The PW-4m also contributed 0.15 equivalents of Fe and 0.342 equivalents of Na. (Note that PW-4m nominally contains 0.1M Na; the as-used PW-4m contained more Na because Na salts of Si and Mo were used in the chemical makeup.) A sample calculation to illustrate use of the ternary diagrams follows:

Consider the WSEP PW-4m spray solidifier flowsheet, which used the following additives;

0.75 moles LiOH per liter of waste at 378 liters/tonne

0.75 moles NaOH per liter of waste at 378 liters/tonne

1.10 moles $\text{Fe}(\text{NO}_3)_3$ per liter of waste at 378 liters/tonne

2.80 moles H_3PO_4 per liter of waste at 378 liters/tonne

Then each liter contains,

1.683 equivalents FP's, or 24.1%

$1.50 + 0.342 = 1.842$ equivalents Na(+Li) or 26.4%

$3.30 + 0.150 = 3.450$ equivalents Fe, or 49.5%

and the M/P ratio is,

$$\frac{1.683 + 1.842 + 3.450 + 0.033}{2.80} = 2.50$$

where 0.033 equivalents are the PW-4m constituents other than FP's, Na, and Fe.

Since the illustrative melt has an M/P ratio of 2.50 it can be found plotted with other melts having M/P ratios of 2.50 in Figures 3.2 and 3.3.

Figures 3.2 and 3.3 describe the variation with spray solidifier melt composition of melting point and leachability, respectively. The melting points shown are actually pour points, i.e., the temperatures at which the melt viscosities become

low enough to allow the melts to drain from a continuous melter (approximately 200 poises). Leachability is expressed as the weight loss, in percent, of -45+60 mesh particles after 72 hours exposure to water at 95 °C. Details of the test procedure are given on page 17 of Reference 27. As a basis for comparison, Pyrex and soft glass gave weight losses of 0.49 and 0.88 percent, respectively, using the test procedure.

3.3.4 In-Pot Melting Process Technology

The in-pot melting modification of the spray solidifier was first demonstrated on an engineering scale at PNL in early 1967. Table 3.4 summarizes the data obtained from developmental in-pot melting runs performed from that time on. The in-pot melting concept was first demonstrated with PW-2 waste.⁽²⁸⁾

The PW-2 flowsheet was the same as used for the continuous melter and was quite amenable to in-pot melting due to the 700 °C melting point of the adjusted waste. As was the case when using the continuous melter it was necessary to add some of the flux as solid NaPO_3 directly to the pot so as to avoid processing a calcine with a melting point close to the operating temperature of the spray calciner. The PW-1 in-pot melting flowsheet that was demonstrated^(18,19) used NaPO_3 entirely as a fluxing agent, the bulk of which was added directly to the pot. Both the PW-1 and PW-2 wastes were readily processed via the in-pot melting concept and definitely indicated the feasibility of this approach. Processing rates in the range of 0.7 to 1.0 tonne/day were readily attained. The melt forming capacity of the pot ranged from 2 to 3 liters/hr which was a factor of two higher than the melt forming capacity of the platinum melter.

During the development of an in-pot melting flowsheet for processing PW-4m waste an evaluation of fluxing agents other

TABLE 3.4. Data From Developmental In-pot Melting Runs
(with Spray Calcination)

Run Number	DSC-4	DSC-6	DSC-8	DSC-9	DSC-13	DSC-35	DSC-40	DSC-41
Waste Type	PW-2	PW-2	PW-1	PW-1	PW-1	PW-4m	PW-4m	PW-4m
Feed Concentration, liters/tonne	454	454	378	378	378	473	473	416
Additives to Waste (378 liters/tonne basis), <u>M</u>	$\left\{ \begin{array}{l} 1.61\text{M H}_3\text{PO}_2, \\ 1.17\text{M LiOH}, \\ 0.6\text{M Ca(NO}_3)_2 \\ \text{and} \\ 0.25\text{M Al(NO}_3)_3 \end{array} \right\}$		None	None	1.0M NaPO ₃	$\left\{ \begin{array}{l} 0.5\text{M ZnO} \\ 0.65\text{M Ca(OH)}_2 \end{array} \right\}$	$\left\{ \begin{array}{l} 0.5\text{M ZnO} \\ 0.65\text{M Ca(NO}_3)_2 \end{array} \right\}$	$\left\{ \begin{array}{l} 0.5\text{M Zn(NO}_3)_2 \\ 0.65\text{M Ca(NO}_3)_2 \end{array} \right\}$
Volume of Feed Fed, liters	253	334	110	64	82	320	205	150
Average Feed Rate, liters/hr	13.3	13.9	13.7	13.6	16.4	17.9	20.5	18
Run Time, hr	19	24	8	4.7	5	18	10	8.3
Calciner Furnace Temp., °C	700	720	700	700	700	700	700	700
Pot Furnace Temp., °C	825	825	850	850	850	950	950	950
Solids Addition to Pot								
Additive Type	NaPO ₃	NaPO ₃	NaPO ₃	NaPO ₃	NaPO ₃	B ₂ O ₃	(Borosilicate Glass Frit)	
Addition Rate, kg/hr	1.77	1.49	5.20	5.6	4.36	1.97	5.5	6.8
Total added, kg	34	36	42	26	22	36	55	56
Concentration (378 liter/tonne basis), g/liter	159	128	380	408	266	138	338	415
Product Collected, kg	104	133	56	33	38	79	79	84
Feed to Product Volume Ratio (378 liter/tonne basis)	5.5	5.3	5.5	5.8	6.0	9.9	6.6	5.0
Product Concentration, liter/tonne	69	70	69	65	63	38	59	75
Processing Rate, tonne/day	0.70	0.74	0.87	0.86	1.04	0.90	1.04	1.04
Melt Formation Rate, liters/hr	2.0	2.2	2.5	2.3	2.7	1.43	2.5	3.2
Pot Material	304L SS	304L SS	304L SS	304L SS	304L SS	304L SS	304L SS	304L SS
Pot Diameter, in.	8	12	8	8	8	8	8	8

than NaPO_3 was undertaken. An appropriate fluxing agent should have the following properties: (20,29,30)

- Relatively low melting point so that fusion can be carried out in stainless steel containers.
- Low corrosivity to stainless steel.
- Ability to combine with calcine to form a relatively homogeneous solid free of void spaces.
- Low leachability.

Compositions of the solid fluxing agents other than NaPO_3 which were considered are given in Table 3.5. These were all glass frits which were obtained commercially or, in the case of the phosphate-containing frits, prepared in the laboratory. Tests were also made using B_2O_3 as the fluxing compound.

Void-free melts were obtained with B_2O_3 and NaPO_3 fluxing, but the products were undesirably leachable and, in the case of NaPO_3 , the melt was considerably more corrosive to stainless steel than other melts as indicated in Table 3.6. Phosphate glass frits I and II yielded homogeneous melts at 950 °C containing 30 wt% PW-4m in laboratory batch tests. The melt proved too corrosive for further consideration however. In a continuous run in a 2-inch diameter pot made of 304L stainless steel the pot wall corroded through after 24 hours at 950 °C. Of the four borosilicate-phosphate glass frits which were examined briefly, composition I yielded the most homogeneous melts, but temperatures above 950 °C were required (the arbitrary upper operating temperature for in-pot melting in 304L stainless steel pots). Coke bottle glass, a soda-lime-silicate formulation, also required temperatures above 950 °C to obtain void free melts. Melts with coke bottle glass also had 2 to 3 vol% of a second phase which floated on the glass and melt and solidified to a soluble yellow microcrystalline phase.

TABLE 3.5. Flux Compositions Used for In-pot Melting Tests

Approximate Composition, wt%	Frit 111(a)	Frit 111-15(a)	Frit 1806(a)	Frit 78-1(a)	Frit 1415(a)	Coke Bottle	Borosilico Phosphate Glass Frit				Phosphate Glass Frit	
							I	II	III	IV	I	II
B ₂ O ₃	26	36	30	23	18		28	30	24	26		
SiO ₂	37	32	36	20	55	73	32	34	28	30		
Na ₂ O-K ₂ O	11	10	16	1	19	16	14.5	16	26	27	8	4
ZnO	18	15									9	9
CaO	2	1.75	6		1	5						
Al ₂ O ₃			4			2	12	13	10	11	10	12
MgO	2	1.75				4						
SrO	2	1.75										
BaO	2	1.75	6									
F			2		1							
PbO				50								
Fe ₂ O ₃				5								
Cr ₂ O ₃				1								
TiO ₂					2							
Co ₃ O ₄					2							
NiO					2							
P ₂ O ₅							13.5	7	12	6	73	75
	100	100	100	100	100	100	100	100	100	100	100	100
Accelerated Leach Rate, % Weight Loss												
First 24 hr	0.09		4.3	11.3	5.6	0.31					3.9	
Second 24 hr	0.05		4.3	10.6	5.0	0.27					4.0	
Third 24 hr	0.02		4.1	3.6	5.5	0.24					4.1	
Overall, 72 hr	0.16		12.2	23.6	15.3	0.82					11.5	

a. Manufactured by American Porcelain Enamel Company, Muskegon, Michigan.

TABLE 3.6. Characteristics of PW-4m In-Pot Melting Compositions

Solid Additives	Leach Rate, %wt Loss ^(c)				304L SS Corr. Rate at 950 °C Average Penetration, mils/mo.	
	First 24 hr	Second 24 hr	Third 24 hr	Cumulative 72 hr	Immersed	Partially Immersed
70 wt% Frit 111 ^(a)	0.13	0.06	0.03	0.22	4	10
40.5 wt% B ₂ O ₃ ^(b)	16	14	11	36	11	12
66.6 wt% N _a PO ₃	30	4.5	4.0	36	>200	>200
70 wt% Frit 78-1 ^(a)	2.4	2.1	2.1	6.5	>200	80
60.5 wt% B ₂ O ₃	55	7	1.1	59	5	80
70 wt% Frit 111-15 ^(a,b)	1.1	1.0	0.9	3.0	2	3

a. Manufactured by American Porcelain Enamel Company, Muskegon, Michigan.

b. 0.5M Zn - 0.65M Ca added to PW-4m solution.

c. -45+60 mesh grains in 95 °C H₂O.

Borosilicate frits are suitable fluxing agents^(25,26) and were studied in most detail. Melts of calcine plus the lead-containing frit (frit 78-1) were about an order of magnitude more corrosive to stainless steel than melts made with borosilicate frits not containing lead. Since frit 78-1 was also relatively leachable, it was rejected from further consideration. The remaining three borosilicate frits (frits 111, 1806, and 1415) all yielded void-free melts at 950 °C, but shared a common characteristic: a second phase was formed similar to that observed with coke bottle glass. The most yellow phase was found in melts prepared with frit 1415. Frits 111 and 1806 were about equal in their tendency to form the yellow phase. Frit 111-15 represented a compromise between higher leach rates resulting from more borate and less yellow phase resulting from reduced silicate.

The flux chosen for in-pot melting Runs SS-12(IPM) and SS-13(IPM) was frit 111-15 (composition given in Table 3.5). The decision was based principally upon considerations of potential pot corrosion and melt quality, i.e., leachability and homogeneity (see Table 3.6).

Frit 111-15 was used in the -6+10 mesh size during developmental Runs DSC-40 and 41 (Table 3.5) and for the WSEP runs. The flux or frit, was added semicontinuously at a feed point located between the spray calciner and the 304L stainless steel waste pots. Feeding rate of the frit was adjusted to produce a melt that nominally contained 70 wt% frit and 30 wt% calcined oxide. The temperature was held at 950 °C to assure an adequate melting rate without significant corrosion of the stainless steel waste pot. Corrosion rates, as shown in Table 3.7, were measured to determine the maximum allowable processing temperature.

TABLE 3.7. In-Pot Melting Corrosion of Stainless Steel

	<u>Corrosion Rate, Mils/month</u>	
	<u>Type 304L</u>	<u>Type 310</u>
950 °C	2	---
1000 °C	130	2
1050 °C	680	16
1100 °C	---	180

Type 310 stainless steel resembles the stainless steel used in the British FINGAL process. Both the chromium and nickel content are higher than in the less expensive 304L stainless steel used in the WSEP runs. An operating temperature of 950 °C was specified for the WSEP runs, which allowed a considerable safety factor since the pot walls were 0.325 inches thick and the time at temperature was only about 1.5 days. The corrosion rates shown in Table 3.7 are for surfaces immersed in melt; substantially higher corrosion rates were found at the melt-vapor interface. Corrosion at the interface was not considered a serious problem because the interface was moving continuously as the pot was filled.

The enhanced corrosivity at the interface was due in part, at least, to the presence of a small amount of second phase material which tended to segregate at the top and toward the bottom of the WSEP in-pot melting products. The second phase appeared as a yellow microcrystalline material in the cooled product. Because it tended to be dispersed in small globules, the total quantity of yellow phase was difficult to determine precisely. The yellow phase was carefully separated from the melt produced in Run DSC-41, a nonradioactive pilot plant in-pot melting developmental run (see Table 3.4), with the following results:

Top yellow phase	Approximately 50 g
Bottom yellow phase	Approximately 100 g
Total weight of melt	89.1 kg.

The flowsheet used in Run DSC-41 was the same as that used in WSEP Run SS-12(IPM) and it is expected that the amount of yellow phase in the latter product was also less than 0.2 wt%.

Analyses obtained on the phases in the DSC-41 product are shown in Table 3.8. Molybdenum was concentrated almost exclusively in the second phase. In fact, laboratory tests indicated that the yellow phase was almost nonexistent in the absence of molybdenum. The yellow phase was much more leachable than the bulk melt and about 20 times more corrosive to stainless steel. Of the long-lived fission products, strontium was not concentrated in the yellow phase but cesium was. This was demonstrated in a special laboratory preparation (DSC-41 used potassium as a stand in for cesium). The yellow phase analyzed 12.3 wt% cesium versus 2.5 wt% in the bulk glass.

Because of the undesirable properties described in the preceding paragraph methods for minimizing the amount of yellow phase in the product were sought. Important factors found were:

- I. The presence of silicon accentuates yellow phase formation.
- II. The quantity of yellow phase increases as calcine:frit ratio increases. (The 30:70 ratio chosen for the WSEP runs was a compromise. Except for increased quantities of yellow phase, satisfactory melts were obtained at 50:50 ratios.)

TABLE 3.8. Characteristics of In-pot Melting Second Phase

	<u>Top Yellow Phase</u>	<u>Bulk Melt</u>	<u>Bottom Yellow Phase</u>
304L SS Corrosion rate at 950 °C, in./yr	0.44	0.02	0.44
Melting points, °C	700	950	975
Density, g/cm ³	3.116	3.102	3.731
Accelerated Leach Test at 950 °C			
% Weight Loss			
First 24 hr	78.2	1.4	22.8
Second 24 hr	4.4	1.1	1.1
Third 24 hr	3.8	1.1	0.68
Overall % wt loss	79.8	3.6	24.2
Composition, wt% ^(a)			
Nd	<1	0.8	1
Ce	<0.1	3	0.5
La	<0.1	3	1
Ba	6	3	5
Mo	7	0.3	8
Sr	0.8	3	5
Fe	1	1	0.05
Cr	1	0.1	0.2
Ca	1	20	10
K	6	0.7	5
Si	<1	8	<0.05
Na	60	30	20
B	0.07	3	0.4

a. The analyses were made by spark source mass spectrography and are estimated to be accurate to a factor of three.

- III. The constituents of the yellow phase tend to dissolve in the glassy matrix as the temperature increases. At 1050 °C the melt compositions used in Runs SS-12(IPM) and 13(IPM) do not produce a yellow second phase.
- IV. The quantity of yellow phase decreases as frit particle size decreases and as more intimate pre-mixing of frit and calcine is achieved.

A large number of chemical additions to the liquid waste prior to calcination were also evaluated. None were very effective in eliminating the yellow phase. (Recent preliminary results indicate additions of V_2O_5 can eliminate the yellow phase.) Calcium and zinc, at 0.65 and 0.50 moles per liter, respectively, were added to the feed for this purpose in Run SS-12(IPM), to yield a product containing 17 wt% PW-4m. No additives were made to the feed in Run SS-13(IPM) and the product contained 28 wt% PW-4m.

A major advantage occurring from the operation of the spray calciner in the in-pot melting mode is that ruthenium volatility is reduced by a factor of approximately twenty. Ruthenium behavior is discussed further in Section 3.4 below.

3.3.5 Pre-Run In-Cell Tests

Prior to each WSEP demonstration run laboratory-scale tests were made in-cell with the actual feed solution to be used in the run. The tests of foaming tendency, melting point, corrosivity, etc., served as a final corroboration of feed makeup and determined the suitability of the feed for spray solidification. Results of these tests are shown in Table 3.9.

TABLE 3.9. Results of Preliminary Radioactive In-cell Laboratory Tests
with Adjusted Spray Solidifier Feeds

WSEP Run	SS-7	SS-8	SS-9	SS-10	SS-11	SS-12 (IPM)	SS-13 (IPM)
Feed Type	PW-1	PW-1	PW-4m	PW-4m	LMFBR	PW-4m	PW-4m
Heat Generation Rate in Feed, W/liter	11.3	8.3	8.0	11.1	16.4	16.2	33.8
Suspended Solids, Vol %	10	Sample was milky white, no way of measuring % solids	<10	75	92	25	32
Corrosiveness of Melt to Pot Material	No visual evidence of corrosion or oxidation	No apparent corrosion	Not determined	No apparent attack on the side which was in melt. The side exposed to air was oxidized.	Not determined	Not determined	Not determined
Product Appearance	Grey, homogenous and glassy	Charcoal color with light gray residue - appears homogenous	Not determined	Dull grayish solid	Dull gray-black solid, smooth surface	Glassy black, shiny smooth	Appears homogenous
Stick Point, °C	800	850	740	800	800	850	Not determined
Initial Melting Point, °C	850	850	950	900	900	850 ^(a)	925 ^(a)

a. After addition of 70 wt% glass frit.

3.4 SUMMARY OF RUTHENIUM VOLATILITY DATA FROM DEVELOPMENTAL SPRAY SOLIDIFIER RUNS

One of the objectives aside from flowsheet development during the developmental spray solidifier runs was to observe and reduce if possible the ruthenium volatility from the solidifier. A summary of ruthenium volatility data obtained during the developmental runs is presented in Table 3.10 along with other pertinent run information.

Although there were some inconsistencies in the data, in general it agreed with the results of the radioactive demonstrations (see Reference 11 and Section 4.4 of this report) and the following generalizations can be made:

- Ruthenium volatilization was unaffected when using steam or nitrogen as the atomizing gas instead of the ordinarily used air.
- Most of the ruthenium was volatilized during the spray calcination step rather than during melting. This is in agreement with laboratory⁽³¹⁾ data which indicated that ruthenium is not appreciably volatilized from phosphate melts.
- The addition of NaNO_2 at concentrations of up to 0.05M (based on 378 liter/tonne feed) to the solidifier feed did not reduce the ruthenium volatility.
- A sugar concentration of 0.2M (based on 378 liters/tonne feed) was required in the solidifier feed before an appreciable reduction in ruthenium volatilization was noted.
- Ruthenium volatility decreased with decreasing feed acidity and appeared independent of the waste type. The nonradioactive runs, however, indicated a stronger

TABLE 3.10. Summary of Ruthenium Volatility Data
from Developmental Spray Solidifier Runs.

DSC Run No.	Waste Type	Additives to Waste, M at 378 liter/tonne	Feed Conc., liters/tonne	Vol. Feed Consumed, liters	Run Time, hr	Feed Acidity, (a,b) N	Actual Ru (a) Conc., M	Calciner Furnace Temp., °C	Melter Furnace Temp., °C	Percent Ru Volatilized	Comments
1A	PW-1	0.55M NaOH, 0.55M LiOH, and 1.78M H ₃ PO ₄	465	327	20	6.5	0.0026	720	1110	64	
1B	PW-1	↓	492	176	10	6.1	0.0025	750	1050	60	Steam atomization
1C	PW-1	↓	492	191	10	6.1	0.0025	750	1050	62	
1D	PW-1	↓	492	201	10	6.1	0.0025	725	1100	72	Steam atomization
2	PW-1	0.5M NaOH, 0.5M LiOH, 1.73M H ₃ PO ₄	454	262	20	6.7	0.0027	720	1100	46	
3	PW-1	↓	454	200	13.5	6.7	0.0027	720	Not used	49	Calcine collected in drum
		+ 0.025M NaNO ₂	454	104	7.0	6.7	0.0027	720	Not used	44	
		+ 0.05M NaNO ₂	454	123	7.8	6.7	0.0027	720	Not used	54	
4	PW-2	0.25M Al ³⁺ , 0.6M Ca ²⁺ , 1.17M LiOH, and 1.61M H ₃ PO ₄	454	80	6	6.0	0.0027	700	825 (Pot)	56	NaPO ₃ to pot
		↓ + 0.085M Sugar	454	106	8	6.0	0.0027	700	825 (Pot)	47	
		↓ + 0.19M Sugar	454	67	5	6.0	0.0027	700	825 (Pot)	20	
8	PW-1	None	378	110	8	6.5	0.0032	700	850 (Pot)	5	NaPO ₃ to pot
12	PW-1	1.0M NaPO ₃	378	67	5.5	7.0	0.0032	700	Not used	1.3	Calcine collected in drum
18	PW-2	0.25M Al ³⁺ , 0.6M Ca ²⁺ , 1.17M LiOH, and 1.61M H ₃ PO ₄	518	325	29.5	6.4	0.0023	700	925	100	NaPO ₃ to melter
19	PW-1	None	303	136	9	7.5	0.004	700	Not used	19	Calcine collected in drum
			227	137	7.6	10.0	0.005	700		19	
20	PW-4m	1.26M LiOH, 0.8M SiO ₂	378	48	4.2	4.2	0.0082	700	1000-1100	<5	B ₂ O ₃ to melter

a. Actual concentrations at the time of processing.

b. As determined by titrating feed to PH-7 for use as basis of reference. (Values were estimated in some cases.)

TABLE 3.10. (contd)

DSC Run No.	Waste Type	Additives to Waste, M at 378 liter/tonne	Feed Conc., liters/tonne	Vol. Feed Consumed, liters	Run Time, hr	Feed Acidity, (a,b) N	Actual Ru (a) Conc., M	Calciner Furnace Temp., °C	Melter Furnace Temp., °C	Percent Ru Volatilized	Comments
22	PW-4m	1.2M Fe ⁺ ₃ , 1.26M NaOH, and 2.46M H ₃ PO ₄	530	126	9	8.2	0.0058	700	1100-1150	2	
23	PW-1	1.0M NaPO ₃ , and 0.69M H ₃ PO ₄	454	105	6.7	4.0	0.0053	700	1150-1175	9	
		0.67M NaPO ₃ , 0.33M NaOH, and 1.0M H ₃ PO ₄	454	81	5.2	5.3	0.0053	700	1150-1175	22	
		0.35M NaPO ₃ , 0.65M NaOH, and 1.34M H ₃ PO ₄	454	74	4.7	6.5	0.0053	700	1150-1175	33	
24	PW-1	None	378	181	12.0	2.5	0.016	700	1150	<0.6	NaPO ₃ to melter
25	PW-4m	None	378	53	4.4	0.7	0.016	700	1150-1175	2.0	NaPO ₃ to melter
26	PW-4m	0.7M Fe ⁺ ₃ , and 0.96M H ₃ PO ₄	458	150	9.5	3.3	0.014	700	1100-1225	7	NaPO ₃ to melter
27	PW-4m	0.9M Fe ⁺ ₃ , 1.5M NaPO ₃ , and 1.35M H ₃ PO ₄	493	298	20	4.6	0.013	700	1150-1175	31	
28	PW-4m	0.7M Fe ⁺ ₃ , 0.2M Al ⁺ ₃ , 1.5M NaPO ₃ , and 1.35M H ₃ PO ₄	522	125	7.7	4.3	0.012	700	1175-1200	60	N ₂ atomization
29	PW-4m	0.7M Fe ⁺ ₃ , 0.2M Al ⁺ ₃ , 0.75M LiOH, 0.75M NaPO ₃ , and 2.1M H ₃ PO ₄	548	85	8.0	4.1	0.0085	760	1150-1200	29	
30	PW-4m	0.9M Fe ⁺ ₃ , 0.2M Al ⁺ ₃ , 0.75M LiOH, 0.75M NaOH, and 2.8M H ₃ PO ₄	573	100	7.0	4.3	0.0054	700	1150-1200	19	
31	PW-4m	0.9M Fe ⁺ ₃ , 0.2M Al ⁺ ₃ , 0.75M LiOH, 0.75M NaOH, and 2.8M H ₃ PO ₄	506	125	8.0	4.9	0.0061	700	1150	38	

a. Actual concentrations at the time of processing.

b. As determined by titrating feed to PH-7 for use as basis of reference. (Values were estimated in some cases.)

TABLE 3.10. (contd)

DSC Run No.	Waste Type	Additives to Waste, M at 378 liter/tonne	Feed Conc., liters/tonne	Vol. Feed Consumed, liters	Run Time, hr	Feed Acidity, (a,b) N	Actual Ru (a) Conc., M	Calciner Furnace Temp., °C	Melter Furnace Temp., °C	Percent Ru Volatilized	Comments
32	PW-4m	0.65M Ca(OH) ₂ , and 0.5M ZnO	454	77	4.2	PH=10	0.0068	700	Not used	2	{ Calcine collected in drum
34	PW-4m	None	378	98	6.3	1.5	0.008	700	Not used	2	{ Calcine collected in drum
		None	378	108	7.0	3.0	0.008	700	Not used	<0.6	
		None	378	99	6.3	4.5	0.008	700	Not used	<3	
35	PW-4m	0.65M Ca(OH) ₂ , and 0.5M ZnO	473	320	18	0	0.0033	700	950 (Pot)	<1	B ₂ O ₃ to pot
36	LMFBR	2.17M Fe ³⁺ , 2.8M NaOH, and 5.66M H ₃ PO ₄	912	99	7	5.4	0.0033	700	1200-1225	<2	
37	LMFBR	↓	976	104	7	5.0	0.003	700	1150	11	
			992	96	6	4.9	0.003	700	1150	17	
38	PW-1	0.65M NaOH, 0.35M NaPO ₃ , and 1.34M H ₃ PO ₄	458	106	6.6	5.4	0.0053	700	1150	34	
39	LMFBR	2.14M Fe ³⁺ , 2.8 NaOH, and 5.82M H ₃ PO ₄	992	55	3.6	5.0	0.002	700	1150	23	
40	PW-4m	0.65M Ca(NO ₃) ₂ , and 0.5M ZnO	473	205	10	0.4	0.003	700	950 (Pot)	<1	Borosilicate frit to pot
41	PW-4m	0.65M Ca(NO ₃) ₂ , and 0.5M Zn(NO ₃) ₂	416	150	8.3	2.3	0.004	700	950 (Pot)	6	Borosilicate frit to pot

a. Actual concentrations at the time of processing.

b. As determined by titrating feed to PH-7 for use as basis of reference. (Values were estimated in some cases.)

dependence of ruthenium volatility on the acidity of phosphate containing waste solutions than was observed during radioactive demonstrations (see Section 4.4).

- The ruthenium volatility from a waste solution not containing phosphate was considerably lower (in many cases less than 5% volatilized) than from one which contained phosphate. This was also observed during radioactive demonstration (see Section 4.4). The mechanism by which phosphate enhances ruthenium volatility was not determined.

3.5 SPRAY SOLIDIFIER OFF-GAS FILTER TESTS

A study was undertaken to evaluate candidate filter types for use as off-gas filters on the spray solidifier. The evaluation consisted of testing filters in a test chamber for performance and cleanability.

The test chamber consisted of a surge drum surmounted by a filter chamber in which two cylindrical filter elements of a given type could be installed. A pulsed air blowback system was provided for filter cleaning. Calcine was added to the chamber supply air via a rotary air lock feeder to provide a dust load to the filters. The pressure drop was recorded at a given face velocity to determine filter permeability and a fraction of the off-gas was drawn through a membrane filter to determine the particulate de-entrainment efficiency of the filters.

Several filter types were tested in the filter test chamber. Results of the testing are presented in Table 3.11. Each filter type was tested for 20 hours at a filter face

TABLE 3.11. Spray Solidifier Off-Gas Filter Test Data

Test No.	Filter Media	(a) Mean Pore Size, microns	(a) 98% Removal Rating For Gases, microns	(b) Initial Filter ΔP in. of water	(c) Minimum Blowback Press. psig	(b) Filter ΔP at Minimum Blowback Press., in. of water	(b) (d) Final Filter ΔP , in. of water	(e) De-entrainment Factor
1	Dutch Twilled Weave Sintered Wire Mesh	----	11	0.80	30	3.1	1.2	2,000
2	Square Weave Sintered Wire Mesh	----	30	0.75	25	2.9	1.0	500
3	Sintered Fiber Metal	41	----	1.1	35	3.4	2.3	500,000
4	Sintered Powder Metal (f)	65	8	0.75	30	3.5	1.5	100,000
5	Wire Wound	50 micron Wire Spacing	----	0.80	40	4.0	1.4	10
6 (g)	Wire Wound	25 micron Wire Spacing	----	0.90	50	2.7	2.7	50
7	Sintered Powder Metal (Internally Reinforced)	65	8	0.70	30	3.0	2.0	50,000

a. Information from the manufacturer.

b. The filter pressure drop was recorded at a filter face velocity of 4 ft/min. and includes the pressure drop across the blowback venturis which was 0.64 in. of water.

c. Represents the minimum blowback air pressure that was necessary to keep the filter pressure drop from exhibiting an increasing trend during the 20 hr. testing period.

d. Represents the filter pressure drop after the filters had been blown back with 50 psig air.

e. Ratio of the total quantity of calcine fed to the filter chamber to that collected downstream of the filters.

f. Filters of the same type as used on the WSEP spray solidifier.

g. Test terminated after 7 hrs.

velocity of 4 ft/min. A PW-1 calcine from a developmental spray calciner run was introduced into the test chamber giving a solids concentration of 0.7 grams per cubic foot of air. The filters were blown back with air using a 2 minute blowback cycle and 2 second pulse. In each test the blowback pressure was initially 20 psig and was increased in 5 psi increments when it was determined that the pressure was not adequate. The inadequacy of the blowback pressure was indicated by an increasing trend in the filter pressure drop and the visual observation of the continued accumulation of calcine on the filters. The increasing trends in filter pressure drop in some cases started out very gradually, but after the filter pressure drop reached a certain point, the rate of increase was greatly accelerated as no calcine was being dislodged from the filter during blowback.

The blowback pressure at which the filter pressure drop did not increase was established for each filter and listed in Table 3.11 as the minimum blowback pressure. These minimums are applicable only to the filter pressure drops of 3 to 4 inches of water encountered during the tests and would be increased for higher levels of filter pressure drop. An increase in these filter pressure drops by a factor of 2, for example, would probably require at least a 50% increase in the minimum blowback pressures listed. This shows the need for bringing the filter pressure drop under control early in the course of a spray solidifier run with adequate blowback pressure before it increases to the point where the blowback pressure necessary to bring it under control cannot be applied without pressurizing the solidifier. The results of the tests as shown in Table 3.11 indicated that a small improvement in the ease of cleaning may be attained with filters other than the sintered powder metal filter used on the solidifier, but at a considerable sacrifice of filtering efficiency.

Final filter testing involved the testing of a reinforced sintered powder metal filter to compare its de-entrainment efficiency and ease of cleaning with the nonreinforced filter used on the spray solidifier. The reinforced filter was identical in shape and dimensions with the nonreinforced filter except for containing a perforated metal support plate (1/16 inch thick with 1/8 inch diameter holes on 3/16 inch equilateral triangular pitch) immediately on the inside wall (downstream side) of the filter element. The perforated plate substantially increased the mechanical strength of the filter element which was deemed necessary following the mechanical failure of the solidifier off-gas filters during Run SS-3.⁽¹¹⁾ As indicated in Table 3.11, the performance of the reinforced powder metal filter was such that it would be suitable for service on the spray solidifier.

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4.0 SPRAY SOLIDIFICATION
PERFORMANCE

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4.0 SPRAY SOLIDIFICATION PERFORMANCE

The final seven radioactive test runs have been completed in WSEP to demonstrate the spray solidification process. A major objective was to increase the concentrations of radionuclides in the waste to permit prediction of the maximum allowable heat generation rate in a receiver pot. Other objectives included determination of the performance of the standard and in-pot melting modification of the spray solidification process coupled with the auxiliary equipment on a variety of waste compositions. Major variables of the demonstration runs are shown in Table 4.1.

Engineering-scale performance of the spray solidification process with highly radioactive waste generally confirmed previous work.^(1,2,3,4,5,6) The processing capacity of the equipment and the distribution of radionuclides in the solidifier condensate were in the range indicated by nonradioactive and radioactive work at PNL.

4.1 OVERALL PROCESSING RATES

Overall processing rates (based on feeding time to the solidifier) ranged from 0.74 to 0.94 tonne/day for PW-1 wastes, from 0.46 to 0.58 tonne/day for PW-4m wastes, and 0.29 tonne/day for an LMFBR waste. During runs demonstrating the in-pot modification of the spray solidification process, overall processing rates ranged from 0.46 to 1.05 tonne/day for PW-4m wastes. These rates represent the production of solidified waste products at 26 to 32 liters/day for PW-1, 24 to 31 liters/day for PW-4m, and 32 liters/day for LMFBR. The production rates during in-pot melting runs ranged from 46 to 60 liters/day of solidified PW-4m waste product. Table 4.2 summarizes the data on processing rates.

TABLE 4.1. Major Demonstration Run Variables

Run	Mode (a)	Pot Diam., in.	Waste Type	Radioactivity Processed, Ci	Equivalent Tonnes Processed	Heat Rate Density, W/tonne	Equivalent (b) Age, yr.
7	A	8	PW-1	3,620,000	1.85	6,860	0.67 (c)
8	A	8	PW-1	1,830,000	1.69	3,930	1.2 (c)
9	A	8	PW-4m	2,030,000	1.26	5,670	2.3 (d)
10	67% A- 33% B	8	PW-4m	2,580,000	1.23	6,790	1.9 (d)
11	A	8	LMFBR	3,110,000	0.54	20,200	2.2 (e)
12 (IPM)	A	8	PW-4m	1,390,000	0.54	9,070	1.3 (d)
13 (IPM)	Bm (f)	8	PW-4m	2,830,000	1.14	11,800	1.0 (d)

a. See Figure 5.2 for WSEP Operating Modes.

b. Out-of-reactor time for fuel with the same heat generation rate.

c. Based on fuel exposed to 20,000 MWd/tonne at 15 MW/tonne.

d. Based on fuel exposed to 45,000 MWd/tonne at 30 MW/tonne.

e. Based on fuel exposed to 100,000 MWd/tonne at 200 MW/tonne.

f. A modified Mode B (see Section 5).

TABLE 4.2. WSEP Spray Solidifier Processing Rates

Run	Type	Aqueous Feed			Feeding Time, hr	Solidified Product			Heat Rate Density, W/liter	Overall Processing Rate ^(a)		
		Heat Rate Density, W/liter	Volume,			Volume,	Fuel Equivalent, tonne	Heat Rate Density, W/liter		Feed, liters/hr	Solidified Waste	
			liters/tonne	liters							liters/tonne	liters
SS-7	PW-1	11.3	452	839	47	34	62	1.85	204	17.9	32	0.94
SS-8	PW-1	8.3	473	800	55	35	59	1.70	114	14.5	26	0.74
SS-9	PW-4m	8.0	630	792	52	54	68	1.26	107	15.2	31	0.58
SS-10	PW-4m	11.1	611	750	56	52	56	1.07	132	13.5	24	0.46
SS-11	LMFBR	16.4	1232	669	45	111	60	0.54	175	14.9	32	0.29
SS-12 (IPM)	PW-4m	16.2	556	301	28	100	54	0.54	90	10.8	46	0.46
SS-13 (IPM)	PW-4m	33.8	352	308	20	57	50	0.88	200	15.4	60	1.05

a. Based on actual feeding time to solidifier.

The general factors affecting processing rates were only qualitatively investigated. In general, the limiting factors affecting the processing rate are the transmission of heat into the calciner to produce a dry free-flowing calcine and the transmission of heat into the melter or pot to produce a fluid melt. These, in turn, are influenced by the feed composition, feed atomization, and furnace temperatures. The processing rate for PW-1, PW-4m, and LMFBR wastes is probably limited by both the calciner and melter at about 20 to 25 liters/hr of feed to the calciner. This is equivalent to approximately 40 liters/day of melt with the PW-1, PW-4m, and LMFBR wastes at 450, 620, and 1200 liters/tonne, respectively. The processing rates for PW-4m waste using the in-pot melting modification of the spray solidification process is probably limited by the 8-inch pot at approximately 72 liters/day of melt. This would be equivalent to a 18 liters/hr feed rate to the calciner with PW-4m waste at 350 liters/tonne and a composition similar to that used in Run SS-13(IPM).

4.2 RADIONUCLIDE HEATING EFFECTS

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

The maximum allowable temperatures established for WSEP are a product temperature of 900 °C and/or a receiver pot wall temperature of 427 °C; if a molten core exists in the receiver pot, the radius of the molten core must not exceed one-half the receiver pot radius. The 900 °C temperature limits

possible corrosion to the stainless steel thermowells used to house the thermocouples at the centerline of the pots. (The wells will probably not be used in production model receiver pots.) The 427 °C wall temperature prevents excessive air oxidation of the container and allows remote handling of the pot without excessive special precautions. Limiting the molten core radius prevents molten waste from contacting the pot wall and thus reduces the corrosion potential.

The temperatures caused by the internal heat generation rate in the seven pots are listed in Table 4.3. During these last seven radioactive demonstrations of the spray solidification process in WSEP, the highest internal heat-rate density was 204 W/liter and was attained in Run SS-7. This represented a thermal maximum in air for the PW-1 waste in an 8-inch diameter pot since the pot centerline and wall temperatures in air were 900 °C and 425 °C, respectively. Previously⁽⁶⁾ the maximum heat-rate density of solidified PW-1 waste in an 8-inch diameter pot stored in air was estimated in the range of 220 to 250 W/liter. The lower value attained in Run SS-7 was due to a lower than anticipated thermal emissivity for the pot wall. The thermal emissivity of the pot wall probably could have been increased had the pot been heat-treated at 800 °C to 900 °C prior to the run to oxidize the pot wall. The maximum heat-rate density for solidified PW-4m and LMFBR wastes for air storage in 8-inch diameter pots would be expected to be in the same range as that for the PW-1 product. Although the PW-4m borosilicate glass product produced during in-pot melting runs has a remelt temperature of about 800 °C, the maximum heat-rate density is limited by the 900 °C centerline temperature restriction and not the molten core restriction to 220 to 250 W/liter for an 8-inch diameter receiver pot when stored in 38 °C air. (Sections 6 and 7 present additional information on pot temperatures).

TABLE 4.3. Receiver Pot Temperatures Caused by Internal Heat Generation

Run	Waste Type	Pot Diam., in.	Pot Material	Total (a) Heat Rate, W	Total (a) Heat Rate Density, W/liter	Type of (b) Filling	Pot Furnace Temperature, °C	Maximum Centerline (c) Temperature During Filling, °C	Steady State (d) Centerline Temperature, °C	Steady State (d) Wall Temperature, °C
SS-7	PW-1	8	304L SS	12,700	204	Batch	Off	980	920	467
SS-8	PW-1	8	304L SS	7,200	120	Batch	Off	830	605	395
SS-9	PW-4m	8	310 SS	7,200	107	Batch	Off	930	594	352
SS-10	PW-4m	8	Mild Steel	7,400	132	Batch	Off	850	611	349
SS-11	LMFBR	8	304L SS	10,500	175	Batch	Off	980	759	406
SS-12(IPM)	PW-4m	8	304L SS	4,900	90	Continuous	900 to 950	980	474	277
SS-13(IPM)	PW-4m	8	304L SS	10,000	200	Continuous	900 to 950	1040	824	420

a. Average of heat rate data from feed analysis and pot calorimetry tests.

b. Batch filling was accomplished by periodic discharge of the melter in 4 to 6 liter batches (23 to 65 liters/hr) via the drain freeze-valve.

c. For the case of batch filling the maximum temperatures resulted immediately following a batch melt addition to the pot.

d. Receiver pot in the furnace with forced air cooling outside the susceptor.

While processing PW-1, PW-4m, and LMFBR wastes during Runs SS-7 through SS-11, the pot was filled by periodic batch discharges of melt from the melter. Batch filling was preferred over continuous filling because of the lesser potential for stalagmite formation at the higher entering melt rates (approximately 23 to 65 liters/hr) and it was not necessary to heat the receiver pot. This technique also permits use of mild steel containers (as in Run SS-10) and the collection of solidified waste with a high heat-rate density such as that in Run SS-7. For PW-4m type phosphate melts an entering melt rate of 23 liters/hr probably represents the minimum filling rate that an unheated 8-inch diameter pot can be successfully filled without serious stalagmite formation problems.

Although a number of temporary surges of the internal pot temperatures occurred (increases in temperatures by approximately 700 °C for Run SS-7) when using the batch technique for filling the pots, the temperatures did not become excessive since the pot was relatively cool prior to the melt dump. Typical receiver pot temperatures during batch dumping of melt (in Run SS-7) are presented in Figure 4.1.

During in-pot melting Runs SS-12(IPM) and SS-13(IPM), PW-4m waste calcine was fused with a borosilicate frit directly in the heated receiver pot. Although the wall temperatures of the 8-inch diameter pots were maintained at 900 to 950 °C during processing, the internal melt temperature was only 1040 °C. This indicates an exceptionally high thermal conductivity for the molten borosilicate product, particularly in view of the fact that during Run SS-13(IPM) the heat-rate density of the melt was 200 W/liter.

Figure 4.2 is a schematic diagram which shows the location of the thermocouples in a receiver pot. One cooling air blower rated at 275 scfm was sufficient to cool the receiver pot and maintain the steady-state centerline temperature of

FIGURE 4.1. Receiver Pot Temperatures During Run SS-7

FIGURE 4.2. Thermocouple Arrangement of Spray Solidifier Receiver Pot

the receiver pot contents at 920 °C and the steady-state pot wall temperatures below 470 °C during Run SS-7 (which contained the highest heat-rate density tested of 204 W/liter). The cooling air blows onto the outside of the furnace susceptor. Direct cooling of the pot wall (inside the susceptor) with 50 scfm of air was also used during this run. A test of internal susceptor air cooling in a previous run⁽⁶⁾ indicated that this added cooling decreased the average pot wall temperature 35 °C below that attained with external susceptor cooling only.

4.3 WASTE VOLUME REDUCTION

Because of the different type wastes and variations in chemical compositions of the waste processed during solidification, the overall volume reduction factors (the volume of aqueous waste at 378 liters/tonne to the volume of solidified waste product) varied from 3.4 to 11.3. Volume reduction factors are summarized in Table 4.4. Estimated values of volume reduction differed from observed values by 2% in Run SS-12(IPM) to a maximum of 16% in Run SS-8, with an average difference of less than 9%. For the first two demonstration runs (Run SS-7 and SS-8) with PW-1 waste, the volume reduction averaged 11.1 which was approximately 11% lower than the average of the estimates values. This difference was due in part to the fact that the product bulk density achieved during filling was lower than the density determined on product samples in the laboratory which were used to calculate the estimated volume reduction factors. The observed volume reduction for PW-1 waste was, however, in good agreement with that achieved in previous runs.⁽⁶⁾ For Runs SS-9 and SS-10 with PW-4m waste, the volume reduction averaged 7.1 and was in good agreement with estimated values. A volume reduction of 3.4 was obtained for an LMFBR waste during Run SS-11. For in-pot

melting Runs SS-12(IPM) and SS-13(IPM) with PW-4m waste, the volume reduction ranged from 3.8 to 6.7. This range in volume reduction resulted when the calcium and zinc additives added to the waste during Run SS-12(IPM) were not added during Run SS-13(IPM).

TABLE 4.4. Volume Reductions

Run	Waste Type	Overall ^(a) Volume Reduction Factor	Estimated ^(b) Volume Reduction Factor	Measured Density of Product, g/ml	Volume of Product, liters/ tonne
SS-7	PW-1	11.3	12.6	3.30	34
SS-8	PW-1	10.8	12.5	3.29	35
SS-9	PW-4m	7.0	7.5	3.31	54
SS-10	PW-4m	7.2 ^(c)	7.6 ^(d)	NA	52 ^(c)
SS-11	LMFBR	3.4	3.7	3.29	111
SS-12(IPM)	PW-4m	3.8	3.7	2.83	100
SS-13(IPM)	PW-4m	6.7	6.2 ^(e)	NA	57

- a. Volume ratio of initial aqueous waste at 378 liters/tonne to the measured volume of the final solidified waste.
 b. Based on laboratory-measured density of the product and the estimated total weight of the adjusted-waste oxides.
 c. Estimated assuming 13% holdup of calcine in the calciner.
 d. Based on a density of 3.31 g/ml.
 e. Based on a density of 2.83 g/ml.
 NA = Not Available.

4.4 VOLATILIZATION OF FISSION PRODUCTS

An important objective during the last seven spray solidification runs was to characterize the path and behavior of volatile fission products which were present in the waste. During the seven demonstration runs, ruthenium, cesium, and tellurium were the only fission products detected that volatilized. Ruthenium volatility ranged from 0.5 to 75%; cesium volatility ranged from 0.002 to 0.3%; and 0.1% of the tellurium was volatilized during one run.

Most of the ruthenium that was volatilized during spray solidification was collected with the solidifier condensate in the WSEP auxiliary evaporator or in the condensate receiver tank. The accumulation of ruthenium in the condensate is shown in Figure 4.3 as a function of the fraction of feed processed for the seven demonstration runs. Table 4.5 lists the ruthenium volatilized from the solidifier along with other variables that could affect ruthenium volatilization.

While processing PW-1, PW-4m, and LMFBR wastes which contained phosphoric acid as an additive, during Runs SS-7 through SS-11, the ruthenium volatilized from the solidifier ranged from 35 to 75%, which was in agreement with nonradioactive tests (see Section 3.4) and previous radioactive demonstration runs. ⁽⁶⁾

The acidity of the wastes processed during Runs SS-8 and SS-10 was reduced prior to each run in an attempt to reduce the ruthenium volatility during solidification. The PW-1 feed for Run SS-8 was pretreated by acid stripping the waste (which included the phosphoric acid additive) in the waste evaporator. After the acid stripping operation and the addition of sodium and lithium hydroxide additives, the acidity (total titratable hydrogen ion to pH 7 used as a basis of reference) of the feed had been reduced from a nominal 9M to 1.6M (based on 378 liters/tonne). Despite the greater than five reduction in feed acidity, 35% of the ruthenium in the feed to the solidifier was volatilized during Run SS-8. Although this represents a reduction from the 50 to 75% volatility experienced in previous spray solidifier runs (SS-1, SS-2, SS-5, SS-6, and SS-7) with the PW-1 flow sheet, it did not indicate the same degree of dependence of ruthenium volatility on feed acidity as was observed during developmental spray solidifier runs with wastes containing phosphate (see Section 3.4). The PW-4m feed for Run SS-10 was also acid stripped, however, 45% of the ruthenium was volatilized.

FIGURE 4.3. Accumulation of Ruthenium in Spray Solidifier Condensate

TABLE 4.5. Ruthenium Vo.

Run	Mode	Waste Type	Specific Feed Volume, liters/tonne	Waste Composition Including Additives (a)										Radioruthenium in Feed to Solidifier		Feed Rate to Solidifier, l/hr	Calci	
				Na ⁺	Al ⁺³	Fe ⁺³	ΣM ⁺	H ⁺ (free)	H ⁺ (total) (e)	NO ₃ ⁻	SO ₄ ⁻²	PO ₄ ⁻³	Ru	Total, Ci	Conc., Ci/liter		Furnace	I
SS-7	A	PW-1	452	0.48	0.074	0.57	4.09	2.30	7.5	3.96	0.0013	1.32	0.0031	22,200	20.2	18	670	4
SS-8	A	PW-1	473	0.38	0.096	0.64	3.42	1.1	1.3	1.44	0.0013	1.28	0.0027	14,400	14.4	15	690	4
SS-9	A	PW-4m	630	0.50	0.20	0.60	3.94	2.10	4.2	4.13	0.0025	1.55	0.0018	10,200	6.7	15	690	4
SS-10	A&B	PW-4m	611	0.62	0.10	0.56	4.33	1.98	2.0	2.41	0.0025	1.78	0.0019	13,100	10.8	14	700	4
SS-11	A	LMFBR	1232	1.15	0.14	0.56	4.33	1.65	2.70	4.14	0.0089	1.74	0.0017	14,400	6.6	15	700	4
SS-12 (IPM)	A	PW-4m	556	0.36	0.20	0.05	4.01	0.14	0.68	3.94	0.0028	0	0.0031	6,800	15.4	11	720 to 740	3
SS-13 (IPM)	Bm	PW-4m	352	0.20	0.33	0.15	3.74	0.46	1.80	3.84	0.0044	0	0.0021	11,000	37.6	15	670 to 700	3

- a. Actual concentrations at time of processing.
- b. Temperatures are measured near the drying chamber wall and range from top to bottom.
- c. Temperature measured in conical bottom section of drying chamber.
- d. Percent of total ruthenium fed to the solidifier.
- e. Acidity as determined by titrating feed to pH-7 (used as a basis of reference).
- f. Determined for the Mode A portion of run only.

TABLE 4.5. Ruthenium Volatilization from the Spray Solidifier

Waste Composition Including Additives ^(a)										Radium Ruthenium in Feed to Solidifier		Feed Rate to Solidifier, l/hr	Calciner Temps., °C			Percent ^(d) Ruthenium Volatilized
Al ⁺³	Fe ⁺³	ΣM ⁺	H ⁺ (free)	H ⁺ (total) ^(e)	NO ₃ ⁻	SO ₄ ⁻²	PO ₄ ⁻³	Ru	Total, Ci	Conc., Ci/ liter	Furnace		Internal ^(b) Drying Chamber	Drying Chamber ^(c) Exit Gas		
8	0.074	0.57	4.09	2.30	7.5	3.96	0.0013	1.32	0.0031	22,200	20.2	18	670	420 to 540	440	59
8	0.096	0.64	3.42	1.1	1.3	1.44	0.0013	1.28	0.0027	14,400	14.4	15	690	400 to 580	460	35
0	0.20	0.60	3.94	2.10	4.2	4.13	0.0025	1.55	0.0018	10,200	6.7	15	690	450 to 600	450	57
2	0.10	0.56	4.33	1.98	2.0	2.41	0.0025	1.78	0.0019	13,100	10.8	14	700	400 to 570	470	45 ^(f)
5	0.14	0.56	4.33	1.65	2.70	4.14	0.0089	1.74	0.0017	14,400	6.6	15	700	430 to 600	470	75
6	0.20	0.05	4.01	0.14	0.68	3.94	0.0028	0	0.0031	6,800	15.4	11	720 to 740	380 to 580	360	1.9
0	0.33	0.15	3.74	0.46	1.80	3.84	0.0044	0	0.0021	11,000	37.6	15	670 to 700	350 to 570	400	0.5

rocessing.
drying chamber wall and range from top to bottom.
ttom section of drying chamber.
the solidifier.
feed to pH-7 (used as a basis of reference).
of run only.

A significant reduction in the amount of ruthenium volatilized from the spray solidifier occurred during Runs SS-12(IPM) and SS-13(IPM) when phosphoric acid was not added to the feed. The 1.9 and 0.5% ruthenium volatilized during Runs SS-12(IPM) and SS-13(IPM), respectively, was in agreement with developmental spray solidification runs with low-acid PW-4m waste which did not contain phosphoric acid (see Section 3.4). As discussed in Section 3.4, the mechanism by which phosphate enhances ruthenium volatilization was not determined.

During the demonstration runs, the quantities of cesium leaving the solidifier with the off-gas were generally higher than could be attributed entirely to entrainment and indicated that cesium was volatilized. During Runs SS-9 through SS-11, cesium was volatilized in the range of 0.06 to 0.3%. The cesium volatilization was probably entirely from the melter since laboratory data on cesium volatility from phosphate melts⁽⁷⁾ can more than account for the quantities of cesium released. During in-pot melting Runs SS-12(IPM) and SS-13(IPM) cesium volatilization ranged from 0.002 to 0.07%.

During Run SS-11, 0.1% of the tellurium in the feed to the spray solidifier was volatilized. The results agreed with the nonradioactive data⁽⁸⁾ wherein from 0.1 to 0.5% of the tellurium volatilized from the spray solidifier.

4.5 SPRAY CALCINER PERFORMANCE

Although some process and equipment difficulties were encountered, they were resolved so that the resultant spray calciner performance was quite satisfactory. Those items which influenced the performance of the process and equipment are discussed below. Pertinent overall spray calciner run parameters are presented in Table 4.6.

TABLE 4.6. Spray Calciner Operating Parameters

Run	Feed					Average (a) Calcination Rate, kg/hr	Average Calciner Pressure, inches of water		Average Calciner Furnace Temp., °C
	Type	Temp., °C	Time, hr	Rate, liters/hr					
				Average	Range				
SS-7	PW-1	30	47	18	14 to 21	3.9	-10	-2	670
SS-8	PW-1	25	55	15	13 to 18	3.0	-8	-2	690
SS-9	PW-4m	30	52	15	8 to 20	4.0	-11	-3	690
SS-10	PW-4m	30	56	14	11 to 18	3.6	-10	-2	700
SS-11	LMFBR	24	45	15	12 to 17	4.1	-10	-2	700
SS-12 (IPM)	PW-4m	32	28	11	9 to 17	1.7	-10 to -6	-4 to 0	720 to 740
SS-13 (IPM)	PW-4m	25	20	15	13 to 18	2.3	-12 to -8	-6 to -2	670 to 700

Run	Atomizing Air (b)			Off-Gas Filters								
	Average Press., psig	Temp., °C	Average Flow, scfm	Pressure Drop, in. of Water			Noncondensable Off-Gas Flow, scfm	Filter Face (c) Velocity ft/min	Chamber Temp., °C	Blowback Gas (d)		
				Start of Run	Maximum	End of Run				Type	Temp., °C	Press., psig
SS-7	44	30	6.5	3.0	5.4	4.8	13	3.7	330	Air	350	42
SS-8	44	30	7.0	4.5	5.4	4.5	13	3.4	340	Air	350	44
SS-9	45	30	6.3	4.5	8.0	4.8	12	3.4	350	Air	350	42
SS-10	43	30	6.2	4.8	9.0	8.0	13	3.3	350	Air	350	40 to 60
SS-11	45	30	7.3	2.7	5.0	3.0	16	3.9	360	Air	350	40
SS-12 (IPM)	45	30	7.8	2.8	3.5	2.6	17	3.5	330	Air	350	40
SS-13 (IPM)	45	30	6.8	3.6	3.6	3.2	18	4.2	340	Air	350	40

- a. Estimated from feed analysis and the average feed rate to the solidifier.
b. A two-fluid internal-mix nozzle was used during all runs.
c. Gas temperature assumed the same as filter chamber temperature.
d. The filters were blown back two at a time during all the runs.

4.5.1 Calciner Feed System

The adjusted waste is pumped through a two-fluid pneumatic atomizing nozzle and sprayed into the top of the calciner.⁽⁹⁾ Air was used as the atomizing gas during the last seven demonstration runs, since it proved to be more reliable than steam during design verification⁽⁴⁾ and nonradioactive tests.⁽¹⁰⁾

With the calciner at operating temperature and the atomizing air on at 40 to 45 psig, the spray calciner was started by feeding water at approximately 15 liters/hr. Water was fed to the calciner for 10 to 20 minutes to permit the calciner temperatures to level out. Feed was then slowly blended with the water over a 1-minute period until only waste was being fed and the water was off. The aqueous feed rate to the solidifier ranged from 9 to 21 liters/hr while processing the PW-1, PW-4m, and LMFBR wastes. Processing rates are summarized in Table 4.2. Shutdown involved an immediate switch to water feeding for 20 to 30 minutes. The use of water during startup and shutdown avoided nozzle plugging problems which result if feed is turned on directly to the hot nozzle or if the nozzle is not adequately flushed at the end of the run.

Internal-mix atomizing nozzles (Spraying Systems Company Setup No. 42) were used during the seven runs. The nozzle used during Run SS-7 performed satisfactorily, but it was necessary to replace it prior to Run SS-8 because the cleanout needle became jammed and would not operate. The next nozzle was used during Runs SS-8, SS-9, and SS-10, but was replaced following SS-10 due to the deposition of 13% of the waste in the calciner during this run. The cleanout needle on this nozzle also became inoperable. The occurrence of deposition during Run SS-10 indicated inadequate feed atomization which was the result of erratic atomizing air flow during the run. During

the majority of Run SS-10, the atomizing air pressure control to the nozzle was somewhat erratic and caused the atomizing air flow to vary as much as 20%. Although the exact cause of the poor air pressure control was not determined, it was probably due to a decreased sensitivity of the pressure control system and observed feed flow fluctuations. Variations in the feed flow were noted during Run SS-10 as indicated by fluctuation of the calciner internal temperatures (as shown in Figure 4.4). This performance in any case points out the importance of controlling the atomizing air and feed flow rates to assure optimum performance of the atomizing nozzle.

During Run SS-11, the newly installed atomizing nozzle with improved atomizing pressure control produced the steadiest internal calciner temperatures (as shown in Figure 4.5) and calcine fall to the melter that has been observed during the radioactive demonstration runs. An inspection of the inside of the solidifier after the run revealed essentially no deposition of calcine.

During Run SS-12(IPM), however, the spray calciner capacity was limited and except for the first few hours of the run it was not possible to exceed a feed rate of 11 liters/hr without producing a significant drop in calciner internal temperatures (as shown in Figure 4.6). Following the run, visual inspections and water capacity checks indicated that there was sufficient calcine scale on the drying chamber walls to reduce the calciner drying capacity approximately 40% below what it had been prior to the run. Mechanical scrapping of the drying chamber walls greatly improved the calciner capacity as indicated in Figure 4.7.

FIGURE 4.4. Spray Calciner Temperatures During Run SS-10

FIGURE 4.5. Spray Calciner Temperatures During Run SS-11

FIGURE 4.6. Spray Calciner Temperatures During Run SS-12(IPM)

FIGURE 4.7. Spray Calciner Capacity Test Data

The cause of the calciner wall scaling during Run SS-12(IPM) was not determined. It was not felt to be characteristic of the feed since this situation did not occur during developmental calciner runs on this feed type. Although poor feed atomization would be suspect, the feed nozzle used during the run was the same one which had performed so satisfactorily during Run SS-11. The atomizing air and feed flow control appeared adequate during Run SS-12(IPM) for proper nozzle operation and an inspection of the nozzle after the run revealed no outward signs of a nozzle malfunction. The scaling apparently was initiated early during Run SS-12(IPM) since the temperatures started dropping sharply shortly after the feed was turned on. It may be that a brief surge in feed flow during this period resulted in the wet spray contacting the hot calciner walls and forming an initial scale. This scale formation may have continued until a significant reduction in feed rate was made so that the feed rate no longer exceeded the drying capacity of the calciner.

A new nozzle was installed prior to Run SS-13(IPM) and the run was successfully completed. Although the feed rate averaged above 15 liters/hr, without a gross drop in calciner temperatures there nevertheless was a decreasing trend throughout the run (as shown in Figure 4.8). This may have indicated that a more thorough cleaning of the drying chamber walls was called for prior to the run. However, inspection of the calciner after the run revealed essentially no scaling of the drying chamber walls occurred during the run.

The feed flow control during most of the runs was barely adequate. The difficulties were due to the insensitivity of the magnetic flowmeter (the sensing element in the feed flow control loop) to changes in feed flow rate. The sensitivity

FIGURE 4.8. Spray Calciner Temperatures During Run SS-13(IPM)

problem occurred primarily because the 15 to 20 liters/hr feed rates desired for the spray solidifier were well below the lower range of the recommended operating range for the flowmeter. Although the flowmeter had the smallest tube diameter (3/16 inch) which would provide sufficient flow area to minimize plugging problems, the resultant fluid velocity was insufficient for good operation. This difficulty with feed flow control can probably be resolved by using other flowmeters or it will probably resolve itself in scaling up the process to the higher rates that will be encountered in most production-scale units.

Due to the high salt and solids content of the feed, the high nozzle operating temperature, and the small diameter of the nozzle feed port (0.1 inch inside diameter), occasional plugs formed on the feed side of the nozzle. The formation of a plug was noted by a sudden drop in the feed flow to the calciner. The nozzle cleanout needle proved thoroughly effective in removing these plug formations when used before a complete stoppage of feed flow occurred. Nonheated atomizing air was used during all of the last seven runs.

On one occasion (during Run SS-7) the air and feed side of the nozzle became partially plugged following a sudden loss in feed flow. The plug resulted when the feed flow ceased and residual feed dried in the hot nozzle. A system was installed which allowed flushing of the air side of the nozzle while on the solidifier by adding small amounts of nitric acid directly to the atomizing air. Following the addition of six 50-milliliter batches of 4M HNO_3 to the atomizing air, normal atomizing air and feed flows were restored to the calciner.

4.5.2 Drying Chamber

In general, all three zones of the calciner furnace were operated at approximately 700 °C while processing the wastes. Higher temperatures were not used while processing PW-1, PW-4m, and LMFBR wastes containing melt-forming additives because of the tendency of these solutions to sinter and stick at temperatures of about 800 °C. Scaling of the heated drying chamber walls only occurred during Run SS-12(IPM) due to poor feed atomization as discussed previously. Scaling was minimal during the other runs.

The net calciner heat requirements during processing ranged from 12 to 18 kilowatts, with about 40% of this used in each of the top two furnace zones. Due to the small holdup and short residence time (6 to 10 seconds) of the waste in the drying chamber, the contribution of the internal heat generation in the waste to the calciner heat requirements was negligible.

The internal calciner wall temperatures were useful indicators of operation by providing immediate response to changes in calciner feed flow which were not indicated by the feed flowmeter. This allowed early feed flow rate corrective action to be taken which would not have otherwise been possible if total reliance on the flowmeter or the dropout rate from the feed tank had been required. Although the temperatures in the top calciner zone ranged from 300 to 500 °C for the seven runs, a temperature of 350 to 400 °C was about optimum for a feed rate of approximately 16 liters/hr. Calciner temperatures during processing are presented in Figures 4.4, 4.5, 4.6, and 4.8.

The free-piston, air-operated vibrator mounted on top of the calciner performed satisfactorily at dislodging calcine from the drying chamber walls during the seven runs; however,

some mechanical difficulties were experienced with it and it was necessary to replace it a number of times. The vibrator was normally actuated for 2 seconds of every minute with an air supply pressure ranging from 40 to 60 psig.

4.5.3 Off-Gas Filtration

The solidifier off-gases exit through 15 square feet of sintered powder metal (316L stainless steel) filters. The filters are cleaned by periodically blowing heated air back through them.

Less than 0.1% of the nonvolatile radioactivity was entrained from the solidifier during the runs as shown in Table 4.7. The fact that the cumulative percent entrainment in some cases is higher than the instantaneous values may indicate that a burst of calcine passed the filters at the start of the run while the filter coat was being established.

TABLE 4.7. Entrainment from the Spray Solidifier

Run	Percent of $^{144}\text{CePr}$ in Feed Entrained from the Solidifier	
	Total Run ^(a)	Instantaneously ^(b)
SS-7	(c)	0.005 to 0.026
SS-8	(c)	0.014 to 0.076
SS-9	0.023	0.21 to 0.33
SS-10	0.079 ^(d)	<0.01
SS-11	0.013	0.002 to 0.034
SS-12 (IPM)	0.014	0.0005 to 0.004
SS-13 (IPM)	0.0011	0.0004 to 0.035

- a. Based on the $^{144}\text{CePr}$ collected in the accumulated solidifier condensate for the total run.
- b. Based on periodic solidifier condensate line samples.
- c. Total entrainment could not be determined due to the contamination of the solidifier condensate as the result of a leak in the solidifier feed system.
- d. For Mode A portion of run only.

With exception of Run SS-10, no difficulties were experienced in controlling the pressure drop across the solidifier off-gas filters as shown in Table 4.6. During Run SS-10 the filter pressure drop increased from 5 to 9 inches of water despite increasing the filter blowback pressure. An inspection of the inside of the solidifier after Run SS-10, revealed considerable calcine deposition in the filter chamber. Apparently as the result of the inadequate feed atomization during the run, wet calcine lodged around the filters and dried to form an impervious cake. The filters were thoroughly flushed prior to Run SS-11 by spraying nitric acid into the upper filter chamber while simultaneously blowing back the filters with saturated steam. Blowing the saturated steam and nitric acid back through the filters proved to be a very effective technique for cleaning them.

Prior to Run SS-11, several of the solenoid valves on the blowback gas supply were either sticking open or closed and leaking excessively. Inspection of the valves (pilot-operated) revealed that they contained Teflon[®] valve discs which had deteriorated as the result of radiation damage and would not allow the pilot or main valves to seat properly. The valves had experienced radiation levels in the range of 1000 to 10,000 R/hr over a period of 1.5 years with only 380 hours of actual operation. All eight valves on the blowback system were replaced with new ones and the system then operated satisfactorily.

Heated air was used during the runs as a blowback gas and proved satisfactory. During the runs, each bank of filters

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was usually blown back for 2 seconds during every 2 minutes. During the runs, with exception of Run SS-10 as discussed earlier, a blowback gas pressure of 40 to 45 psig maintained the filter pressure drop between 2.5 to 5 inches of water. The use of 40 psig air (350 °C) as blowback gas added approximately 1.5 scfm of air to the solidifier off-gas system. Also, during these last runs, the filter blowback system was usually turned off for 10 to 30 minutes during discharge of the melter. However, this did not adversely affect the filter pressure drop.

The calciner was normally maintained under a vacuum of 10 to 12 inches of water to accommodate the pressure surges during filter blowback. The air inleakage through the flanged connections on the solidifier (particularly on the melter) ranged from 5 to 10 scfm, and represented 20 to 30% of the total off-gas flow.

4.6 PERFORMANCE OF THE MELTER

The calcined waste drops from the spray calciner directly into the melter⁽⁹⁾ where it is converted to a melt. During Runs SS-7 through SS-11 in which the platinum melter was used, the melt was discharged batchwise through the drain freeze-valve. This procedure was preferred over continuous discharge⁽⁶⁾ because it avoided stalagmite formation problems in the receiver pot and allowed the filling of unheated pots.

As shown in Table 4.8, the internal melt temperature measured near the bottom of the melter was generally 40 to 90 °C below the furnace temperature. This melt temperature ranged from 1050 to 1150 °C during processing of PW-1, PW-4m, and LMFBW wastes. Figures 4.9 and 4.10 show typical melter

TABLE 4.8. Melter Operating Parameters

Run	Feed Type	Melt Heat Rate Density, W/liter	Melter Furnace		Melt (a) Temperature, °C	Calculated Melt Production Rate, liters/hr	Melt Discharge	
			Average Temperature, °C	Average Gross Power, kW			Method	Rate, liters/hr
SS-7	PW-1	204	1125	14.7	1060	1.32	Batch	65
SS-8	PW-1	114	1140	15.0	1050	1.07	Batch	52
SS-9	PW-4m	107	1175	15.3	1100	1.30	Batch	23
SS-10	PW-4m	132	1190	16.0	1150	1.0	Batch	24
SS-11	LMFBR	175	1180	16.0	1140	1.33	Batch	34

a. The maximum measured melt temperature (near the bottom of the melter).

FIGURE 4.9. Melter Temperatures During Run SS-7

FIGURE 4.10. Melter Temperatures During Run SS-10

temperatures during processing of the wastes. The melt level was about 5 to 6 liters when batches in the melter were discharged. The time at which to discharge the melter was determined by the amount of waste fed between batches and the melter internal temperatures. The 5 to 6-liter level in the melter was usually indicated when the internal melt temperature located 5-1/2 inches from the melter bottom (3.9 liter level) increased to almost equal the temperature at the lower part of the melter.

Following Run SS-11, the platinum melter was removed from the melter furnace and it was found that the melter had four large indentations in the side of it as shown in Figure 4.11. The melter at the time of removal had experienced approximately 650 hours of intermittent service with temperatures ranging from 900 to 1200 °C and pressures of -25 to +10 inches of water. The melter had been visually examined prior to Run SS-5 after approximately 220 hours of service, and it had one slight indentation located in the same area as the indentation labeled Number 2 in Figure 4.11, but it was considerably less pronounced. Measurements taken on the melter indicated that the diameter of the melter had been reduced as much as 2 inches in some spots as the result of the indentations. The exact cause of the distortion of the platinum melter was not determined. A similar distortion of a platinum melter occurred at Brookhaven National Laboratory⁽¹¹⁾ and was attributed to the negative melter operating pressure and the reduced creep resistance of the platinum caused by the long process exposures. A subsequent Brookhaven melter was fabricated with increased wall thickness and stiffener rings welded to the outside melter wall to increase strength.

The platinum melter is shown in Figure 4.12 shortly after fabrication. A summary of the melter fabrication and operating history is provided below. Pertinent items during fabrication were:

Position I
Neg 701124-2

Position II
Neg 701124-4

Position III
Neg 701124-5

FIGURE 4.11. Distorted Spray Solidifier Platinum Melter

Neg 0662221-4

FIGURE 4.12. Spray Solidifier Platinum Melter Shortly After Fabrication

- The rolled sides, the conical bottom section, and the tubing for the drain and weir tubes were of >99.95% platinum and supplied by Engelhard Industries.
- The above mentioned components along with the top cover (including 6 nozzles) salvaged from the first WSEP melter⁽⁵⁾ were assembled at Battelle-Northwest into the melter as shown in Figure 4.12.
- All welds were made using the Tungsten Inert Gas Process.
- All materials were X-rayed before and after welding and all welds were inspected by an authorized Battelle-Northwest representative.
- The completed assembly was hydrostatically tested at 5 psig for 2 hours and then installed in B-Cell on the WSEP spray solidifier in September 1966.

Pertinent items during operation were:

- The melter was first put into service during Run C (October 1966) of the spray solidifier design verification tests.⁽⁴⁾
- The radioactive service was started with Run SS-1 (January 1967) and continued through Run SS-11 (February 1970).
- The melter was removed from the furnace (June 1967) following Run SS-2 so that the freeze valve heaters could be replaced. The melter appeared in good condition at that time with exception of a bent drain tube which was straightened.
- Total heated hours through Run SS-11 (900 to 1200 °C) were about 650.
- Total number of heating-cooling cycles (room temperature to greater than 900 °C) were 18. The melter heatup rate was generally about 150 to 200 °C/hr.

- The melts processed included PW-1, PW-2, PW-4m, and LMFBP phosphate adjusted wastes.
- The melter pressure was generally 0 to -12 inches of water while at temperature and on occasion it surged as high as 10 inches of water and as low as -25 inches of water.
- Pressure pulses as the result of filter blowback were imposed upon the inside of the melter to an incremental stress of 15 to 30 psi at a rate of about 2 to 4 times per minute for a total of about 100,000 cycles.

4.6.1 Melt Drain System

During Run SS-7 through SS-11 the melt was discharged successfully in batches from the melter using the drain freeze-valve cooling system installed prior to Run SS-5.⁽⁶⁾

To batch discharge the melter, the air to the cooling coil of the drain freeze-valve was turned off. When the melter started draining (which usually occurred 2 to 3 minutes after the air had been turned off), the solidifier vacuum was reduced to approximately 2 inches of water to speed the drainage and the filter blowback system was turned off to avoid pressurizing the solidifier. The air was turned back on to the drain valve coil shortly after the melter quit draining a steady stream and started to drip. The blowback system and solidifier vacuum were restored to normal approximately 2 to 3 minutes after the melter had quit dripping. A typical batch of 4 to 6 liters of melt usually drained steadily for 4 to 20 minutes and then dripped for another 2 to 4 minutes before the drain tube sealed. On several occasions, difficulties occurred in sealing the drain tube primarily as the result of not letting the melter completely empty out before trying to seal it. On

several occasions it was necessary to reduce the melter furnace temperature approximately 100 °C in order to stop the melter from dripping. Usually, the blowback system was off about 10 to 20 minutes during the dump procedure, but this did not have any detrimental effect on the solidifier off-gas filter pressure drop.

The cooling air flow rates to the drain freeze-valve coil and the weir coil were 5 to 8 and 3 to 7 scfm, respectively, during the runs. The temperatures at the drain and weir tubes were 800 to 840 °C at these air flow rates. When the air was turned off to the drain freeze-valve coil, the temperature at the drain tube increased to 950 to 1040 °C. The PW-1 melts were batch discharged from the melter at rates of 50 to 65 liters/hr; the PW-4m melts were considerably more viscous and discharged at rates of 23 to 24 liters/hr; and the LMFBR melt was discharged at a rate of 34 liters/hr. In all cases, batch discharge allowed filling of unheated receiver pots without stalagmite formation. However, a filling rate of 23 liters/hr probably represents the minimum rate at which an unheated 8-inch diameter pot can be filled with PW-4m melt without stalagmite formation problems.

4.6.2 Effect of Internal Heat Generation

The net heat requirement to form a fluid melt from the entering waste calcine is about 1.5 to 2.5 kilowatts for a melt production rate of 1.2 liters/hr. The highest heat rate density of 204 W/liter was attained for a PW-1 melt in Run SS-7. This heat rate density accounts for 50 to 80% of the net heat requirement in a melt volume of 6 liters. However, due to the continuous variation of melt volume from 0 to 6 liters (during batch dumping) and due to the high heat losses from the melter (about 12 kilowatts), the effect of internal heat generation was not apparent.

4.7 IN-POT MELTING PERFORMANCE

The in-pot melting technique involved melting the spray calcined waste directly in the final storage container with a borosilicate glass frit.

To adapt the spray solidifier for in-pot melting, the platinum melter and melter furnace assembly were removed from the solidifier and a transition piece (spool-piece) was fabricated which coupled the spray calciner directly to the receiver pot. The spool-piece shown in Figure 4.13 was a 6-inch diameter tube rolled from 11 gage 304L stainless steel sheet metal with vee flanges welded at each end to attach it to the calciner outlet and pot fill head assembly. The spool-piece was provided with (1) a removeable quartz glass window to allow viewing down into the pot with the aid of a mirror, (2) two two-inch diameter access nozzles, one of which was used to add solid flux to the pot, (3) a ten-inch diameter bellows to allow for thermal expansion, (4) an air-operated vibrator to vibrate the spool-piece when desired, and (5) a one-inch thick outside covering of Kaowool insulation to reduce heat loss.

Since all the flux required for in-pot melting is added directly to the pot, a solids addition system was required. The system used was the same as that used during Runs SS-3 and SS-4⁽⁶⁾ in that solids were added in small batches to the suction side of an air-operated jet and conveyed pneumatically into the process cell and discharged into a screen-covered hopper on the solids feeder. The solids feeder as shown in Figure 4.13 consisted of a section of pipe attached to a nozzle on the spool-piece with two air-operated ball valves which served as an air lock so that solids could be added

FIGURE 4.13. In-Pot Melting and Solids Addition Systems

without loss of solidifier vacuum. A vibrator was also attached to aid transport of the solids.

The in-pot melting proceeded without any difficulties during Runs SS-12(IPM) and SS-13(IPM). The receiver pot furnace was started initially with the bottom three zones set at 925 to 950 °C and the top three zones at 850 °C. As the bottom zones were filled, the respective furnace zone temperature was reduced and the furnace zone was eventually turned off. The upper furnace zone temperatures were increased to 925 to 950 °C as required so that at least two zones above the melt level were at temperature.

During the first 5.5 hours of Run SS-12(IPM) the pot kept up easily with the calciner at an average melt formation rate of 2.7 liters/hr with rates as high as 3 liters/hr being attained at the start of the run. (Due to heat loss out the bottom of the pot the capacity should be limited at the start of a run.) During the remainder of the run the melt formation rate was only 1.75 liters/hr as the result of the reduced feed rate to the calciner. The average melt formation rate for this run was 1.9 liters/hr and was equivalent to an overall waste processing rate of 0.46 tonne/day.

During Run SS-13(IPM), the pot easily kept up with the calciner at a melt-forming rate of approximately 2.5 liters/hr. For this run the flowsheet was modified such that excess aluminum in the feed stock solutions was substituted for the zinc and calcium additives used during Run SS-12(IPM) and this increased the waste concentration in the product to 28 wt% from the 17 wt% in SS-12(IPM). The increased product waste concentration and the 2.5 liters/hr melt formation rate resulted in an average processing rate of 1.05 tonne/day during Run SS-13(IPM) which was 80% higher than the highest processing

rate attained for the PW-4m waste during previous spray solidification runs using the platinum melter.

The progress of the in-pot melting runs was followed by viewing through the spool piece window and observing the pot internal temperatures. Although no real detail was visible in the pot, the presence of a red glow in the pot gave assurance that the melting was progressing satisfactorily. The window was kept relatively free of calcine during the first half of Run SS-12(IPM) via a window wiper. During the last half of this run and all of Run SS-13(IPM), the window was streaked with calcine and viewing was somewhat limited as the result of deterioration of the hypolon rubber wiper blade due to the high spool piece temperatures (200 to 300 °C). The pot internal temperatures provided the best indication of how the pot filling was progressing. As shown in Figures 4.14 and 4.15, the pot centerline temperatures would start dropping as the melt level entered a respective zone, reaching a minimum of 650 to 700 °C, when the zone was about half full and then increasing as the zone completed filling. When the zone was filled as indicated by a centerline temperature in excess of 900 °C, the respective furnace zone temperature was reduced and eventually turned off. As indicated in Figures 4.14 and 4.15, the borosilicate melt possessed a relatively high thermal conductivity since the pot centerline temperature did not exceed 1040 °C despite pot wall temperatures of 900 to 950 °C and a heat rate density of 200 W/liter during Run SS-13(IPM). This would indicate that the borosilicate melt during processing (average melt temperature of 900 °C or greater) has an effective thermal conductivity in the range of 4 to 7 W/(m²)(°C/m).

FIGURE 4.14. Pot Temperatures During Run SS-12(IPM)

FIGURE 4.15. Pot Temperatures During Run SS-13(IPM)

The feed to the calciner was discontinued at the end of each run due to the sustained decrease in the pot Zone 1 center-line temperature and due to the fact that no red glow was visible in the pot. Approximately 20 minutes after the feed was turned off a red glow was again visible in the pot. The Zone 1 furnace was turned off and cooling air was turned on to all furnace zones using one blower (275 scfm) about 1 to 3 hours after the feed had been turned off.

Inspection of the 8-inch diameter, 304L stainless steel pots following Runs SS-12(IPM) and SS-13(IPM) revealed that they had been filled to a height of 68 and 64 inches, respectively. This was short of the planned level of 72 inches but is not surprising in view of high heat losses at the top of the pot since the pot was only effectively heated to the 78 inch level. A higher level probably could have been obtained had a significant reduction in feed rate been made. Although the surface of the products was somewhat irregular, all the material appeared to have been molten. There was a light film of calcine on the upper internal pot surfaces, but no accumulation of calcine was apparent.

The borosilicate glass frit was added as -6 +10 mesh particles to the pot during the runs via the previously-mentioned solids addition system. The frit was added in 1 kilogram batches with the number of batches added per hour depending on the feed rate to the calciner, so as to theoretically give a ratio of calcine to frit of 30:70 by weight. The batch addition rate ranged from 4 to 6 batches/hr during the runs. The solids feeder system performed satisfactorily during the run with a total of 109 and 106 kilograms of frit being added during Runs SS-12(IPM) and SS-13(IPM), respectively.

4.8 GENERAL PERFORMANCE AND OPERATING HISTORY

4.8.1 Waste Composition Effects

During the WSEP spray solidification runs relatively few processing problems resulted from waste composition. Two runs with PW-1 waste, four runs with PW-4m waste, and one run with LMFBR waste demonstrated adequate performance with wastes from light water reactor fuels, advanced light water reactor fuels, and fast reactor fuels, respectively.

Detailed waste compositions for the seven runs and other pertinent data on the feeds to the solidifier are listed in Table 9.1 of the Appendix. Summary feed composition ranges for the six spray solidification runs are shown in Table 4.9. Feeds to the spray solidification process were prepared using actual Purex high-level waste and concentrated radio-rare earths (Mostly $^{144}\text{CePr}$) solutions to provide the desired self-heat generation rate in the solidified product. However, because the radioactive solutions sometimes contained excess aluminum and rare earths compared to the standard waste compositions, actual composition of the wastes processed varied somewhat from the desired composition. (See Section 3 for the details of the effects of these changes in composition.) The ability to handle these variations in themselves points out the flexibility of the solidification system.

The excess aluminum in the Purex waste was used as a partial substitute (10 to 13%) for the 0.93M iron in Runs SS-7 and SS-8 with PW-1 waste, (15 to 30%) for the 1.1M iron additive in Runs SS-9 and SS-10 with PW-4m waste, and (20%) for the 2.17M iron additive in Run SS-11 with LMFBR wastes. Although aluminum served as a partial iron substitute during

TABLE 4.9. Summary of Waste Composition Ranges

Constituents	PW-1 Waste, $\underline{M}^{(a)}$		PW-4m Waste, $\underline{M}^{(a)}$		LMFBR Waste, $\underline{M}^{(a)}$	
	Nominal	Actual ^(b)	Nominal	Actual ^(b)	Nominal	Actual ^(b)
Na^+	0.138	0.47 to 0.57	0.10	0.19 to 0.83	0.1	3.75
Al^{+3}	0.001	0.09 to 0.12 ^(c)	0.001	0.16 to 0.34 ^(c)	0.001	0.46 ^(c)
Fe^{+3}	0.93	0.69 to 0.8	0.05	0.07 to 1.0	0.16	1.81
$(\text{Y+RE})^{+3}$	0.12	0.12 to 0.13	0.274	0.28 to 0.33	0.528	0.53
NO_3^-	7.5	1.8 to 4.7	6.66	3.6 to 6.9	4.75	13.5
<u>Additives</u>						
Na^+	0.5	Included above	0.97 ^(d)	Included above	3.4	Included above
Fe^{+3}	---	-----	1.10 ^(d)	Included above	2.17	Included above
PO_4^{-3}	1.7	1.58 to 1.6	2.80 ^(d)	0.003 to 2.87	5.58	5.68

a. Molarities are based on 378 liter/tonne feed.

b. Based on analysis of the composite feed (including additives).

c. Excesses result from the presence of excess aluminum in the Purex high level waste.
The excess aluminum was substituted for iron.

d. These additives were not added during Runs SS-12(IPM) and SS-13(IPM).

Runs SS-12(IPM) and SS-13(IPM), it was still a factor of approximately 200 in excess of the 0.001M nominal aluminum concentration for the PW-4m waste.

All chemical additives were added directly to the feed for Runs SS-7 through SS-11 while the flux for the PW-4m waste during Runs SS-12(IPM) and SS-13(IPM) was added as a borosilicate frit directly to the receiver pot.

4.8.2 Related Equipment

Performance of the primary spray solidifier equipment has been discussed in the preceding sections. The operating history of this equipment (which includes all nonradioactive tests) is summarized in Table 4.10. Discussion of other related equipment is presented below.

Seal Pot

A secondary vent line from the solidifier provided for relief of solidifier pressure if it increased to atmospheric level during operation. A water-seal pot in the line overflows directly into a condensate receiver tank (TK-117).

The calciner seal pot is an 8-inch diameter by 36-inch long section of pipe which is closed at each end and contains inlet and outlet piping arranged in such a way that maximum pressure differentials of up to 20 inches of water are required to allow gas to flow from the calciner to the condensate tank. Backward flow of seal water to the solidifier is not possible. During the runs the solidifier was vented occasionally through the seal pot during filter blowback as the result of a decrease in venting capacity of the solidifier off-gas system which sometimes occurred when a liquid or gas sample was being taken.

TABLE 4.10. Spray Solidification Equipment Operating History Through Run SS-13(IPM)

Equipment	Construction Material	Temp, °C	Pressure, in. of Water	Chemical	Total Operating Time, hr	Comments
Calciner shell	310 SS	200 to 700	-20 to +5	Atomized liquid and calcined waste; water and HNO ₃ vapors; oxides of nitrogen; oxides of sulfur; air	900	
Calciner furnace	Nichrome V elements and Tipersul insulation	650 to 750	-0.5	Cell air	1000	
Off-gas filters No. 2	Sintered 316L SS powder metal filters (1/16 in. thick)	200 to 400	-20 to +5	Calcined waste, water and HNO ₃ vapors, oxides of nitrogen, oxides of sulfur, and air	450	
Feed nozzle No. 4	303 SS (external-mix)	50 to 130	20 to 30 psig		47	Replaced prior to Run SS-8 because of a malfunctioning cleanout needle.
No. 5	303 SS (internal-mix)	50 to 130	20 to 30 psig	Liquid waste and air	141	Replaced after Run SS-10 because of deposition in calciner (see Section 4.5.1).
No. 6	303 SS (internal-mix)	50 to 130	20 to 30 psig		73	Replaced after Run SS-12(IPM) because of scaling of drying chamber walls (see Section 4.5.1).
No. 7	303 SS (internal-mix)	50 to 130	20 to 30 psig		20	
Calciner vibrator No. 4	Mild Steel	50 to 100	30 to 40 psig	Air	164	Replaced during Run SS-9 when it quit vibrating.
No. 5	Mild Steel	50 to 100	30 to 50 psig	Air	73	Replaced prior to Run SS-11 as it would not vibrate
No. 6	Mild Steel	50 to 100	30 to 50 psig	Air	60	Replaced during Run SS-12(IPM) when it quit vibrating.
No. 7	Mild Steel	50 to 100	30 to 50 psig	Air	14	Replaced prior to Run 13(IPM) as it would not vibrate.
No. 8	Mild Steel	50 to 100	30 to 50 psig	Air	20	

TABLE 4.10. (contd)

Equipment	Construction Material	Temp, °C	Pressure, in. of Water	Chemical	Total Operating Time, hr	Comments
Calciner seal pot	304L SS	30 to 50	-20 to +5	Water	900	
Melter	Platinum	700 to 1200	-20 to +5	Calcined and molten waste and vapors	650	After Run SS-11, indentations were noted in the sides of the melter (see Section 4.6).
Melter furnace	Kanthal A-1 elements, K-28 and Fiberfrax insulation	800 to 1250	-0.5	Cell air and receiver pot vapors	730	Internal furnace leads failed after 500 hr of operation prior to Run SS-3 and had to be replaced (see Refer- ence 6).
Melter freeze- valve cooling coil assembly	Hastelloy X coils	800 to 1100	-0.5	Cell air and receiver pot vapors	420	
Receiver pot furnace	Kanthal A-1 elements Tipersul insulation Hastelloy-X Susceptor	600 to 950	-0.5	Cell air	300	

However, this could have usually been prevented by adjusting the solidifier vacuum prior to and during sampling.

Receiver Pot Furnace

The six-zone resistance-heated receiver pot furnace (and cooler) performed well in transferring heat to or from the receiver pot. The furnace was not operated during Runs SS-7 through SS-11 as the receiver pots were unheated and the furnace provided cooling function only. Indirect cooling by forced air around the outside of the furnace susceptor was sufficient to maintain the steady-state centerline temperatures of the receiver pot contents below 920 °C and the steady-state pot wall temperatures below 470 °C during Run SS-7 which had the highest internal heat generation rate (12.7 kilowatts) of the seven runs.

During Runs SS-12(IPM) and SS-13(IPM) the furnace was operated to fuse the waste calcine and borosilicate frit directly in the receiver pot. The furnace operated very satisfactorily at temperatures up to 950 °C. See additional discussion in Section 4.2 and 4.7.

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5.0 AUXILIARY PROCESS SYSTEMS
PERFORMANCE

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5.0 AUXILIARY PROCESS SYSTEMS PERFORMANCE

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

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

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

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

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

In the WSEP auxiliary system, vapors from the solidification system which are not acceptable for discharge without further treatment are first routed through a condenser to the evaporator. The solidifier condensate is concentrated in the evaporator (along with incoming feed in some cases). The vapors from the evaporator are decontaminated from entrained aerosols in the evaporator tower by impingement plates, bubble caps, and a mist eliminator and then they are condensed. The evaporator condensate is further decontaminated and concentrated in the acid fractionator where nitric acid is recovered. The vapors from the fractionator are again condensed and about 90% of the fractionator distillate is recycled to the evaporator as acid stripwater, while the remaining 10% is collected as an intermediate to low-level waste stream. The remaining gases are

treated by high efficiency filtration, scrubbing, and additional filtration before discharge to the atmosphere. Figure 5.1 illustrates the WSEP auxiliary process system.

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

1. The radionuclides in the immediate effluent (solidifier off-gases) have been decontaminated by factors of 1.4 to 200 so that the effluent remains as a high to intermediate-level waste. The larger value is for an in-pot melting run.
2. The decontamination of process off-gases by the WSEP auxiliary system is adequate for the final gaseous effluent stream, but is inadequate for the final aqueous effluent stream which contains a radionuclide concentration that is above 10CFR20⁽²⁾ release limits by factors as high as 16,000.
3. The volumes and radionuclide content of the immediate effluent (evaporator bottoms) and recovered acid (fractionator bottoms) are relatively small and can be recycled to the solidifier feed and to a fuel reprocessing plant, respectively. To be released to the environment, the fractionator distillate stream would require additional decontamination.

A summary of information on typical effluents resulting from the spray solidification process is presented in Table 5.1. During spray solidification Runs SS-7 through SS-11, from 39% to 73% of the radioruthenium fed to the solidifier was volatilized from the solidifier and accumulated in the auxiliary evaporator. Volatilization of ruthenium was only 1.9% and 0.05% during Runs SS-12 and SS-13, respectively, using the spray solidification in-pot melting technique. Nonvolatile entrainment represented by cerium was less than 0.014%.

FIGURE 5.1. WSEP Auxiliary Process System

TABLE 5.1. Typical Effluents Resulting From Spray Solidification During Mode A Operation (a)

Stream	Solution	Volume, liters/ liter feed	Radioactive Ruthenium, Ci/Ci in feed	Gross Radio- activity less Ruthenium, Ci/Ci in feed	Potential Disposal
Evaporator Bottoms	4M HNO ₃	0.4 ^(c)	0.55 (0.01) ^(b)	3.8×10^{-4} ($<7 \times 10^{-4}$) ^(b)	Recycle to solidifier feed or to fuel repro- cessing plant waste concentrator
Fractionator Bottoms	8M HNO ₃	0.3 - 0.4	5×10^{-3}	$10^{-5} - 10^{-7}$	Reuse in fuel repro- cessing plant
Accumulated Fractionator Distillate	0.05M HNO ₃	0.2 - 0.7	3×10^{-6}	$10^{-9} - 10^{-10}$	Reuse in fuel repro- cessing plant
Scrubber Bottoms	2M to 0M NaOH	0.6 ^(d)	5×10^{-5}	$10^{-9} - 10^{-10}$	Intermediate level waste treatment or combine with high level waste
Final Off-Gas From Scrubber	Air	—	$10^{-8} - 10^{-9}$	$10^{-11} - 10^{-12}$	To building ventila- tion filters
Final Off-Gas to Stack	Air	—	$<10^{-10}$	$10^{-12} - 10^{-13}$	To atmosphere

a. Average of data taken from Spray Solidification Runs SS-7 through SS-11.

b. Average data from Inpot Melting Runs SS-12 and SS-13.

c. Assumes a working volume of 300 liters in the evaporator. This volume is present at start of run and must either be continuously recycled or batch recycled to the feed.

d. Assumes a working volume in the scrubber of 500 liters. This volume is present at the start of the run and must be recycled batchwise to the feed.

5.1 OPERATING MODES

The need to demonstrate how the treatment of effluents from solidification can be integrated into a fuel reprocessing plant using existing equipment such as waste evaporator and acid recovery system or done separately prompted the selection of three different operating modes in WSEP. These are designated in WSEP as Modes A, B, C; and are described in References 3, 4, and 5. Figure 5.2 shows the three operating mode options for WSEP. To date, Mode A and B were tested with the spray solidification process; Mode C was not tested.

Applications of the modes in a fuel reprocessing plant are visualized as shown in Figure 5.3. During Mode A operation, the evaporator bottoms is an additional effluent stream which must be recycled back to the solidifier feed or to the waste concentrator in a fuel reprocessing plant. In Mode B and C operation, the evaporator bottoms are mixed with incoming waste. Typical effluent data for Mode A operation for the auxiliary system during Runs SS-7 through SS-13 are summarized in Table 5.1. The only Mode B operation demonstrated was during the last 33% of Run SS-10. During Run SS-13, a modified Mode B was used for the entire run where solidifier condensate was routed to a separate condensate receiver. Normally the solidifier condensate is accumulated and decontaminated in the auxiliary evaporator.

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

FIGURE 5.2. WSEP Process Mode Options

FIGURE 5.3. Operating Mode Applications in a Fuel Reprocessing Plant

Mode C operation was not demonstrated during the spray solidification runs because provisions are not included in WSEP for continuous injection of melt-making additives to the concentrated high-level waste from the evaporator and continuous boiling of the chemically-adjusted feed could possibly cause undesirable and excessive solids precipitation. Since the basic difference between Modes B and C is holdup time of the concentrated waste before it is fed to the solidifier, little incentive existed to add the necessary equipment for Mode C operation.

5.2 RUTHENIUM CONTROL

The process effluents from spray solidification are contaminated primarily by volatilized ruthenium. Ruthenium can easily be volatilized during both solidification and evaporation. Several general relationships for minimizing the volatilization of RuO_4 were summarized in References 3 to 6.

These include:

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

A combination of these methods may prove advantageous.

The data presented in the following sections were obtained primarily from References 7 through 15.

During spray solidification Runs SS-7 through SS-11, from 39% to 73% of the radioruthenium fed to the solidifier was volatilized from the solidifier and accumulated in the auxiliary evaporator. Ruthenium volatilization from the solidifier

during SS-12 and SS-13 using the in-pot melting technique was only 1.9% and 0.05%, respectively. Figure 5.4 presents the accumulation of radioruthenium (^{106}Ru) in the WSEP auxiliaries as a function of percent of feed fed to solidifier.

The auxiliary evaporator serves as a decontamination stage between the spray solidifier and the nitric acid fractionator. During Runs SS-7 through SS-13(IPM), the evaporator was operated with a bottoms acidity of 3 to 6M HNO_3 but generally less than 5M HNO_3 and a overhead acidity of less than 1M HNO_3 , thus reducing the potential for ruthenium volatilization. Although volatilization of ruthenium was typically kept below 1% of that present in the evaporator bottoms by maintaining low acidity in the evaporator, it may be desirable to decrease the the ruthenium volatilization from the evaporator by the continuous addition of a reductant to the evaporator. Reductants have been shown to decrease ruthenium volatility,^(16,17) but no such reductants were added to the evaporator during Runs SS-7 through SS-13(IPM).

Stripwater (fractionator distillate) was recycled back to the evaporator to strip nitric acid while maintaining the evaporator overheads between 0.1 and 0.4M HNO_3 . Auxiliary evaporator and acid fractionator operating conditions for Runs SS-7 through SS-13(IPM) are shown in the appendix in Figures 9.5 through 9.11. These include: volume, specific gravity, solution temperature, stripwater addition rate, and overhead acidity. Other operating data for the evaporator as well as other auxiliaries is presented in Table 9.3 in the appendix.

Performance of the auxiliary system was primarily assessed by determining decontamination factors at each stage in the system. Data on decontamination factors across the evaporator and fractionator are presented in Table 5.2 to show the effects of evaporator bottoms and overhead acid concentration on

FIGURE 5.4. Accumulation of Ruthenium in WSEP Auxiliaries

TABLE 5.2. Decontamination Factors Across the WSEP Auxiliary Evaporator and Fractionator

SS Run	Mode	Solution in Evaporator	Additive	Evaporator					Fractionator				
				Average Acidity, M HNO ₃		Cumulative Ruthenium DF (a)	Cumulative Cerium DF (a)	Instantaneous Cerium DF (b)	Average Acidity, M HNO ₃		Cumulative Ruthenium DF (c)	Cumulative Cerium DF (c)	Instantaneous Cerium DF (d)
				Bottoms	Distillate				Bottoms	Distillate			
7	A	Nitric Acid plus Solidifier Condensate	Strip Water	4.3	0.3	52	9.8×10^2	$10^3 - 10^4$	8.0	0.07	4.8×10^3	5.8×10^4	—
8	A	Nitric Acid plus Solidifier Condensate	Strip Water	4.0	0.2	1.1×10^2	2.4×10^4	$10^3 - 10^6$	8.7	0.04	7.8×10^2	2.3×10^3	—
9	A	Nitric Acid plus Solidifier Condensate	Strip Water	4.3	0.2	87	1.5×10^3	$10^3 - 10^4$	8.1	0.06	$>6.5 \times 10^2$	NA	—
10	A	Nitric Acid plus Solidifier Condensate	Strip Water	4.0	0.2	1.2×10^2	1.7×10^4	10^4	7.4	0.04	NA	NA	—
10	B	Nitric Acid, Solidifier Condensate plus HL Waste	Strip Water	3.0	0.2 to 0.6	3.7×10^2	3.3×10^5	$10^4 - 10^6$	7.0	0.03	$1.2 \times 10^{3(e)}$	$1.2 \times 10^{3(e)}$	—
11	A	Nitric Acid plus Solidifier Condensate	Strip Water	5.7	0.4	3.5×10^2	73.5×10^2	$10^2 - 10^3$	9.1	0.1	6.3×10^2	1.3×10^3	$10^2 - 10^4$
12	A	Nitric Acid plus Solidifier Condensate	Strip Water	4.1	0.2	14	>4	$10^2 - 10^3$	8.2		7.5×10^2	7.1×10^3	$10^2 - 10^4$
13	Bm	Nitric Acid plus HL Waste	Strip Water	3.2	0.4	3.6×10^3	2.2×10^4	$10^4 - 10^6$	7.8	0.008	3.7×10^2	8.6×10^2	$10^2 - 10^3$

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

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

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

d. Instantaneous concentration of component in fractionator/instantaneous concentration of component in the condensed fractionator overhead.

e. Total run including both Mode A and B.

NA Not Available.

ruthenium DF's. Cumulative ruthenium DF's* across the evaporator varied from a low of 14 to a high of 370. The lowest DF_c occurred in the Mode A Run SS-12(IPM) while the highest DF_c occurred in the Mode B portion of Run SS-10. The low DF_c is probably caused by internal contamination of the system as indicated by the fact that the ruthenium accumulation in the fractionator only decreased by a factor of about 6 compared to previous spray runs while the ruthenium accumulation in the evaporator decreased by a factor of about 50 (decreased volatilization from the solidifier). This is particularly evident since the modified solidifier condenser and condenser offgas filtering system was used during Run SS-12(IPM).

The increase in the ruthenium DF_c during the Mode B portion of Run SS-10 is due to the method of calculating the DF. During the Mode B portion of Run SS-10, about 775 liters of Purex high-level waste (1WW) containing 1.8×10^5 curies of total radioactivity were transferred to the evaporator in 50 liter batches, hourly. Figure 5.5 shows the WSEP tank volumes during Run SS-10 while Figure 9.8 in the appendix shows the evaporator and fractionator operating parameters. The accumulation of ruthenium in the fractionator during the Mode A portion of Run SS-10 remained relatively constant. During the Mode B portion of the run, the ruthenium accumulation rate increased by a factor of 2.5 indicating an increase in the ruthenium volatilization from the evaporator bottoms. This increased ruthenium volatilization was due to the increased ruthenium concentration and evaporator acidity in the evaporator bottoms and increased boilup rate during Mode B.

The radionuclide distribution for Runs SS-7 through SS-13(IPM) is summarized in Table 5.3. The equivalent feed radioruthenium accumulated in the fractionator bottoms was

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

FIGURE 5.5. WSEP Tank Volumes

TABLE 5.3. Radionuclides in Effluent Stream for Total Run
Spray Solidification

SS Run Mode	Fraction of Equivalent Feed Radioactivity in Effluent Stream for Total Run ^(b)													
	¹⁰⁶ Ru (Radium)						¹⁴⁴ CePr (Radioactivity)							
	7	8	9	10	10	10	11	12 (IPM)	13 (IPM)	7	8	9	10	10
	A	A	A	A	B	Total Run	A	A	Bm	A	A	A	A	B
Solidifier Condensate Receiver (TK-117)	—	—	—	—	—	—	—	—	4.9 × 10 ⁻³	—	—	—	—	—
Evaporator (TK-113)	6.1 × 10 ⁻¹	3.9 × 10 ⁻¹	5.7 × 10 ⁻¹	4.5 × 10 ⁻¹	2.1 ^(a)	1.0 ^(a)	7.3 × 10 ⁻¹	1.9 × 10 ⁻²	—	2.6 × 10 ^{-2(e)}	5.7 × 10 ^{-2(e)}	2.3 × 10 ⁻⁴	7.9 × 10 ⁻⁴	2.4 × 10 ⁻¹
Fractionator (TK-115)	1.2 × 10 ⁻²	3.6 × 10 ⁻³	6.5 × 10 ⁻³	4.0 × 10 ⁻³	7.8 × 10 ⁻³	5.3 × 10 ⁻³	2.1 × 10 ⁻³	1.4 × 10 ⁻³	3.4 × 10 ⁻⁴	2.7 × 10 ⁻⁵	1.2 × 10 ⁻⁵	NDG	2.3 × 10 ⁻⁷	7.1 × 10 ⁻⁷
Fractionator Distillate Receiver (TK-116)	2.9 × 10 ⁻⁶	4.8 × 10 ⁻⁶	2.7 × 10 ⁻⁶	6.0 × 10 ⁻⁷	1.3 × 10 ⁻⁵	4.8 × 10 ⁻⁶	5.3 × 10 ⁻⁶	1.9 × 10 ⁻⁶	3 × 10 ⁻⁶	4.7 × 10 ⁻¹⁰	1.0 × 10 ⁻⁹	NDG	NDG	5.6 × 10 ⁻¹⁰
Off-Gas Scrubber (TK-118)	5.1 × 10 ⁻⁵	2.5 × 10 ⁻⁵	1.8 × 10 ⁻⁵	3.4 × 10 ⁻⁵	2.7 × 10 ⁻⁵	3.2 × 10 ⁻⁵	1.9 × 10 ⁻⁵	3.1 × 10 ⁻⁵	2.6 × 10 ⁻⁶	NDG	4.3 × 10 ⁻⁸	8.8 × 10 ⁻⁹	2.1 × 10 ⁻¹⁰	<1.7 × 10 ⁻⁹
Off-Gas from Scrubber	—	—	6.8 × 10 ⁻⁹	2.0 × 10 ⁻¹⁰	5.1 × 10 ⁻¹⁰	1.3 × 10 ⁻⁹	1.8 × 10 ⁻⁸	1.0 × 10 ⁻⁸	1.1 × 10 ⁻⁸	—	—	9.9 × 10 ⁻¹²	1.4 × 10 ⁻¹⁰	6.3 × 10 ⁻¹²
Off-Gas to Stack ^(c,d)	<3 × 10 ⁻¹³	<3 × 10 ⁻¹⁰	6.8 × 10 ⁻¹¹	—	—	<2.0 × 10 ⁻¹⁰	<2 × 10 ⁻¹⁰	<4 × 10 ⁻¹⁰	2.2 × 10 ⁻¹⁰	3.6 × 10 ⁻¹³	<4.9 × 10 ⁻¹³	5.0 × 10 ⁻¹⁴	—	—
Ratio (Fractionator Distillate Radioactivity to 10CFR20)	1.0 × 10 ⁴	1.4 × 10 ⁴	4.6 × 10 ³	—	—	4.9 × 10 ³	1.6 × 10 ⁴	1.1 × 10 ⁴	8 × 10 ³	2.2 × 10 ²	1.8 × 10 ²	—	—	—
Ratio (Scrubber Off-Gas Radioactivity to 10CFR20)	—	—	6.5 × 10 ¹	1.9 × 10 ²	4.9 × 10 ²	2.1 × 10 ³	4.9 × 10 ²	1.9 × 10 ²	3.9 × 10 ²	—	—	4.8	1.3 × 10 ⁴	6.0 × 10 ²
Ratio (Stack Off-Gas Radioactivity to 10CFR20)	<4 × 10 ⁻⁴	—	1.7 × 10 ¹	—	—	<4 × 10 ⁻⁴	<4 × 10 ⁻⁴	<4 × 10 ⁻⁴	<4 × 10 ⁻⁴	1.6 × 10 ⁻²	<8.2 × 10 ⁻⁴	1.1 × 10 ⁻²	—	—

- a. Fraction of feed radioactivity for Mode B and total run includes radioactivity fed to TK-113 from Mode B feed tank (TK-112) during Mode B.
- b. Total curies of component gained in auxiliary tank/total curies of component fed to the solidifier for total run.
- c. Total curies of component in off-gas/total curies of component fed to solidifier for total run.
- d. Based on total noncondensable gas flow of 40 scfm.
- e. A small stream of feed leaked to the evaporator through a faulty control valve causing a high accumulation of ¹⁴⁴CePr. The actual entrainment was about 1 × 10⁻²% based on instantaneous stream samples.
- NDG No detectable gain in radioactivity.

TABLE 5.3. Radionuclide Distribution in WSEP Auxiliaries for Spray Solidification Runs SS-7 Through SS-13(IPM)

Fraction of Equivalent Feed Radioactivity in Effluent Stream for Total Run ^(b)															
¹⁰⁶ Ru (Radiatoruthenium)							¹⁴⁴ CePr (Radiocerium)								
9	10	10	10	11	12 (IPM)	13 (IPM)	7	8	9	10	10	10	11	12 (IPM)	13 (IPM)
A	A	B	Total Run	A	A	Bm	A	A	A	A	B	Total Run	A	A	Bm
—	—	—	—	—	—	4.9 × 10 ⁻³	—	—	—	—	—	—	—	—	1.1 × 10 ⁻⁵
5.7 × 10 ⁻¹	4.5 × 10 ⁻¹	2.1 ^(a)	1.0 ^(a)	7.3 × 10 ⁻¹	1.9 × 10 ⁻²	—	2.6 × 10 ⁻² ^(e)	5.7 × 10 ⁻² ^(e)	2.3 × 10 ⁻⁴	7.9 × 10 ⁻⁴	2.4 × 10 ⁻¹ ^(a)	7.9 × 10 ⁻² ^(a)	1.3 × 10 ⁻⁴	1.4 × 10 ⁻³	—
6.5 × 10 ⁻³	4.0 × 10 ⁻³	7.8 × 10 ⁻³	5.3 × 10 ⁻³	2.1 × 10 ⁻³	1.4 × 10 ⁻³	3.4 × 10 ⁻⁴	2.7 × 10 ⁻⁵	1.2 × 10 ⁻⁵	NDG	2.3 × 10 ⁻⁷	7.1 × 10 ⁻⁷	3.9 × 10 ⁻⁷	<4 × 10 ⁻⁷	2.4 × 10 ⁻⁶	4.7 × 10 ⁻⁶
2.7 × 10 ⁻⁶	6.0 × 10 ⁻⁷	1.3 × 10 ⁻⁵	4.8 × 10 ⁻⁶	5.3 × 10 ⁻⁶	1.9 × 10 ⁻⁶	3 × 10 ⁻⁶	4.7 × 10 ⁻¹⁰	1.0 × 10 ⁻⁹	NDG	NDG	5.6 × 10 ⁻¹⁰	1.9 × 10 ⁻¹⁰	8 × 10 ⁻¹⁰	<2 × 10 ⁻¹⁰	<2 × 10 ⁻⁹
1.8 × 10 ⁻⁵	3.4 × 10 ⁻⁵	2.7 × 10 ⁻⁵	3.2 × 10 ⁻⁵	1.9 × 10 ⁻⁵	3.1 × 10 ⁻⁵	2.6 × 10 ⁻⁶	NDG	4.3 × 10 ⁻⁸	8.8 × 10 ⁻⁹	2.1 × 10 ⁻¹⁰	<1.7 × 10 ⁻⁹	<7.0 × 10 ⁻¹⁰	7.7 × 10 ⁻⁹	NDG	NDG
6.8 × 10 ⁻⁹	2.0 × 10 ⁻¹⁰	5.1 × 10 ⁻¹⁰	1.3 × 10 ⁻⁹	1.8 × 10 ⁻⁸	1.0 × 10 ⁻⁸	1.1 × 10 ⁻⁸	—	—	9.9 × 10 ⁻¹²	1.4 × 10 ⁻¹⁰	6.3 × 10 ⁻¹²	2.2 × 10 ⁻¹¹	1.4 × 10 ⁻¹¹	3.2 × 10 ⁻¹¹	1.5 × 10 ⁻¹⁰
6.8 × 10 ⁻¹¹	—	—	<2.0 × 10 ⁻¹⁰	<2 × 10 ⁻¹⁰	<4 × 10 ⁻¹⁰	2.2 × 10 ⁻¹⁰	3.6 × 10 ⁻¹³	<4.9 × 10 ⁻¹³	5.0 × 10 ⁻¹⁴	—	—	1.5 × 10 ⁻¹²	3 × 10 ⁻¹²	2.0 × 10 ⁻¹²	<7.4 × 10 ⁻¹³
4.6 × 10 ³	—	—	4.9 × 10 ³	1.6 × 10 ⁴	1.1 × 10 ⁴	8 × 10 ³	2.2 × 10 ²	1.8 × 10 ²	—	—	—	1.3 × 10 ²	2.2 × 10 ²	1.5 × 10 ²	3 × 10 ³
6.5 × 10 ¹	1.9 × 10 ²	4.9 × 10 ²	2.1 × 10 ³	4.9 × 10 ²	1.9 × 10 ²	3.9 × 10 ²	—	—	4.8	1.3 × 10 ⁴	6.0 × 10 ²	1.2 × 10 ³	3.8 × 10 ¹	7.0 × 10 ¹	5.8 × 10 ¹
1.7 × 10 ¹	—	—	<4 × 10 ⁻⁴	<4 × 10 ⁻⁴	<4 × 10 ⁻⁴	<4 × 10 ⁻⁴	1.6 × 10 ⁻²	<8.2 × 10 ⁻⁴	1.1 × 10 ⁻²	—	—	3.4 × 10 ⁻³	7.8 × 10 ⁻³	2.4 × 10 ⁻³	<2 × 10 ⁻³

tal run includes radioactivity fed to TK-113 from Mode B feed tank (TK-112)

nk/total curies of component fed to the solidifier for total run.

s of component fed to solidifier for total run.

n.

through a faulty control valve causing a high accumulation of ¹⁴⁴CePr.
on instantaneous stream samples.

from 0.034% during the modified Mode B portion of Run SS-13(IPM) where the solidifier condensate was routed to a separate receiver tank to 1.2% during the Mode A portion of Run SS-7. These values were generally typical of previous WSEP runs.^(3,4,5,6) In general, these values indicate that the accumulation of ruthenium in the fractionator is not a direct function of the ruthenium present in the evaporator since the accumulation of ruthenium in the fractionator does not follow ruthenium increases in the evaporator. This suggests that prior to the installation of the new modified solidifier condenser and condenser off-gas filtering system gas phase carryover of ruthenium from the solidifier condenser off-gas was as important as the volatilization of ruthenium from the evaporator.

The problem of ruthenium volatilization from the WSEP auxiliary evaporator was investigated by defining instantaneous DF's (DF_i 's)* across the evaporator. Generally, these DF_i 's for the first series of phosphate glass solidification and pot calcination runs varied inversely with the nitric acid concentration in the evaporator bottoms and resulting distillate as shown in Figure 5.6.^(3,4) This indicated that ruthenium volatility increases with increasing acidity in the evaporator bottoms. During the spray solidification runs there was no apparent correlation of DF_i and the distillate acidity. However, an apparent correlation does exist between the DF's and overhead acidity during the acid stripping operations prior to Runs SS-8 and SS-10 as seen in Figures 5.7 and 5.8, respectively. The generally low DF_i 's for ruthenium in Figure 5.6 were attributed to vapor phase flow of ruthenium from the solidifier which was only partially scrubbed in the solidifier condenser as indicated by the presence of ruthenium in the solidifier condenser off-gas.

* Instantaneous concentration of component in evaporator bottoms/instantaneous concentration of component in evaporator overheads.

FIGURE 5.6. Ruthenium Volatilization from WSEP Auxiliary Evaporator

$$DF_i = \frac{\text{INSTANTANEOUS CONCENTRATION OF Ru-103, 106 IN BOTTOMS (TK-113)}}{\text{INSTANTANEOUS CONCENTRATION OF Ru-103, 106 IN DISTILLATE (E-113)}}$$

FIGURE 5.7. Ruthenium Volatilization During Run SS-8
Batch Waste Concentration and Acid-Stripping

FIGURE 5.8. Ruthenium Volatilization from the WSEP Auxiliary Evaporator During Run SS-10

This vapor phase flow of ruthenium apparently had less effect on DF_i 's during the phosphate glass and pot calcination runs. Another possible cause of the generally low DF_i 's and no correlation between DF 's and evaporator distillate acidity could be the contamination of the auxiliary system by the continual buildup or adsorption of ruthenium of the stainless steel piping and other auxiliary equipment. Stainless steel has been shown to adsorb ruthenium⁽¹⁸⁾ onto its surface. Also, the presence of nitrogen oxides increased the evaporator overhead acidity (Section 5.4) resulting in no equilibrium between the evaporator bottoms acidity and the evaporator overhead acidity.

The use of the modified solidifier condenser and condenser off-gas filtering system apparently reduced the carryover of ruthenium in the noncondensable gas stream. The solidifier condenser off-gas contained $6.4 \times 10^{-2} \mu\text{Ci}/\text{cm}^3$ of ^{106}Ru during Run SS-10 with the old condenser and $2.9 \times 10^{-5} \mu\text{Ci}/\text{cm}^3$ of ^{106}Ru during Run SS-12(IPM) where the in-pot melting technique and modified solidifier condenser were used.

As seen in Figure 5.9, the accumulation in the fractionator during Runs SS-11 and SS-12 was not linear as was the case in previous spray solidification runs. There was a factor of about 2 to 6 decrease in ruthenium accumulation over Runs SS-7 through SS-10. This indicates that gas phase flow of ruthenium previously experienced in the spray solidification runs did contribute significantly to the ruthenium accumulation in the fractionator. Some of this reduction during Runs SS-12(IPM) and SS-13(IPM) may be attributed to the reduction in ruthenium volatilization from the solidifier. During Run SS-11, ruthenium accumulation seemed to level out after an initial jump early in the run. Basing the accumulation in the fractionator on the evaporator condensate stream samples, the total

FIGURE 5.9. Comparative Accumulation of Ruthenium in Fractionator

accumulation should have been a factor of about 20 less. This fact indicates that the initial jump in ruthenium accumulation may have been caused primarily by radioruthenium contamination early in the run.

During the first 37 hours of Run SS-8, it was found that recycling the strip water at 60 liters/hr through the spray nozzle into the solidifier condenser did somewhat decrease the rate of ruthenium accumulation in the fractionator. This indicated that a 25-40% reduction in the concentration of radionuclides was realized with the water addition. Also during Run SS-12(IPM) using the new modified solidifier condenser, strip water was sprayed at about 40 liters/hr through the condenser to help improve ruthenium decontamination. The average concentration of ruthenium in the condenser off-gas during Run SS-12 was a factor of about 200 less than the concentration during Run SS-11. This was primarily attributed to the decrease in ruthenium volatilization from the solidifier using the in-pot melting technique. However, some reduction in ruthenium concentration was attributed to the water spray as indicated by the factor of about 10 increase in the ruthenium concentration in the solidifier condenser off-gas during Run SS-13 where no water spray was added through the condenser and the ruthenium volatilization was typical of that from Run SS-12.

Gas sampling techniques were initiated during Run SS-9 (Section 5.5) and prior to Run SS-11, the modified solidifier condenser and condenser off-gas filtering system was installed (Section 5.6). The average concentrations of radionuclide in the process off-gas are summarized in Table 5.4 while cumulative DF's across the WSEP process condensers and process off-gas filters are summarized in Table 5.5. The cumulative ruthenium DF's across the solidifier condenser ranged from 1.4×10^3 to 5.4×10^3 based on data from Runs SS-11, SS-12(IPM), and SS-13(IPM). The ruthenium DF's across the solidifier

TABLE 5.4. Average Concentration of Radionuclides in the Process
Off-Gas During Runs SS-9 Through SS-13(a)

SS Run Number	Solidifier Condenser		Off-Gas from Condenser		Evaporator Condenser		Fractionator Condenser	
	Off-Gas, $\mu\text{Ci}/\text{cm}^3$		Filter, $\mu\text{Ci}/\text{cm}^3$		Off-Gas, $\mu\text{Ci}/\text{cm}^3$		Off-Gas, $\mu\text{Ci}/\text{cm}^3$	
	^{106}Ru	$^{144}\text{CePr}$	^{106}Ru	$^{144}\text{CePr}$	^{106}Ru	$^{144}\text{CePr}$	^{106}Ru	$^{144}\text{CePr}$
10	6.4×10^{-2}	1.0×10^{-3}	—	—	—	—	—	—
11	5.7×10^{-3}	4.3×10^{-5}	2.8×10^{-6}	2.6×10^{-6}	3.4×10^{-7}	9.3×10^{-7}	5.0×10^{-6}	3.3×10^{-7}
12 (IPM)	2.9×10^{-5}	6.8×10^{-5}	2.2×10^{-6}	4.4×10^{-5}	8.7×10^{-7}	4.8×10^{-5}	5×10^{-7}	7×10^{-7}
13 (IPM)	3×10^{-4}	5×10^{-4}	3.2×10^{-6}	4.0×10^{-4}	8.3×10^{-6}	6.7×10^{-4}	2.0×10^{-7}	3.8×10^{-8}

SS Run Number	Off-Gas from High		Final Off-Gas from Scrubber			
	Efficiency Filter, $\mu\text{Ci}/\text{cm}^3$		$\mu\text{Ci}/\text{cm}^3$		Ratio to 10CFR20	
	^{106}Ru	$^{144}\text{CePr}$	^{106}Ru	$^{144}\text{CePr}$	^{106}Ru	$^{144}\text{CePr}$
9	—	—	1.3×10^{-8}	1.9×10^{-9}	6.5×10^1	4.8
10	—	—	2.4×10^{-7}	8.5×10^{-7}	1.2×10^3	2.1×10^3
11	4.4×10^{-8}	1.3×10^{-8}	9.8×10^{-8}	1.5×10^{-8}	4.9×10^2	3.8×10^1
12 (IPM)	—	2×10^{-9}	3.6×10^{-8}	2.0×10^{-8}	1.9×10^2	7.0×10^1
13 (IPM)	1.7×10^{-8}	2.1×10^{-8}	7.8×10^{-8}	2.3×10^{-8}	3.9×10^2	5.8×10^1

a. Average values for entire run.

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

SS Run	Average DF ^(a)					
	¹⁰⁶ Ru			¹⁴⁴ CePr		
	11	12 (IPM)	13 (IPM)	11	12 (IPM)	13 (IPM)
Solidifier Condenser (E-111)	1.4×10^3	6.3×10^3	5.4×10^3	6.5×10^2	2.6×10^3	2.1×10^4
Solidifier Condenser Off-Gas Filter ^(b)	2.0×10^3	9.5	95	16	15	1.1
Evaporator Condenser (E-113)	6.5×10^4	1.1×10^4	1.3×10^3	8.3×10^2	56	3.3
Fractionator Condenser (E-115)	58	6.3×10^2	1.0×10^2	48	NA	4.5×10^3
High Efficiency ^(b) Filter (F-112)	1.1×10^2	1.1×10^2	12	25	3.9×10^2	1.8

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

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

NA Not Available.

condenser off-gas filter have varied from a high of 2.0×10^3 during Run SS-11 to a low of 9.5 during Run SS-12. Instantaneous DF's across the filter have generally agreed with the cumulative DF's.

Most of the ruthenium that volatilizes from the evaporator is condensed by the evaporator condenser and accumulated in the fractionator. From 3.4×10^{-7} to 8.3×10^{-6} $\mu\text{Ci}/\text{cm}^3$ of ^{106}Ru were present in the evaporator condenser off-gas based on Runs SS-11 through SS-13. Ruthenium DF's across the evaporator condenser averaged about 3×10^4 . This was a factor of about 6 increase over the DF across the solidifier condenser.

A total of 0.034 to 1.2% of the equivalent ruthenium fed to the solidifier accumulated in the fractionator. The fractionator nitric acid concentration was maintained at about 7 to 9M, and the resulting fractionator overheads acidity ranged from about 0.03 to 0.07M HNO_3 using a tower internal reflux ratio varying from about 0.008 to 0.1. The ruthenium DF_c across the fractionator varied from a low of 6.3×10^2 to 4.8×10^3 . The ruthenium DF_i 's across the fractionator ranged from less than 100 to greater than 1000 and were typically greater than 100.

Ruthenium that escapes the WSEP acid fractionator is mostly condensed by the fractionator condenser and then either recycled back to the evaporator as stripwater or accumulated in a separate distillate receiver. Typically, 90% of the fractionator distillate was recycled back to the evaporator while the remaining 10% was accumulated in the fractionator distillate receiver. Average stripwater rates to and boil-off rates from the evaporator are listed in the Appendix Table 9.2. The distillate receiver accumulated generally about 0.0001% of the equivalent ruthenium fed to the solidifier. The fractionator distillate (final aqueous process effluent) contained a concentration of radionuclides which was above 10CFR20 release limits by a factor as high as 4.1×10^4 .

The off-gas leaving the fractionator condenser varied from 2×10^{-7} to 5×10^{-6} $\mu\text{Ci}/\text{cm}^3$ of ruthenium. Ruthenium DF's across the fractionator condenser varied from 58 to 6.3×10^2 .

Approximately 20 scfm of noncondensable gases leaving the fractionator condenser are filtered through a high efficiency filter before entering the off-gas scrubber. The filtering efficiency for radioruthenium based on gas samples ranged from a low of 12 during Run SS-13 (attributed most likely to contaminated sample lines and to the low level radioactivity being measured) to 1.1×10^2 during both SS-11 and SS-12. Most of the remaining radioruthenium in the process off-gas was removed in the off-gas scrubber where from 0.00026 to 0.0051% of the equivalent radioruthenium fed to the solidifier accumulated in the scrubber bottoms. Accumulation of radioruthenium in the scrubber during Runs SS-7 through SS-13 is shown in Figure 5.4.

The final process off-gas leaving the off-gas scrubber contained concentrations of radioruthenium that were factors of 65 to 1200 above 10CFR20 release limits. However, the final process off-gases were filtered twice more and discharged into the main building ventilation system where they were mixed with about 120,000 scfm of air before entering the stack. This large dilution by the main building ventilation flow and the additional filtration reduced the ruthenium concentration to below detection limits for the available counting equipment (see Figure 9.12, appendix). During the last spray solidification runs, the radioruthenium in the stack gases was at least 1200 times less than the 2×10^{-10} $\mu\text{Ci}/\text{cm}^3$ 10CFR20 release limit. This value is conservative because it assumes all radioruthenium emitted to the off-gas is from WSEP processing. Other sources of radionuclides in the facility are ventilation air from eight other high-level radioactivity cells and process vent effluents from other in-cell activities.

5.3 CONTROL OF OTHER RADIONUCLIDES

With spray solidification, a relatively small amount (less than 0.1%) of nonvolatile constituents were entrained from the solidifier and accumulated in the auxiliary evaporator. Cumulative decontamination factors (DF_c) for nonvolatiles represented by $^{144}\text{CePr}$ across the WSEP evaporator ranged from a low of 74 for Run SS-12 to a high of 3.3×10^5 during the Mode B portion of Run SS-10. Instantaneous decontamination factors (DF_i 's) for nonvolatiles across the auxiliary evaporator based on $^{144}\text{CePr}$ ranged from about 10^2 to 10^6 . These data agree quite well with data from the previous spray solidification, phosphate glass, and pot calcination runs.

Typical entrainment from the WSEP auxiliary evaporator was less than 1% of the nonvolatiles present in the evaporator. The overall DF's for nonvolatiles represented by $^{144}\text{CePr}$ from the original aqueous waste through the auxiliary system to the recovered acid in the fractionator ranged from about 10^4 to 10^6 . Comparable DF's to the fractionator distillate were typically 10^9 . Accumulation of nonvolatile radionuclides in the WSEP auxiliaries is shown in Figure 5.10.

The spray solidifier off-gases contained about 20 scfm of noncondensibles from inleakage and 6 to 8 scfm of solidifier atomizing air. The presence of this noncondensable gas stream significantly affects decontamination, and efforts to keep air inleakage minimized should be applied to commercial applications. Overall, the nonvolatile constituents in the noncondensable gas flow were sufficiently removed by the auxiliary system to levels that were not as significant as compared to radioruthenium.

Decontamination factors for nonvolatiles represented by $^{144}\text{CePr}$ across the solidifier condenser were 6.5×10^2 , 2.6×10^3 and 2.1×10^4 for Runs SS-11, SS-12(IPM), and

FIGURE 5.10. Accumulation of Nonvolatiles in WSEP Auxiliaries

SS-13(IPM), respectively. Nonvolatile DF's across the process condenser and filter are presented in Table 5.5. The DF's across the evaporator condenser were 8.3×10^2 , 56, and 3.3 for SS-11, SS-12, and SS-13, respectively, and across the fractionator condenser were 48 for SS-11, and 4.5×10^3 for SS-13. The inconsistency and low DF's were probably caused by system contamination which also was shown to have affected the ruthenium DF's as well.

DF's across the solidifier condenser off-gas filter were 16, 15, and 1.1 for SS-11, SS-12(IPM), and SS-13(IPM), respectively. The low DF for Run SS-13 indicated that either the filter had failed or that the sample lines were contaminated. Visual inspection of the condenser off-gas filter after the run (Figure 5.11) revealed that the filter media had partially slipped out of the filter cannister as the result of the failure of the adhesive which bonded the media to the cannister walls. It was therefore possible for a portion of the off-gas to bypass the filter media which would result in the low DF observed. The inlet side of the filter was darkened by the presence of ruthenium and other radionuclides while the outlet remained the same color as new filtering media. There was no evidence of corrosion of the aluminum filter media supports as has been the case with the high efficiency process filter prior to the off-gas scrubber.

The particulate DF's across the process filter prior to the off-gas scrubber were 25, 3.9×10^2 , and 1.8 for Runs SS-11, SS-12, and SS-13, respectively. These represent filtering efficiencies of 96, 99.8, and 44%, respectively. Again, the inconsistency and low DF's indicate that either the filter had failed or that the gas sample lines had become contaminated with radionuclides.

Neg 703320-3

INLET

Neg 703320-1

OUTLET

Neg 703320-2

FIGURE 5.11. Failed Solidifier Condenser Off-Gas Filter

The accumulation of nonvolatiles in the off-gas scrubber was generally nondetectable or at most the equivalent fraction of feed radiocerium was less than 10^{-9} . The off-gas leaving the scrubber contained a concentration of radiocerium that was above 10CFR20 release limits by factors of about 50. However, the nonvolatile radioactive constituent concentration in the off-gas entering the atmosphere were well below 10CFR20 release limits after the scrubber off-gas was filtered twice more and diluted by other building and process air.

5.4 NITROGEN BALANCE

From 33% to 73% of the nitrogen that volatilized from the solidifier was removed from the off-gases in the solidifier condenser. The remaining 66% to 27% was probably present as oxides of nitrogen which were carried through the condenser in the gas phase. A 10% increase in nitrogen absorption occurred during 37 hours of Run SS-8 when fractionator distillate was sprayed into the solidifier condenser. The specific changes of nitrogen content at the various points in the auxiliary system are listed in Table 5.6. The off-gas scrubber containing from 0.5 to 2M NaOH absorbed from 8% to 39% of the equivalent nitrogen fed to the solidifier. During spray solidification Runs SS-7 through SS-13, the off-gas scrubber solutions (NaOH) were being neutralized by oxides of nitrogen to varying degrees and nitrogen was lost to the stack as indicated by the failure to account for 5% to 50% of the nitrogen added to the system. Generally nitrogen losses were less than 15%.

Figure 5.12 shows the typical accumulation of nitrogen and ruthenium in the caustic scrubber (taken during Runs SS-9 and SS-11). During Run SS-9, 10% of the nitrogen was recovered in the scrubber solution. During Run SS-11 the off-gas scrubber was inadvertently started with 0.44M NaOH instead of the usual 2M NaOH. The nitrogen oxides neutralized the scrubber solution

TABLE 5.6. Nitrogen Balance for Spray Solidification
Runs SS-7 Through SS-13(IPM)

SS Run	Net Change, kg N						
	7	8 ^(a)	9	10	11	12 (IPM)	13 (IPM)
Feed to Solidifier (TK-114)	-45	-17	-45	-41 ^(b)	-39	-17	-27 ^(d)
Evaporator (TK-113)	+3.0	-6.2	-1.5	+1.6	-20	-10	-3.5
Fractionator (TK-115)	+36	+17.0	+13	+18	+35	+15	+18
Accumulated Fractionator Distillate (TK-116)	+0.2	+0.2	+1.2	+0.4	+0.6	+0.1	+0.2
Scrubber (TK-118)	+8.0	+1.7	+12.0	+5.2	+3.0	+6.4	+4.5
Product	+0.05	+0.01	—	—	—	—	—
Melter Condensate (TK-117)	—	—	—	—	—	—	+5.3
Percent Recovery	104	95	85	86	48	68	95
Percent Feed Nitrogen in Scrubber	18	10	27	21	8 ^(c)	39	26
Percent Feed Nitrogen in Solidifier Condensate ^(f)	64	50 (60) ^(e)	73	50	37	46 ^(e)	33

- a. The scrub solution used during Run SS-8 was distilled water.
b. Includes 16 kg nitrogen added during Mode B operation (TK-112 to TK-113).
c. The scrubber became neutralized after 30% of the feed was fed to the solidifier.
d. Includes 9 kg of nitrogen from the 2M HNO₃ addition to the evaporator.
e. Fractionator distillate spray addition to solidifier condenser.
f. Determined from instantaneous stream samples.

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FIGURE 5.12. Typical Scrubber Operating Conditions

at a fairly constant rate until about 37% of the feed was fed to the solidifier, at which time the bottoms were completely neutralized. At this time, the nitrogen accumulation rate in the scrubber solution started to decrease sharply until at about 60% feed fed no more nitrogen accumulated. Extrapolating from the first part of the run, 20% to 30% of the equivalent feed nitrogen should have been removed by the scrubber, if the scrubber solution had not become acidic before the end of the run. Therefore, 12% to 19% of the nitrogen escaped with the scrubber off-gas. The motive air to the process vent jet dilutes the WSEP off-gases by about a factor of two. The nitrogen losses from the WSEP system could be reduced by increasing the caustic in the scrubber bottoms by about a factor of two.

5.5 PROCESS OFF-GAS SAMPLING

Gas sampling techniques were initiated prior to the last series of five phosphate glass runs in an attempt to provide engineering-scale data to permit better definition of the type, form, and extent of radioactivity present in the process off-gas. During spray solidification Runs SS-11 through SS-13(IPM), final process off-gas leaving the scrubber, gaseous effluents from the solidifier condenser, evaporator condenser and fractionator condenser, the gaseous effluents from the high efficiency process filter prior to the scrubber were sampled for both particulate and volatile forms of radioactivity. This was accomplished by routing a side stream of the gaseous effluent through first a glass fiber filter and then a 2M KOH scrubber. The sampling systems are shown in References 6 and 19.

The condenser off-gas sampling equipment consists of three separate samplers on one common vacuum header. Each sampler includes a flowmeter (0 to 1.2 ft³/min at STP) and a vacuum

gage (0 to 30 inches of mercury). The sample packages which are used in conjunction with the samplers contain 25 mm Gelman Type A glass fiber filter to collect particulates, a fritted gas dispenser, and a 200 ml-2M KOH scrubber to absorb the volatile components such as RuO_4 .

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

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

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

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

5.6 NEW MODIFIED SOLIDIFIER CONDENSER

A modified solidifier condenser and condenser off-gas filtering system as shown in Figure 5.13 was installed prior to Run SS-11 to improve decontamination of the solidifier off-gas. The bottom half of the condenser tubes were filled with Pall rings (reduced from 5/8-inch to 1/2-inch diameter by mechanical press) to improve the condenser performance.

Neg 700405-2

Neg 700405-5

FIGURE 5.13. New Solidifier Condenser and Condenser Off-Gas Filtering System

Filling the tubes completely with Pall rings would have substantially increased the pressure drop across the condenser to a point that vacuum requirements for the spray solidifier could not be met.

Pressure drop tests across a 71-inch 1/2 Sch.-80 pipe which is similar to the condenser tubes in inside diameter and length were made and Figure 5.14 shows the results of these tests. The pressure drop was determined as a function of air flow and total Pall ring fill in the tube. As a result of these tests it was found that the solidifier condenser tubes should only be filled 1/2 full with the modified Pall rings.

5.7 PROCESS CONTROL OF WSEP AUXILIARY SYSTEM

Nitric acid and water recovery from the solidifier off-gas in WSEP is dependent on both efficient decontamination in the evaporator and fractionator and acid concentration in the fractionator. Decontamination data from the evaporator and fractionator have been compromised by the inability to maintain constant acid conditions in the evaporator bottoms. While the evaporator overhead conductivity monitor has provided an excellent indication of the overhead acid concentration, attempts to manually adjust boilup and stripwater recycle controller set points to maintain the overhead conductivity at some fixed value and observe the constraints of liquid volume and acid concentration of the two vessels as feed conditions vary have not been successful.

An objective of Run SS-13(IPM) was to demonstrate automatic control of the WSEP auxiliaries. During the run, 2M HNO_3 was fed to the evaporator at about 14 liters/hr to simulate solidifier condensate since the actual solidifier condensate was collected separately. During the automatic control periods,

FIGURE 5.14. Pressure Drop Test for New Solidifier Condenser Using a 1/2-inch SCH 80 Pipe Packed with Pall Rings

steady operation was not obtained as illustrated by the evaporator and fractionator operating parameters shown in the appendix (Figure 9.11).

Six standard, three-mode controllers were used in three cascade loops to control the auxiliary equipment as shown in Figure 5.15. One controller sensed the evaporator weight factor and cascaded its output to the setpoint of the controller on the evaporator tube bundle steam flow. Another similar system controlled the steam flow to the fractionator tube bundle as an inverse function of fractionator specific gravity. A third system controlled the stripwater recycle flow rate as a direct function of the overhead conductivity.

During the initial automatic control test of the auxiliaries and again during Run SS-13, it was found that the specific gravity measurement in the fractionator was a function of the boilup rate which resulted in poor control. Therefore, specific gravity control could not be used for controlling the steam flow. While a control system based on a weight factor measurement was adequate to maintain stable operating conditions, it did not perform the primary function of the system, namely to maintain the fractionator bottoms at 10M HNO_3 .

Another problem that occurred twice during Run SS-13 was that the evaporator dip tubes were inadvertently vented causing an upset in automatic control.

During subsequent auxiliary tests and in analog simulations, the very long time constants of the evaporator and fractionator were realized, explaining the instabilities that had been observed during these early tests. To avoid overshoot and subsequent loss of water from the auxiliary system to the fractionator distillate receiver, the weight factor controllers were operated with zero reset. However, it was found that the 3-mode controllers available could not be operated as

FIGURE 5.15. Basic Instrumentation for Automatic Control of WSEP Auxiliaries

proportional-only instruments and some long-term cycling resulted. To eliminate this problem, the General Electric 412 process control computer that has been used as a data logging device was programmed to set the set point on the controllers for the steam flow to the evaporator and fractionator tube bundles. The computer was programmed to calculate the set points in direct proportion to the deviation of the measured weight factors from the desired operating weight factor. In addition, the computer was programmed to limit the minimum steam flow to maintain boiling in the evaporator and fractionator at all times, and to limit the maximum steam flow to avoid pressurization of the auxiliary evaporator and fractionator by excessive boilup. Also, the computer was used to periodically vent the weight factor and specific gravity dip tubes in the evaporator to avoid plugging of the dip tubes during operation.

5.8 AUXILIARY HANDLING OF PUREX WASTE

Fission product waste solutions contain precipitates which may interfere with liquid transfer, storage, or evaporation. While amorphous, noncaking precipitates can be handled at concentrations up to 50 vol%; in WSEP, very small quantities of heavy, caking precipitates can plug pipes and equipment. Thus, proper design and operation requires a good knowledge of the precipitate characteristics. The precipitates present in a given waste solution depend to a large extent upon the chemical flowsheet used in the reprocessing plant and during the subsequent treatment of the waste. In general, the PW-1, PW-4m, and LMFBR solutions used in demonstration Tests SS-7 through SS-12(IPM) were representative of typical Purex plant wastes. That is, they contained the full gamut of expected precipitate types, although the comparative amounts of precipitate varied with each waste.

The volume of settled solids in actual samples of the feed solutions used in Runs SS-7 through SS-13(IPM) ranged from 10 to 65% and were typically greater than 30%. The majority of the solids encountered in the spray solidification feeds contains molybdenum, phosphorous, and zirconium, and is a zirconium phosphomolybdate compound. The solids are hydrous, amorphous precipitates which have never been observed to cake in the laboratory even after standing several months. In PW-4m, LMFBR, and PW-1 waste the phosphomolybdate compound is predominant and the solids are gelatinous and noncrystalline. When the PW-1, PW-4, and LMFBR wastes are continuously boiled, the precipitates lose their gelatinous characteristics and become a very loose, easily-suspended precipitate (even after prolonged settling). The handling of spray solidification feeds in feed tanks, evaporators, and transfer lines was not considered to be a major problem.

5.9 GENERAL PERFORMANCE OF AUXILIARY EQUIPMENT

The auxiliary equipment performed satisfactorily during Runs SS-7 through SS-13(IPM). Some feed pump problems and deterioration of plastic insulation on electrical and instrument wiring within the cell occurred but did not affect the results of any runs. All five runs were completed without an interruption. Table 5.7 is a compilation of the general operating experience of the WSEP auxiliary equipment.

5.9.1 Pumps

The feed pumps used during spray solidification Runs SS-7 through SS-13(IPM) were a modified in-line pump assembly using a conventional Deanline[®] centrifugal pump. The pumps contained double mechanical, water-lubricated seals with graphite rotating

[®] RTM Dean Brothers Pumps, Inc.

TABLE 5.7. WSEP Auxiliary Equipment Operating Summary
[Through Spray Solidification Run SS-13(IPM)]

Equipment	Construction Material	Temp., °C	Avg. Press., in. Water	Chemical	Operating Time, hr	Remarks
Feed Tanks	304L SS	25 to 60	-5	Darex, Purex, TBP-25 Type Waste	4070	Agitators used 3200 hr.
Condensate Tanks	304L SS	25	-10 to 20	H ₂ O, Dilute HNO ₃	3548	Submerged pump used 1780 hr.
Caustic Scrubber	304L SS	25 to 40	-10 to 20	Dilute NaOH	3548	Circulation pump used 1780 hr.
Evaporator	A-55 Ti	110	-10 to 20	Boiling Waste	3324	Minor titanium corrosion caused by fluoride ion during early DVT runs
Fractionator	A-55 Ti	115	-10 to 20	8 to 12M HNO ₃	3324	
Solidifier Condenser	A-55 Ti	100 to 200	-10 to 20	HNO ₃ Vapors	3502	Localized vapor entry corrosion caused by volatilized sulfate (up to 0.06 in.) during early DVT Runs 3 and 4
Evaporator Condenser	A-55 Ti	100 to 110	-10 to 20	Dilute HNO ₃	3324	
Fractionator Condenser	304L SS	100 to 110	-10 to 20	H ₂ O, Dilute HNO ₃	3324	
Feed Pumps	304L SS	60		Adjusted Waste	1800	Changed from the original inline pump to conventional pump prior to Run PG-3
					845	New pump jumper (see Appendix Table 9.5 for pump history)
Flowmeters:						
Feed, magnetic	Vitreous enamel liner. Platinum sealed elec- trodes. Inconel flowtubes.	30 to 80	~100	Concentrated Wastes	2582	Occasional intermittent readings due to lead wire failures. Also frequent shifts in calibration and loss of sensitivity, partially attributed to low WSEP flow rates.
Condensate, magnetic	(same as above)	25 to 40	~100	Condensate	2734	Two units (1150 hr/unit) did not operate during last 5 phosphate glass runs primarily due to elec- trical lead failures.
Condensate, electronic rotameter		30 to 80	10 to 30	Dilute Acid Water	3202	The meter was reliable for recycle flow measurement of stripwater.
Filters, Process Off-Gas						
Process Vent	Glass-asbestos with aluminum separators in 304L SS housing	50 to 70	-20	Predominantly Air, Nitrogen Oxides		Not changed during SS-7 through SS-10 but was changed after completing the last series of phosphate glass runs and prior to SS-11.

rings. Isolation valves were installed on the pump assembly to prevent loss of feed if the seals failed and to allow remote changeout in approximately 4 hours without transferring the feed out of the feed tank.

Feed pump operating experience is summarized in Table 9.5 (appendix). Pump life is decreased by start and stop operation and is substantially increased by thorough water flushing after each run. In an extended pump operating test with nonradioactive feed, a similar pump was operated continuously for 553 hours before the seals failed.

5.9.2 Feed Control System and Flow Measurement

Operation of the feed control system over the range of about 10 to 20 liters/hr was only fair because measurement of this low feed flow rate to the solidifier with a magnetic flowmeter was frequently inadequate. The automatic feed controller receives an input signal from the magnetic flowmeter and delivers an output signal to the feed control valve. Difficulties experienced with the magnetic flowmeters occurring in many early WSEP runs included loss of signal, frequent shifts in calibration (partially due to low flow rates required), and failure of electrical wire insulation. Reliability was increased significantly by changing the electrical wire periodically. The wire insulation failures are described below. A 1/2-inch Hammel Dahl valve with a No. 5 spline trim was used to control the feed to the solidifier. Special flushing procedures are used prior to and after feeding to keep the feed line satisfactorily free of solids deposition.

5.9.3 Evaporator and Acid Fractionator

The WSEP evaporator and fractionator which are capable of boilup rates as high as 530 and 310 liters/hr, respectively, performed satisfactorily. Operating conditions for the evaporator are shown in Figures 9.5 through 9.11 and are discussed

in Section 5.2. A conductivity measurement of the condensed evaporator overheads was used to determine the overhead acidity, and thereby control the stripwater (fractionator distillate) recycle flow to the evaporator.

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

Again as in previous WSEP runs, chemical complexants were added to the titanium evaporator and fractionator vessels to minimize fluoride-induced corrosion. Aluminum nitrate was added to the vessels during every run; however, when waste solutions are boiled in the evaporator, enough iron, zirconium, and aluminum ionic complexants are normally present in the waste solution to inhibit corrosion.

5.9.4 Filters

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

5.9.5 Electrical and Instrument Wiring

During spray solidification Runs SS-7 through SS-13(IPM), less extensive deterioration of wiring insulation occurred since most of the wiring that used linear polyethylene as insulation had been replaced with a more flexible and less expensive neoprene rubber-insulated wire.

5.9.6 Aqueous Sampling

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

Gas sampling equipment was installed prior to Run SS-11 to collect samples of process off-gas at various points in the auxiliary system. Gas sampling is discussed in Section 5.5.

5.9.7 Material Balances

Specific balance data for spray solidification Runs SS-7 through SS-13(IPM) are presented in appendix Table 9.3. Except for radioruthenium, the recovery of individual elements was good.

Analysis for ruthenium in the ceramic product was very unreliable by either chemical or radiochemical analysis. Consequently, a total material balance for ruthenium was difficult to make. However, recently a new method of counting WSEP melt samples for obtaining relative percent recoveries of ^{106}Ru , ^{137}Cs , and ^{95}Nb was successfully tested and evaluated.⁽²⁰⁾ Analysis for ruthenium in the liquid streams in WSEP is easily obtained from a radiochemical gamma energy analysis (GEA). The overall material balances for spray solidification Runs SS-7 through SS-13 are shown in Table 5.8.

TABLE 5.8. Overall Material Balances for Spray
Solidification Runs SS-7 Through SS-13(IPM)

<u>Run</u>	<u>Percent Recovery</u>	
	<u>Volume</u>	<u>Mass</u>
7	94	91
8	92	93
9	110	101
10	94	93
11	91	90
12 (IPM)	100	99
13 (IPM)	96	98

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6.0 FILLED RECEIVER
POT PERFORMANCE

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6.0 FILLED RECEIVER POT PERFORMANCE

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

Experimental measurements are made on each receiver to aid in characterizing the thermal conductivity, leachability, chemical and physical stability, and corrosivity of the solidified waste and to aid in characterizing the suitability and compatibility of the receiver and solidified wastes. This section presents a summary of the experimental measurements that have been made for the receivers from spray solidifier demonstration Runs 7 through 13. Data from Runs SS-1 through SS-6⁽²⁾ are included where it is considered appropriate.

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

Table 6.1 is a summary of overall receiver pot fill data. Waste type, receiver diameter and material, and the weight and volume of solidified product for the last seven spray solidifier demonstrations are included with bulk density and laboratory determined density. There is close agreement between measured bulk density and measured laboratory sample (grab sample) density. The density data indicate that there are a few voids in the solidified waste.

6.1 THERMAL CONDUCTIVITY

A regression analysis of the effective thermal conductivity (k_{eff}) for spray solidified waste as a function of average product temperature has been completed. The data from WSEP demonstration Runs SS-1 through SS-6 were included with the data for WSEP Runs SS-7 through SS-11. Figure 6.1 shows the calculated effective thermal conductivity of the combined phosphate solidified waste and waste receivers based on experimentally determined heat generation rate and temperatures. The line for the least squares curve fit has been drawn through the data. The data from SS-12(IPM) and SS-13(IPM) for the borosilicate waste with the spray in-pot melting process is shown in Figure 6.2.

The k_{eff} of the products from each feed type (PW-1, PW-2, and PW-4m) was compared by statistical techniques to determine if k_{eff} should be treated independently. However, it was not possible to determine if the variation in k_{eff} between spray product types is real or due to variations in measurements. The data showed that the effective thermal conductivity for spray solid over the temperature range from 100 °C to 650 °C should be treated independent of solidifier feed type and constant at approximately $1.2 \text{ W/m}^2(\text{°C/m})$. That is to say there is no apparent dependence on temperature in the temperature region where the waste is a solid.

TABLE 6.1. Receiver Pot Fill Data

WSEP Run Number	Waste Type	Pot Diam., in.	Pot Material	Volume of Product, (a) liters	Weight of Waste Product, kg	Bulk Density, (b) kg/l	Laboratory Sample Density, kg/l
SS-7	PW-1	8	304L SS	62.2	197	3.2	3.3
SS-8	PW-1	8	304L SS	59	170	2.9	3.3
SS-9	PW-4m	8	310 SS	67.6	194	2.9	3.1
SS-10	PW-4m	8	Mild Steel	56	176	3.1	NA
SS-11	LMFBR	8	304L SS	60	188	3.1	3.3
SS-12 (IPM)	PW-4m	8	304L SS	54	162	3.0	2.83
SS-13 (IPM)	PW-4m	8	304L SS	50	150	3.0	NA

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

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

NA Not available

IPM In pot melting

FIGURE 6.1. Effective Thermal Conductivity of Spray Solidifier Phosphate Ceramic Waste

FIGURE 6.2. Effective Thermal Conductivity of Spray Solidifier Borosilicate Glass Waste

The k_{eff} of the borosilicate waste is more dependent on temperature as shown in Figure 6.2. Over the temperature range from 100 °C to 650 °C the thermal conductivity fits the equation:

$$k_{\text{eff}} [\text{watts}/(\text{m}^2)(^\circ\text{C}/\text{m})] = 0.00095 (\bar{T}, ^\circ\text{C}) + 0.75$$

Above 650 °C the waste is in a softened or molten state and the thermal conductivity rises rapidly.

The unusual thermal conductivity values reported for SS-6⁽³⁾ are real and as yet are not fully understood. Core drill samples of the product being taken in SSETF may provide a more thorough understanding of the exceptionally high thermal conductivity. No apparent changes in volume or composition occurred during the testing and handling of this receiver pot, but the pot did experience an inadvertant thermal cycle shortly after it was filled.⁽³⁾

6.2 GAMMA SPECTRUM ANALYSIS AND RADIATION PROFILES

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

The gross gamma scans are accomplished by positioning an ionization chamber approximately 6 inches from the pot near

the midpoint of each of the six pot zones. Detailed analysis of the fission product spectrum at various locations in waste containers will be accomplished later in the Solids Storage Engineering Test Facility⁽¹⁾ where core drilled samples are underway.

Figure 6.3 shows the results of the gross gamma scans for spray solidification Runs 7 through 13. The dose rate measurements have been normalized to Zone 4 which is located near the midplane of the filled portion of the receiver. The purpose of normalization was to show the characteristic "banana shape" radiation profile that one would expect from a homogeneous, uniform distribution of fission products. Actual data from gross gamma dose rate measurements are presented in Table 6.2. Intermediate and wall thermocouple temperature measurements, also normalized to Zone 4, are presented in Figure 6.4 for Zones 1 through 6 to further substantiate the product uniformity.

The fill height of solidified waste relative to the pot zones is shown for each waste receiver on Figures 6.3 and 6.4. Obviously, the amount of product in the receiver pot affects the shape of both the radiation and temperature profiles.

All of the radiation profiles indicate that the solidified waste in WSEP demonstration Runs SS-7 through SS-13 is uniformly distributed. The temperature profiles indicate that there are no "hot spots" within these waste containers that might lead to premature receiver failure or invalidate assumptions for effective thermal conductivity calculations.

6.3 WASTE RECEIVER DIMENSIONS AND PHYSICAL DATA

Each waste receiver that is used in a WSEP demonstration run is carefully examined prior to transfer to the hot cell.

(a) ALL READINGS NORMALIZED TO ZONE 4 = 1.0

FIGURE 6.3. Normalized Gross Gamma Scans of Spray Solidifier Receiver Pots

TABLE 6.2. Gross Gamma Dose Rates for SS-7 Through SS-13 Receiver Pots

Waste Container Zone	Dose Rate $\times 10^{-4}$ rad/hr						
	SS-7 Scanned On	SS-8 Scanned On 4/4/69	SS-9 Scanned 4/1/69	SS-10 Scanned On 4/25/69	SS-11 Scanned On 3/12/70	SS-12 (IPM) Scanned On 4/20/70	SS-13 (IPM) Scanned On 5/14/70
1	Data not taken	1.6	2.4	1.0	2.0	1.0	2.1
2		2.3	2.6	2.0	3.5	2.0	4.5
3		2.8	2.6	2.3	4.0	2.1	5.5
4		2.8	2.6	2.5	4.0	2.0	5.8
5		2.8	2.6	2.4	4.0	1.8	5.8
6 (bottom)		2.7	2.4	2.2	3.5	1.8	5.7

FIGURE 6.4. Normalized Temperature Data for Spray Solidifier Receiver Pots

Prefill dimensions are taken of the receiver wall thickness, receiver length, and receiver diameter at several locations. No significant dimensional changes were detected for spray solidification Runs SS-7 through SS-13 after the receivers were filled.

Satisfactory wall thickness measurements of the waste receivers after the receivers have been filled have been made using an ultrasonic wall thickness scan system. Table 6.3 summarizes the data for the spray solid receiver pots for before and after-fill measurements. The receiver pots have maintained their initial wall thickness through processing and various storage times. The wall pieces that are removed during core drilling will also be used to determine wall thickness.

The receiver diameter and length were measured for each of the spray solidification runs in the final test series. The purpose of these measurements is to detect gross changes in pot dimensions during the processing cycle. The fill portion of the waste solidification cycle is, in general, the most severe part of the cycle with respect to environmental conditions. Table 6.4 summarizes the prefill and after-fill measurements of pot diameter and length for the last five spray solidification runs. The diametral measurements were made using dial indicating micrometers which allow accuracies within 0.025 inches. However, data are reported to the nearest 0.1 inches which is adequate for determination of gross changes. No diameter changes of more than 0.1 inches occurred in any receiver pot indicating that very little, if any, change occurred.

Figure 6.5 shows photographs of an 8-inch receiver pot prior to installation in the cell. The pot wall thermocouples are readily visible. The interior thermocouples were inserted

TABLE 6.3. Spray Solid Receiver Pot Wall Thickness Data*

Zone No.	SS-7, 8 in. Pot		SS-11, 8 in. Pot		SS-12, 8 in. Pot		SS-13, 8 in. Pot	
	Prefill 12/11/68	Afterfill 11/5/70	Prefill 3/4/70	Afterfill 11/6/70	Prefill 4/7/70	Afterfill 11/9/70	Prefill 11/10/70	Afterfill 11/10/70
1	0.314	0.312	0.325	0.319	0.336	0.325	0.302	0.306
1-1/2	0.312	0.304	0.323	0.327	0.330	0.327	0.303	0.305
2	0.312	0.308	0.325	0.327	0.333	0.327	0.303	0.295
2-1/2	0.312	0.304	0.323	0.319	0.332	0.323	0.302	0.307
3	0.312	0.304	0.323	0.319	0.333	0.329	0.303	0.304
3-1/2	0.310	0.308	0.324	0.317	0.333	0.326	0.304	0.301
4	0.310	0.306	0.324	0.320	0.331	0.328	0.303	0.300
4-1/2	0.312	0.307	0.324	0.317	0.330	0.332	0.302	0.303
5	0.310	0.308	0.323	0.317	0.334	0.332	0.304	0.303
5-1/2	0.312	0.309	0.320	0.316	0.335	0.331	0.303	0.306
6	0.314	0.306	0.322	0.317	0.334	0.332	0.303	0.304
6-1/2	0.312	0.310	0.320	0.314	NA	0.329	0.305	0.307

* SS-8, SS-9, SS-10 had not been scanned at report time.

NA - Not available.

TABLE 6.4. Spray Solidifier Waste Receiver Prefill and Afterfill Dimensions

Run No.	Distance from Top of Pot, in.	Prefill Diam., in.		Afterfill Diam., in.		Prefill Pot Length, in.	Afterfill Pot Length, in.
		Maximum	Minimum	Maximum	Minimum		
SS-7	24	8.7	8.6				
	56	8.7	8.5	NA	NA	95.5	NA
	80	8.7	8.6				
SS-8	24	8.7	8.6	8.7	8.7		
	56	8.7	8.6	8.7	8.7	95.6	NA
	80	8.7	8.6	8.7	8.7		
SS-9	24	8.7	8.6	8.7	8.7		
	56	8.7	8.6	8.7	8.6	NA	NA
	80	8.7	8.6	8.7	8.6		
SS-10	24	8.6	8.6	8.7	8.6		
	56	8.6	8.6	8.7	8.7	95.9	96.0
	80	8.7	8.6	8.7	8.6		
SS-11	24	8.7	8.6	8.5	8.5		
	56	8.7	8.6	8.5	8.5	96.0	NA
	80	8.7	8.6	8.5	8.5		
SS-12(IPM)	24	8.7	8.6				
	56	8.7	8.6	N/A	N/A	95.8	NA
	80	8.7	8.6				
SS-13(IPM)	24	8.6	8.6	8.6	8.6		
	56	8.6	8.6	8.7	8.6	95.9	96.0
	80	8.6	8.6	8.7	8.6		

NA Not available.

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FIGURE 6.5. Spray Solidifier 8 in. Waste Receiver Pot

into the thermal wells through Conax glands. Connection to the pot for thermocouple readout is through the L-shaped thermocouple arm and Cannon connector. The intermediate and center line thermocouples can and have been replaced remotely where thermocouples became inoperative.

6.4 WASTE RECEIVER WELDING

The waste receiver pots in this series have been welded and leak checked. Table 6.5 shows the before-fill and after-welding helium mass spectrometer leak rates. The basic concepts and principles that have been applied to seal welding the waste receivers have worked very well.⁽²⁾ Some difficulty was encountered with in-cell components that are subject to radiation damage.

6.5 WASTE RECEIVER CALORIMETRY

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

Table 6.6 shows the results of the calorimeter measurements and the back-calculated end-of-run heat generation rates for each spray solidifier filled waste receiver in this series. The decay half-life that was used for the end-of-run heat generation rate calculation was 284 days (CePr-144). The calorimeter measurements are considered to be accurate within $\pm 10\%$ based on comparisons with material balance calculations from each of the runs and the reproducibility of calorimetry results.

TABLE 6.5. Spray Solidifier Receiver Pot Leak Rates

<u>Run No.</u>	<u>Leak Rate, atm. cm³/sec</u>	
	<u>Before fill</u>	<u>After fill</u>
SS-7	1.1×10^{-7}	None
SS-8	2.6×10^{-7}	5.3×10^{-7}
SS-9	NA	2.1×10^{-7}
SS-10	8.0×10^{-9}	5.4×10^{-7}
SS-11	NA	1.7×10^{-7}
SS-12	NA	8×10^{-7}
SS-13	NA	4.1×10^{-7}

TABLE 6.6. Spray Solid Waste Receiver Pot Calorimetry

<u>Run No.</u>	<u>Calorimetry Date</u>	<u>Heat Generation Rate, kW</u>	<u>Fill Date</u>	<u>Heat Generation Rate at Fill Date, kW</u>
SS-7	1/21/69	11.4	12/11/68	12.6
SS-8	2/11/69	7.4	2/6/69	7.6
SS-9	4/4/69	7.0	3/27/69	7.2
SS-10	5/2/69	7.1	4/24/69	7.4
SS-11	3/10/70	9.8	3/4/70	10.0
SS-12	4/13/70	4.8	4/7/70	4.9
SS-13	5/18/70	9.5	5/12/70	9.6

NA - Not available.

6.6 RECEIVER POT INTERNAL PRESSURE

No pressure data was collected on the receiver pots from WSEP Runs SS-7 through SS-13 while the pots were stored in B-Cell. These receiver pots were left open to ambient cell pressure. Hence, it is not possible to arrive at a meaningful conclusion regarding the stability (chemical or radiolytic) during B-Cell storage.

Waste receiver Pots SS-4, SS-8, and SS-10 were subsequently transferred to SSETF where pressure monitoring has been done on a continuous basis using pressure transducers. During SSETF storage, no pressurization of these containers was observed under high or low temperature storage conditions.

6.7 RECEIVER POT WALL TEMPERATURES

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

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

FIGURE 6.6. Pot Wall Temperatures in Air and in Air-Cooled Receiver Pot Furnace

at the receiver midplane. The calculated and measured values of wall temperature compare favorably for the 0.6 emissivity condition except for SS-10 and 11 which appear to compare more favorably with 0.8 emissivity. The measured temperature values are within the calculated range of temperatures for expected emissivity values for the pot surfaces.

6.8 GRAB SAMPLE LEACH RATES

Grab samples of solidified waste from SS-7, SS-8, and SS-9 were collected as the melt flowed from the melter to the receiver pot. Leach rates for Cs-137 and Ce-144 are being obtained on the samples. The standard or slow leach method based on the work of Paige⁽⁵⁾ using recirculating distilled water at 25 °C is being used. A static leach test is being used for very long leach times (from 12 to 56 weeks) to reduce analytical requirements. The static test samples are maintained in beakers of static water at ambient temperature and the water is sampled every 12 weeks.

The data shown in Figure 6.7 are typical of spray solid radioactive samples. The scatter of the data for a given sample can be large as shown by SS-7 and SS-8. The data tend to show a decreasing leach rate for the time of the tests shown. The highest leach rate is for Cs-137 for SS-7 at 2×10^{-3} g/cm²-day while the SS-8 Ce-144 leach rate is the lowest at 2×10^{-9} g/cm²-day.

6.9 ENVIRONMENTAL TESTING

The WSEP demonstration runs from this latter series of spray solid runs are important to the environmental test program. SS-8, SS-9, and SS-10 waste receivers are undergoing further and more extensive evaluation.^(3,4) These three

FIGURE 6.7. Leach Rate Data for Spray Solid

waste receivers and one from the first series (SS-4) are being used to determine the product and container characteristics. The importance of this work lies in obtaining information about radiation stability, chemical stability, and thermal stability of the solidified waste. Equally as important are the corrosion resistance and environmental stability of the waste receiver pot.

REFERENCES FOR SECTION 6

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7.0 PROJECTED FLOWSHEETS FOR
PW-4m AND LMFBR WASTES

7.0 PROJECTED FLOWSHEETS FOR PW-4m AND LMFBR WASTES

While it is desirable for a waste solidification facility to be capable of processing wastes which differ widely in chemical and radiochemical compositions, demonstration of all possible waste variations in the WSEP program is impractical. Experience in fuel reprocessing and projections of future fuel reprocessing requirements led to the selection of four generalized types of Purex acid wastes. Two of these wastes, Purex 1 and 2, were discussed in the WSEP Volume 6 report where the first series of spray solidification runs were discussed.⁽¹⁾ The second two wastes types, PW-4m and LMFBR, are shown in Table 3.1 and were tested during the last series of spray solidification runs.

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

The fission product heat generation rate in waste from one tonne of the 45,000 MWd/tonne and LMFBR core fuels is presented in Figure 7.1. Both the initial heat generation rate levels of the waste and its later aged levels must be considered in filling a pot. The initial heat generation rate

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

in a solidified waste may not be compatible with economical heat dissipation in a final storage environment such as a salt mine; consequently, an aging period may be required. If aging of the solidified waste (to permit radionuclide decay) in an interim storage basin is used, the container can be loaded with a higher heat generation rate than the final storage environment may allow. The aging before storage of the pots in salt depends on economic choice. However, a proposed Federal Regulation suggests that solidification of all high level wastes be completed before the fuel has been out of the reactor for five years.⁽⁴⁾ Figure 7.2 shows the ages required to meet present temperature limitations for filling a 6- and an 8-inch diameter pot with spray solidified product for storage in either water or air. Two sets of curves are shown; one set is for spray solidification using a melter and the other is for spray solidification using in-pot melting. For the in-pot melting process a solid waste composition containing 50 wt% waste oxides is used. Solidification can be performed at an earlier age out of reactor if a lower waste oxide percentages is used.

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

Since the PW-4m and LMFBR spray solidified melter products have nominal melting temperatures of 900 °C, the centerline

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

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

and wall temperature limits were used to determine the maximum heat generation rates shown in Figure 7.2 for the 6-inch and the 8-inch diameter pots such as were used in the WSEP program. Although the PW-4m and LMFBR spray solidified in-pot melting product has a nominal remelt temperature of 800 °C, the 900 °C centerline temperature limit is reached before the molten core limit is attained.

Data from both nonradioactive⁽⁵⁾ and radioactive WSEP demonstrations have been used in projecting typical chemical flowsheets for spray solidification. Sufficient confidence in radioactive demonstration has been reached to specify most of the necessary details for flowsheets with PW-4m and LMFBR wastes using either a melter or the in-pot melting scheme. Figure 7.3 shows a Mode A flowsheet for the solidification of one tonne of PW-4m waste aged 0.8 years (out of the reactor) using spray solidification with a melter and Figure 7.4 is a Mode A flowsheet for the solidification of one tonne of PW-4m waste aged 1.5 years and using the in-pot melting technique. The aging time for each waste is the minimum out-of-reactor time prior to spray solidification for which the maximum allowable heat generation rate is obtained for an 8-inch diameter waste container stored in air. As seen in Figure 7.2, considerably higher heat rate densities can be attained if the pots are filled and cooled in water.

FIGURE 7.3. Typical Flowsheet for Processing One Tonne of PW-4m Waste with Mode A Operation (spray solidifier with melter).

FIGURE 7.4. Typical Flowsheet for Processing One Tonne of PW-4m Waste with Mode A Operation (spray solidifier with in-pot melting).

FLOW SHEET CODE FOR FIGURES 7.3 AND 7.4STREAM

1. Incoming waste from processing one tonne of power reactor fuel with an integrated exposure of 45,000 MWd/tonne at a specific power of 30 MW/tonne. The computer program ISOGEN was used to determine the fission product data for this reactor fuel. The total fission product values do not include the transuranium or the transplutonium values. The ^{144}Ce values include its naturally occurring daughter ^{144}Pr .
2. Nonradioactive chemical additives to the raw waste. Additives for PW-4m include 2.8M phosphoric acid (75 wt%), 0.75M lithium hydroxide, 0.97M sodium hydroxide, and 1.1M ferric nitrate for the melter flow sheet and based on a feed concentration of 378 liters/tonne.
3. Chemically adjusted waste, or feed to the spray calciner.
4. Gas flow to atomize the incoming feed prior to calcination in the spray calciner. Approximately 6.2 scfm of unheated air is used with an internal-mix atomizing nozzle (Spraying Systems Co., Setup No. 42 is used here).
5. Gas flow for back pulsing the porous metal filters to dislodge collected calcine fines. Air heated to about 350 °C and at 40 to 60 psig is used here with a nominal 2-minute cycle and a 2-second pulse. A nominal effective flow of 1.5 scfm of air was used for the 8 sets of filter venturis.
6. Solid additive (flux) to the in-pot melting process. Sodium borosilicate frit (111-15) particles at -6 +10 mesh are added (see Section 3.3.4 for frit composition) to produce a melt that contains 50 wt% waste oxides.

7. Not used.
8. Solidifier condensate. A total of 60% of the total nitrate is assumed present in this stream.
9. Solidifier noncondensables and entrained particles not removed by the solidifier condenser. A total of 40% of the total nitrates is estimated for this stream. A total gas flow of 13 scfm including inleakage at the solidifier is used for this stream.
10. Melt flow to receiver. Actual flow may be continuous or by periodic batches.
11. Evaporator bottoms. The bottoms will be recycled and eventually returned to the solidifier. They may be recycled to the solidifier feed or to the high level liquid waste system of the reprocessing plant. A total of 100 liters of 5M HNO_3 was arbitrarily selected to represent the volume to be recycled for each tonne equivalent of waste processed. (Not included in balance)
12. Evaporator strip water. A HNO_3 concentration of 0.02M is used here.
13. Evaporator overheads. A HNO_3 concentration of 0.5M is used here.
14. Solidifier noncondensibles and entrained particles not removed in the evaporator condenser. A total of 40% of the total nitrate is assumed present in this stream.
15. Fractionator bottoms. A HNO_3 concentration of 10M is used for calculations. This stream can be used for fuel element dissolution or possibly in solvent extraction scrub streams.
16. Fractionator distillate.

17. Fractionator distillate. This can be used as makeup water for fuel dissolution, solvent extraction scrub streams, or it can be treated as low level waste.
18. Scrubber solution, approximately 1 to 2M NaOH. Twenty-five percent of the nitrate from the solidifier is removed by the scrubber.
19. System off-gas. Fifteen percent of the total feed nitrate is present in this stream.
20. Solidified ceramic or glass product. Pot is welded and stored.

The in-pot melting process is not a continuous process and consequently the processing rate is dependent on the pot size. However, for the flow sheet shown in Figure 7.4 the pot does not impose a limit. (With an 8-inch diameter pot, a melt formation rate of approximately 2 liters/hr is near optimum). The heat rate density and maximum heat generation rate in the pots for either in-pot melting or spray solidification with a melter are dependent on the pot diameter.

A flowsheet is not presented for LMFBR waste because the LMFBR waste as shown in Table 3.1 and as demonstrated during spray solidification Run SS-11 was adjusted by adding chemicals to make it nearly identical to PW-4m. Slight differences included the presence of antimony and tin, and volatile selenium and tellurium in the LMFBR waste as discussed in Section 3. To process the LMFBR core fuel, an aging period of 1.6 and 2.4 years is needed prior to solidifying in 8-inch diameter air cooled pots with the spray melter and in-pot melting systems, respectively. After the dilution by additive chemicals the solid wastes would occupy 110 liters/tonne using the spray melter process and 70 liters/tonne using the spray in-pot melting process. Further information on processing simulated LMFBR waste is presented in Sections 4 and 9.

Both the water and the acid from the fractionator require reuse or further treatment. Although the chemical level of fission products in each WSEP demonstration run represented 45,000 MWd/tonne thermal fuel and LMFBR core fuel at 100,000 MWd/tonne, the radioactive fission product spectrum used did not represent that value. In order to project WSEP data to expected 45,000 MWd/tonne and LMFBR core exposure, the same fractional distribution of radionuclides to the auxiliaries

as given in Table 5.3 was used for evaluation of each run. This exercise increased particular radionuclides to the appropriate curie level that would exist if the waste was solidified at the age shown in Table 7.1 where the fractionator results are shown. On this basis, approximately 2000 curies of ruthenium, 10 curies of $^{144}\text{CePr}$ and less than 1 curie of ^{90}Sr are found in the fractionator bottoms per tonne of 45,000 MWd/tonne thermal fuel processed when using the spray-melter process. When in-pot melting is used, the ruthenium content is reduced by a factor of approximately 10. For 100,000 MWd/tonne LMFBR core fuel, the fractionator will accumulate approximately 3300 curies of ruthenium, less than 1 curie of $^{144}\text{CePr}$, and less than 0.1 curies of ^{90}Sr . The gross $\beta + \gamma$ in the acid using waste from 45,000 MWd/tonne thermal fuel will range from 280 to 1400 $\mu\text{Ci/ml}$ for the in-pot melting process to 3000 to 11,000 $\mu\text{Ci/ml}$ using the spray-melter process. For the 100,000 MWd/tonne LMFBR core fuel waste using the spray-melter process, the gross $\beta + \gamma$ will be approximately 17,000 $\mu\text{Ci/ml}$.

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

The ratio of the radionuclide concentration in the final distillate to 10CFR20 release limits was obtained by projecting run data as shown in Table 7.2. While ^{90}Sr and $^{144}\text{CePr}$ concentrations are approximately 30 to 100 times the 10CFR20 release limits⁽⁷⁾ for the 45,000 MWd/tonne thermal fuel waste, ^{106}Ru is the controlling constituent at approximately 300,000 times its limit. Another careful distillation would,

TABLE 7.1. Projected Radionuclides in Fractionator Acid
Per Tonne of Equivalent Fuel Processed^(a)

Run No.	Waste Type	Operating Mode	Age of Waste, ^(c) yr	Projected Fractionator Acid Radioactivity ^(a,b)		
				¹⁴⁴ CePr, Ci	⁹⁰ Sr, Ci	Ru (Total), Ci ^(d)
7	PW-1	A	0.5	2.0	1.3	2280
8	PW-1	A	0.5	9.0	0.58	680
9	PW-4m	A	0.8	NDG	NDG	2080
10	PW-4m	A,B	0.8	0.41	0.04	1700
11	LMFBR	A	1.5	0.97	0.04	3360
12 (IPM)	PW-4m	A	1.5	1.3	0.24	280
13 (IPM)	PW-4m	B-Modified	1.5	NDG	NDG	120

- a. Based on activity distribution data in Table 5.3 and Reference 2 for LMFBR waste and Reference 3 for PW-4m and PW-1 thermal reactor waste fission product spectrums.
- b. Based on the production of 10M nitric acid, the nominal acid volume will range from 150 to 250 liters/tonne.
- c. Age of waste is based on WSEP established maximum temperatures using 8-inch diameter pots with air cooling.
- d. Ruthenium data does not include the effect on the ruthenium of the recycle of the solidifier condensate (containing approximately 50% of the ruthenium in the raw waste for the spray-melter runs) to the feed tank. This would increase the projected values by a factor of about 2. (Reference 9)

NDG = No detectable gain.

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

Nuclide	10CFR20 ^(c) Limit, $\mu\text{Ci/ml}$	PW-4m Waste ^(a)		LMFBR Waste ^(b)	
		Projected Distillate, ^(d) $\mu\text{Ci/ml}$	Ratio Projected Distillate to 10CFR20 Limit	Projected Distillate, ^(d) $\mu\text{Ci/ml}$	Ratio Projected Distillate, to 10CFR20 Limit
$^{144}\text{CePr}$	1×10^{-5}	3.3×10^{-4}	33	6.7×10^{-3}	670
^{90}Sr	3×10^{-7}	3.3×10^{-5}	110	2.9×10^{-4}	970
^{106}Ru	1×10^{-5}	3.8 (spray melter)	3.8×10^5	30	3×10^6
		1.3 (in-pot melting)	1.3×10^5		

- a. PW-4m waste from fuel irradiated to 45,000 MWd/tonne at 30 MW/tonne and 0.8 years out of reactor for the spray-melter runs and 1.5 years out-of-reactor for the spray in-pot melting runs. Projections are based on Runs 9 and 10 for the spray-melter, and Runs 12 and 13 for in-pot melting.
- b. LMFBR waste from core fuel irradiated to 100,000 MWd/tonne at 200 MW/tonne and 1.5 years out-of-reactor. Projection is based on Run SS-11.
- c. USAEC Code of Federal Regulations, Title 10, Part 20, Table II, Column 2.
- d. A distillate volume of 300 liters is used but actual volumes depend on feed type, etc., and may vary from 200 to 400 liters/tonne of waste.

in general, bring all values, except possibly ^{106}Ru to below 10CFR20 release limits. The distillate could also be used as makeup water in the reprocessing plant,⁽⁶⁾ however, if an additional distillation is made, the bottoms would be recycled to the waste evaporator or to the solidifier feed.

The same observations can be made for the final distillate from processing of LMFBR core fuel as were made for the 45,000 MWd/tonne thermal fuel. By projecting the data from the one LMFBR spray solidifier run that was made, the final distillate is found to be approximately 1000 and 700 times the 10CFR20 limits for ^{90}Sr and $^{144}\text{CePr}$, respectively and 3,000,000 times 10CFR20 limits for ^{106}Ru .

The ruthenium content in the fractionator and fractionator distillate is due primarily to the fact that approximately 0.5 percent of the total ruthenium in the solidifier off-gas remains airborne in the gas stream from the solidifier condenser. This is discussed in more detail in Section 5.

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

The secondary effect of the recycle of ruthenium to the solidifier feed stream has not been demonstrated. However, for the continuous recycle of the evaporator bottoms (50% of the ruthenium in the raw waste volatilized during solidification) about a two-fold increase in the total ruthenium concentration in the auxiliary process streams could be expected at steady state.⁽⁹⁾

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8.0 FUTURE WORK

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8.0 FUTURE WORK

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

8.1 EQUIPMENT AND PROCESS REQUIREMENTS

It is desirable to reduce the volatilization of ruthenium from the spray solidifier (i.e., by reducing feed acidity and/or adding a chemical reductant to the feed) when processing wastes containing phosphate. Ruthenium volatility from the spray solidifier is not a problem (<5%) when phosphate is not added to the waste as is the case for the in-pot melting modification where all the flux is added directly to the pot.

To assure adequate feed atomization, improved control of the feed rate to the solidifier is desired. The addition of a mechanical scraper to the bottom conical section of the calciner could also aid in eliminating downtime required to remove deposition in this area.

An extended spray solidification run (on the order of 1000 hours) would be helpful in identifying any process problems associated with long-term operation, and establishing equipment reliability. This test could probably be performed with equally valid results with a nonradioactive solidification system.

The governing mechanism which affects calciner and melter capacity should be established to provide information for scale-up. A suitable construction material which is less expensive than platinum is desirable for the continuous melter.

8.2 FILLED POT PERFORMANCE

Four of the waste containers from the spray solidification demonstration runs are undergoing environmental testing in the Solid Storage Engineering Test Facility (SSETF).⁽¹⁾

The SSETF is a special facility in A-Cell of the Chemical and Materials Engineering Laboratory⁽²⁾ in which as many as 16 WSEP product containers can be subjected to a controlled environment storage. The facility consists of test pods in which various storage conditions can be provided under carefully controlled conditions. Storage temperatures up to 100 °C in water and up to 600 °C in air will be studied. The SSETF was activated in January 1969, with installation of the first pot-pod combination.

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

The variables involved in the test plan are:

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

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

Insight into product and container properties will be gained through this study. Specifically, the product will be

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

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

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

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

TABLE 8.1. SSETF Environmental Tests of Spray Solidifier Receiver Pots

<u>WSEP Demonstration Run Number</u>	<u>Feed Type</u>	<u>Container Material</u>	<u>Fill Date, month/ year</u>	<u>Initial Heat Generation Rate, kW</u>	<u>SSETF Test Started month/ year</u>	<u>Storage Medium</u>
SS-4	PW-2	Mild Steel	9/68	5100	9/69	Water
SS-8	PW-1	304L SS	2/69	6700	1/70	Air
SS-9	PW-4m	310 SS	3/69	7200	6/70	Air
SS-10	PW-4m	Mild Steel	4/69	7400	2/70	Water

REFERENCES FOR SECTION 8

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

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APPENDIX 9.09.1 RUN DESCRIPTION

This appendix briefly describes WSEP radioactive Runs SS-7 through SS-13(IPM). Following the run descriptions, general information for all runs on feed compositions, solidifier and auxiliary equipment operating parameters and results, material balances and feed pump experience are presented in Tables 9.1 to 9.5, respectively. Schematic diagrams of the equipment arrangement for Mode A and Mode B operation are shown in Figures 9.1 and 9.2, respectively. WSEP solidifier and auxiliary equipment flow diagrams are shown in Figures 9.3 and 9.4, respectively. WSEP auxiliary evaporator and fractionator operating parameters are shown in Figures 9.5 to 9.11. Figure 9.12 shows a schematic of the process off-gas ventilation system. Startup, normal operating and shutdown procedures for the spray solidification system are presented in Reference 1 Section 5.

Run SS-7

The seventh demonstration of the spray solidification process was completed during December 1968. Run SS-7 was the fifth radioactive demonstration of the spray solidification process with a PW-1 (sulfate-free) waste flowsheet.

During Run SS-7, waste equivalent to processing 1.85 tonnes of power reactor fuel (20,000 MWd/tonne at 15 MW/tonne) with an equivalent aging time of 0.7 years was processed to produce 197 kilograms of ceramic product. The 62 liters of radioactive ceramic produced a heat-rate density of 204 W/liter (12,700 watts total based on pot calorimetry and analytical data) in an 8-inch diameter 304L stainless-steel melt receiver.

TABLE 9.1. Nominal and Actual Feed Compositions Used in Spray Solidification Runs SS-7 Through SS-13(IPM)

Waste Component	WSEP Subs.	PW-1 Nominal M(a)	Actual PW-1(a,b) Concentration, M		PW-4m Nominal M(a)	Actual PW-4m Concentration, M(a,b)				LMFBR Nominal M(a)	Actual(a,b) LMFBR, M	
			SS-7	SS-8		SS-9	SS-10	SS-12(IPM)	SS-13(IPM)		SS-11	SS-11
H ⁺ (d)		3.7	2.8(9.0)	1.38(1.6)	4.3	3.5(7.0)	3.2(3.3)	0.2(1.0)	0.43(1.68)	0.5	5.38(8.8)	
Fe ⁺³	(c)	0.93	0.7	0.8	0.05	1.0	0.90	0.06	0.11	0.16	1.81	
Cr ⁺³		0.012			0.012					0.046		
Ni ⁺²		0.005			0.008					0.023		
Al ⁺³	(c)	0.001	0.09	0.12	0.001	0.18	0.16	0.33	0.31	0.001	0.46	
Na ⁺		0.138	0.57	0.47	0.10	0.90	1.0	0.53	0.19	0.1	3.75	
U ⁺⁶		0.01			0.01							
NO ₃ ⁻		6.5	4.74	1.8	6.5	6.89	3.90	5.8	3.59	4.75	13.5	
SO ₄ ⁻²		--			--					--		
PO ₄ ⁻³		0.003			0.003					0.06		
SiO ₃ ⁻²		0.01			0.01							
Cs ⁺ + Rb ⁺	K ⁺	0.042			0.092					0.229		
Sr ⁺²		0.0155			0.036					0.04		
Ba ⁺²		0.0195			0.041					0.068		
(Y + RE) ⁺³	RE ⁺³	0.12	0.13	0.12	0.274	0.31	0.32	0.33	0.28	0.528	0.53	
Zr ⁺⁴		0.065			0.143					0.222		
MoO ₄ ⁻² + TcO ₄ ⁻²	MoO ₄ ⁻²	0.079			0.161					0.30		
Ru ⁺⁴		0.0032	0.0037	0.0033	0.0032	0.003	0.0031	0.0046	0.002	0.005	0.0054	
Ru ⁺⁴	Fe ⁺³	0.0288			0.0786					0.215		
Rh ⁺²	Co ⁺²	0.0074			0.013					0.06		
Pd ⁺²	Ni ⁺²	0.017			0.043					0.16		
Ag ⁺ + Cd ⁺²	Cu ⁺²	0.0016			0.0041					0.029		
TeO ₄ ⁻²	SO ₄ ⁺²	0.0064			0.014					--		
TeO ₄ ⁻²					--					0.034		
SeO ₄ ⁻³					--					0.005		
Sn ⁺⁴ + In ⁺³	Sn ⁺⁴				--					0.011		
Sb ⁺³					--					0.003		
Additives to Waste												
Li ⁺		0.5			0.75					--		
Na ⁺		0.5			0.972			None		3.4		
Fe ⁺³	(c)	--			1.10				None	2.17		
Ca ⁺²		--			--			0.65		--		
Zn ⁺⁴		--			--			0.50		--		
PO ₄ ⁻³		1.78	1.58	1.6	2.80	2.58	2.87	None		5.58	5.68	
Borosilicate(e)					--			533 g/l (To Pot)	320 g/l (To Pot)			
Final Feed												
Concentration, liters/tonne			452	473		630	611	556	352		1232	
Specific Gravity at 25 °C			1.31	1.22		1.34	1.27	1.28	1.26		1.35	
Solids, vol%			32	32		45	42	31	10		65	
ΣM _T ⁺			4.89	4.28		6.56	7.0	5.9	3.48		14.1	
ΣM _T ⁺ /P			2.75	2.65		2.83	2.5	--	--		2.5	
Total Radioactivity, Ci/liter			3070	2280		2390	3443	4608	9190		4112	
Radioruthenium, Ci/liter			24.2	18		11.1	17.5	22.6	35		21.6	
Total Heat Rate Density, W/liter			11.3	8.4		7.98	11.1	16.2	33.8		16.4	

- a. Values are reported on a 378 liter/tonne basis.
- b. Values reported are total concentrations including additives (if any) as determined by chemical analysis of the waste. All other chemical compositions were added quantitatively as given by nominal values.
- c. Excess aluminum in radioactive feedstock solutions was substituted for part of total iron requirement.
- d. The value in brackets represents a total acidity as determined by titrating the waste to PL-7 (used as a basis of reference).
- e. Added as -6+10 mesh frit (111-15) directly to the receiver pot (see Section 3 for composition).

Spray Solidification Run Number	SS-7	SS-8	SS-9	SS-10	SS-11	SS-12 (IPM)	SS-13 (IPM)
Date	12/9/68 12/11/68	2/4/69 2/4/69	3/24/69 3/28/69	4/21/69 4/24/69	3/2/70 3/4/70	4/6/70 4/7/70	5/11/70 5/12/70
Operating Mode ^(a)	A	A	A	67% A - 33% B	A	A	B-Modified
Feed							
Type	PW-1	PW-1	PW-4m	PW-4m	LMFBR	PW-4m	PW-4m
Concentration, liters/tonne	452	473	630	611	1232	556	352
Heat Rate Density, W/liter	11.3	8.3	8.0	11.1	16.4	16.2	33.8
Temperature, °C	30	25	30	30	24	32	25
Feed Rate, liters/hr	17.9	14.5	15.2	13.5	14.9	10.8	15.4
Total Feed Processed, liters	839	800	792	750	669	301	308
Total Feed Time, hr ^(b)	47	55	52	56	45	28	20
Number of Feed Interruptions	1	1	2	1	0	2	0
Total Time Feed Off ^(c)	4	0.5	7.0	3.5	0	4.4	0
Total Curies in Feed to Solidifier	3,620,000	1,830,000	2,030,000	2,582,000	3,110,000	1,387,000	2,830,000
Total Curies of Ruthenium in Feed to Solidifier	22,000	14,400	10,200	13,100	14,400	6,800	11,000
Atomizing Feed Nozzle ^(d)							
Atomizing Gas	Air	Air	Air	Air	Air	Air	Air
Gas Flow, scfm	6.5	7.0	6.3	6.2	7.3	7.8	6.8
Gas Pressure, psig	44	44	45	43	45	45	45
Gas Temperature, °C	30	30	30	30	30	30	30
Calciner Vibrator							
Cycle, min	1	1	1	0.25 to 1	1	0.5 to 1	1
Pulse, sec	2	2	2	2 to 5	2	2 to 4	2
Air Supply Pressure, psig	45	50	50 to 55	50 to 60	50	50 to 80	50
Solidifier Off-Gas Filters ^(e)							
Blowback Gas	Air	Air	Air	Air	Air	Air	Air
Gas Temperature, °C	350	350	350	350	350	350	350
Gas Pressure, psig	42	44	42	40 to 60	40	40	40
Blowback Cycle, min	2	2	2	2	2	2	2
Blowback Pulse, sec	2	2	2	2	2	2	2
Filter Pressure Drop, in. of water							
Start of Run	3.0	4.5	4.5	4.8	2.7	2.8	3.6
Maximum	5.4	5.4	8.0	9.0	5.0	3.5	3.6
End of Run	4.8	4.5	4.8	8.0	3.0	2.6	3.2
Air Inleakage to Solidifier, scfm	5	5	5	5	8	8	10
Total Noncondensable Gas Flow to Filters, scfm	13	13	12	13	16	17	18
Filter Chamber Temperature, °C	330	340	350	350	360	330	340
Total Gas Flow to Filters (at chamber temp.), cfm	55	51	51	50	59	53	63
Filter Face Velocity (at chamber temp.), ft/min.	3.7	3.4	3.4	3.3	3.9	3.5	4.2
Calciner							
Furnace Temperature, °C	670	690	690	700	700	720-740	670-700
Drying Chamber Temperatures, °C							
Top Internal ^(f)	420	400	450	400	430	380	350
Bottom Internal ^(g)	540	580	600	570	600	580	570
Exit Gas ^(h)	440	460	450	470	470	360	400
Average Pressure, in. of water							
Normal	-10	-8	-11	-10	-10	-10 to -6	-12 to -8
During Blowback	-2	-2	-3	-2	-2	-4 to 0	-6 to -2
Average Furnace Power, kW							
Atomizing Air On Only	12	NA	NA	12	14	13	13
Feed On	30	22	NA	23	27	20	27
Solids Addition							
Type	--	--	--	--	--	Borosilicate Frit (111-15)	Borosilicate Frit (111-15)
Size, mesh	--	--	--	--	--	-6+10	-6+10
Addition Point	--	--	--	--	--	To Pot	To Pot
Addition Method	--	--	--	--	--	Batch	Batch
Batch Size, kg	--	--	--	--	--	1	1
Batch Rate, batches/hr	--	--	--	--	--	~4	~5
Total Added	--	--	--	--	--	109	106
Melter							
Furnace Temperature, °C	1125	1140	1175	1190	1180	--	--
Internal Melt Temperature, °C	1060	1050	1100	1150	1140	--	--
Drain Freeze-Value Temperature, °C							
While Frozen	780	820	820	825	840	--	--
While Draining	900	930	950	1030	1035	--	--
Melt Production Rate, liters/hr	1.3	1.1	1.3	1.0	1.3	1.9 (Pot)	2.5 (Pot)
Melt Discharge Method	Batch	Batch	Batch	Batch	Batch	--	--
Melt Discharge Rate, liters/hr	65	52	23	24	34	--	--
Average Furnace Power, kW	14.7	15.0	15.3	16.0	16.0	--	--
Receiver Pot and Product							
Pot Furnace Temperature, °C							
Zone Being Filled and Those Above	OFF	OFF	OFF	OFF	OFF	900 to 950	900 to 950
Zones Below	OFF	OFF	OFF	OFF	OFF	OFF	OFF
Receiver Pot							
WSEP Number	42	40	36	54	47	48	
Material	304L SS	304L SS	310 SS	Mild Steel	304L SS	304L SS	304L SS
Diameter (OD), in. ⁽ⁱ⁾	8.60	8.65	8.65	8.60	8.65	8.67	8.60
Wall Thickness, in. ⁽ⁱ⁾	0.312	0.323	0.330	0.320	0.320	0.333	0.304
Length, in. ⁽ⁱ⁾	95.5	95.6	96.0	95.9	96.0	95.8	95.9
Depth of Product in Pot, in. ^(j)	80	74	81	70	76	68	64
Product Volume, liters	62	59	68	56	60	54	50
Product Weight, kg	197	170	194	176	186	162	151
Product Density, kg/liter							
Bulk	3.16	2.9	2.87	3.14	3.1	3.0	3.0
Measured ^(k)	3.30	3.3	3.31	NA	3.29	2.8	NA
Initial Product Melting Point, °C ^(l)	850	850	950	900	900	850	925
Feed to Solid Volume Ratio							
Actual	13.5	13.6	11.7	11.7 ^(m)	11.2	5.6	6.2
Based on 378 liter/tonne Feed	11.3	10.8	7.0	7.2	3.4	3.8	6.6
Equivalent Waste, tonne	1.85	1.7	1.26	1.07 ^(m)	0.54	0.54	0.88
Unit Product Volume, liters/tonne	33.6	35	53.7	52	111	100	57
Average Processing Rate, tonne/day	0.94	0.74	0.58	0.46	0.29	0.46	1.05
Fission Product Heat in Pot, W							
Based on Feed Analysis	12,700	6700	7200	8400	10,900	4900	10,400
Based on Pot Calorimetry	12,600	7600	7200	7400	10,000	4900	9600
Heat Generation Rate Density, W/liter ⁽ⁿ⁾	204	120	107	132 ^(o)	175	90	200
Total Radioactivity in Pot, Ci ^(p)	3,620,000	1,826,000	2,030,000	2,232,000 ^(m)	3,100,000	1,387,000	2,830,000
Total Radioruthenium in Pot, Ci ^(p)	8650	8600	4400	6280 ^(m)	3600	6700	11,000
Equivalent Age of Waste, years	0.67 ^(q)	1.2 ^(q)	2.3 ^(r)	1.9 ^(r)	2.2 ^(s)	1.3 ^(q)	1.0 ^(q)
Centerline Temperature, °C ^(t)							
In Air Cooled Furnace	920	605	594	611	759	474	824
In Air	900	NA	520	539	608	435	785
In Water	547	285	283	337	378	278	563
Wall Temperature, °C ^(t)							
In Air Cooled Furnace	467	395	352	349	406	277	420
In Air	425	NA	285	279	288	228	344
In Water	25	40	40	40	44	40	50
Effective Thermal Conductivity, W/(m ²) (°C/m) ^(u)							
In Air Cooled Furnace	1.16	1.4	1.14	1.30	1.28	1.18	1.28
In Air	1.11	NA	1.14	1.31	1.41	1.12	1.17
In Water	1.0	1.2	1.09	1.15	1.35	0.98	1.01
Radiation Reading at 6 Inches, rad/hr ^(v)	NA	28,000	26,000	25,000	40,000	21,000	58,000
Pot Leakage, atm-cm ³ /sec ^(w)	NA	5.3 × 10 ⁻⁷	2.1 × 10 ⁻⁷	5.4 × 10 ⁻⁷	1.7 × 10 ⁻⁷	8.0 × 10 ⁻⁷	4.1 × 10 ⁻⁷

a. Equipment arrangements for Mode A, Mode B, and Mode B-Modified is shown in Figures 9-1 and 9-2

Blowback Gas	Air	Air	Air	Air	Air	Air	Air
Gas Temperature, °C	350	350	350	350	350	350	350
Gas Pressure, psig	42	44	42	40 to 60	40	40	40
Blowback Cycle, min	2	2	2	2	2	2	2
Blowback Pulse, sec	2	2	2	2	2	2	2
Filter Pressure Drop, in. of water							
Start of Run	3.0	4.5	4.5	4.8	2.7	2.8	3.6
Maximum	5.4	5.4	8.0	9.0	5.0	3.5	3.6
End of Run	4.8	4.5	4.8	8.0	3.0	2.6	3.2
Air Inleakage to Solidifier, scfm	5	5	5	5	8	8	10
Total Noncondensable Gas Flow to Filters, scfm	13	13	12	13	16	17	18
Filter Chamber Temperature, °C	330	340	350	350	360	330	340
Total Gas Flow to Filters (at chamber temp.), cfm	55	51	51	50	59	53	63
Filter Face Velocity (at chamber temp.), ft/min.	3.7	3.4	3.4	3.3	3.9	3.5	4.2
<u>Calciner</u>							
Furnace Temperature, °C	670	690	690	700	700	720-740	670-700
Drying Chamber Temperatures, °C							
Top Internal(f)	420	400	450	400	430	380	350
Bottom Internal(g)	540	580	600	570	600	580	570
Exit Gas(h)	440	460	450	470	470	360	400
Average Pressure, in. of water							
Normal	-10	-8	-11	-10	-10	-10 to -6	-12 to -8
During Blowback	-2	-2	-3	-2	-2	-4 to 0	-6 to -2
Average Furnace Power, kW							
Atomizing Air On Only	12	NA	NA	12	14	13	13
Feed On	30	22	NA	23	27	20	27
<u>Solids Addition</u>							
Type	--	--	--	--	--	Borosilicate Frit (111-15)	Borosilicate Frit (111-15)
Size, mesh	--	--	--	--	--	-6+10	-6+10
Addition Point	--	--	--	--	--	To Pot	To Pot
Addition Method	--	--	--	--	--	Batch	Batch
Batch Size, kg	--	--	--	--	--	1	1
Batch Rate, batches/hr	--	--	--	--	--	~4	~5
Total Added	--	--	--	--	--	109	106
<u>Melter</u>							
Furnace Temperature, °C	1125	1140	1175	1190	1180	--	--
Internal Melt Temperature, °C	1060	1050	1100	1150	1140	--	--
Drain Freeze-Value Temperature, °C							
While Frozen	780	820	820	825	840	--	--
While Draining	900	930	950	1030	1035	--	--
Melt Production Rate, liters/hr	1.3	1.1	1.3	1.0	1.3	1.9 (Pot)	2.5 (Pot)
Melt Discharge Method	Batch	Batch	Batch	Batch	Batch	--	--
Melt Discharge Rate, liters/hr	65	52	23	24	34	--	--
Average Furnace Power, kW	14.7	15.0	15.3	16.0	16.0	--	--
<u>Receiver Pot and Product</u>							
Pot Furnace Temperature, °C							
Zone Being Filled and Those Above	OFF	OFF	OFF	OFF	OFF	900 to 950	900 to 950
Zones Below	OFF	OFF	OFF	OFF	OFF	OFF	OFF
Receiver Pot							
WSEP Number	42	40	36	54	47	48	
Material	304L SS	304L SS	310 SS	Mild Steel	304L SS	304L SS	304L SS
Diameter (OD) in. (i)	8.60	8.65	8.65	8.60	8.65	8.67	8.60
Wall Thickness, in. (i)	0.312	0.323	0.330	0.320	0.320	0.333	0.304
Length, in. (i)	95.5	95.6	96.0	95.9	96.0	95.8	95.9
Depth of Product in Pot, in. (j)	80	74	81	70	76	68	64
Product Volume, liters	62	59	68	56	60	54	50
Product Weight, kg	197	170	194	176	186	162	151
Product Density, kg/liter							
Bulk	3.16	2.9	2.87	3.14	3.1	3.0	3.0
Measured (k)	3.30	3.3	3.31	NA	3.29	2.8	NA
Initial Product Melting Point, °C ^(l)	850	850	950	900	900	850	925
Feed to Solid Volume Ratio							
Actual	13.5	13.6	11.7	11.7 ^(m)	11.2	5.6	6.2
Based on 378 liter/tonne Feed	11.3	10.8	7.0	7.2	3.4	3.8	6.6
Equivalent Waste, tonne	1.85	1.7	1.26	1.07 ^(m)	0.54	0.54	0.88
Unit Product Volume, liters/tonne	33.6	35	53.7	52	111	100	57
Average Processing Rate, tonne/day	0.94	0.74	0.58	0.46	0.29	0.46	1.05
Fission Product Heat in Pot, W							
Based on Feed Analysis	12,700	6700	7200	8400	10,900	4900	10,400
Based on Pot Calorimetry	12,600	7600	7200	7400	10,000	4900	9600
Heat Generation Rate Density, W/liter ⁽ⁿ⁾	204	120	107	132 ^(o)	175	90	200
Total Radioactivity in Pot, Ci	3,620,000	1,826,000	2,030,000	2,232,000 ^(m)	3,100,000	1,387,000	2,830,000
Total Radium in Pot, Ci ^(p)	8650	8600	4400	6280 ^(m)	3600	6700	11,000
Equivalent Age of Waste, years	0.67 ^(q)	1.2 ^(q)	2.3 ^(r)	1.9 ^(r)	2.2 ^(s)	1.3 ^(q)	1.0 ^(q)
Centerline Temperature, °C ^(t)							
In Air Cooled Furnace	920	605	594	611	759	474	824
In Air	900	NA	520	539	608	435	785
In Water	547	285	283	337	378	278	563
Wall Temperature, °C ^(t)							
In Air Cooled Furnace	467	395	352	349	406	277	420
In Air	425	NA	285	279	288	228	344
In Water	25	40	40	40	44	40	50
Effective Thermal Conductivity, W/(m ²)(°C/m) ^(u)							
In Air Cooled Furnace	1.16	1.4	1.14	1.30	1.28	1.18	1.28
In Air	1.11	NA	1.14	1.31	1.41	1.12	1.17
In Water	1.0	1.2	1.09	1.15	1.35	0.98	1.01
Radiation Reading at 6 Inches, rad/hr ^(v)	NA	28,000	26,000	25,000	40,000	21,000	58,000
Pot Leakage, atm-cm ³ /sec ^(w)	NA	5.3 × 10 ⁻⁷	2.1 × 10 ⁻⁷	5.4 × 10 ⁻⁷	1.7 × 10 ⁻⁷	8.0 × 10 ⁻⁷	4.1 × 10 ⁻⁷

- Equipment arrangements for Mode A, Mode B, and Mode B-Modified is shown in Figures 9.1 and 9.2.
- Total hours feed was actually being fed to the solidifier.
- Total hours that feed was off between time feed first fed to solidifier and time feed was shut off to end run.
- An internal-mix, two-fluid atomizing nozzle (Spraying System Co., Setup No. 42) was used during all of the runs.
- Solidifier off-gas filters consisted of 15 sintered powder metal (316L SS) filter elements with a total filter surface area of 15 ft². The filter elements were cleaned two at a time by blowing gas back through them.
- Temperature measured 2 in. down from top near wall.
- Temperature measured 60 in. down from top near wall.
- Temperature measured in conical bottom section of drying chamber.
- Average of prefill measurements made out of cell prior to run.
- Includes approximately 4 in. of product from Run SS-6.
- Laboratory measurement of grab samples taken as melt flowed from the melter or directly from the receiver pot.
- Values reported from in-cell tests with samples of the actual radioactive waste prior to each run.
- Assuming 13% holdup of product in the calciner.
- Based on average of heat rate data from feed analysis and pot calorimetry tests.
- Based on pot calorimetry data only.
- Assuming ruthenium not found downstream of solidifier was in product.
- Out-of-reactor time for fuel with some heat generation rate and exposed to 20,000 MWd/tonne at 15 MW/tonne.
- Out-of-reactor time for fuel with some heat generation rate and exposed to 45,000 MWd/tonne at 30 MW/tonne.
- Out-of-reactor time for fuel with some heat generation rate and exposed to 200,000 MWd/tonne at 100 MW/tonne.
- Usually the average of temperatures in Zones 3, 4, and 5.
- Based on average pot temperatures and heat rate density.
- Maximum radiation dose rate from pot measured with unshielded ionization chamber.
- Leakage into the sealed, evacuated receiver pot after a run as determined by a helium leak check using a mass spectrometer type leak detector.

TABLE 9.2. Spray Solidifier Operating Parameters and Results for Runs SS-7 Through SS-13(IPM)

TABLE 9.2. Spray Solidifier Operating Parameters and Results for Runs SS-7 Through SS-13(IPM)

TABLE 9.3. WSEP Auxiliary Operating Parameters and Results During Spray Solidification Runs SS-7 Through SS-13

WSEP Auxiliary Data Spray Solidification Run	SS-7	SS-8	SS-9				SS-10		SS-11	SS-12	SS-13
Operating Mode or Type of Run (a)	A	A	Acid Run 1	PW-4m Run	Acid Run 2	Evap. Run	A	B	A	A	Bm (b)
<u>Evaporator (TK-113) Average Operating Conditions</u>											
Bottoms, M HNO ₃	4.3	4.0	4.0	4.3	4.7	3.4	4.0	3.0	5.7	4.1	3.2
Overheads, M HNO ₃	0.34	0.15	0.2	0.2	0.2	0.04	0.18	0.4	0.4	0.2	0.58
Boiloff Rate, liters/hr	70	77	91	93	110	160	70	130	58	46	78
Strip Water Addition Rate, liters/hr	60	61	96	79	99	170	60	90	45	40	60
Volume, liters - Start	415	342	212	321	301	271	312	450	756	414	390
- End	418	330	321	301	271	284	450	320	87	329	350
E-111 Water Spray - liters/hr	-	60	-	53	-	-	-	-	-	40	-
<u>Fractionator (TK-115) Average Operating Conditions</u>											
Bottoms, M HNO ₃	7.9	8.7	6.7	8.1	7.6	8.5	7.4	7.0	9.1	8.2	8.0
Overheads, M HNO ₃	0.07	0.04	<0.07	0.06	0.04	<0.01	0.04	0.03	0.1	0.01	0.008
Boiloff Rate, liters/hr	66	77	89	88	95	170	65	140	56	42	64
Reflux Ratio	0.2	0.2	0.28	0.28	0.26	0.15	0.4	0.2	0.28	0.30	0.40
Volume, liters - Start	389	540	530	555	779	975	428	635	570	410	371
- End	652	547	555	779	975	876	635	678	637	556	646
<u>Fractionator Distillate Receiver (TK-116)</u>											
Bottoms, M HNO ₃ - Start	0.03	0.03	5.6	5.2	0.17	5.7	0.25	0.29	<0.01	<0.001	<0.001
- End	0.05	0.04	5.2	0.17	5.7	6.1	0.29	0.05	0.06	0.01	0.006
Volume, liters - Start	246	290	463	276	441	261	226	178	206	414	771
- End	544	822	276	857	216	257	178	555	719	473	841
<u>Off-Gas Scrubber (TK-118)</u>											
Recirculation Rate, liters/min	<30	30	30	30	30	30	30	30	30	30	30
Bottoms, M NaOH - Start	2.00	0.06	2.0	1.4	0.01	<0.001	1.9	1.4	0.44	1.58	2.06
- End	0.037	0.09	1.4	0.01	<0.001	<0.001	1.4	0.8	<0.01	0.42	1.39
Volume, liters - Start	397	732	476	533	733	771	484	448	423	441	459
- End	466	806	533	714	771	810	448	477	419	559	450
<u>Solidifier Condensate Receiver (TK-117)</u>											
Bottoms, M HNO ₃ - Start	-	-	-	-	-	-	-	-	-	-	3 × 10 ⁻⁴
- End	-	-	-	-	-	-	-	-	-	-	0.34
Volume, liters - Start	-	-	-	-	-	-	-	-	-	-	455
- End	-	-	-	-	-	-	-	-	-	-	745
Accumulation Rate - liter/hr	-	-	-	-	-	-	-	-	-	-	14.5

a. Equipment arrangements for Mode A and Mode B are shown in Figures 9.1 and 9.2, respectively.

b. Bm = modified Mode B operation. The solidifier condensate was routed to a separate receiver (TK-117) 2M nitric acid was added to the evaporator roughly at the same rate of condensate produced to simulate the condensate.

TABLE 9.4. Overall Material Balances for Spray Solidification Runs SS-7 Through SS-13

		SS-7	SS-8	SS-9		SS-10	SS-11	SS-12	SS-13
				Acid Run I	PW-4m Run	Acid Run II			
Feed to Solidifier (TK-114)	Initial, liters	926	970	—	915	—	840	390	500
	Final, liters	87	119	—	123	—	90	207	198
	Net Change, liters	-839	-851	—	-792	—	-750	-183	-302
	kg	-1091	-995	—	-1021	—	-940	-202	-381
	N, kg	-45	-17.2	—	-45.1	—	-25.3	-20.3	-17
Feed to Auxiliary Evaporator (TK-112) (Mode B Operation)	Initial, liters	—	—	—	—	—	776	—	—
	Final, liters	—	—	—	—	—	80	—	—
	Net Change, liters	—	—	—	—	—	-696	—	—
	kg	—	—	—	—	—	-737	—	—
	N, kg	—	—	—	—	—	-16.3	—	—
Solidifier Condensate Receiver (TK-117)	Initial, liters	—	—	—	—	—	—	—	455
	Final, liters	—	—	—	—	—	—	—	745
	Net Change, liters	—	—	—	—	—	—	—	290
	kg	—	—	—	—	—	—	—	290
	N, kg	—	—	—	—	—	—	—	5.3
Auxiliary Evaporator (TK-113)	Initial, liters	415	378	212	321	332	312	756	414
	Final, liters	418	305	321	301	271	320	87	329
	Net Change, liters	3	-73	321	-20	-61	8	-669	-85
	kg	-1	-87	109	-20	-56	10	-871	-110
	N, kg	3	-6.2	—	1.5	—	1.6	-38.9	-10
Fractionator (TK-115)	Initial, liters	389	517	530	555	781	428	570	410
	Final, liters	652	565	555	779	975	478	637	556
	Net Change, liters	263	48	25	224	194	250	67	146
	kg	309	67	38	287	204	291	109	164
	N, kg	35.8	17	—	12.8	—	17.9	35.3	15
Fractionator Condenser (E-115)	Initial, liters	—	—	109	33	67	49	42	50
	Final, liters	—	—	33	67	17	49	48	50
	Net Change, liters	—	—	-76	34	-50	0	6	0
	kg	—	—	-76	34	-50	0	6	0
									-39
Fractionator Distillate Receiver (TK-116)	Initial, liters	246	307	463	276	441	226	206	414
	Final, liters	554	830	276	857	216	555	719	473
	Net Change, liters	298	523	-187	581	-180	329	513	159
	kg	298	523	-204	581	-180	329	513	59
	N, kg	0.2	0.2	—	1.2	—	0.4	0.6	0.1
Off-Gas Scrubber (TK-118)	Initial, liters	397	732	476	533	733	484	423	441
	Final, liters	466	808	533	714	771	477	419	559
	Net Change, liters	69	76	57	181	38	-7	-4	118
	kg	41	76	55	181	38	-10	-4	89
	N, kg	8.0	1.7	—	12.0	—	5.2	3.0	6.4
Product	Initial, liters	3	0	—	0	—	0	0	0
	Final, liters	65	59	—	76.6	—	56	63	54
	Net Change, liters	62	59	—	76.6	—	56	63	54
	kg	197	195	—	189	—	176	186	162
									150
Net Change	Volume, liters	-144	-218	-72	276	-59	-192	-207	0.02
	Mass, kg	-247	-221	-83	44	-40	-273	-263	-17
	N, kg	2	-4.5	—	-21.3	—	-16.5	-20.3	-5.5
Percent Recovery of Feed	Volume, liters	94	92	96	110	97	94	91	100
	Mass, kg	91	93	96	101	98	93	90	99
	N, kg	104	95	—	85	—	86	66	68

TABLE 9.5. Feed Pump Experience During WSEP Spray Solidification Runs

Pump ^(a) No.	Service, Runs	Feed Type	Hours	Run Date	Remarks
P-12	SS-4	PW-2	42	9/12/68	P-12 failed after 297 hr of operation during a flushing operation following Run SS-8.
	SS-5	PW-1	45	10/16/68	
	SS-6	PW-1	77	11/4/68	
	SS-7	PW-1	65	12/9/68	
	SS-8	PW-1	68	2/3/68	
			297	Total	
P-14	SS-9	PW-4m	61	2/25/69	P-14 failed during subsequent use with the phosphate glass process.
	SS-10	PW-4m	65	3/25/69	
			126		
P-17	SS-11	LMFBR	50	2/24/70	P-17 was used 68 hr during Run PG-11. P-17 was not used after Run SS-12 and did not fail.
	SS-12	PW-4m	36		
			154		
P-18	SS-13	PW-4m	36	5/11/70	P-18 was used 83 hr during Runs PC-7 and PC-8 and did not fail.

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

ARRANGEMENT FOR RUNS SS-7, 8, 9, 11 AND 12(IPM)

FIGURE 9.1. Equipment Arrangement for Mode A Spray Solidification Runs

ARRANGEMENT FOR RUNS SS-10 and SS-13(IPM)

FIGURE 9.2. Equipment Arrangement for Mode B Spray Solidification Runs

H-3-21001

FIGURE 9.3. WSEP Solidification Equipment Flow Diagram

FIGURE 9.4. WSEP Auxiliary Equipment Flow Diagram

FIGURE 9.5. WSEP Auxiliary Evaporator and Fractionator Operating Parameters During Run SS-7

FIGURE 9.6. WSEP Auxiliary Evaporator and Fractionator Operating Parameters During Run SS-8

FIGURE 9.7. WSEP Auxiliary Evaporator and Fractionator Operating Parameters During Run SS-9

FIGURE 9.8. WSEP Auxiliary Evaporator and Fractionator Operating Parameters During Run SS-10

FIGURE 9.9. WSEP Auxiliary Evaporator and Fractionator Operating Parameters During Run SS-11

FIGURE 9.10. Auxiliary Evaporator and Fractionator Operating Parameters During Run SS-12

FIGURE 9.11. Auxiliary Evaporator and Fractionator Operating Parameters During Run SS-13

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

FIGURE 9.12. Schematic Diagram of Ventilation System for Process Off-Gases (Also see Figure 5.1.)

The steady-state pot centerline temperature in the air-cooled furnace was 920 °C and the centerline-to-wall temperature difference was 453 °C. These values calculate out to give an effective thermal conductivity of $1.16 \text{ W/(m}^2)(^\circ\text{C/m)}$ [$0.67 \text{ Btu/(hr)(ft}^2)(^\circ\text{F/ft)}$] for the ceramic product. Pot centerline and wall temperatures while hanging in air were 900 and 425 °C, respectively, and represent a thermal maximum pot in air.

The solidifier was fed 839 liters of adjusted PW-1 feed at 452 liters/tonne in 47 hours at an average feed rate of 17.9 liters/hour. The feed containing 3,620,000 curies of radioactivity including 22,200 curies of radioactive ruthenium was reduced in volume by a factor of 13.5, or 11.3 on a 378 liters/tonne basis.

Difficulty was experienced during the first 23 hours of the run with feed control as the magnetic flowmeter was inoperable and manual feed control was required. The atomizing feed nozzle became partially plugged as a result and a four-hour shutdown was required to unplug it. The nozzle was flushed by adding small amounts of nitric acid directly to the atomizing air. The flowmeter was made operable during the shutdown and the last 24 hours of the run was completed trouble-free using automatic feed control. No indication of wall scaling in the solidifier was given by the solidifier internal and wall temperatures. The floating-type pneumatic vibrator on top of the solidifier removed the calcine powder successfully from the drying chamber.

The filter pressure drop averaged about 5 inches of water throughout the run indicating that the blowback system performed quite satisfactorily. The melter furnace operated at 1125 °C with an internal melt temperature of 1060 °C. The melter was batch dumped through the drain freeze valve 11 times in about

6 liter batches at 5 to 6 hour intervals. The average processing rate was 0.94 tonne/day. The pot furnace was not used during Run SS-7 and no stalagmites formed in the pot.

During the entire run, 61% of the ruthenium and 2.7% of the other combined radioactive species in the feed to the solidifier accumulated in the WSEP evaporator. The accumulation of the nonvolatile radioactive species was a factor of forty higher than the entrainment during SS-5 and SS-6. This high value was partially caused by a feed line flush which occurred after 23 hours of feed-on time (radioactivity in the feed line was flushed to the evaporator) but was primarily due to a poorly seated valve (feed tank to evaporator intertie) which is normally closed. This valve between the feed line and the evaporator was leaking a small stream of feed into the evaporator. Therefore, about 59% of the ruthenium fed to the solidifier was volatilized and less than 1% of the nonvolatile species were entrained from the solidifier.

The solidifier condenser absorbed 64% of the nitrogen volatilized from the solidifier while the remaining 36% was probably present as oxides of nitrogen and carried through the condenser in the gas phase.

An equivalent of 1.2% of the ruthenium fed to the solidifier accumulated in the fractionator. This ruthenium volatilized from the auxiliary evaporator and some was carried through the evaporator in the gas phase.

The cumulative decontamination factor, DF_C , across the WSEP auxiliary evaporator for ruthenium was 52. Instantaneous DF_i 's ranged from 5.1×10^2 to 1.3×10^3 . Again, as in previous runs, a nearly constant buildup of ruthenium in the acid fractionator indicated a direct gas phase flow of ruthenium from the solidifier condenser to the evaporator condenser.

Cumulative DF for $^{144}\text{CePr}$ representing nonvolatiles was 9.8×10^2 across the evaporator. Instantaneous DF's ranged from 2.5×10^3 to 4.1×10^4 .

The DF across the fractionator for ruthenium was 4.8×10^3 and for $^{144}\text{CePr}$ was 5.8×10^3 . Instantaneous DF's for ruthenium averaged greater than 10^3 and agreed with the cumulative value.

The final condensate stream contained a fraction of equivalent feed radioactivity equal to 2.9×10^{-6} for ruthenium and 4.7×10^{-10} for $^{144}\text{CePr}$. These values were above 10CFR20 release limits by factors of 1×10^4 and 2.2×10^2 , respectively. Fractional losses of radioactivity by the off-gases to the stack were well below the 10CFR20 release limits. The off-gas to the stack is measured after it is combined and significantly diluted by the building ventilation.

Run SS-8

The eighth demonstration of the spray solidification process was completed during February 1969. Run SS-8 was the sixth and final radioactive demonstration of the spray solidification process with a PW-1 (sulfate-free) waste flowsheet. During Run SS-8, simulated Purex waste equivalent to that resulting from the reprocessing of 1.7 tonne of power reactor fuel (20,000 MWd/tonne at 15 MW/tonne) with an equivalent aging time of 1.2 years was interfused in 170 kilograms of solid waste product. The 59 liters of solid waste produced a heat-rate density of 120 W/liter (7200 watts total based on the average of feed analysis and data pot calorimetry tests) in an 8-inch diameter 304L stainless steel product receiver pot. The average steady-state pot centerline temperature in the air-cooled furnace was 605 °C with an average centerline-to-wall temperature drop of 210 °C. The heat-rate density and temperature drop indicate an effective thermal conductivity of $1.4 \text{ W/(m)}^2 (\text{°C/M}) [0.82 \text{ Btu/(hr)} (\text{ft}^2) (\text{°F/ft})]$ for the phosphate ceramic product.

The solidifier was fed 800 liters of low acid, PW-1 waste at 473 liters/tonne in 55 hours. Feed additives included NaOH, LiOH, and H_3PO_4 . The feed contained 1,830,000 curies of radioactivity including 14,400 curies of ruthenium.

About 14 hours into the run, the feed flow and the air flow to the atomizing nozzle began to fluctuate and remained erratic throughout the run except during the half-hour period about midway through the run while feeding water to the spray calciner. The flow of calcine from the spray calciner into the melter became erratic after 27 hours of processing feed and progressively worsened. After 54 hours of calcining feed, the flow of calcine into the melter stopped completely due to a bridge of calcine in the calciner cone over the melter inlet nozzle. The feed was shut off to the calciner after trying, unsuccessfully, for an hour to dislodge the bridge of calcine with the calciner vibrator. The vibrator was actuated manually with an air supply pressure of 60 psig and continuous operations for up to 1.5 minutes, but no appreciable quantity of calcine fell into the melter. The melter vacuum decreased sharply about 1 to 2 inches of water below the calciner vacuum at time the calcine bridged over in the calciner cone. Also, the temperature in the calciner cone began to rise steadily after the plug developed. The filter pressure drop remained nearly constant and no change was observed in the main calciner temperatures. These combined evidence indicated the problem was limited to the area of the calciner cone and that no major scale-up problems were involved in either the calciner drying or filter chambers.

The filter pressure drop averaged about 4 to 5 inches of water throughout the run indicating that the blowback system performed quite satisfactorily.

While the spray calciner was cooling down, the bridge of calcine was broken by rodding and an estimated 20 kilograms of calcine was brought down using the calciner vibrator. The calcine appeared free-flowing and no chunks were observed. Two additional batches of melt were made with each batch held for about two hours at 1000 °C to 1100 °C before being drained to the receiver pot.

An inspection of the calciner after the run revealed that some scale on the calciner drying chamber walls had occurred since the previous inspection (prior to Run SS-7), but not to the extent that special cleaning was necessary.

The melter furnace was operated at a temperature of 1170 °C and the melter was discharged batchwise through the drain freeze-valve in batches of 5 to 7 liters. The melt drained into the pot receiver at an average rate of 52 liters/hour and the drain freeze-valve was resealed within 5 minutes following each batch dump. A total of 10 melt samples were taken during the run with four samples taken from one melt batch at spaced intervals. The analyses of the melt samples indicated that the radio-nuclides were uniformly distributed throughout each batch of melt and throughout the total melt drained into the unheated melt receiver during the run.

Prior to the run, the simulated PW-1 waste including the phosphoric acid additive was acid-stripped in the auxiliary evaporator. After the stripping operation and the addition of the sodium and lithium hydroxide additives, the total acidity of the feed had been reduced from a nominal 9M to 1.6M (based on 378 liters/tonne). Despite the factor of five reduction in feed acidity, 35% of the ruthenium in the feed to the solidifier was volatilized during Run SS-8. Although this represents a reduction from the 50 to 70% volatility experienced

in previous spray solidifier runs with the PW-1 flowsheet, it did not bear out the strong dependence of ruthenium volatility on feed acidity found in nonradioactive spray solidifier studies (see Section 3.4).

As in previous spray solidification runs, there was an excessive rate of ruthenium accumulation in the acid fractionator, in the fractionator distillate receiver, and in the scrubber indicating a direct gas phase flow of ruthenium from the solidifier condenser through the auxiliary equipment. Also as during previous runs, the concentration of ruthenium in the off-gases leaving the solidifier condenser was about an order of magnitude higher during the first hour of the run than during the remainder of the run. From 20 to 25% of the total ruthenium collected in the acid fractionator accumulated during the first hour of the run (i.e. during less than 2% of the total elapsed run time). This initial 20%/hr accumulation rate was significantly greater than the nearly constant ruthenium accumulation rate of 1.2%/hr for the last 45 hours of the run. Based on "steady-state" ruthenium accumulation rate for the acid fractionator, about 25 to 35% of the total ruthenium gained in the acid fractionator was due to startup (transient) conditions and would not be present in a truly continuous run. Similar "transient" accumulation rates were observed for the fractionator distillate receiver and the WSEP scrubber. The cause of the transient ruthenium concentration in the solidifier condenser off-gases is not known.

During Run SS-8, it was found that recycling the strip water to the evaporator via the solidifier condenser significantly decreased the rate of ruthenium accumulation in the acid fractionator and in the fractionator distillate receiver. During the first 37 hours of the run about 60 liters/hr of

fractionator distillate was pumped to a spray nozzle in the top (gas inlet end) of the solidifier condenser. The rate of accumulation of ruthenium in the fractionator and in the fractionator distillate receiver was reduced by a factor of 2 to 4 below the rates observed without the water addition to the solidifier condenser.

This reduction indicated that the concentration of ruthenium in the solidifier condenser off-gases was reduced 25 to 50% of the concentration without the water addition. The fraction of $^{144}\text{CePr}$ in the solidifier condenser off-gases were reduced by about a factor of 4 by the water addition and about 20% of the oxides of nitrogen (an additional 10% of the total nitrogen entering the solidifier condenser) was scrubbed by the water addition.

The decontamination factors (DF's) across the evaporator were typical of those obtained with waste in the evaporator bottoms (i.e. a Mode B operation). About 50 liters of the feed consumed accumulated in the evaporator during the run as a result of feed leaking directly into the evaporator through a faulty control valve in the solidifier feed loop. The cumulative DF for ruthenium and $^{144}\text{CePr}$ across the WSEP auxiliary evaporator was 1.1×10^2 and 2.4×10^4 , respectively. The instantaneous DF for ruthenium across the evaporator ranged from 5.2×10^2 to 1.0×10^3 during the first part of the run (with water spray to solidifier condenser), increased to 5.2×10^3 during the latter part of the run, and increased to 4.4×10^4 after the feed was off to the solidifier.

The instantaneous DF for nonvolatiles represented by $^{144}\text{CePr}$ was about 3×10^5 during the first part of the run, about 3×10^6 during the last part of the run, and increased to about 5×10^6 after the feed was off to the solidifier.

The cumulative DF across the fractionator for ruthenium and for $^{144}\text{CePr}$ was 7.8×10^2 and 2.3×10^3 , respectively. The instantaneous DF across the fractionator for ruthenium ranged from 7.0×10^2 to 2.0×10^3 during the first part of the run, decreased to 4.6×10^2 during the last part of the run, and increased to 5.1×10^3 after the feed was off to the solidifier. The instantaneous DF across the fractionator for $^{144}\text{CePr}$ ranged from 20 to 80 during the first part of the run, decreased to about 2 during the last part of the run, and was 80 after the feed was off to the solidifier.

The fractionator distillate accumulated a fraction of the total equivalent feed radioactivity equal to 5.7×10^{-6} for ruthenium and 1.2×10^{-9} for $^{144}\text{CePr}$. The concentrations of ^{106}Ru and $^{144}\text{CePr}$ in the fractionator distillate at the end of the run were above 10CFR20 release limits by factors of 1.4×10^4 and 1.8×10^2 , respectively.

The fractional losses of radioactivity in the off-gases to the stack were less than 2×10^{-10} for ruthenium and less than 5×10^{-13} for nonvolatiles (represented by $^{144}\text{CePr}$). These losses were below 10CFR20 release limits by factors of greater than 4×10^{-4} and greater than 3×10^{-2} , respectively.

Nitrogen analyses of the solidifier condensate accounted for 58% of the total nitrogen volatilized from the solidifier during the first part of the run and for 50% during the last part of the run (without the water addition to the solidifier condenser). The remaining 40 to 50% of the total nitrogen (as oxides of nitrogen) were partially scrubbed in the auxiliary equipment with 10% being removed in the off-gas scrubber which contained distilled water. About 25% of the nitrogen fed to the solidifier was unaccounted for indicating that it escaped with the auxiliary off-gas leaving the scrubber.

Run SS-9

The ninth demonstration of the spray solidification process was completed during March 1969. Run SS-9 was the first radioactive demonstration of the spray solidification process with a PW-4m waste flowsheet. The PW-4m waste was a simulated low-salt, high fission product containing Purex waste equivalent to that resulting from the reprocessing of power reactor fuel irradiated to 45,000 MWd/tonne at a power level of 30 MW/tonne.

During Run SS-9, simulated PW-4m waste equivalent to that resulting from reprocessing 1.26 tonnes of power reactor fuel with an equivalent aging time of 2.3 years was processed to produce 194 kilograms of ceramic product. The 68 liters of radioactive product produced a self-generating heat rate density of 107 W/liter (7200 watts total based on analytical and pot calorimetry data) in an 8-inch diameter 310 stainless steel melt receiver. The average steady-state pot centerline temperature in the air-cooled furnace was 594 °C with an average centerline-to-wall temperature difference of 242 °C. These values indicate an effective thermal conductivity of $1.14 \text{ W/(m}^2\text{)} (\text{°C/m}) [0.66 \text{ Btu/(hr)} (\text{ft}^2) (\text{°F/ft})]$ for the ceramic product.

The solidifier was fed 792 liters of adjusted PW-4m feed (additives of LiOH, NaOH, $\text{Fe}(\text{NO}_3)_3$, and H_3PO_4 at 630 liters/tonne in 52 hrs. The feed containing 2,030,000 curies of radioactivity including 10,200 curies of radioruthenium was reduced in volume by a factor of 11.7 or 7.0 on a 378 liters/tonne basis.

In general, the spray solidifier and its principal components (atomizing nozzle, off-gas filters, and feed control system) performed satisfactorily. Two periods of mechanical difficulty with the pneumatic vibrator were encountered. The feed was interrupted both times with replacement of the vibrator required the final time.

The melter furnace operated at 1175 °C with an average internal melt temperature of 1100 °C. The melt was discharged batchwise 12 times to the receiver pot from the melter via the drain freeze-valve in 5 to 6 liter batches at 4 to 6 hour intervals. The PW-4m melt was considerably more viscous than either PW-1 or PW-2 melts and as a result it took 2 to 3 times longer to discharge the melt than in previous runs. Despite the slower discharge rate, a uniform fill of the unheated receiver pot was attained.

In addition to demonstrating solidification of PW-4m waste, particular emphasis was placed upon the investigation of the distribution of radioactivity in the decontamination equipment (auxiliaries) located downstream of the spray solidifier. A total of 57% of the ruthenium fed to the solidifier was volatilized or entrained and then collected in the WSEP auxiliary evaporator. Instantaneous values ranged from 54% to 56% and agreed with the cumulative value. On the other hand, only 0.022% of the nonvolatiles (represented by $^{144}\text{CePr}$) were entrained from the solidifier. The cumulative decontamination factor (DF_c) across the auxiliary evaporator for ruthenium was 87. Instantaneous DF's for ruthenium ranged from 3.4×10^2 to 1.9×10^3 . Corresponding values for $^{144}\text{CePr}$ (representing nonvolatiles) ranged from 5.2×10^3 to 1.8×10^4 .

A total of 0.65% of the equivalent ruthenium fed to the solidifier accumulated in the acid fractionator. This was a factor of about 2 less than that accumulated during Run SS-7. The cumulative DF across the fractionator for ruthenium was 6.5×10^2 . The instantaneous ruthenium DF's ranged from 5×10^2 to 5.8×10^3 .

Review of data had suggested that the source of at least part of the ruthenium collected in auxiliary system components during runs was not that fed to the solidifier, but material

plated or trapped on filters, pipe walls, etc. In an attempt to "decontaminate" and qualitatively define the extent of this material, 188 liters of 5.6M nitric acid and 180 liters of 6M nitric acid were fed to the solidifier before and after the radioactive feed portion of SS-9, respectively. The acid flow rate was about 15 liters/hour. Review of data indicated that ruthenium buildup in auxiliaries during these acid or nonradioactive feed periods was negligible when compared to the radioactive feed portion of Run SS-9.

Instantaneous ruthenium DF's for the evaporator during the above two acid runs ranged from 2.8×10^4 to 1.9×10^5 . The fact that better decontamination factors are attained without radioactive feed supports the assumption initially based on a nearly linear accumulation of ruthenium in the acid fractionator, that much of the contamination of equipment downstream of the evaporator is the result of a noncondensable gas stream from the solidifier. This gas stream results in the deposition in the fractionator distillate and the aqueous phase of the scrubber of about 2.6×10^{-6} and 1.8×10^{-5} of the ruthenium fed to the solidifier, respectively. During the last 12 hours of the radioactive portion of Run SS-9, fractionator distillate was added as a spray to the process condenser (installed directly downstream of the solidifier and between the solidifier and auxiliary evaporator). No obvious scrubbing effect was attained with this technique.

After the final acid run, a 12-hr acid strip of the auxiliary evaporator bottoms was performed. The instantaneous ruthenium DF's during this period ranged from 5.6×10^3 to 2.7×10^4 . The DF's averaged 10 times greater than during the feed-on period. However, these values were well below the expected values for ruthenium DF's.

The final distillate stream contained an equivalent fraction of feed radioactivity equal to 2.7×10^{-6} for ruthenium. The concentration of ruthenium was above the 10CFR20 release limit by a factor of 4.6×10^3 . The $^{144}\text{CePr}$ in the distillate was not detectable and therefore was assumed to be at least 100 times less than the ruthenium value.

During Run SS-9 work was also begun on gas sampling techniques in attempts to provide engineering-scale data that would permit better definition of the type, form, and extent of radioactivity present in the process off-gas streams. Gaseous effluent from the scrubber was sampled for both particulate and volatile forms of activity by routing a side stream of the effluent through first a glass fiber filter and then a 2M KOH solution. Analysis of filters revealed that the primary contributor to the "particulate" activity is ^{106}Ru . The scrub solution contained a negligible amount of radioactivity indicating that no volatile components were leaving the final process off-gas or that the ruthenium was adsorbed on the filters. Calculations indicated that the order of magnitude for the ^{106}Ru concentration in the process off-gas was $10^{-8} \text{ } \mu\text{Ci/cm}^3$, while that for $^{144}\text{CePr}$ was about a factor of 10 less. These radionuclide concentrations were above 10CFR20 release limits by 50 and 3.2 for ruthenium and $^{144}\text{CePr}$, respectively. The process off-gases are filtered, combined, filtered again, and significantly diluted (factor of about 2.9×10^3) before entering the stack for discharge to the atmosphere. After the filtration and dilution, the ratio to 10CFR20 release limits was 1.7×10^{-1} for ruthenium and 1.1×10^{-2} for $^{144}\text{CePr}$.

Run SS-10

The tenth demonstration of the spray solidification of high-level radioactive waste was completed during April 1970.

During Run SS-10, a simulated low-salt, high fission product Purex waste (PW-4m) equivalent to that resulting from the reprocessing of 1.23 tonne of power reactor fuel (45,000 MWd/tonne at 30 MW/tonne) with equivalent aging time of 1.9 years was processed.

The solidifier was fed 750 liters of PW-4m feed (additives of $\text{Fe}[\text{NO}_3]_3$, $\text{Al}[\text{NO}_3]_3$, LiOH , NaOH , and H_3PO_4) at 611 liters/tonne in 55.5 hours. The feed contained 2,582,000 curies of radioactivity including 13,100 curies of ruthenium.

During the run the flow of calcine from the spray calciner into the melter was difficult to maintain and was more erratic than in previous runs. Early in the run the feed was interrupted to rod out what was thought to be a partial calcine bridge in the conical bottom outlet of the calciner. However, the rodding dislodged very little calcine, and increased vibration of the calciner was required for the remainder of the run to maintain calcine flow to the melter. The filter pressure drop also increased from 5 to 9 inches of water during the run despite increasing the filter blowback pressure. This was the first time since Run SS-3 that a significant increase in filter pressure drop had occurred during a run.

During the majority of the run the atomizing air pressure control to the internal-mix spray nozzle was somewhat erratic and as a result caused the atomizing air flow to vary as much as 20%. Although the exact cause of the poor air pressure control is not known, it was probably the result of a number of things including feed flow fluctuations and decreased sensitivity of the pressure control system.

An inspection of the inside of the solidifier was made after the run. Calcine deposits were found in the conical

bottom section of the calciner and considerable deposition was noted in the filter chamber, as caked calcine was lodged around the bottom section of the filters. This would explain the erratic calcine flow and the increase in filter pressure drop during the run. The calciner drying-chamber walls were relatively clean.

In all cases, the deposits appeared to be the result of wet calcine depositing and drying to form a cake. These deposits suggest inadequate feed atomization which was probably the result of the erratic atomizing air flow during the run. This performance points out the importance of controlling the atomizing air and feed flow rates.

Based on pot calorimetry tests and volume reduction data it was estimated that approximately 13% of the product accumulated in the calciner as a result of the deposition during the run. A thorough flush of the system was required prior to resuming spray solidifier operation.

The melter furnace was operated at a temperature of 1190 °C and was discharged batchwise through the drain freeze-valve in melt batches of 5 to 6 liters. The melt was quite viscous as in Run SS-9 and the melter drain rate averaged approximately 24 liters/hr. Although an adequate fill of the unheated receiver pot was attained, the filling rate during the run probably represents the minimum for an unheated receiver with PW-4m melt without serious stalagmite formation problems.

The 8-inch diameter mild steel pot was filled with 56 liters of radioactive ceramic product which calorimetry measurements indicated had a heat generation rate of 7400 watts. The steady-state centerline temperature in the air-cooled furnace was 611 °C and the centerline-to-wall temperature difference was 262 °C. These values indicate an effective thermal conductivity of $1.30 \text{ W/(m}^2)(\text{°C/m})$ [$0.75 \text{ Btu/(hr)(ft}^2)(\text{°F/ft})$] for the ceramic product.

During the last third of Run SS-10, operation was changed from Mode A to Mode B by feeding 776 liters of Purex high-level waste (LWW) from the evaporator feed tank (TK-112) to the waste evaporator (TK-113).

Forty-five percent of the ruthenium in the feed processed during Mode A was volatilized from the solidifier. This indicated that a factor of two reduction in the total acidity of the feed during an acid strip prior to the run did not significantly reduce ruthenium volatility from the solidifier. Only 0.08% of the $^{144}\text{CePr}$ representing the nonvolatiles in the feed processed during Mode A was entrained from the solidifier.

Nitrogen analysis of the solidifier condensate indicated that approximately 50% of the nitrogen fed to the solidifier was present in the condensate. The remaining 50% of the nitrogen apparently carried through the condenser as nitrogen oxides.

The instantaneous ruthenium decontamination factors (DF's) across the evaporator during Mode A were a factor of 75 to 100 below instantaneous DF's observed while acid stripping waste solution both before and after feeding the solidifier. This would indicate that the majority of the ruthenium in the evaporator overheads during Mode A was the result of ruthenium being carried through in the gas phase from the solidifier condenser. A total of 0.4% of the ruthenium in the feed processed during Mode A accumulated in the fractionator indicating a cumulative ruthenium DF of 1.2×10^2 across the evaporator during Mode A. The cumulative DF for nonvolatiles across the evaporator during Mode A was 1.7×10^4 .

During Mode B the ruthenium accumulation rate in the fractionator increased by a factor of 2.5 over that during Mode A and indicated an appreciable increase in the ruthenium

volatilized from the evaporator. The increase in ruthenium evolution was due to the increased evaporator acidity, ruthenium concentration, and boilup rate during Mode B. Although 0.78% of the ruthenium in the feed processed during Mode B accumulated in the fractionator which was a factor of 2 higher than during Mode A, it was within the range of Mode A data attained from previous runs. The cumulative DF's during Mode B for ruthenium and nonvolatiles were 3.7×10^2 and 3.3×10^5 , respectively.

The cumulative DF across the fractionator was 1.2×10^3 for both ruthenium and nonvolatiles for the total run.

A total of $4.8 \times 10^{-4}\%$ of the ruthenium and $1.9 \times 10^{-8}\%$ of the nonvolatiles fed to the solidifier accumulated in the fractionator distillate receiver during the run. The concentration of radionuclides in the distillate were above the 10CFR20 release limits by factors of 4.9×10^3 for ^{106}Ru and 1.3×10^2 for $^{144}\text{CePr}$ representing nonvolatiles.

At the end of the run, $3.2 \times 10^{-3}\%$ of the ruthenium and less than $7 \times 10^{-8}\%$ of the nonvolatiles fed to the solidifier were present in the off-gas scrubber. The accumulation rate of ruthenium in the scrubber during the run was unaffected by the change from Mode A to Mode B and essentially ceased during an end-of-run acid strip after the feed had been turned off to the solidifier. This along with the fact that approximately seven times as much ruthenium accumulated in the scrubber during the run than in the fractionator distillate receiver indicated that considerable ruthenium was carried through the auxiliaries with the noncondensable gas stream. A total of 21% of the nitrogen fed to the solidifier also accumulated in the scrubber during the run.

The average concentration of radionuclides in the solidifier condenser off-gas was $6.4 \times 10^{-2} \mu\text{Ci}/\text{cm}^3$ for ^{106}Ru and $1.0 \times 10^{-3} \mu\text{Ci}/\text{cm}^3$ for $^{144}\text{CePr}$ as obtained from gas samples taken during the run. The radionuclides in the solidifier condenser off-gas could account for the majority of the ruthenium accumulated in the fractionator.

Gas samples of gaseous effluent from the scrubber (TK-118) were also taken during the run. The results of the sampling suggest that the ^{106}Ru and $^{144}\text{CePr}$ concentrations in the off-gas exceeded 10CFR20 release limits by factors of 1200 and 2100, respectively. However, when the scrubber off-gas was filtered and combined with building ventilation air, the radioactivity released with the off-gas to the stack was well below 10CFR20 limits.

Run SS-11

The eleventh demonstration of the spray solidification process was completed during March 1970. Run SS-11 was the first spray solidifier run with LMFBR waste; however, the waste as processed was not too different from the PW-4m waste that was demonstrated in Runs SS-9 and SS-10. Differences were a slightly changed fission product spectrum and the addition of selenium, tellurium, antimony, and tin since these elements become more significant in the higher burnup fast reactor fuels. The completion of Run SS-11 marked the completion of the radioactive spray solidifier runs using a high temperature platinum melter.

During Run SS-11, a simulated waste equivalent to that resulting from the reprocessing of 0.54 tonne of LMFBR core fuel (100,000 MWd/tonne at 200 MW/tonne) with an equivalent aging time of 2.2 years was processed to produce 186 kilograms

of ceramic product. The 60 liters of radioactive ceramic produced a heat rate density of 175 W/liter (10,500 watts total based on analytical and pot calorimetry data) in an 8-inch diameter 304L stainless steel melt receiver. The steady-state pot centerline temperature in the air-cooled furnace was 759 °C, and the centerline-to-wall temperature difference was 353 °C. These values indicated an effective thermal conductivity of $1.28 \text{ W/(m}^2)(^{\circ}\text{C/m)}$ [$0.72 \text{ Btu/(hr)(ft}^2)(^{\circ}\text{F/ft)}$] for the ceramic product.

The solidifier was fed 669 liters of adjusted LMFBR feed (additives of NaOH, $\text{Fe}[\text{NO}_3]_3$, and H_3PO_4 based on 378 liters/tonne) at 1230 liters/tonne in 45 hr. The feed containing 3,110,000 Ci of radioactivity including 14,400 Ci of radioactive ruthenium was reduced in volume by a factor of 11.2 or 3.4 on a 378 liters/tonne basis.

The operation of the spray solidifier was very smooth. The principal process factors (atomization, filter operation, atomizing air and feed flow control) performed very satisfactorily. A newly installed atomizing nozzle with improved atomizing air pressure control produced the steadiest internal calciner temperatures and calcine fall to the melter that was observed during the radioactive spray runs. An inspection of the inside of the solidifier after the run revealed that essentially no deposition of calcine occurred during the run.

During the run 73% of the ruthenium in the feed processed was volatilized from the solidifier. Although the ruthenium volatility was higher than in some previous runs, it was in general expected for the phosphoric-acid-containing feed. Only 0.013% of the nonvolatiles in the feed processed during the run were entrained from the solidifier. This represents a cumulative decontamination factor (DF) for nonvolatiles across the solidifier off-gas filters of 7.7×10^3 which is in agreement with instantaneous DF's which ranged from 2.9×10^3 to 6.0×10^4 .

The LMFBR melt was batch discharged from the melter via the drain freeze-valve into the unheated stainless steel receiver pot. The melter drain rate during discharge averaged approximately 34 liters/hr which is about a 40% faster drain rate than that attained with PW-4m melt during Run SS-10. Although it was necessary to reduce the melter temperature approximately 50 to 100 °C after each dump to seal the freeze-valve and stop the melter from dripping, an even fill of the receiver pot was achieved.

Following the run the platinum melter was removed from the melter furnace and it was found that the melter had four large indentations in the side of it as shown in Figure 4.11. The melter at the time of removal had experienced approximately 650 hours of intermittent service with temperatures ranging from 900 to 1200 °C and pressures of -25 to +10 inches of water. The melter had been visually examined prior to Run SS-5 after approximately 220 hours of service, and it had one slight indentation located in the same area as the indentation labeled Number 2 in Figure 4.11, but it was considerably less pronounced. The exact cause of the distortion of the platinum melter was not determined. A similar distortion of a platinum melter occurred at Brookhaven National Laboratory and was attributed to the negative melter operating pressure and the reduced creep resistance of the platinum caused by the long process exposures. A subsequent Brookhaven melter was fabricated with increased wall thickness and stiffener rings welded to the outside melter wall to increase strength.

Auxiliary system performance improved substantially during Run SS-11 with the addition of a new modified solidifier condenser and condenser off-gas filtering system. This system was added prior to Run SS-11 to improve decontamination of the

solidifier off-gas. The bottom half of the condenser tubes were filled with Pall rings (reduced from 5/8-inch to 1/2-inch diameter by mechanical press) to improve the condenser performance by providing additional surface for scrubbing and breaking up the laminar gas flow in the condenser tubes. Filling the tubes completely would have substantially increased the pressure drop across the condenser to a point that vacuum requirements for the spray solidifier could not be met.

During Run SS-11, 73% of the ruthenium in the feed to the solidifier volatilized and accumulated in the auxiliary evaporator while only 0.013% of the $^{144}\text{CePr}$ representing non-volatiles entrained from the solidifier. Cumulative decontamination factors (DF_c 's) based on gas sample data across the solidifier condenser were 1400 for ^{106}Ru and 6500 for $^{144}\text{CePr}$. This was an improvement over previous results by factors of 10 to 100. Instantaneous DF 's across the solidifier condenser off-gas filter were 2.0×10^3 for ^{106}Ru and 36 for $^{144}\text{CePr}$. The latter value for $^{144}\text{CePr}$ is lower than expected (typically should be greater than 10^3) which could indicate some internal contamination in sample lines and gas samplers or possibly a bad filter.

Volatilization of the LMFBR fission product tellurium was determined to be 0.1% of the total fed to the solidifier. This agreed with nonradioactive data where 0.1 to 0.5% of the tellurium volatilized from the solidifier.

The accumulation of ruthenium in the auxiliaries was generally typical of previous runs. However, the ruthenium accumulation in the fractionator was not linear as was the case in previous spray solidification runs. The ruthenium accumulation leveled out after an initial jump early in the run. Basing the accumulation in the fractionator on the evaporator

condensate stream samples, the total accumulation should have been a factor of 20 less. This fact indicates that the ruthenium accumulation may have been caused primarily by internal contamination (radionuclide deposition in pipes, etc.) early in the run.

Decontamination of the solidifier condensate was generally better than in previous spray solidification runs. Instantaneous ruthenium DF's across the auxiliary evaporator including the evaporator condenser, ranged from 4.4×10^3 to 1.3×10^5 , but still no apparent correlation between instantaneous ruthenium DF's and evaporator overhead acidity. Previously, this would have indicated that ruthenium was being carried through the evaporator in the gas phase from the solidifier condenser and not the result of being volatilized from the evaporator. However, gas sample data from the solidifier condenser off-gas filter indicated that only a small amount of radionuclides were in the noncondensable process off-gas to the evaporator. Therefore, the noncorrelation probably is attributed to oxides of nitrogen not being scrubbed out completely by the solidifier condenser. The solidifier condenser stopped only 37% of the total nitrogen in the solidifier off-gas. Part of the remaining 63% was scrubbed out by the evaporator condenser increasing the evaporator acidity, and resulting in no correlation between ruthenium instantaneous DF's and evaporator overhead acidity. The low $^{144}\text{CePr}$ instantaneous DF's (2.9×10^2 to 2.4×10^3) were attributed to some internal contamination of the auxiliary systems.

Ruthenium equivalent to $2.1 \times 10^{-1}\%$ of that fed to the solidifier accumulated in the fractionator indicated a cumulative ruthenium DF of 350 across the evaporator, and that less than $4 \times 10^{-5}\%$ of the $^{144}\text{CePr}$ representing nonvolatiles accumulated in the fractionator indicated a cumulative DF for

nonvolatiles of greater than 350. The cumulative DF's across the fractionator was 6.3×10^2 for ^{106}Ru and 1.3×10^3 for $^{144}\text{CePr}$.

The concentration of radionuclides that accumulated in the fractionator distillate (80% of the distillate was recycled to evaporator as nitric acid strip water while the remaining 20% is collected in a receiver tank) was above 10CFR20 release limits by 1.6×10^4 for ^{106}Ru and 2.2×10^2 for $^{144}\text{CePr}$.

The average instantaneous DF's across the high efficiency process filter were 1.1×10^2 for ^{106}Ru and 25 for $^{144}\text{CePr}$ (representing particulate DF). The DF for particulates was lower by a factor of about 100 than in previous runs, but agreed closely with the average particulate DF across the solidifier condenser off-gas filter.

The off-gas scrubber was inadvertently started with only 0.44M NaOH instead of the usual 2M NaOH. The scrubber became neutralized after 30% of the feed had been fed to the solidifier at which time the accumulation rate of nitrogen dropped off rapidly until at 60% feed, fed no more nitrogen accumulated. The neutralization of scrubber bottoms is attributed to the oxides of nitrogen present in the off-gas to the scrubber. A total of only 7.7% of the nitrogen fed to the solidifier accumulated in the scrubber. Using the nitrogen accumulation rate before the scrubber became neutralized and extrapolating for the entire run indicates that about 25 to 30% of the feed nitrogen should have accumulated in the scrubber. Indications were that about 50% of the equivalent feed nitrogen escaped with the scrubber off-gas. The nitrogen recovery for the auxiliary system was the lowest of any WSEP run.

The final process off-gas leaving the scrubber was above 10CFR20 release limits by factors of 4.9×10^2 for ^{106}Ru and

3.8×10^1 for $^{144}\text{CePr}$. However, after the scrubber off-gas was filtered twice more and combined with building ventilation air, the radioactivity released with the off-gas to stack was well below release limits.

Run SS-12(IPM)

The twelfth demonstration of the spray solidification process was completed during April 1970.

Run SS-12(IPM) was successfully completed using the in-pot melting technique wherein spray calcined PW-4m waste was melted with a borosilicate glass frit directly in the final storage container. The WSEP spray calciner had been coupled directly to the receiver pot for this run via a special spool-piece as shown in Figure 4.13, and the solid frit was added directly to the pot via a solids feeder attached to the spool-piece.

During Run SS-12(IPM), a simulated waste equivalent to that resulting from the reprocessing of 0.54 tonne of power reactor fuel (45,000 MWd/tonne at 30 MW/tonne) with an equivalent aging time of 1.3 years was processed to produce 162 kilograms of product. The 54 liters of radioactive solid produced a heat rate density of 90 W/liter (4900 watts total based on analytical and pot calorimetry data) in an 8-inch diameter 304L stainless steel melt receiver. The steady-state pot centerline temperature in the air-cooled furnace was 474 °C, and the centerline-to-wall temperature difference was 197 °C. These values indicated an effective thermal conductivity of $1.18 \text{ W/(m}^2)(^\circ\text{C/m)}$ [$0.65 \text{ Btu/(hr)(ft}^2)(^\circ\text{F/ft)}$] for the product. The effective thermal conductivity of the product while molten during processing was approximately 3 to 4 times higher than this and consequently pot centerline temperatures did not exceed 980 °C despite pot wall temperatures of 900 to 950 °C.

The calciner was fed 301 liters of adjusted PW-4m feed (additives of $\text{Ca}(\text{NO}_3)_2$ and $\text{Zn}(\text{NO}_3)_2$ at 556 liters/tonne in 28 hours. The resulting calcine was combined with 109 kilograms of borosilicate glass frit in the receiver pot. The feed containing 1,387,000 Ci of radioactivity including 6800 Ci of radioactive ruthenium was reduced in volume by a factor of 5.6, or 3.8 on a 378 liters/tonne basis.

During the first 4 hours of Run SS-12(IPM) the spray calciner average feed rate was approximately 15 liters/hr, and the in-pot melting process easily kept up with the calciner at a melt forming rate of approximately 2.7 liters/hr. For the remainder of the run, however, the spray calciner capacity was limited for some unknown reason and it was not possible to exceed a feed rate of 11 liters/hr (a melt forming rate of 2.0 liters/hr) without producing a significant drop in the calciner internal temperatures.

The spray calciner feed was interrupted twice during Run SS-12(IPM) for a total of 4.4 hours. The first shutdown was made to enable an evaluation of why the calciner capacity was limited, and the second was made while a failed calciner vibrator was replaced. The performance of the spray calciner off-gas filters was very satisfactory during the run as the filter pressure drop was maintained at 3.3 inches of water and only 0.014% of the particulates were entrained from the calciner.

Following the run, an inspection of the inside of the spray calciner was made to determine, if possible, the cause of the reduced feed capacity during the run.

Although there was some calcine scale on the upper half of the drying chamber walls it did not appear excessive. Since no particular problems were observed with the feed nozzle

it was reinstalled and a capacity check of the calciner was made with water feed. The check consisted of feeding water to the calciner at several different rates and observing the resulting internal calciner temperatures. Results of the test indicated that the calciner drying capacity was about 40% below what it was prior to and at the start of Run SS-12(IPM). The reduction in capacity was arrived at by comparing the feed rates before and after Run SS-12(IPM) which were required to drop the internal calciner temperature to the same level.

A thorough check of the calciner furnace electrical system was then made to see if it was the problem. However, resistance readings on the furnace elements while both hot and cold revealed them to be in good condition and also voltage and current reading of all furnace circuits with the furnace at temperature were normal. The feed nozzle was again removed from the calciner and a rod was inserted through the feed nozzle port to scrape the calciner walls to see if there was sufficient scale on the walls to cause the apparent loss in heat transfer. The scraping was observed to dislodge a fair amount of calcine from the walls although the scale did not appear to be more than about 1/8 inch thick in any one spot. The scraping covered the top half of the calciner and only about 3/4 of the way around the circumference since internal thermocouple did allow scrapping all the way around. After completion of the scraping operation a radiation scan of the calciner revealed that the radiation reading on the top half of the calciner had been reduced approximately 50%.

Since the calciner walls appeared fairly clean a new feed nozzle was installed and another capacity check of the calciner was made with water. The results of the test are presented in Figure 4.7 along with the results of the previous test and data

from Runs SS-11 and SS-12(IPM). As shown in Figure 4.7 the calciner capacity during this test was in agreement with data from Run SS-11 and the start of Run SS-12(IPM) and indicated that scale formation on the calciner walls was definitely the cause of the reduced capacity during Run SS-12(IPM). This was further brought out during the capacity test since top calciner external wall temperatures in the area which was not scraped as mentioned earlier were 50 °C higher than those where the wall had been scraped, indicating that a large percentage of the heat flux into the calciner was through the walls from which the scale had been removed.

The cause of the calciner wall scaling during Run SS-12(IPM) was not determined. It was not felt to be characteristic of the feed since this situation did not occur during developmental calciner runs on this feed type. Although poor feed atomization would be suspect, the feed nozzle used during the run was the same one which had performed so satisfactorily during Run SS-11. The atomizing air and feed flow control appeared adequate during Run SS-12(IPM) for proper nozzle operation and an inspection of the nozzle after the run revealed no outward signs of a nozzle malfunction. The scaling apparently was initiated early in the run since the temperatures started dropping sharply shortly after the feed was turned on. It may be that a brief surge in feed flow during this period resulted in the wet spray contacting the hot calciner walls and forming an initial scale. This scale formation may have then continued until a significant reduction in feed rate was made such that the feed rate no longer exceeded the drying capacity of the calciner. Based on the results of the final water capacity test it was decided to proceed with preparations for Run SS-13(IPM).

During Run SS-12(IPM) the WSEP auxiliaries were operated in a Mode A arrangement.

The accumulation of radionuclides in the auxiliaries was generally typical of previous runs except for the accumulation of radioruthenium in the auxiliary evaporator. Ruthenium volatilization from the solidifier was only 1.9% of the ruthenium in the feed to the solidifier. This represented the lowest ruthenium volatilization for any spray solidification run through Run SS-12(IPM). The decrease during this run was anticipated from results of cold development runs and was explained by the absence of phosphoric acid in the feed to the spray calciner.

During Run SS-12(IPM) the solidifier condenser off-gas contained an average of $2.9 \times 10^{-5} \mu\text{Ci}/\text{cm}^3$ of ^{106}Ru which is a factor of about 200 less than the ^{106}Ru concentration during Run SS-11. This is attributed to the decrease in ruthenium volatilization from the spray solidifier during Run SS-12(IPM) and to the 140 liter/hr water spray to the solidifier condenser which helped scrub out more of the ruthenium. This spray was pumped from the fractionator distillate receiver to the solidifier condenser. The concentration of $^{144}\text{CePr}$ remained about the same during Runs SS-11 and SS-12(IPM) and averaged $6.8 \times 10^{-5} \mu\text{Ci}/\text{cm}^3$ during Run SS-12(IPM). The cumulative DF across the solidifier condenser was 6.2×10^3 for ^{106}Ru and 2.6×10^3 for $^{144}\text{CePr}$.

The solidifier condenser and condenser water spray stopped 46% of the total nitrogen in the solidifier off-gas. This was an increase of 9% over Run SS-11 and this increase is attributed to the water spray to the condenser. However, this increase was much less than what was initially expected. Part of the remaining 54% that remained in the gas phase was scrubbed out

by the evaporator condenser increasing the evaporator acidity and resulting in no equilibrium between the evaporator bottoms acidity and evaporator overhead acidity.

The off-gas from the solidifier condenser is filtered through a high efficiency filter before entering the evaporator. The off-gas leaving the solidifier condenser off-gas filter contained an average of 2.2×10^{-6} $\mu\text{Ci}/\text{cm}^3$ of ^{106}Ru and 4.4×10^{-5} $\mu\text{Ci}/\text{cm}^3$ of $^{144}\text{CePr}$. These values indicated average instantaneous decontamination factors (DF's) across the filter of 8 for ^{106}Ru and 1.5 for $^{144}\text{CePr}$. These DF's were considerably less than during Run SS-11. This is possibly an indication that the filter had partially failed.

The auxiliary evaporator operated on about 5M HNO_3 . Instantaneous ruthenium DF's across the evaporator ranged from 1.8 to 2.2×10^3 . These values were considerably less than during Run SS-11. There was again, as in most previous spray solidification runs, no apparent correlation between evaporator overhead acidity and instantaneous ruthenium DF's. This is attributed to an increased overhead acidity from oxides of nitrogen not being scrubbed out completely by the solidifier condenser and by internal contamination of the system. The fraction of equivalent feed ruthenium accumulated in the fractionator was 1.4×10^{-3} which indicated a cumulative ruthenium DF of 14 across the evaporator, while the fraction of $^{144}\text{CePr}$ accumulated was 2.4×10^{-6} which indicated a cumulative DF for nonvolatiles of 74.

The fraction of equivalent feed radioactivity that accumulated in the fractionator distillate receiver was 2×10^{-6} for ^{106}Ru representing a cumulative DF across the fractionator of 7.5×10^2 . There was no detectable gain of $^{144}\text{CePr}$ in the fractionator distillate receiver. The concentration

of radionuclides in the fractionator distillate (final aqueous effluent) was above 10CFR20 release limits by factors of 1.1×10^4 for ^{106}Ru and 1.5×10^2 for $^{144}\text{CePr}$ representing non-volatiles. Throughout the run, fractionator distillate was pumped at 140 liter/hr to the solidifier condenser from the fractionator distillate receiver.

The off-gas scrubber bottoms (initially 1.6M NaOH) was continually neutralized by the presence of nitrogen oxides in the off-gas to the scrubber. The final concentration in the scrubber bottoms was 0.42M NaOH. A total of 39% of the nitrogen fed to the solidifier accumulated in the scrubber. This was highest accumulation of nitrogen in the scrubber for any WSEP run and is attributed to poor removal of nitrogen oxides by the auxiliary evaporator and fractionator and associated condensers and towers.

The fraction of equivalent feed radioactivity that accumulated in the off-gas scrubber was 1.0×10^{-8} for ^{106}Ru , agreeing with data from Run SS-11. The final process off-gas leaving the scrubber contained an average of $3.6 \times 10^{-8} \mu\text{Ci}/\text{cm}^3$ of ^{106}Ru and $2.0 \times 10^{-8} \mu\text{Ci}/\text{cm}^3$ of $^{144}\text{CePr}$ representing an equivalent fraction of feed radioactivity of 1.0×10^{-8} for ^{106}Ru and 3.2×10^{-11} for $^{144}\text{CePr}$. These values are above 10CFR20 release limits by factors of 1.9×10^2 for ^{106}Ru and 7.0×10^1 for $^{144}\text{CePr}$. However, after the scrubber off-gas was filtered twice and combined with building ventilation air, the radioactivity released with the off-gas to the stack was well below 10CFR20 release limits.

Run SS-13 (IPM)

The thirteenth and final demonstration of the spray solidification process was completed during May 1970. Run SS-13 (IPM)

was the second radioactive demonstration using the in-pot melting technique where spray calcined PW-4m waste was melted with a borosilicate glass frit directly in the final storage container. As in Run SS-12(IPM) the WSEP spray calciner was coupled directly to the receiver pot via a special spool-piece and the solid frit was added directly to the pot.

During Run SS-13(IPM), a simulated Purex waste equivalent to that resulting from the reprocessing of 0.88 tonne of power reactor fuel (45,000 MWd/tonne at 30 MW/tonne) with an equivalent aging time of 1.0 years was processed to produce 151 kilograms of product. The 50 liters of radioactive solid produced a heat rate density of 200 W/liter (10,000 watts total based on the average of analytical pot calorimetry data) in an 8-inch diameter 304L stainless steel receiver pot. The steady-state pot centerline temperature in the air-cooled furnace was 824 °C, and the centerline-to-wall temperature difference was 404 °C. These values indicate a calculated effective thermal conductivity of $1.28 \text{ W/(m}^2)(^{\circ}\text{C/m)}$ [$0.74 \text{ Btu/(hr)}(\text{ft}^2)(^{\circ}\text{F/ft)}$] for the product. As during Run SS-12(IPM) the effective thermal conductivity of the product while molten during processing was approximately 3 to 5 times higher than this and consequently pot centerline temperatures did not exceed 1040 °C despite pot wall temperatures of 900 to 950 °C.

The calciner was fed 308 liters of PW-4m feed at 352 liters/tonne in 20 hours. The resulting calcine was combined with 106 kilograms of borosilicate glass frit in the receiver pot. The feed containing 2,830,000 Ci of radioactivity including 11,000 Ci of radioactive ruthenium was reduced in volume by a factor of 6.2, or 6.6 on a 378 liters/tonne basis.

The spray calciner performed satisfactorily during Run SS-13(IPM) at an average feed rate of 15.4 liters/hr. The in-pot melting process easily kept up with the calciner at a melt-forming rate of approximately 2.5 liters/hr. For this run the flowsheet was modified such that excess aluminum in the feed stock solutions was substituted for the zinc and calcium additives used during Run SS-12(IPM) and this increased the waste concentration in the product from 17 to 28 wt%. The increased product waste concentration and the 2.5 liters/hr melt formation rate resulted in an average processing rate of 1.05 tonne/day during Run SS-13(IPM) which was 80% higher than the highest processing rate attained for the PW-4m waste during previous spray solidification runs using the platinum melter.

Ruthenium volatilization from the solidifier during Run SS-13(IPM) was only 0.5% of the ruthenium in the feed to the solidifier. This represents the lowest ruthenium volatility for any of the spray solidification runs and is due to the absence of phosphoric acid in the feed to the solidifier, since all the glass-forming flux was added directly to the melt pot.

The performance of the spray calciner off-gas filters was very satisfactory during the run as the filter pressure drop was maintained at 3.6 inches of water and only 0.001% of the particulates were entrained from the calciner.

Modified Mode B operation of the WSEP auxiliaries was used during Run SS-13(IPM). This included routing the solidifier condensate to a separate receiving tank as illustrated in Figure 9.2.

An objective of Run SS-13(IPM) was to demonstrate automatic control of the WSEP auxiliaries. This included using cascade control loops with the evaporator weight factor controller cascaded to the evaporator tube bundle steam controller and the fractionator specific gravity controller cascaded to the fractionator tube bundle steam controller.

During the run $2M$ HNO_3 was fed to the evaporator at about 14 liters/hr to simulate solidifier condensate since the actual solidifier condensate was collected separately. During the automatic control periods steady operation was not obtained as illustrated by the evaporator and fractionator operating parameters shown in Figure 9.11. One main problem was that the fractionator specific gravity signal was adversely affected by the fractionator boilup which resulted in poor control. Also twice during the run the evaporator dip tubes were inadvertently vented causing an upset in automatic control.

The solidifier condenser stopped only 26% of the total nitrogen feed to the solidifier while the remaining 74% remained as nitrogen oxides in the gas phase and was partially scrubbed out by the evaporator tower and condenser. The removal of nitrogen oxides by the evaporator condenser increased the overhead acidity and again resulting in no correlation with instantaneous ruthenium DF's.

During Run SS-13(IPM) the solidifier condenser off-gas contained an average of 3×10^{-4} $\mu Ci/cm^3$ of ^{106}Ru and 5×10^{-4} $\mu Ci/cm^3$ of $^{144}CePr$ while the off-gas leaving the condenser filter contained 3.2×10^{-6} $\mu Ci/cm^3$ of ^{106}Ru and 4×10^{-4} $\mu Ci/cm^3$ of $^{144}CePr$. These values indicated a DF of 94 for ruthenium and a DF of 1.3 for $^{144}CePr$ across the high efficiency filter. The low DF for $^{144}CePr$ indicates that either the filter had failed or there was internal contamination of gas sample lines. The concentration of $^{144}CePr$ in the off-gas from the filter increased by a factor of about 10 over that during Run SS-12(IPM). Visual inspection of the condenser off-gas filter after Run SS-13(IPM) revealed that the filter media had partially slipped out of the filter canister as the result of the failure of the adhesive which bonded

the media to the canister walls. It was therefore possible for a portion of the off-gas to by-pass the filter media which would result in the low DF observed above. The inlet side of the filter was darkened by the presence of ruthenium and other radionuclides while the outlet remained the same color as new filtering media. There was no evidence of corrosion of the aluminum filtering media supports as has been the case with the high efficiency process filter prior to the off-gas scrubber. The cumulative DF across the solidifier condenser was 5.4×10^3 for ^{106}Ru and 2.1×10^4 for $^{144}\text{CePr}$.

The accumulation of radionuclides in the auxiliaries during Run SS-13(IPM) was generally the same as Runs SS-11 and SS-12(IPM).

Prior to this modified Mode B run, 450 liters of Purex 1WW containing 370,000 Ci of total radioactivity including 23,000 Ci of radioruthenium were transferred to the auxiliary evaporator. During the run the evaporator bottoms were slowly acid stripped. Instantaneous ruthenium DF's across the evaporator were typically greater than 10^4 while instantaneous $^{144}\text{CePr}$ DF's were typically greater than 10^5 . There was no decrease in DF's when the feed was started to the solidifier. The equivalent fraction of feed ruthenium accumulated in the fractionator was 3.4×10^{-4} indicating a cumulative evaporator ruthenium DF of 3.6×10^3 while the fraction of feed $^{144}\text{CePr}$ accumulated was 4.7×10^{-6} indicating a cumulative DF for non-volatiles of about 10^4 .

The fraction of equivalent feed radioactivity that accumulated in the fractionator distillate receiver was 3×10^{-6} for ^{106}Ru representing a cumulative DF across the fractionator of 3.7×10^2 . There was no detectable gain of $^{144}\text{CePr}$ in the fractionator distillate receiver. Instantaneous ruthenium DF's across the fractionator were typically greater than 10^2 while instantaneous $^{144}\text{CePr}$ DF's were greater than 10^5 .

The fractionator distillate (final aqueous effluent) contained about 8×10^{-5} Ci/liter of ^{106}Ru and 6×10^{-5} Ci/liter of $^{144}\text{CePr}$. These values were about 10CFR20 release limits by factors of 8×10^3 for ^{106}Ru and 3×10^3 for $^{144}\text{CePr}$ representing nonvolatiles.

The equivalent fraction of feed ruthenium accumulated in the off-gas scrubber was 2.6×10^{-6} while there was no detectable gain of $^{144}\text{CePr}$ in the scrubber. The final process off-gas leaving the scrubber contained an average of 7.8×10^{-8} $\mu\text{Ci}/\text{cm}^3$ of ^{106}Ru and 2.3×10^{-8} $\mu\text{Ci}/\text{cm}^3$ of $^{144}\text{CePr}$. These values are about 10CFR20 release limits by factors of 3.9×10^2 for ^{106}Ru and 5.8×10^1 for $^{144}\text{CePr}$. As in all previous WSEP runs the scrubber off-gas was filtered and combined with building ventilation air before being released to the atmosphere and as a result the concentration of radioactivity in the off-gas was well below 10CFR20 release limits.

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