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Pacific Northwest Laboratories
Richland, Washington 99352

AEC Research and Development Report

WASTE SOLIDIFICATION PROGRAM
SUMMARY REPORT

VOLUME 11

EVALUATION OF WSEP HIGH LEVEL
WASTE SOLIDIFICATION PROCESSES

JUNE 1972

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Waste Disposal
and Processing

WASTE SOLIDIFICATION PROGRAM SUMMARY REPORT
VOLUME 11
EVALUATION OF WSEP HIGH LEVEL
WASTE SOLIDIFICATION PROCESSES

By

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July 1972

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at Hanford Engineering Development Laboratory

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ABSTRACT

Successful demonstrations of the solidification of high-level radioactive waste by the pot, spray, and phosphate glass solidification processes have been performed in WSEP. A total of 33 demonstrations have been completed. More than 50 million curies of radionuclides have been processed and collected in 6-, 8- and 12-inch diameter containers. The results of these runs have been evaluated and are presented in this report.

Results from WSEP have been used to develop design concepts and waste management economics for application of the WSEP solidifiers in industrial plants. Material balance flow-sheets were developed and design concepts were made for a 5 tonne/day reprocessing plant for both the high salt, sulfate-containing PW-2 waste, and for the relatively pure fission product PW-4m waste used in WSEP. Economic comparisons of the entire waste management scheme were made. An overall comparison of the WSEP type solidification processes indicates an apparent slight preference of the spray solidification process over pot calcination, with the phosphate glass process having the fewer number of advantages for the cases studied.

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:

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1.0 INTRODUCTION

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1.0 INTRODUCTION

During the 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 separated from human environment by storage in man-made vaults of high integrity or in geologically isolated formations.

A considerable amount of development on techniques for solidification of high level wastes has taken place in the past 17 years and is still progressing. Four processes for solidification of high level liquid wastes have been developed in the United States to the point of radioactive demonstrations

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

on an engineering scale. The four processes are pot calcination, spray solidification, phosphate glass solidification, and fluidized bed calcination. Two waste solidification methods which have received considerable development effort abroad are the pot vitrification process in France and the FINGAL borosilicate glass process in the United Kingdom.

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, intermediate level wastes have been processed at the Idaho Chemical Processing Plant (ICPP), now operated by the Allied Chemical Company, since 1963.

Pot calcination (developed by Oak Ridge National Laboratory), spray solidification (developed by Battelle-Northwest), and phosphate glass solidification (developed by Brookhaven National Laboratory), have been demonstrated at Hanford on an engineering scale with full radioactivity levels for the Atomic Energy Commission. The purpose of this cooperative, high-level waste solidification demonstration program has been to provide the technological bases which would enable industry to adopt and implement at the earliest possible time the practice of solidifying the high-level liquid waste from the reprocessing of nuclear fuel. The radioactive demonstrations of the three alternative processes have been conducted in the Waste Solidification Engineering Prototypes (WSEP) at Hanford.

The WSEP is a pilot plant which was designed to provide the information required for the technical, economic, and

safety evaluations of the pot, spray, and phosphate glass processes. A detailed description of the WSEP has been previously reported.⁽¹⁾ A summary of the basic technology associated with the pot, spray, and phosphate glass solidification processes has also been reported.⁽²⁾

As a means of presenting the data from the radioactive demonstrations on a current basis, the results from a particular series or sequence of runs with each solidification process have been reported in individual documents during the course of the program (References 3 through 8). The results of the performance of the associated auxiliary equipment and measurements on the solidified waste for the various series of runs have also been maintained on a current basis in References 3 through 8.

It is the purpose of this document to compile and assess the pertinent data which have been obtained from the demonstration program and with the perspective which has been achieved through the operation of the equipment, present an evaluation and comparison of the processing parameters, product characteristics and economics associated with each solidification system.

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2.0 SUMMARY

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2.0 SUMMARY

Radioactive demonstration tests with three solidification processes in the WSEP have been completed. Results of these test runs have been evaluated and assessed with design concepts for solidification facilities for a hypothetical reprocessing plant having a capacity of 5 tonnes/day of irradiated fuel.

2.1 WASTE SOLIDIFICATION STUDIES IN WSEP

Successful demonstrations of the solidification of high-level radioactive waste by the pot, spray, and phosphate glass solidification processes have been performed in WSEP. A total of 33 demonstrations have been completed as of September, 1970: 9 by pot solidification, including one using the rising level glass (RLG) technique; 11 by phosphate glass solidification, and 13 by spray solidification, including two tests using the in-pot melting variation. More than 50 million curies of radionuclides have been processed and collected in 6-, 8- and 12-inch diameter containers. The maximum self-generating heat rate values in the solidified wastes for an 8-inch diameter pot ranged from 204 W/liter for the spray solid to 93 W/liter for the pot calcine.

The WSEP effluent treatment (auxiliary) equipment reduced radionuclides in the stack gas to well below 10CFR20* concentrations. The final liquid effluent from the WSEP processes contained radoruthenium that was 1000 to 100,000 times 10CFR20* concentrations and therefore would require more treatment before release to the environment. Nonvolatile radionuclides were present to a much smaller extent, and would present a less significant problem of removal.

* Code of Federal Regulations, Title 10, Part 20, Appendix B Table II, Columns 1 and 2, August 9, 1966.

The pots of solidified wastes from the WSEP runs are undergoing testing to determine the effects of storage temperature, environment (air or water), radiation, and feed type on the physical and chemical properties of the solidified wastes.

2.1.1 Pot Solidification

The pot calcination system is ready for application in industrial plants. The rising level glass (RLG) modification of this process requires appreciable additional development effort prior to such an application.

Entrainment from the pot calciner, when operated as in WSEP, can be expected to be 0.3 to 1%. The amount of ruthenium volatilized from the pot calciner will be between 5 and 30%. There appear to be two distinct modes of ruthenium volatilization where for certain conditions (low sodium, low sulfate and early wall scaling), less than 10% volatilization can be expected from the pot calciner. Otherwise the volatilization can be as much as 30%.

Sulfate-containing and sulfate-free wastes are readily solidified by pot calcination. Phosphate is preferred over sulfate to suppress alkali metal volatilization because of solids precipitation problems in the aqueous waste with sulfate. Aluminum-containing wastes are also readily processed.

Foaming in the calciner pot can sometimes cause losses of waste from the pot; however, the addition of anti-foam to the pot in two WSEP runs appeared to prevent foaming and improve process stability.

Satisfactory filling of the calcine pot with significant heat generation rates (heat rate densities to 93 W/liter in an 8-inch diameter pot) was accomplished using a six-zone heating-cooling furnace and a simple three-step reduction of furnace temperatures based upon pot wall and calcine temperatures at various stages of the calcination cycle.

The volume of solidified waste from each equivalent tonne of fuel processed in WSEP was approximately 45 liters/tonne for all pot calciner wastes.

Equipment operation for the pot calcination system was satisfactory. A standard dip tube, purged with an air-steam condensate mixture, proved most satisfactory for level control in the pot. It is anticipated that on a production basis the process can be adequately controlled with the dip tube and about 3 centerline thermocouples and without measuring wall temperatures.

A self-cleaning off-gas line as developed and used in WSEP is believed essential for continuous use of the pot calciner; otherwise vent line blockage by entrained calcine can occur after several runs.

Based on one run, the amount of ruthenium volatilization from the RLG pot will be approximately 15%. Temperature control with the RLG process was satisfactory and is similar to the spray in-pot melting process (summarized below). A heat rate density of 310 W/liter was obtained in a 6-inch diameter pot.

The volume of solidified waste per equivalent tonne of fuel processed in WSEP was 32 liters/tonne for the RLG run where 50 wt% waste oxides were combined with 50 wt% sodium borosilicate additives.

2.1.2 Spray Solidification

The spray solidification processes are ready for application in industrial plants. Use of the platinum melter system is not recommended; however, other suitable options are available.

Entrainment from the spray solidifier through sintered stainless steel filters can be expected to be 0.001 to 0.1%.

The amount of ruthenium volatilized from the spray-melter process with a phosphate melt can be as high as 75%; however, a factor of two decrease in volatilization can be achieved with low acid concentration in the waste. Ruthenium volatilization is expected to be 0.5 to 2% when making borosilicate products where phosphoric acid is omitted.* For wastes containing sulfate, only phosphate-containing flowsheets have been developed. Ruthenium volatilization during in-pot melting will be the same as for the phosphate containing spray-melter system.

Sulfate-containing wastes can be processed with the spray-melter process under a moderately narrow range of chemical flowsheet and operating conditions; close control is required to prevent sulfate volatilization in the melter and foaming in the waste storage container. Sulfate wastes are readily processed when spray in-pot melting is used, but a phosphate-based melt is required and close control is again necessary to prevent foaming in the storage container.

Sulfate-free wastes are readily solidified with the spray solidification process. Aluminum containing wastes are readily processed with the borosilicate system. Modest amount of aluminum (up to approximately 15% of the total cationic normality) can be processed with the spray-melter phosphate system without significantly modifying the chemical additives presently used.

Uniform filling of unheated pots without appreciable voids in the final solids can be accomplished with the spray melter process at pot filling rates as low as 15 liters/hr (in 3 to 7 liter batches). A slightly higher rate of about 25 liters/hr is near the minimum filling rate for the viscous PW-4m type of phosphate melt. Filling rates significantly lower than these

* The borosilicate system was demonstrated in WSEP spray solidifier tests using only the in-pot melting technique. This system could also be used with continuous melting (and with a nonplatinum melter).

require maintaining the pot temperature at the "slumping" point (25 to 300 °C below the melting point) of the solidified waste by either heating the pot or restricting the amount of cooling provided. A maximum heat rate density of 204 W/liter was obtained in an 8-inch diameter pot. Receiver pot temperature control during filling was satisfactorily demonstrated using air cooling only.

Temperature control during filling of the in-pot melting pot is satisfactory. The low remelt temperature of the solidified waste results in a partially molten product at temperatures of 600 °C for PW-2 and 800 °C for PW-4m, which causes the effective thermal conductivity to increase markedly with increasing temperature. This feature reduces the amount of pot wall cooling required to maintain pot centerline temperatures during filling below approximately 800 and 1000 °C for sulfate and nonsulfate wastes, respectively, and allows filling the pot with waste having high rates of self-heat generation. A maximum heat rate density of 200 W/liter was obtained in an 8-inch diameter pot.

The average volume of solidified waste from each equivalent tonne of reactor fuel processed ranged from 33 to 64 liters/tonne for the spray-melter phosphate system and 57 to 100 liters/tonne for the in-pot melting borosilicate system. The waste volume with the borosilicate system can be reduced to as low as 30 liters/tonne by increasing the waste content to 50 wt%.

The principal equipment disadvantage with the spray-melter process using the phosphate system is the platinum melter.* Platinum is very expensive, it is structurally weak,

* The borosilicate system can be used with a nonplatinum melter (such as 50% chromium-50% nickel, Corronel-230 or Type 310 stainless steel alloys) at temperatures up to 1100 °C. With the phosphate flowsheet developed for sulfate containing wastes, the melter may be made of the alloy Corronel-230 if the temperature is limited to 1000 °C.

and it has a very low thermal emissivity (which requires increased operating temperatures in the melter furnace). Elimination of a melter is achieved with the in-pot melting process.

With either spray process, feed atomization must be good to prevent calcine caking within the spray calciner.

2.1.3 Phosphate Glass Solidification

The phosphate glass process requires some design modification and verification for continuous operation to make it appropriate for application in industrial plants. This requirement involves improvements in the denitrator-evaporator and the transport of the concentrated solution, and a replacement of the platinum melter.

Entrainment from the combined denitrator and melter can be expected to be 0.1 to 0.3% when using the WSEP design. The amount of ruthenium volatilized is 5 to 10% and is independent of Purex waste composition within the range of those tested in WSEP.

Sulfate-containing wastes are readily handled by the process. However, the sulfate is completely volatilized from the melter, and the melter condensate is then a high level waste that requires treatment by a separate process, such as vacuum distillation. The nitric acid distillate and bottoms would be recycled and the sulfate distillate would be disposed of by a method such as incorporation in asphalt.

Sulfate-free wastes can cause solids formation and plugging in the denitrator-evaporator and melter feed system. Improvement of the flowsheets may be possible. The PW-4m waste characteristics were more satisfactory than the PW-1 characteristics in this respect; however, a lower concentration factor, boiling point, and denitration percentage was obtained.

Uniform filling of pots without appreciable voids can be accomplished at very low melt addition rates (steady drip) if the receiver pot is held at 600 °C (approximately the remelt temperature of the phosphate glass). It should also be possible to fill unheated pots batchwise at the rate of 15 liters/hr (in 3 to 7 liter batches) which was accomplished with the spray solidifier. Mild steel pots can be used for all wastes and filling methods. Temperature control during filling of the receiver pots is satisfactory. Maximum heat rate densities of 317 and 198 W/liter were obtained in 6- and 8-inch diameter pots respectively.

The average volume of solidified waste from each equivalent tonne of thermal reactor fuel processed ranged from 40 liters/tonne for PW-2 sulfate waste to 108 liters/tonne for PW-1 nonsulfate waste.

The principal equipment disadvantage with the phosphate glass process is the platinum melter, which has the same disadvantages as the spray-melter used for phosphate melts. Slurry handling in the denitrator and the melter feed system requires some improvement to make the process sufficiently reliable for industrial application. It is believed that difficulties with these operations can be resolved with an improved evaporation system (such as a wiped film evaporator) coupled to a modified melter feed system (such as a screw pump). The melter airlift feed system may be adequate for cases where several fold higher melter feed rates to larger melters would be encountered. In these cases, control of higher slurry rates is inherently easier, and larger melters should provide more freeboard.

2.1.4 Solidifier Effluent Control

Conversion of high-level aqueous wastes to solids results in one or more effluent streams with lower levels of radioactivity.

In WSEP the immediate solidifier effluent was treated by auxiliary equipment consisting of an evaporator, an acid fractionator, condensers, filters and a caustic scrubber.

The following generalizations can be stated regarding the effluents from the WSEP processes:

1. The solidifier feed was decontaminated by factors of 1.3 to 200 for radoruthenium and 100 to 100,000 for radiocerium (representing nonvolatile constituents of the feed), thus the immediate effluent from the solidification step still remained as a highly contaminated waste.
2. The cleanup of the highly contaminated solidifier effluent by the WSEP effluent treatment system was adequate for the final gaseous effluent stream, with decontamination factors from the solidifier feed to the stack of 10^{10} for radoruthenium and 10^{12} for radiocerium representing nonvolatiles.
3. The cleanup in the WSEP effluent treatment system was inadequate for the final aqueous effluent stream by factors of three to five orders of magnitude, based on values in 10CFR20.
4. The volumes and total radionuclide content of the immediate effluents from solidification are relatively small compared to those associated with the contaminated nitric acid and condensate streams recovered from the solvent extraction process during fuel reprocessing. Consequently, these effluents can be sent to disposal facilities associated with a fuel reprocessing plant. Studies also indicate that the effluent from the WSEP effluent treatment system can be reasonably recycled for reuse in fuel reprocessing plants.

Decontamination factors were used as a measure of the performance of the WSEP effluent treatment system. Decontamination

factors from the solidifier feed to the recovered nitric acid were typically 10^3 for radoruthenium and between 10^5 and 10^7 for radiocerium. Radoruthenium decontamination factors from the solidifier feed to the final acid fractionator condensate were typically between 10^5 and 10^6 with the lower value being more representative of the spray calciner-melter process. Decontamination factors to the final condensate were approximately 10^8 to 10^9 for radiocerium. Decontamination factors from the feed to the off-gas scrubber were typically between 10^5 and 10^6 for radoruthenium. Radiocerium accumulation in the scrubber was generally nondetectable ($DF > 10^9$). The scrubber accumulated between 4 and 40% of the nitrogen in the feed to the solidifier. The total loss of nitrogen to the stack (presumably as NO_x) was typically less than 10% but higher losses occurred during some spray solidification runs and the one rising level glass run where more oxides of nitrogen were produced by the solidifiers.

The undiluted off-gas stream from the process scrubber was typically above 10CFR20 values by factors of less than 500 for radoruthenium and less than 300 for nonvolatile radiocerium. However this 5 to 50 SCFM gas stream was filtered twice more and combined with building ventilation air before it was discharged from the stack where the radioactive content was generally less than detectable.

Correlation of evaporator ruthenium decontamination data was generally compromised by particulate carryover and by lack of adequate vapor-liquid contact between the solidifier and the evaporator. A modified solidifier condenser containing Pall rings for improved vapor-liquid contact followed by a high efficiency filter, reduced the ruthenium carryover beyond the evaporator. Spraying water into the condenser was only modestly successful in scrubbing out additional uncondensed ruthenium and nitrogen oxide gases.

Overall performance of the auxiliary equipment during the WSEP runs was satisfactory. Exceptions were some feed pump failures, occasional plugging of pipes and gradual deterioration of the insulation on the electrical and instrument wiring within the hot cell.

2.1.5 Evaluation of Solidified Waste from WSEP Processes

The 33 pots of WSEP solidified waste are being used for a demonstration of interim storage of prototypical high level solidified wastes. Ten of the pots are in individual, specially controlled environments of air or water in the Solids Storage Engineering Test Facility (SSETF); the remainder are being stored at ambient air temperatures.

To date one-third of the pots have been core-sampled and the product properties of the radioactive solids correspond closely to those predicted from measurements made on laboratory-prepared nonradioactive solids. The oldest WSEP pot that has been core-drilled, SS-4, had been stored 3.5 years at the time of sampling.

Four basic forms of solidified waste were produced in the WSEP program: friable calcine cakes (pot calcination process), phosphate-based ceramics (spray calciner-melter process), phosphate-based glasses (phosphate glass process), and borosilicate glasses (rising level glass and in-pot melting processes). All of the products filled the pots quite homogeneously, as shown by axial and radial radioactivity and temperature measurements. Minor fission product segregation (cesium enrichment in the top portions of the product) was found in the only pot calcine process pot sampled thus far.

Results of an empirical dispersibility test, in which the range of particle sizes is measured after a standard physical impact, indicate the physical structure of the radioactive

solids tested to date is similar to that of nonradioactive solids of the same chemical composition and thermal history. All but one of the four phosphate glass pots sampled were found to be completely devitrified. Most of the devitrification is believed to have usually occurred in the few hours during the initial cool-down of the melt rather than during interim storage.

Effective thermal conductivity of the solidified wastes ranges from approximately $0.35 \text{ W/(m}^2)(^\circ\text{C/m)}$ * for the porous pot calcine product to 0.9 to $1.3 \text{ W/(m}^2)(^\circ\text{C/m)}$ for the coherent ceramic and glass products. The thermal conductivity of the phosphate ceramic did not vary with temperature between 100 and 600°C ; an increase in thermal conductivity with rising temperature was observed for the other product forms.

No significant pressurization of any of the WSEP pots has been observed.

The use of Types 304L and 310 stainless steel and mild steel (for processes with a separate melter) pots has been demonstrated. Pot wall thickness measurements to date indicate negligible corrosion. Thermowell failure was experienced in two phosphate glass pots; however, none of the five thermowell samples core-drilled from one of the pots was corroded significantly, indicating a very localized leak.

Leach rates of the radioactive glass products are in the range of 5×10^{-6} to $10^{-4} \text{ g/cm}^2\text{-day}$; leach rates of the phosphate ceramic and devitrified phosphate glass are in the range 10^{-4} to $5 \times 10^{-3} \text{ g/cm}^2\text{-day}$. About 25% of the cesium in the radioactive pot calcine was leached into water within one week.

2.2 USE OF WSEP RESULTS FOR APPLICATION IN INDUSTRIAL PLANTS

Results from WSEP have been used to develop design concepts and waste management economics for application of the

* $\text{W/(m}^2)(^\circ\text{C/m}) \times 0.578 = \text{Btu/(hr)(ft}^2)(^\circ\text{F/ft)}$.

WSEP solidifiers in industrial plants. Material balance flow-sheets were developed and design concepts were made for a 5 tonne/day reprocessing plant for both the high salt, sulfate-containing PW-2 waste, and for the relatively pure fission product PW-4m waste used in WSEP.

A summary of the comparative information for the various processes is presented in Table 2.1. This comparison is based on information developed in WSEP studies and in the design concepts and cost analyses developed in this report for a 5 tonne/day plant. An overall order of process performance shown at the bottom of Table 2.1, indicates an apparent slight preference of the spray solidification process over pot calcination, with the phosphate glass process having the fewer number of advantages for the cases studied.

TABLE 2.1. Overall Comparison of Waste Solidification Processes (5 tonne/day Reprocessing Plant)

	Type of Waste	Pot Calcination	Spray Solidification		Phosphate Glass
			Borosilicate	Phosphate	
Waste Management Costs	Clean	Average	Low	Average	High
(Minimum Cost Cases)	Sulfate	High	(Process Not Developed)	Average-High	Average
Amenability to Scale-up	Most	Multiple Lines	Good ^(a)	Good ^(a)	Good
Flexibility for Varying Wastes	Most	Very Good	Good	Fair	Fair
Radionuclides in Solidifier Vapors	Most	Average	Low ^(b)	High ^(b)	Average
Solidified Waste-Form	Most	Friable Calcine	Glass	Ceramic	Glass
-Overall Characteristics	Most	Poor	Good	Good	Fair-Good
Simplicity, Reliability, Maintainability ^(c)	Most	All Similar			
Safety Considerations ^(c)	Most	All Similar			
Overall Readiness for Commercial Application	Most	Best	Good	Fair-Good	Fair
Order of Overall Process	} Clean	2	1 (Best)	2	3
Preference from WSEP Tests		2	(Process Not Developed)	1 (Best)	3

a. If in-pot melting is used, multiple lines are probable.

b. Entrainment is very low in both spray solidification systems, but ruthenium volatilization is high with the phosphate system.

c. Specific differences in these categories do exist, but overall differences appear insignificant.

2.2.1 Design Concepts for Solidification and Waste Management

Design concepts were developed for possible industrial application of each of the three solidifiers demonstrated in the WSEP. These concepts are for a hypothetical plant which reprocesses spent LWR fuels at the rate of 5 tonnes/day at 75% operating efficiency, for an annual reprocessing rate of 1370 tonnes of fuel. The high level waste from this hypothetical reprocessing plant has the same composition as that for the high-salt, sulfate-containing waste designated PW-2 in WSEP tests, or the relatively pure fission product waste without sulfate designated PW-4m. The off-gas from the solidifier in each case is routed back to the plant's high level waste evaporator after being scrubbed by recycled strip water from the plant's acid fractionator.

The more important equipment information for the design concepts in this study is summarized in Table 2.2. The lower thermal conductivity of the pot calcine generally requires more waste aging time before solidification than with the other processes. Also, the batch-limited capacities of pot calcination and the in-pot-melting step of the spray-in-pot-melting process require multiple pot lines for the hypothetical plant.

Design concepts for the spray solidifier were developed for converting wastes to borosilicate glasses or to phosphate ceramics. The borosilicate system permits the use of smaller calciners and melters and the use of nonplatinum melters. However, borosilicate systems have not yet been developed for use with sulfate-containing wastes. Such systems generally result in two phases within the solidified waste. It should be noted, however, that the trend in reprocessing is toward sulfate-free systems, and this is expected to become essentially universal in future plants.

TABLE 2.2. Summary of Design Information for Solidifier Concepts

Range for Min. Age to Max. Age Evaluated at Solidification Time		Pot Calciner	Spray Solidifier				Phosphate Glass
			Phosphate Melt		Borosilicate Melt		
			Melter	IPM ^(a)	Melter	IPM	
	Sulfate-Containing PW-2 Waste						
	Pot Diameter, in.	6-24	10-24	10-24	-- (b)	-- (b)	8-20
	Age, yr (c)	0.4-5.1	0.5-2.3	0.5-2.3	--	--	0.4-2.2
	Pots/day	7.8-0.6	3.2-0.6	3.2-0.6	--	--	3.2-0.6
	No. of Pot Lines	12-7	1	4-1	--	--	1
	Heat/Pot, kW	6.6-7.9	13.9-17.1	13.9-17.1	--	--	14.6-19.0
	Calciner Diameter, in. } × Height, ft	6-24 × 10	36 × 20	36 × 20	--	--	--
	Solid Waste liter/te	71	78	78	--	--	50
	Evaporator Diameter, in. } × Length, in.	--	--	--	--	--	18 × 48
	Melter Diameter, in. } × Height, in.	--	26 × 36	(Pot)	--	--	24 × 34
	Pot Material	SS	MS	SS	--	--	MS
	Waste Without Sulfate, PW-4m						
	Pot Diameter, in.	6-10	6-12	--	6-12	6-12	8-20
	Age, yr (c)	2.1-5.0	0.5-2.0	--	1.0-3.0	1.0-3.0	0.7-3.3
	Pots/day	4.6-1.7	6.3-1.6	--	3.8-1.0	3.8-1.0	5.4-1.0
	No. of Pot Lines	4-3	1	--	1	5-2	1
	Heat/Pot, kW	6.6-7.2	15.5-20.1	--	15.5-21.4	15.5-21.4	14.6-19.0
	Calciner Diameter, in. } × Height, ft	6-10 × 10	30 × 15	--	18 × 8	18 × 8	--
	Solid Waste, liter/te	42	57	--	35	35	85
	Evaporator Diameter, in. } × Length, in.	--	--	--	--	--	15 × 42
	Melter Diameter, in. } × Length, in.	--	21 × 29	--	10 × 14 ^(d)	(Pot)	18 × 25
	Pot Material	SS	MS	--	MS	SS	MS

a. IPM = In-Pot-Melter

b. Borosilicate glass compositions have not been developed for PW-2 wastes for this study; such compositions appear to be possible, but generally result in 2 phases.

c. Age = Total out-of-reactor time.

d. This melter is Corronel-230 or equivalent; all other cases use platinum melters.

An improved mathematical model was developed for the scale-up of feeding times for pot calcination, based on non-radioactive and radioactive test results with the WSEP equipment. The model is based on radial deposition of calcine scale on the pot wall, with allowance for formation of a cylindrically-shaped void.

The proposed limits for ultimate disposal of wastes in a salt mine^(1,2) present restrictions in the waste processing options. For all processes, the maximum amount of radioactive decay heat in a container which is acceptable in the proposed salt mine is more restrictive than process limitations. For the processes which convert the wastes to glasses or ceramics, the proposed limits would require solidification within two to three years out-of-reactor time if maximum-sized containers as limited by process considerations are used. For pot calcination and spray in-pot melting, the proposed limits will require an increase in the number of parallel pot lines to maintain capacity.

Concepts for interim aqueous storage and interim on-site storage of solidified wastes were based on ORNL studies⁽³⁾ and applied to the solidification concepts.

A simplified design concept for the solidified waste containers was developed in this study. All the cylindrical containers are similar, with differences primarily in the use of mild steel or stainless steel and in the shape of the internal thermocouple well. Also, the containers for pot calcination include an integral baffle for de-entrainment.

Heat removal aspects of alternative designs of containers for solid radioactive waste were studied. Systems investigated were annular containers, containers with internal fins, containers with multiple internal cooling ports, metal-waste composites, and layered systems of metal and waste. For

maximizing the heat removal from a single container, the containers with multiple internal cooling ports are the most promising, with improvements up to a factor of 10 possible with no change in outer pot diameter. Heat removal from annular containers can be increased by factors greater than three times that for simple cylinders at constant cylinder diameters. For pots with internal fins, for the layered waste-metal systems, and for the mixed waste-metal systems, increased heat removal from a pot by factors of about two are possible in the ranges of practical conditions.

2.2.2 Economics of Waste Management

Economic comparisons of the waste management schemes were made for the WSEP processes. The economic comparisons are discounted cash flow analyses based on processing waste from fuel exposed to 33,000 MWd/tonne. The radioactive decay heat in the waste is based on calculations made with the ORIGEN code using the data contained in Reference 1. Comparisons are made for both PW-4 and PW-2 type wastes (see Section 3) with the specific volumes of both the liquid and solid waste adjusted for 33,000 MWd/tonne. Results of these comparisons for the minimum-cost cases are summarized in Table 2.3. The higher thermal conductivity of the solidified waste from the spray solidification processes and the phosphate glass process proved to be a distinct economic advantage. The higher thermal conductivity permits solidification without any interim liquid storage, thus avoiding a large investment in storage tanks and associated facilities. It was, however, necessary to dilute the solidified waste with nonradioactive chemicals to permit solidification without interim liquid storage in the case of the PW-4 waste. In the case of the PW-2 waste, only the phosphate glass solid required dilution. It is possible to dilute the pot calcination product to the point where solidification without interim liquid cooling can also be accomplished, but the dilution required was so high that it did not show a cost advantage.

TABLE 2.3. Summary Comparison of Minimum Waste Management Costs

Process	Pot Calcination	Spray Melter (Non-Platinum)		Spray Melter (Platinum)	Spray In-Pot Melting	Phosphate Glass
		Air Cooled (a)	Water Cooled (a)			
<u>PW-4 Type Waste</u>						
Interim Storage, yr						
Liquid	15	0	0	0	10	0
Solid	12	5	5	5	58	5
Total Cost, mills/MWH	30.2	28.1	26.0	30.8	31.2	33.6 ^(c)
<u>PW-2 Type Waste</u>						
Interim Storage, yr						
Liquid	15	0	--	--	0	0
Solid	17.5	5	--	--	5	5
Total Cost, mills/MWH	42.3	32.7	--	--	40.5	33.5 ^(b)

a. Water cooling can be (and was) used for the design concepts for the air cooled case; for the water-cooled case, water cooling is mandatory.

b. Does not include the cost for treating sulfate condensate from the solidifier melter.

c. Costs were slightly less than this for 15 year aqueous storage. This case was preferred because of the greater uncertainty in long-term aqueous storage costs and because of the much lower capital investment with this case.

From the minimum total costs encountered at zero aqueous storage time for the spray and phosphate glass processes, the costs increase to maxima at about 2.5 years liquid storage for PW-4 waste and at 5 to 7.5 years liquid storage for PW-2 wastes. The total costs then decrease for longer liquid storage times. At 15 to 20 years liquid storage times the costs become about equal to those at zero liquid storage. For the pot calcination process, the total costs are highest at zero liquid storage and decrease with increasing liquid storage times.

With the PW-4 type waste, the spray melter system with the nonplatinum melter provided the lowest cost of 28.1 mills/MWh, pot calcination is next at 30.2 and the phosphate glass process is the highest with 33.6 mills/MWh. Table 2.3 also shows that the spray melter cost can be further reduced by adjusting conditions to incorporate more heat in the pots such that water cooling is required. However, that level of specific heat is higher than is believed reasonable. With PW-2 type waste where the solid is more dilute for all the processes, the spray melter process with a nonplatinum melter is still the lowest cost process at 32.7 mills/MWh, the phosphate glass process is second at 33.5 and the pot calcination is the most expensive at 42.3 mills/MWh. However, the cost of treating the sulfate condensate from the phosphate glass process, when solidifying PW-2 waste, is not included.

2.2.3 Qualitative Comparison of Solidifiers

Overall qualitative comparisons of the three processes were also made for process characteristics other than costs. Such comparisons, however, are strongly dependent upon the conditions for each reprocessor's situation. For the general conditions in this study, the comparisons should only be used as trend indicators.

Except for the phosphate glass process, all the processes are essentially ready for commercial application, but all processes do need minor amounts of research and development, such as characterizing the specific solid waste and determining the fate of halides during solidification. In addition, the spray processes need modest R&D on atomizing nozzle scale-up and melter materials and reliability studies; the phosphate glass process requires melter feed system studies and studies on melter materials and melter reliability.

For scale-up beyond about 0.5 to 2 tonnes of spent fuel per day, the pot calcination process requires a number of parallel pot lines to achieve higher capacity. The in-pot-melting step used as an optional melting technique with the spray calciner also needs multiple pot lines (1 to 5 pot lines with one spray calciner) for higher capacity.

The continuous spray and phosphate glass processes should be capable of reasonable scale-up, but not all the specific scale-up factors are established.

All the processes are reasonably flexible for processing Purex type wastes which contain "conventional" constituents. However, the pot calcination process has generally the most flexibility to process a variety of waste compositions. When used to convert wastes to borosilicate glasses, the spray process is the next most flexible for varying waste compositions. The spray (with a phosphate system) and the phosphate glass processes are somewhat less versatile with some variations in waste composition.

In this study, the parallel pot lines of the pot calcination process require the most pieces of major process equipment, but also require the fewest different types of major process equipment pieces. The other processes (including the variations of the spray process) are approximately similar in overall major equipment needs.

For processing PW-2 waste with the cases studied here, the pot calcination equipment is somewhat more complicated and consequently should be the most difficult to maintain. Otherwise, there appears to be little difference in overall reliability of the three processes with PW-2 waste.

For processing PW-4m waste, spray in-pot-melting with the borosilicate system appears to be somewhat simpler overall and therefore should be easier to maintain than the other processes. The multiple pot calcination equipment appears to be most complicated, but the spray continuous platinum melter system and the phosphate glass systems are expected to present the most maintenance problems. Reliability of any of the processes appears to be approximately comparable with the others.

The brief safety survey in this study revealed no major differences in safety characteristics among the three processes. However, the pot calcination and spray in-pot-melting processes do have higher in-process inventories of radionuclides than the other techniques. In general operational and accident safety characteristics of the three processes are comparable to typical operations in fuel reprocessing.

The amount of radioactive materials in the off-gases from any of the processes is expected to be in the acceptable range. Entrainment in the off-gases is lowest with the spray solidifier and highest with the pot calciner; ruthenium volatilization is lowest with the spray solidifier making borosilicate glasses, and is highest with the spray solidifier when making phosphate glasses; volatilization of ruthenium is intermediate with the other processes.

REFERENCES FOR SECTION 2

1. U.S. Federal Register, Appendix F to 10CFR50, Policy Relating to the Siting of Commercial Fuel Reprocessing Plants and Related Waste Management Facilities, November 14, 1970.
2. ORNL Staff, Siting of Fuel Reprocessing Plants and Waste Management Facilities, USAEC Report ORNL-4451, July 1970.
3. R. S. Dillon, J. J. Perona, and J. O. Blomeke. A Model for the Economic Analysis of High Level Radioactive Waste Management, USAEC Report ORNL-4633, November 1971.

3.0 BACKGROUND AND DESCRIPTION OF PROCESSES

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3.0 BACKGROUND AND DESCRIPTION OF PROCESSES

3.1 PROCESS DEVELOPMENT AND DESCRIPTION

The WSEP program was designed to compare three high level waste solidification processes on an engineering scale under identical, highly radioactive conditions. The processes, pot solidification, spray solidification, and phosphate glass solidification, were developed independently and carried through laboratory-scale and nonradioactive pilot-plant scale tests, at Oak Ridge National Laboratory, Hanford, and Brookhaven National Laboratory, respectively. A rising level glass modification of pot solidification and the in-pot melting modification of spray solidification, developed to a lesser degree, were included in the final stages of the WSEP program. Figure 3.1 illustrates pertinent differences in the processes. Only brief descriptions of each process will be presented in this summary document. Readers desiring more background or process information will find a comprehensive bibliography in Section 3.3.4.

3.1.1 Pot Calcination

Pot calcination is a batch process in which the predominately nitrate wastes are calcined to oxides by heating to 900 °C. The equipment required includes a multiple zone heating and cooling furnace, 304L stainless steel processing pots which become the final containers for the solidified wastes, an off-gas line which can be washed down continuously, and an off-gas condenser.

Only minor chemical adjustments to the waste are required before processing. It is necessary that sufficient nonvolatile anions, such as sulfate or phosphate, be present in the waste to form stable salts of cesium, rubidium, and sodium. The oxides of these metals may be volatilized unless the ratio

$$\frac{\text{Chem. equivalents sulfate or metaphosphate}}{\text{Chem. equivalents alkali metals}} \geq 1.$$

FIGURE 3.1. Outline of the WSEP Waste Solidification Processes

For wastes containing significant quantities of sulfate the following expression must also be satisfied to suppress loss of sulfate by volatilization:

$$\frac{\text{Chem. equivalents (alkalis + alkaline earths)}}{\text{Chem. equiv. (sulfate + metaphosphate + metaborate + silicate)}} \geq 1.1$$

Calcium is preferable to magnesium as an alkaline earth additive because of the nature of the solids obtained. Dibutyl phosphate from decomposition of tributyl phosphate, the Purex plant solvent extractant, causes foaming in the pot and must be removed by extended nitric acid digestion of the waste. Alternatively, commercial antifoam agents can be added to the pot during processing.

The pot calcination batch processing cycle may be divided into three major periods. First is the period of filling and concentrating at a constant maximum feed rate. In the second major operational period, the feed rate must be reduced gradually because precipitation from the saturated solution forms a scale on the pot walls which grows in thickness and lessens heat transfer to the boiling sludge. Finally, when the feed rate has been reduced to an unprofitably low rate, the feed is shut off and the third major period, that of drying and final calcining, occurs. The presence of internal heat from decay of radioactive constituents requires cooling of the pot wall before the material at the center of the pot has reached its final maximum temperature so that the center temperature will not exceed that desired. (Higher temperatures can result in severe corrosion and potentially undesirable volatilization of some constituents.)

The final product of pot calcination is a porous friable calcine cake with a low thermal conductivity and a relatively high solubility in aqueous solutions.

3.1.2 Rising Level Glass (RLG) Modification

High Level wastes can also be converted to a glassy product in essentially unmodified pot calcination equipment by the addition of appropriate chemicals to the wastes before and/or during processing. Conversion to a glass yields a less dispersible product with improved thermal conductivity. Type 310 rather than 304L stainless steel pots are used for increased high temperature corrosion resistance. As developed by ORNL, the rising level glass modification of the pot calcination process is somewhat similar to the FINGAL process developed in England,⁽¹⁾ however significant differences exist in the chemical formulation used, in the processing temperature, and in the off-gas treatment.

The glass-making additives used in the single radioactive demonstration of the rising level glass process in WSEP were H_3BO_3 , $NaNO_3$ and SiO_2 . They were added to yield the following melt composition:

B_2O_3	21 wt%
SiO_2	17
Na_2O	13
Waste Inerts (Fe, Cr, Ni oxides)	2
Fission Product Oxides	<u>47</u>
	100 wt%

In order to prevent excessive solids formation the waste solution was diluted and heated to 60 °C before addition of H_3BO_3 . Colloidal SiO_2 was added directly to the pot.

The rising level glass process gets its name from the mode of operation. As the solution of waste plus glass-making additive is pumped into the heated pot, three distinct layers form. In order from top to bottom they are made up of boiling solution, calcine, and molten glass. As the run progresses the volume of molten glass increases until the pot is filled to the desired

level. Some foaming, associated with decomposition of residual nitrates in the viscous initial melt at 650-700 °C, occurs in the RLG process but laboratory tests indicated minimum foaming for the waste composition used in the WSEP run.

The RLG process has not received as much development work as the other WSEP solidification techniques and cannot be considered an established process without further investigation.

3.1.3 Spray Calciner-Melter Process

The spray calciner-melter process developed at Hanford is a continuous process which converts aqueous high level waste to a rock-like microcrystalline product. The equipment required includes a radiant-heat spray calciner with integral off-gas filtration, a close-coupled platinum melter (the melter off-gases exit through the calciner), and a mild steel receiver pot.

Desired solidified waste properties are obtained by chemical additions made to the high level waste prior to processing or, as solids, directly to the melter during processing. The chemical additives are chosen to produce melts which will flow freely from the platinum melter yet will have a sufficiently high sintering temperature or "stick point" so that the calcine does not adhere to the hot walls of the calciner. Chemical additions must be made to a given sulfate-free waste composition to obtain ($\pm 15\%$) the following chemical equivalent ratios:

$$\frac{\text{Na}}{\text{FP}^*} = 1.0$$

$$\frac{\text{Fe}}{\text{FP}^*} = 2.0$$

$$\frac{\text{PO}_3^-}{\text{FP}^*} = 1.48$$

* For wastes derived from LWR fuels, the net fission product (FP) cation chemical equivalents per metric ton of uranium processed are approximately proportional to the fuel exposure and can be calculated as follows,
 $\Sigma \text{FP cation chem. equiv.} \approx 0.015$ (average exposure of the fuel, MWd/tonne).

This procedure will yield a melt containing 2.7 metal cation equivalents per mole of metaphosphate ($M^+/P = 2.7$). The sodium is added as the nitrate or hydroxide, the iron as ferric nitrate and phosphate as orthophosphoric acid.

Sulfate-containing wastes require a special melt formulation to prevent excessive volatilization of sulfur trioxide. A melt makeup procedure is presented below that will satisfactorily retain sulfate during the solidification of wastes from those Purex flowsheets in which ferrous sulfamate is used as the plutonium reductant:

1. Satisfy the following chemical equivalent ratios in the solidifier feed:

$$\begin{array}{rcl} \frac{PO_3^-}{SO_4} & = & \geq 0.925 \\ \frac{Na}{PO_3^-} & = & 1.33 \\ \frac{Fe + Al}{PO_3^-} & = & 1.33 \\ \frac{Ca + FP}{PO_3^-} & = & 1.33 \end{array} \left. \vphantom{\begin{array}{rcl} \frac{Na}{PO_3^-} \\ \frac{Fe + Al}{PO_3^-} \\ \frac{Ca + FP}{PO_3^-} \end{array}} \right\} M^+/P = 4.0$$

2. Add $NaPO_3$ directly to the melter so that moles $NaPO_3 = 0.75$ (moles H_3PO_4 added to the solidifier feed).

This procedure will yield a melt with an M^+/P ratio of 2.71. Aluminum is added as the nitrate; calcium and sodium may be added as the nitrates or hydroxides. In many of the WSEP spray solidifier runs lithium was substituted for 50% of the additive sodium, which yielded a slightly lower melting point. In a commercial plant this advantage would probably not outweigh the additional expense.

Spray calcination-melting is a continuous two-step process. In the first step the waste-plus-additive solution is pumped

through an atomizing nozzle into a spray calciner operating with a wall temperature of about 700 °C. A finely divided calcine powder is formed, part of which falls directly into the platinum melter and part of which collects on the off-gas filters. The off-gas filters must therefore be blown-back on a regular cycle. In the second step of the process the calcine powder is fused to a flowable melt in the platinum melter at 1000-1100 °C. The platinum melter is batch dumped to the mild steel receiver pots.

The WSEP spray solidifier chemical flowsheets were phosphate-based because phosphate solids are nonabrasive and easily suspended in the feed solution and because, by proper adjustment of the chemical composition, sulfate can be retained in the low-melting low-viscosity melts. The borosilicate flowsheets developed for the in-pot melting process below can also be utilized with the spray calciner-melter. Borosilicate melts are less corrosive than phosphate melts and can be processed in melters made of metals other than platinum, i.e., the Inconel melter used in the French pot vitrification process.⁽²⁾

3.1.4 In-pot Melting

Spray calcined waste can be mixed with a suitable fluxing agent and fused directly in a furnace-heated stainless steel pot which then serves as the final storage vessel. This process, called the in-pot melting process, has the advantage of eliminating the expensive platinum melter from the system. Higher processing rates can be achieved because stainless steel has a much higher emissivity than platinum. The in-pot melting process also accommodates more variation in viscosity of the melt formulations since the melt is never drained from one container to another. Special equipment requirements include a continuous solids feeder for the fluxing agent and a multiple zone pot furnace.

Most waste compositions can be readily calcined to an oxide powder in the spray calciner, without modification by chemical additions, hence the only chemical flowsheet additive is a fluxing agent which is added directly to the pot in a continuous or semi-continuous flow mode. A relatively low-melting borosilicate glass frit appears to be the best fluxing agent. The frit used in the WSEP demonstrations had the following composition: B_2O_3 , 36 wt%; SiO_2 , 32 wt%; Na_2O , 5 wt%; K_2O , 5 wt%; ZnO , 15 wt%; alkaline earth oxides, 7 wt%. Melts containing as little as 50 wt% frit, the remainder being waste oxides, are readily formed by in-pot melting. The WSEP runs used 70 wt% frit in order to minimize the formation of a microcrystalline, molybdenum-rich second phase (discussed further in Section 6).

Sulfate-containing waste calcines cannot be satisfactorily melted with borosilicate frits. When attempted, most of the sulfate separates as a water soluble second phase. The flowsheet described in the preceding section (3.1.3) for processing sulfate-containing wastes by spray solidification is also applicable for processing these wastes by in-pot melting. The $NaPO_3$ is simply metered into the pot rather than a platinum melter.

Processing by in-pot melting consists essentially of coupling the pot, which will be the ultimate solidified waste storage vessel, directly to the spray calciner. Glass frit is metered into the top of the pot at a rate calculated to give the desired ratio of frit and waste oxides in the final melt. In the WSEP runs, the 304L stainless steel pots were held at 950 °C during the run and complete fusion of frit and calcine was effected. Heating of the pot must be continued for approximately two hours after cessation of feeding to assure complete fusion of the last material fed to the pot.

Borosilicate glasses, which are more resistant to devitrification than phosphate glasses, are easily formed by in-pot

melting. Although in-pot melting was coupled to a spray calciner in the WSEP tests, alternate calcination techniques, such as fluid bed calcination, could be used.

3.1.5 Phosphate Glass

Phosphate glass solidification is a continuous process to convert high level wastes to a glass. The equipment required includes a titanium or Zircalloy denitrator-evaporator, a platinum melter and platinum off-gas line, a means of metering the thick syrupy evaporator bottoms to the melter, and a mild steel receiver pot. The WSEP denitrator-evaporator was a calandria evaporator and utilized an air lift recirculator to feed the melter. (Nonradioactive tests indicated a wiped-film evaporator could offer significant advantages in this service.)

An additional step is required if the waste being processed contains sulfate. Sulfate is volatilized quantitatively from the phosphate glass melter, forming an intermediate level waste containing H_2SO_4 , HNO_3 and traces of H_3PO_4 . A method of decontaminating the H_2SO_4 waste stream by vacuum distillation to a level of radioactivity which would permit disposal in asphalt was demonstrated in the WSEP program and is described in Reference 3. The HNO_3 and H_3PO_4 separated from the H_2SO_4 are recycled to the nitric acid recovery and high level waste solidification processes, respectively.

The chemical adjustments required for the phosphate glass process consist mainly of adding orthophosphoric acid to the high level wastes to obtain a metaphosphate melt (Σ cation equivalents/ PO_3^- equivalents = 1). Additions of ferric nitrate and sodium hydroxide are made as required to adjust the melting point and viscosity of the melt and to optimize properties of the aqueous feed solution during the denitration-evaporation

step. The additives for a given waste composition can be calculated by satisfying the following chemical equivalent ratios ($\pm 10\%$):

$$\frac{\text{Fe} + \text{Al}}{\text{FP}^*} \geq 1$$

$$\frac{\text{Na}}{\text{Fe} + \text{Al} + \text{FP}^*} = 0.5$$

$$\frac{\text{PO}_3^-}{\text{Fe} + \text{Al} + \text{Na} + \text{FP}^*} = 1.0$$

Residual dibutylphosphate can cause foaming in the denitrator-evaporator. The foaming can be controlled by intermittent additions of small amounts of commercial silicone antifoam agents.

The phosphate glass process is unique in that the two-step process is all liquid. Also, most of the nitrates are evolved as HNO_3 rather than NO_x which simplifies recovery. In the first step, the concentrate from the denitrator-evaporator, operating at 125 to 135 °C, is fed continuously to a platinum melter where, in the second step, it is converted to molten glass at 1100-1150 °C. The melter is batch-dumped into a nonheated mild steel pot.

Phosphate glass devitrifies rapidly at temperatures above 550 °C and becomes much more leachable. Therefore, it is desirable that the melt be quenched rapidly in the receiving pots, perhaps by water cooling the pots. The WSEP phosphate glass pots were not water-cooled until completion of processing and the contents of most are completely devitrified.

3.2 WSEP PROGRAM HISTORY

3.2.1 WSEP Design

In 1962, the Hanford Laboratories, predecessor of the Pacific Northwest Laboratory, was authorized by the Division of

* FP equivalents ≈ 0.015 (fuel exposure, MWd/tonne).

Reactor Development, U.S. Atomic Energy Commission, to initiate design-development, procurement and fabrication of equipment for an engineering-scale demonstration of promising solidification processes using actual high-level radioactive wastes. The decision to construct the Waste Solidification Engineering Prototypes (WSEP) was made possible by the large amount of laboratory and cold pilot plant research and development on waste solidification processes conducted at Oak Ridge National Laboratory, Brookhaven National Laboratory and Hanford Laboratories. Information on these supporting studies, which continued during much of the WSEP program, can be found in the references given in Section 3.2.4.

The WSEP equipment was constructed to provide process evaluation on a meaningful engineering scale. The design capacity was established as 10-40 and 10-20 liters/hr of concentrated liquid waste, instantaneous and average rates, respectively. This capacity is equivalent to the waste from about one tonne of power reactor fuel per day.

The equipment was modular-designed to fit in a large radiochemical cell, 22-ft x 25-ft x 30.5-ft in height, with viewing windows and master-slave manipulators located on three sides. The solidification processes shared a common feed makeup and off-gas treatment system (see Figure 3.2). Detailed design features of all of the WSEP equipment are given in Reference 4.

Design of WSEP started in September of 1962 and equipment installation in the cell was completed by October, 1964.

3.2.2 Design Verification Tests

Design verification testing of the solidification equipment was carried out prior to starting the radioactive demonstration of each process in order to:

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FIGURE 3.2. Process Features of the Waste Solidification Engineering Prototypes.

1. Analyze equipment performance and make design modifications, if necessary.
2. Establish optimum operating procedures.
3. Define operating limits.

Eight pot calcination and two rising level glass DVT runs were made between October 1964 and August 1966; ten spray calciner DVT runs were made between September 1965 and October 1966; seven phosphate glass DVT runs were made between January 1966 and May 1967.

The design verification tests served their purpose well. Very few design changes were required during the actual radioactive demonstrations. Repeated failures of the resistance heaters on the platinum melter freeze valves prompted design of an air-cooled freeze valve.⁽⁵⁾ Transfer of the viscous phosphate glass denitrator-evaporator solution to the melter was a problem and a substitute auger mechanism was tried in the last radioactive phosphate glass run.⁽⁶⁾ The WSEP ventilation system was modified to provide adequate vacuum for the spray solidifier. All other process changes made in the course of the radioactive investigations were instituted without changes in design of the equipment. Highlights of the DVT runs are presented below.

Pot Calcination Design Verification Tests^(4,7)

The eight pot calcination DVT runs in 8 and 12-inch diameter pots demonstrated good reliability and operability of the equipment. The pot furnace, a six-zone 175 kW induction heated (Hastelloy-X susceptor) unit, proved very reliable. Four methods of pot liquid level detection were employed. A thermal type liquid level probe developed at ORNL (consisting of a thermocouple imbedded in a solid bar of stainless steel-jacketed copper) and a steam purged, bubbler-type, weight factor probe were satisfactorily used for continuous level

control by regulating feed addition to the pot. A time domain reflection technique (utilizing nanosecond pulses down a rigid coaxial cable probe in the calciner pot) and interpretation of pot thermocouples were also used.

Both low and high heat flux (the available furnace power for high flux was approximately double that for the low flux) methods of operating the pot calcination process were demonstrated. Overall processing rates were almost identical, but during low flux operation decontamination factors from the pot were a factor of five better. A straight section of 2-inch pipe was used for an off-gas line during the early runs. Deposits of entrained calcine combined with wet off-gas vapors presented a source of plugging, and contamination release during the removal of the pot. To reduce this potential a 3-inch jacketed line was installed. By continuously refluxing 2 to 10 liters/hr of the off-gas, the line was washed and maintained free of all solid deposits. The reflux was drained away from the line and combined with the pot condensate.

Eight wastes (Darex, Purex Low and High Iron, Purex Low and High Sulfate, TBP-25, FTW-65, and PW-1) were tested for performance in the prototype pot calcination equipment. Several of these wastes included nonradioactive elements to simulate fission products from power reactor fuel burnups of up to 20,000 MWd/tonne. All wastes performed satisfactorily except the Purex Low Iron, which produced excessive foaming.

The final two DVT runs demonstrated the rising level glass process with FTW-65 and PW-1 wastes. For these runs melt forming chemicals, including NaNO_3 , LiNO_3 and H_3PO_4 , were added. The first run was very successful, and demonstrated significant processing rate enhancement by feeding the pot via film flow down the centerline thermowell; in the second run, however, a hole developed in the bottom of the pot after 29 hours due to corrosion of the 310 stainless steel. The 30 liters of molten

waste that leaked from the failed pot were safely contained by the induction furnace susceptor without damage to other equipment. A less corrosive borosilicate type melt formulation was used in the WSEP demonstration of the rising level glass process.

Spray Solidifier Design Verification Tests^(4,8)

The ten spray solidifier DVT runs demonstrated the general operability of the equipment and the achievement of design processing rates. Melter and pot furnace reliability was demonstrated and the satisfactory use of mild steel receiver pots was established. Powder de-entrainment from the calciner off-gas was effectively accomplished with sintered stainless steel filters.

Performance of the external-mix spray nozzle used in all of the DVT runs was never completely satisfactory. Coarse droplets generally existed in the center core of the spray pattern when either air or steam atomization was used. These droplets formed deposits on the calciner walls and in the core at the bottom of the calciner. Occasionally the latter were extensive enough to plug the calciner outlet to the melter. This situation was rectified in the WSEP demonstrations by the use of internal-mix nozzles with air atomization, which proved quite satisfactory.

The platinum melter developed a leak during the eighth DVT run after 440 hr service at 900-1250 °C. The failure was due to inadvertently dropping a stainless steel chain into the melter. Phosphorus from the melt alloyed with platinum under localized reducing conditions, causing embrittlement and fracturing at grain boundaries.

Liquid level in the melter was best determined by visual observation through a window in the top of the melter and by internal melter temperature readings. A microwave pulse

reflectometer probe was tested for melt level detection in several runs and worked satisfactorily until the ceramic insulators in the probe were dissolved by the melt.

Three waste compositions were used in the spray solidification DVT's: design base IWW, PW-1 and PW-2. Satisfactory melts were prepared from PW-1 and PW-2, sulfate retention in the melt being demonstrated in the latter case. The single run with design base IWW was unsuccessful, however, in that the melt contained a high melting, predominantly rare earth phosphate, phase which could not be drained from the melter and ultimately had to be removed by hand. This experience demonstrated the importance of making the proper chemical additions in a melt-forming process.

Phosphate Glass Design Verification Tests^(4,9)

Seven phosphate glass DVT runs were made using 12-inch pots. During the course of the DVT runs several equipment modifications were made which helped assure the success of the highly radioactive phosphate glass runs which followed. Corrosion problems with the denitrator-evaporator agitator and in the melter off-gas and melter condenser drain lines were detected and corrected. After the fourth DVT run the lid of the platinum melter was found to have buckled excessively and had to be repaired. Additional thermal expansion measurements were made and the melter system design was altered slightly to prevent any further recurrence of this problem.

The biggest overall difficulty during the phosphate glass process DVT's was with the system which transports the concentrate from the denitrator to the melter. The concentrate is a viscous slurry and plugging can occur when the slurry is not kept flowing fast enough to avoid the settling of solids. Plugging of the denitrator-evaporator level and specific gravity tubes was also a major problem. Two waste compositions, PW-1 and PW-2, were used in the test program. It was found that most of the plugging

problems occurred while processing PW-1. Relatively few problems were encountered while concentrating PW-2 wastes, which contain large quantities of sulfate.

A platinum pulse reflectometer probe for measurement of melt level was tested and found unsatisfactory, primarily because of destruction of spacing insulators and some glass retention within the probe.

Both 304L stainless and mild steel pots were satisfactorily filled with phosphate glass product during the DVT tests. In the sixth run a high aluminum content waste was processed successfully. In the fourth run, excessive phosphoric acid was added to the waste solution to yield a metal ion equivalent to phosphorus ratio of 0.7 rather than the desired ratio of 1.0, and the run had to be terminated prematurely because of plugging problems. Processing rates were also extremely low due to the very high melt viscosity encountered. A melt product rate of 2.8 to 5.6 liters/day was the maximum achieved, compared to the normal 17 to 33 liters/day. This experience, as well as that cited for the spray solidification LWW DVT run illustrates the importance of proper melt formulation in processes which utilize a continuous melter.

3.2.3 High-Level Radioactive Tests

Thirty-three radioactive demonstration runs were completed between November 1966 and October 1970. Four reference waste compositions were used to bracket the anticipated range of compositions for high-level wastes coming from aqueous reprocessing of power reactor fuels by Purex-type flowsheets. They are shown in Table 3.1. The PW-1 and PW-2 compositions represent the types of high level waste that can be generated by the first U.S. commercial reprocessing plant; the PW-4m composition represents the "cleaner" waste which will be typical of second generation commercial reprocessing plants.

TABLE 3.1. Nominal Chemical Composition of High-Level Liquid Wastes for WSEP Demonstrations

Constituent	Concentration, Molarity at 378 liters/tonne ^(a)			
	PW-1	PW-2	PW-4m	LMFBR
<u>General Chemical Composition of Inert Materials</u>				
Na	low	high	low	low
Fe	high	med	low	low
SO ₄	0	high	0	0
<u>Nominal Chemical Composition of Inert Materials</u>				
H	3.70	3.90	0.50	0.50
Fe + Al	0.93	0.44	0.050	0.16
Cr	0.012	0.024	0.012	0.046
Ni	0.005	0.010	0.008	0.023
Na	0.14	0.93	0.10	0.10
U	0.010	0.010	0.010	0.010
Hg	<0.001	<0.001	<0.001	---
NO ₃	7.5	5.4	2.4	4.7
SO ₄	---	0.87	---	---
PO ₄	0.003	0.006	0.003	0.060
SiO ₃	0.010	0.010	0.010	---
F	<0.001	<0.001	<0.001	---
$\sum M^{+ (b)}$	3.03	2.48	0.37	0.83
kg oxide/ tonne	31.7	28.1 ^(c)	4.6	9.7

Expected Chemical Composition of Major Materials from Nuclear Fission

Constituent ^(d)	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 (Mo)	0.014	0.031	0.060
Sr	0.015	0.036	0.040
Ba	0.019	0.041	0.068
Cs (K)	0.035	0.078	0.21
Rb (K)	0.007	0.014	0.019
Y+RE ^(e)	0.12	0.27	0.53
Zr	0.065	0.14	0.22
Ru (Fe for 0.9 Ru)	0.032	0.082	0.22
Rh (Co)	0.007	0.013	0.060
Pd (Ni)	0.017	0.043	0.16
Ag (Cu)	0.0008	0.0016	0.019
Cd (Cu)	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
$\sum M^{+ (b)}$	0.91	2.10	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. Does not include the sulfate. If sulfate is not volatilized, approximately 27 kg/tonne of additional oxides are formed.
d. Chemical substitutes used in WSEP demonstration runs are shown in parentheses.
e. RE is rare earth elements.

The LMFBR waste composition was included as another example of a "clean" waste which also contained significantly higher comparative concentrations of certain fission products, such as Sn and Sb.

Since waste from the processing of 20,000 to 100,000 MWd/MT exposure fuel was not available, it was synthesized for the WSEP runs by combining:

1. Hanford Purex plant IWW (from special runs designed to minimize the amount of aluminum and sulfate in the waste).
2. Rare earth fission product concentrate obtained from the Atlantic Richfield Hanford Company waste treatment facility.
3. Inert chemicals.

The Purex IWW provided the entire fission product spectrum, albeit in much lower concentrations than will be present in power reactor wastes, and assured the presence of typical non-radioactive Purex waste constituents, such as solvent degradation products. The rare earth fission product concentrate was used to obtain fission product heat generation rates (predominantly from $^{144}\text{CePr}$) comparable to those in power reactor wastes. Finally, inert isotopes were added to achieve the nominal fission product and nonfission product chemical composition of the wastes, as defined in Table 3.1. Iron, nickel, etc. were substituted for some of the more expensive chemicals after laboratory tests showed no difference in performance. The substitutes used are shown in Table 3.1.

Chemical additions were made to the nominal waste solutions in order to obtain proper processing characteristics and desired properties in the solidified product. As has been discussed, these chemical adjustments varied depending upon the solidification process. The actual chemical composition of the feed solution for each WSEP solidification run is shown in Table 3.2.

TABLE 3.2. Actual Chemical Composition of High-Level Liquid Feed Solutions for WSEP Demonstrations(a)

Run No.	Type of Waste	Adjusted Feed Vol., liter/tonne (b)	Solidifier Feed Composition, M in adjusted feed (c,d)																					
			H ⁺	Li ⁺	Na ⁺	K ⁺	Ca ⁺²	Sr ⁺²	Ba ⁺²	Mn ⁺²	Co ⁺²	Ni ⁺²	Cu ⁺²	UO ₂ ⁺²	Al ⁺³	Cr ⁺³	Fe ⁺³	Y+RE ⁺³	Zr ⁺⁴	MoO ₄ ⁻²	RuNO ₃ ⁺³	NO ₃ ⁻¹	SO ₄ ⁻²	PO ₄ ⁻³
PC-1	PW-2	440 (e)	3.60	0	1.06	0.036	0.215 (e)	0.013	0.017	0.025	0.0064	0.023	0.0014	(0)	(0.017)	0.021	0.382	0.103	0.056	0.068	0.0027	5.33	0.753	(0.003)
	PW-2	400	---	0	0.827	0.040	0.180	0.015	0.018	0.027	0.007	0.035	0.0015	(0.007)	0.212	0.019	0.212	0.113	0.061	0.075	0.0030	(5.43)	0.590	(0.01)
	PW-2	420	---	0	0.738	0.038	0.158	0.014	0.018	0.026	0.0066	0.033	0.0014	(0.009)	0.349	(0.018)	0.067	0.108	0.059	0.071	0.0029	(5.39)	0.566	(0.009)
	PW-1	370	---	0	0.484	0.043	0	0.016	0.020	0.029	0.0076	0.023	0.014	(0.010)	0.112	0.012	0.838	0.123	0.066	0.081	0.0033	(6.64)	0.272	(0.003)
	PW-1	410	2.39	0	0.590	0.039	0	0.014	0.018	0.027	0.0068	0.020	0.0015	(0.009)	0.120	0.011	0.738	0.111	0.060	0.073	0.0030	(5.99)	0.329	(0.003)
	PW-2	390	3.44	0	1.04	0.041	0.084	0.015	0.019	0.028	0.0072	0.026	0.0016	(0.010)	0.339	0.023	0.091	0.116	0.063	0.077	0.0062	5.40	0.607	(0.006)
	PW-1	385	2.16	0	0.187	0.041	0	0.015	0.019	0	0.0073	0.022	0.0016	(0.010)	0.128	0.012	(0.785)	0.118	0.064	0.078 ¹	0.0031	6.48	(0)	0.062
	PW-4m	460	2.63	0	0.205	0.076	0	0.029	0.034	0	0.0109	0.041	0.0034	(0.008)	0.099	0.010	0.041	0.296	0.118	0.132	0.0026	4.93	(0)	0.090
	PW-4m	777 (f)	1.02	0	0.666	0.045	0	0.017	0.020	0	0.0065	0.025	0.0020	(0.005)	0.083	0.0058	0.040	0.199	0.070	0.078	0.0023	3.79	(0)	(0.002)
SS-1	PW-1	455	2.9	.46	0.606	0.035	0	0.013	0.016	0.026	0.0062	0.004	0.0013	(0.008)	0.059	0.010	0.79	0.099	0.054	0.054	0.0027	5.10	(0.008)	1.48
	PW-1	455	3.8	.46	0.33	0.035	0	0.013	0.016	0.026	0.0062	0.004	0.0013	(0.008)	0.059	0.010	0.79	0.099	0.054	0.054	0.0021	5.35	(0.008)	1.46
	PW-2	582	2.73	0.760	0.591	0.027	0.390	0.010	0.013	0	0.0048	0.018	0.0010	(0.006)	0.198	0.016	0.268	(0.078)	0.042	0.051	0.0030	4.29	(0.57)	0.95
	PW-2	560	3.71	0.790	0.689	0.028	0.405	0.010	0.013	0	0.0050	0.018	0.0011	(0.007)	0.209	0.016	0.280	(0.081)	0.044	0.053	0.0014	4.82	(0.59)	1.09
	PW-1	446	4.47	0.424	0.568	0.035	0	0.013	0.017	0	0.0063	0.019	0.0014	(0.008)	0.161	0.010	0.636	0.161	0.055	0.067	0.0027	5.42	(0.006)	1.42
	PW-1	521	4.57	0.363	0.432	0.030	0	0.011	0.014	0	0.0054	0.016	0.0012	(0.007)	0.076	0.0087	0.578	0.109	0.047	0.057	0.0028	4.86	(0.005)	1.44
	PW-1	452	2.34	0.418	0.480	0.035	0	0.013	0.016	0	0.0062	0.019	0.0013	(0.008)	0.074	0.010	0.574	0.109	0.054	0.066	0.0031	3.85	(0.005)	1.32
	PW-1	473	1.10	0.400	0.376	0.034	0	0.012	0.016	0	0.0059	0.018	0.0013	(0.008)	0.096	0.010	0.639	0.096	0.052	0.063	0.0026	1.44	(0.005)	1.28
	PW-4m	630	2.30	0.450	0.540	0.055	0	0.022	0.025	0	0.0078	0.031	0.0025	(0.006)	0.108	0.0072	0.600	0.186	0.086	0.097	0.0018	4.13	(0.008)	1.55
	PW-4m (g)	611	1.98	0.464	0.625	0.057	0	0.022	0.025	0	0.0080	0.032	0.0025	(0.006)	0.101	0.0074	0.557	0.198	0.088	0.100	0.0019	2.41	(0.009)	1.78
	LMFBR (h)	1232	1.65	0	1.15	0.070	0	0.012	0.021	0	0.0184	0.056	0.0089	(0)	0.141	0.014	0.555	0.163	0.068	0.092	0.0017	4.14	(0)	1.74
	PW-4m	556	0.14	0	0.360	0.063	0.442	0.024	0.028	0	0.0088	0.035	0.0028	(0.007)	0.224	0.0082	0.041	0.221	0.097	0.109	0.0031	3.94	(0)	(0.002)
	PW-4m	352	0.46	0	0.204	0.099	0	0.039	0.044	0	0.0140	0.055	0.0044	(0.011)	0.333	0.013	0.118	0.301	0.154	0.173	0.0021	3.86	(0)	(0.003)
PG-1	PT1	483	6.97	0	0.700	0.033	0	0.012	0.015	0	0.0058	0.021	0.0013	(0.008)	0.079	0.019	0.250	0.094	0.051	(0.102)	0.0027	3.66	0.704	2.29
	PW-2	470	---	0	0.567	0.034	0	0.012	0.016	0	0.0060	0.022	0.0013	(0.008)	0.193	0.019	0.200	0.096	0.052	(0.105)	0.0029	3.51	0.756	2.70
	PW-2	586	4.19	0	0.639	0.027	0	0.010	0.013	0	0.0048	0.018	0.0010	(0.006)	0.157	0.015	0.142	0.077	0.042	0.051	0.0024	3.13	0.561	2.21
	PW-2	458	5.28	0	0.726	0.035	0	0.013	0.016	0	0.0061	0.022	0.0013	(0.014)	0.145	0.020	0.243	0.095	0.054	0.065	0.0050	3.71	0.685	2.77
	PW-2	540	---	0	0.840	0.029	0	0.011	0.014	0	0.0052	0.019	0.0011	(0.007)	0.134	0.017	0.134	0.399	0.046	0.055	0.0021	3.49	0.840	3.15
	PW-1	666	4.88	0	1.57	0.024	0	0.0088	0.011	0	0.0042	0.013	0.0009	(0.009)	0.236	0.0068	0.272	0.068	0.037	0.045	0.0023	4.03	(0.004)	3.67
	PW-1	1143	2.94	0	0.913	0.014	0	0.0051	0.0064	0	0.0024	0.0073	0.0005	(0.017)	0.138	0.0040	0.159	0.040	0.021	0.026	0.0013	2.35	(0.002)	2.14
	PW-1	889	5.10	0	1.23	0.018	0	0.0066	0.0083	0	0.0031	0.012	0.0007	(0.004)	0.068	0.0051	0.446	0.102	0.028	0.034	0.0014	3.19	0.003	3.39
	PW-2	644	5.99	0	0.816	0.025	0	0.0091	0.011	0	0.0043	0.016	0.0009	(0.006)	0.088	0.014	0.190	0.123	0.038	0.046	0.0020	3.58	0.514	2.47
	PW-4m	722	5.92	0	0.817	0.048	0	0.019	0.021	0	0.0070	0.026	0.0021	(0)	0.209	0.0063	0.107	0.309	0.075	0.084	0.0019	3.68	(0.008)	3.04
	PW-4m	1023	3.95	0	0.495	0.034	0	0.013	0.015	0	0.0049	0.019	0.0015	(0)	0.155	0.0044	0.026	0.044	0.053	0.059	0.0012	2.73	(0.005)	1.67
PW-4m (i)	1198	3.04	0	0.461	0.029	0	0.011	0.013	0	0.0042	0.016	0.0013	(0)	0.158	0.0038	0.023	0.092	0.045	0.051	0.0032	2.43	(0.005)	1.68	
LMFBR	1916	5.25	0	0.659	0.045	0	0.0079	0.013	0	0.0118	0.036	0.0057	(0)	0.138	0.0091	0.109	0.180	0.044	0.059	0.0018	3.45	(0)	1.98	

a. Includes solutions and slurries added separately to solidifier but not solids added to melter.

b. Does not include correction for H₂O or acid spray, antifoam, etc.

c. Estimated or calculated values are given in parentheses.

d. Feeds also contained an estimated 0.002-0.01M SiO₃ from HLW feed materials.

e. Includes 40 liter/tonne of 2.4M Ca(NO₃)₃ added directly to the pot.

f. Includes 72 liter/tonne of 21.5 wt% colloidal suspension of SiO₂ (0.37 moles SiO₂/liter of feed) added directly to the pot.

g. Feed also contained 0.41M B₂O₃.

h. The feed also contained 0.012M TeO₄⁼, 0.0015M SeO₄⁼, 0.0034M Sn⁺⁴, and 0.00092M Sb⁺³.

i. Feed also contained 0.34M Zn⁺⁺.

j. The feed also contained 0.0067M TeO₄⁼, 0.0010M SeO₄⁼, 0.0022M Sn⁺⁴, and 0.00059M Sb⁺³.

(The minor variations from nominal waste compositions which occurred in some instances due to the sulfate and aluminum content of the Purex IWW are included in the table.)

Approximately 400-1000 liters of waste were prepared for each radioactive demonstration run, depending upon the pot size to be used. Actual running time for the radioactive demonstration runs averaged about 50 hours. The runs were spaced at about six week intervals to allow time for after-fill pot measurements, data evaluation, and preparation for the succeeding run.

A total of 4,930 kg of solidified waste generating 193 kilowatts of fission product heat was encapsulated. Summary details of the runs are shown in Table 3.3. The three base waste solidification processes were all proven to be operable under remote conditions as originally designed. In addition, the two in-pot melting runs proved this process to have many attractive features. The single run of the least well-developed process, the rising level glass process, was only partially satisfactory and indicated that some operating problems remain to be solved.

More detailed reviews of process performances in WSEP and descriptions of the solidified products are presented in Sections 4.0, 5.0, and 6.0.

3.2.4 WSEP Waste Solidification Bibliography

WSEP Program Reports

Results of the WSEP program have been reported in a series of eleven comprehensive reports, of which this report is the last. These reports cover process technology, equipment description, and detailed descriptions of all the runs. The first ten reports in the series are:

TABLE 3.3. WSEP Radioactive Demonstration Runs

Run No.	Date of Run	Processing Summary			Pot Description		Filled Pot Summary							
		Waste Type PW	Avg Feed Rate, liters/hr	Process Rate Tonne/Day	Diam. in.	Material of Construction	Volume of Solid, Liters	Bulk Density, kg/liter	Fill Height, inches	Total MCi	Total Heat Rate, kW	Heat Rate Density W/liter	ΔT, (c) °C	Temp. (c) °C
PC-1	Nov. 1966	2	13.8	0.73 (a)	12	304L	105 (b)	1.3	~72	0.09	0.60	5.7	70	140 (d)
PC-2	Feb. 1967	2	14.7	0.79	12	304L	105	1.2	~72	0.43	1.7	0.6	235	485
PC-3	Feb. 1967	2	12.3	0.72	8	304L	60	1.4	~72	0.38	1.8	30	220	410
PC-4	Jun. 1967	1	14.7	0.96	12	304L	110	1.3	~72	0.65	2.7	23.7	312	477
PC-5	Jul. 1967	1	13.2	0.78	8	304L	55	1.4	~72	1.15	4.3	78	495	725
PC-6	Sep. 1967	2	8.5	0.57	8	304L	60	1.3	~72	1.3	5.1	85	700	940
PC-7	Aug. 1970	1	10.7	0.64	8	304L	60	1.2	~72	1.4	5.6	93	753	1012
PC-8	Sep. 1970	4m	7.9	0.40	6	304L	34	1.3	~72	1.2	4.8	141	604	856
PC-9 (RLG)	Oct. 1970	4m	9.0	0.30	6	310	~16	3.5	35	1.4	5.6	310	370	635
Avg 0.65										£8.00	£31.8			
PG-1	Nov. 1967	2	14.6, 13 (e)	0.53	12	Mild Stl.	92	2.7	50	0.35	1.6	17	89	316 (d)
PG-2	Dec. 1967	2	14	0.38	8	304L	35	2.9	43	0.40	1.7	49	135	355
PG-3	Jan. 1968	2	16	0.21	8	Mild Stl.	35	2.8	43	0.60	3.3	95	255	655 (d)
PG-4	Mar. 1968	2	7.5	0.34	8	Mild Stl.	73	2.9	89	1.1	4.2	57	175	510 (d)
PG-5	Apr. 1968	1	10.0, 11.5 (e)	0.24	12	Mild Stl.	113	2.8	61	2.2	8.8	78	352	712
PG-6	May, 1968	1	10.5	0.28	8	304L	62	2.8	75	2.4	9.6	155	380	780
PG-7	Jul. 1969	2	17.0	0.58	8	310	67	2.7	81	2.8	9.8	146	401	782
PG-8	Aug. 1969	4m	13.0	0.39	8	Mild Stl.	67	2.9	81	2.3	8.8	132	350	710
PG-9	Oct. 1969	4m	25.0	0.47	6	304L	27	2.8	58	1.0	4.2	158	204	566
PG-10	Oct. 1969	4m	22.0	0.34	6	304L	29	2.9	63	2.6	9.3	317	369	827
PG-11	Dec. 1969	LMFBR	18.0	0.20	8	304L	60	2.9	73	3.3	11.9	198	417	834
Avg 0.39										£19.1	£73.7			
SS-1	Jan. 1967	1	16.3	0.84	12	304L	38	3.2	21	0.08	0.28	7.5	30	170
SS-2	Apr. 1967	1	13.8	0.72	8	304L	48	3.2	58	0.42	2.1	44	70	315
SS-3	Jul. 1968	2	11.3	0.46	12	304L	39	2.7	21	0.42	1.6	40	80	315
SS-4	Sep. 1968	2	12.3	0.53	8	Mild Stl.	56	2.9	68	1.4	5.1	93	220	505
SS-5	Oct. 1968	1	16.7	0.90	8	304L	66	3.2	80	2.5	8.2	127	270	633
SS-6	Nov. 1968	1	17.7	0.82	8	304L	65	3.2	79	3.0	10.0	168	305	767
SS-7	Dec. 1968	1	17.9	0.94	8	304L	62	3.2	75	3.6	12.7	204	453	928
SS-8	Feb. 1969	1	14.5	0.74	8	304L	59	2.9	72	1.8	7.2	120	210	605
SS-9	Mar. 1969	4m	15.2	0.58	8	310	68	2.9	83	2.0	7.2	107	242	594
SS-10	Apr. 1969	4m	13.5	0.46	8	Mild Stl.	56	3.1	68	2.6	7.9	141	262	610
SS-11	Mar. 1970	LMFBR	14.9	0.29	8	304L	60	3.1	73	3.1	10.5	175	353	754
SS-12 (IPM)	Apr. 1970	4m	10.8	0.46	8	304L	54	3.0	66	1.4	4.9	90	197	474
SS-13 (IPM)	May, 1970	4m	15.4	1.05	8	304L	50	3.0	61	2.8	10.0	200	404	824
Avg 0.68										£24.7	£87.3			
										££51.8	££193			

- a. Based on feed time plus drying and cooling time for all pot calcine runs.
b. Product volume estimated from receiver pot temperatures and feed consumption for all pot calcine runs.
c. Receiver pot setting in furnace with cooling air on.
d. Receiver pot setting in furnace with cooling air off.
e. Two feed batches were used.

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J. E. Mendel and J. L. McElroy, Waste Solidification Program Volume 10, Evaluation of Solidified Waste Products, BNWL-1666, Battelle-Northwest, Richland, Washington, July 1972.

Hanford Quarterly Reports

To assure prompt and widespread dissemination of the results of the high level waste solidification studies at Hanford, quarterly reports were issued from 1959-1971. These are listed on Page 3.25, along with a notation of the specific waste solidification processes which are dealt with in each quarterly report. Editors of the quarterly reports were D. W. Pearce, April, 1959 - April, 1961; E. R. Irish, June 1961 - March, 1964; A. M. Platt, June, 1964 - January, 1969; A. G. Blasewitz, April, 1969 - January, 1971; and K. J. Schneider, April, 1971. The reports were titled, Quarterly Progress Report - Research and Development Activities - Fixation of Radioactive Residues.

Quarter	Year	Report Number	Pot Calcination	Rising Level Glass*	Spray Solidification	In-Pot Melting*	Phosphate Glass
	<u>1959</u>						
First		HW-60584			x		
Second		HW-61635			x	x	
Third		HW-63048			x	x	
Fourth		HW-63949	x	x	x		
	<u>1960</u>						
First		HW-65209	x	x	x	x	
Second		HW-66571			x		
Third		HW-67334	x		x		
Fourth		HW-68193	x	x	x	x	
	<u>1961</u>						
First		HW-69176	x				
Second		HW-70517	x	x	x		
Third		HW-71374	x	x	x	x	
Fourth		HW-72324	x		x		
	<u>1962</u>						
First		HW-73412			x		
Second		HW-74375			x		
Third		HW-75290	x	x	x		
Fourth		HW-76262	x		x		
	<u>1963</u>						
First		HW-77299	x		x		
Second		HW-78188	x		x		
Third		HW-79140			x		
Fourth		HW-80526			x		x
	<u>1964</u>						
First		HW-81862			x	x	x
Second		HW-83320			x		x
Third		HW-84467			x		x
Fourth		HW-84603	x		x		x
	<u>1965</u>						
First		BNWL-76	x		x		
Second		BNWL-139	x	x	x		x
Third		BNWL-170	x	x	x		
Fourth		BNWL-213			x		
	<u>1966</u>						
First		BNWL-267			x		
Second		BNWL-306			x		x
Third		BNWL-365		x			x
Fourth		BNWL-410	x		x		x
	<u>1967</u>						
First		BNWL-434	x		x		x
Second		BNWL-507	x		x		x
Third**		BNWL-677	x		x		
Fourth		BNWL-771	x		x		x
	<u>1968</u>						
First		BNWL-824			x		x
Second		BNWL-889			x		x
Third		BNWL-923			x		x
Fourth		BNWL-1003			x		x
	<u>1969</u>						
First		BNWL-1074			x		x
Second		BNWL-1186			x		x
Third		BNWL-1263			x	x	x
Fourth		BNWL-1311			x		x
	<u>1970</u>						
First		BNWL-1401			x	x	x
Second		BNWL-1494		x		x	x
Third		BNWL-1533	x	x	x		x
Fourth		BNWL-1557		x	x		x
	<u>1971</u>						
First***		BNWL-1578		x		x	x

* Experiments prior to 1966 involved batchwise preparation of melts, mostly sulfate-based, in stainless steel pots. The experimental results are relevant to the RLG and in-pot melting processes, although flowsheets and procedures differed considerably.

** This report covers the four-month period July through October, 1967. Succeeding reporting periods are February-April, May-July, August-October, and November-January.

*** Final report in series.

Background Information

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4.0 EVALUATION OF THE WSEP SOLIDIFICATION PROCESSES

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4.0 EVALUATION OF THE WSEP SOLIDIFICATION PROCESSES

Section 4 presents a summary and evaluation of the data obtained with the pot, spray and phosphate glass processes during the WSEP demonstration runs. Some comparisons are made with data obtained during the development of these processes.

4.1 POT SOLIDIFICATION

Nine radioactive pot solidification runs were made in WSEP.^(1,2) Eight runs were made with the pot calcination process and one run was made using the rising level glass (RLG) technique. The pot calcination process is essentially ready for commercial use; however, further development is required for the rising level glass system.⁽¹⁾

The essential features of the pot solidification equipment are shown in Figure 4.1. The calcine pot sits in a six zone heating-cooling furnace and is surmounted by a self-cleaning vent line and a fill head that connects the pot to process and instrument lines.^(1,3) The stainless steel calcine pot and the location of the pot and furnace thermocouples are shown in Figure 4.2.

The RLG process will be discussed separately in Section 4.1.6; however, data for the RLG run will be presented in the following tables and figures with the pot calcination data.

4.1.1 Overall Processing Rates

Feed composition (concentration), pot size, and internal heat generation rates were the major variables which affected the processing rates. Startup procedure, initial feed rate, feed rate at feed shutoff, available furnace power, and interruptions also affected the processing rates for a given feed composition, pot size, and internal heat generation rate.

FIGURE 4.1. Pot Solidifier Self Cleaning Vent Line and Fill Head in WSEP

Other factors which influenced the overall rates slightly were: 1) approximately 1 kg/hr of steam condensate was added to the pot during most runs to purge the pot weight factor dip tube during the feed period; 2) five to ten liters of condensed pot vapors were returned to the pot during the run to wash the lower section of the pot vent line and the pot throat; 3) a run was started with 10 to 30 liters of water accumulated in the pot from a vent line flush; and 4) during the last two pot runs, approximately 1 kg/hr of antifoam solution was added to the pot to stabilize foaming.

A consistent startup procedure was used to avoid high and random feed rates during the early stages of the runs. The 6, 8 and 12-inch pots were limited to a maximum rate at startup of approximately 17, 30 and 50 liters/hr, respectively (60 liters/hr would be suitable for the 12-inch pots). During WSEP DVT* testing, maximum water boilup rates of 60 and 90 liters/hr were achieved with 8 and 12-inch diameter pots; however, rates were limited to 30 and 60 liters/hr, respectively, ^(4,5) to minimize entrainment by limiting the superficial vapor velocity in the pot to approximately 1.2 ft/sec (about 85 liters/hr-ft² boiloff). The WSEP pots had nominal inside diameters of 6, 8 and 11.4 inches.

Table 4.1 summarizes the data on processing rates for the pot runs in WSEP. The feed and processing rates can be compared as shown in Figure 4.3. The average feed rate to the pot calciner increased substantially with pot diameter; increasing from 10 to 15 to 22 liters/hr for 6, 8 and 12-inch diameter pots. The increase in overall processing rate was less sensitive to pot diameter because the calcination and cooling time (final bake-out period after feeding was

*DVT = Nonradioactive design verification tests of the WSEP equipment prior to radioactive service.

TABLE 4.1. Pot Solidifier Feeding and Run Data

Solidifier Run Number	PC-1	PC-2	PC-3	PC-4	PC-5	PC-6	PC-7	PC-8	PC-9 (RLG)
Operating Mode	A	B	A-Modified	C	C	A	A	A	A
Pot Size (a)	12	12	8	12	8	8	8	6	6
Waste Type	PW-2	PW-2	PW-2	PW-1 (b)	PW-1 (b)	PW-2	PW-1	PW-4m	PW-4m
Feed Volume, liters/tonne	400	400	420	370	410	390	385	460	705
Feed Temperature, °C	30	30	70	<70	50 to 60	35	35	NA	65
Feed Consumed, liters	850	940 (c)	553	1060 (d)	515	460 (e)	500	340	393
Additive Stream to Pot, liters	(CaNO ₃) 85	--	--	--	--	--	(Antifoam) 31	(Antifoam) 36	(SiO ₂) 40
Total Feed Time, hr	43.7	42	31	42	28	43 (e)	36.5 (f)	36	43.2 (g)
Total Drying and Cooling Time, hr	24	22	14	30	11	8 (e)	9	6	--
Average Feed Rate, liters/hr	19.5	22.4	17.8	25	18.4	10.7 (e)	12.5 (f)	9.4	9.1
Overall Average Processing Rate, liters/hr	13.8	14.7	12.3	14.7	13.2	8.5	10.7	7.9	9.0
Feed Added Prior to Calcine Deposition, (i) liters	500	550	240	250	88	125	100	20	--
Feed Rate at Feed Off, liters/hr	2	5	5	5	3	2	5	3	NA
<u>Process</u>									
Pot Furnace Temperature, °C	850	850	850	900	900	850	900	900	950
Pot Vacuum, in. of water	20	15	15	15	15	15	10	10	10
System Off-Gas, scfm	1.5	2	1.5	1 to 2	1 to 2	1 to 2	<5	<5	<5
<u>Radioactivity</u>									
Total Radioactivity in Feed to Pot, (j) kCi	85	430	375	650	1150	1300	1400	1200	1400
Radioruthenium in Feed to Pot, kCi	9.2	35	32	47	18	36	3.8	2.3	1.8
Feed Heat Rate Density, W/liter	0.7	1.85	3.2	11	2.4	8.3	11.2	14.2	14.3
Fission Product Heat to Pot, W	600	1700	1800	2700	4300	5100	5600	4800	5600
Ruthenium Volatilized from Pot, %	14	30	31	5	3	13 (h)	6	11	15
¹⁴⁴ CePr Entrainment from Pot, %	0.04	~0.04	0.29	NA	NA	1.2 (h)	0.15	1.2	0.38
<u>Equivalent Spent Fuel Waste</u>									
Waste to Pot, tonne	2.2	2.3	1.4	2.8	1.25	1.2 (e)	1.3	0.74	0.56
Average Processing Rate, tonnes/day	0.73	0.79	0.96	0.72	0.78	0.57 (e)	0.64	0.4	0.3
Equivalent Age of Waste, (k) yr	37	6.2	3.4	4.8	1.4	1.1	3.0	2.0	1.2

NA - Not Available

- a. PC-9(RLG) pot was 310 SS. All others were 304L.
b. Early PW-1 runs contained excessive amounts of sulfate.
c. Does not include 99 liters of water to pick up feed heel.
d. Includes 60 liters expelled from pot due to foaming.
e. Feeding extended to obtain maximum fill. Run was interrupted three times and had two extensive delays.
f. Feed was off 2.5 hours during run. Average feed rate includes down time.

- g. Feed was off 15 hours during run.
h. Data is through first shutdown only including the calcining-cooling cycle.
i. Volume at which scale deposition started on the pot wall in the lower zones.
j. Radioactivity was predominantly ¹⁴⁴CePr.
k. Based on heat generation rate in pot and ISOGEN program. See Section 7.

Values Used for Pot Feeding Model (See Appendix A)
 Calculated for PW-2 Waste with Nominal WSEP Operating Parameters

$\rho = 1.3 \text{ kg/liter}$, $W = 0.16 \text{ kg/liter}$, $W_p = 0.4 \text{ kg/liter}$
 $k = 0.2 \text{ Btu/hr-}^\circ\text{F-ft}$, $\Delta T = 1320^\circ\text{F} = 733^\circ\text{C}$, $\lambda = 2200 \text{ Btu/liter}$
 $L = 6 \text{ ft}$, $\Delta L = 0.75 \text{ ft}$, $n = 0.5$, Max Feed Rate = 86.4 l/hr-ft^2

Data Obtained from Model

Pot Size, in. ID	90% Feed Fill				100% Feed Fill			
	Hours at Max Rate	Hours at Falling Rate	Total Hours	Avg Rate liter/hr	Hours at Max Rate	Hours at Falling Rate	Total Hours	Avg Rate liter/hr
6	11.5	5.1	16.7	15.0	11.5	10.3	21.9	12.7
8	9.7	12.1	21.8	19.8	9.7	21.1	30.8	15.6
12	7.6	31.9	39.5	24.7	7.6	52.3	59.8	18.1
16	6.7	51.4	58.1	26.2	6.7	83.2	89.9	18.9

Pot Size, in. ID	105% Feed Fill			
	Hours at Max Rate	Hours at Falling Rate	Total Hours	Avg Rate liter/hr
6	11.5	16.0	27.5	10.6
8	9.7	31.0	40.6	12.4
12	7.6	74.5	82.1	13.9
16	6.7	118.0	124.7	14.3

FIGURE 4.3. Pot Calciner Feed Rate Dependence on Pot Size

terminated) increased significantly for large diameter pots. The average processing rate increased from 8 to 12 to 14 liters/hr for 6, 8 and 12-inch diameter pots.

Typical pot feed rate curves for 6, 8 and 12-inch diameter pots are shown in Figure 4.4. The falling rate portion of the curves is exponential (straight line on semi-log paper) for all runs except PC-6 and 7. Both of these pots had nearly the same high internal heat rate density and yet both unexpectedly fell below the corresponding feed rate capacity, caline density, and effective thermal conductivity of similar 8-inch pots with less internal heat. The constant feed rate portion of the curve represented approximately 40 to 50% of the feed delivered to the pots and was independent of pot diameter.

A mathematical model for predicting average pot feed rates was derived and is presented in the appendix. The model is based on the WSEP method of pot calcination (a constant feed rate period followed by a falling feed rate period). The model was used to predict typical average feed rates using PW-2 waste and typical WSEP conditions. Results are shown in Figure 4.3. The model predicts that the average feed rate increases with diameter for small diameter pots but becomes independent of diameter beyond about a 15 inch-diameter pot.

The model also shows the effect of completely filling a pot (Figure 4.3). A significantly faster feed rate is attained (19 versus 26 liters/hr for large diameter pots) if the pot feed is shut off at 90% of the required feed volume for filling a pot.

Increased internal heat generation rates increased the overall processing rate (i.e., feeding, calcining, and cooling) by decreasing the calcining and cooling time following feed shutoff because the calcine would come to its maximum temperature more rapidly. Pot calcining and cooling time is plotted in Figure 4.5 as a function of pot diameter and internal heat rate

FIGURE 4.4. Typical WSEP Pot Feed Rates

FIGURE 4.5. Pot Calcination Calcining and Cooling Times

density. Most data were obtained with 8-inch diameter pots and an excellent correlation exists. The data for the 12-inch pots show considerable scatter. As shown in Figure 4.5 it is postulated that for very high heat rate densities in a given diameter pot, the calcining and cooling time approaches a point that is independent of the pot diameter. However, because the maximum allowable heat rate density in a pot decreases with increasing diameter, calcining and cooling times for each diameter will not necessarily overlap those for other diameter pots and will normally increase with pot diameter. For pots containing the maximum allowable heat rate densities, the calcining and cooling time, in hours, will equal 850 divided by the heat rate density.

Average processing rates for Purex waste using 8-inch diameter pots in cold ORNL and WSEP development tests were 10 and 14 liters/hr, respectively, ^(6,7) in line with the radioactive run results.

It should also be noted that the feed and processing rates will increase as the effective heated length of the calcine pot is increased. The increase will not be directly proportional to length, if the pot is operated as in WSEP, since the initial boiloff rate period is limited by diameter and is independent of pot length.

4.1.2 Radionuclide Heating Effects

The high concentrations of radionuclides in high level solidified wastes produce high internal temperatures even when the receiver pot is cooled. The maximum allowable temperatures established for WSEP were a product (solidified waste) temperature of 900 °C and/or a receiver pot wall temperature of 427 °C (800°F). The 900 °C temperature prevented excessive corrosion to the stainless steel thermowells used to house the thermocouples at the centerline of the pots. The 427 °C wall

temperature prevented excessive air oxidation of the container and allowed remote handling of the pots without excessive special precautions.

The internal heat generation rates and the resulting temperatures in the WSEP pot calcine pots are listed in Table 4.2. It was established that the maximum allowable heat-rate density in an 8-inch diameter pot was approximately 85 to 90 watts/liter (approximately 5300 watts total) during Runs PC-6 and PC-7 when the 900 °C centerline restriction was exceeded in both runs. During Run PC-8, a 141 watt/liter heat-rate density (4800 watts total) produced an 865 °C centerline temperature in a 6-inch diameter pot. From these data an average effective thermal conductivity, K_{eff} , (includes pot and solid product) of 0.35 W/(m²)(°C/m) was established for the pot calciner (see Section 6.2.2). Pot temperature considerations and limitations are discussed in Section 8.8.

Data obtained from pot wall temperatures indicated that the emissivity of the calcine pot was 0.8.^(1,2) The minimum emissivities obtained with all WSEP pots were about 0.6 for those that were unoxidized.

Pot and furnace temperature control techniques were developed in the first series of pot runs⁽²⁾ to assure adequate calcination while preventing excessive calcine temperatures. The control technique allows for the need to start cooling parts of the pot contents while other parts are still heating. The general procedure was as follows:

- Reduce furnace temperature about 200 °C in individual zones when the pot wall temperature is nearly equal to the furnace control temperature.
- Shut off furnace heat to a zone when the centerline or intermediate temperature of ≥600 °C indicated that the calcine was dry. In large diameter pots (≥12 inches) a

TABLE 4.2. Pot Solidifier Product Data Summary

Solidifier Run Number	PC-1	PC-2	PC-3	PC-4	PC-5	PC-6	PC-7	PC-8	PC-9(RLG)
Pot Size (a)	12	12	8	12	8	8	8	6	6
Feed Type	PW-2	PW-2	PW-2	PW-1	PW-1	PW-2	PW-1	PW-4m	PW-4m
Product Weight, kg	151	141	86	166	86	80	73	46	64
Product Volume, (b) liters	105	105	60	110	55	60	60	34	~16 (plus ~2 as calcine)
Bulk Density, kg/liter	1.26	1.18	1.43	1.38	1.43	1.33	1.22	1.34	~3.5 (glass)
Volume Reduction, Feed to Solid	8	9	9	9.1	9.4	7.7	8.3	10	22
Adjusted Volume Reduction (Based on feed at 378 liters/tonne)	7.6	8.5	8.1	9.3	8.7	7.5	8.2	8.2	12
Product Unit Volume, liters/tonne	50	45	47	41	43	50	46	46	32
Fission Product Heat in Pot, W	600	1700	1800	2700	4300	5100	5600	4800	5600
Heat Generation Rate Density, W/liter	5.7	16	30	24	78	85	93	141	310
Pot Radiation Reading at 6-in., (e) kR/hr	25	24	39	38	49	57	32	55	51
<u>Pot Steady State Temperature Data</u>									
Centerline Temperature, (c) °C									
In Air-Cooled Furnace	NA	415	410	630 (d)	900 (d)	NA	1025	872	740
In Air at ~40 °C	140	NA	NA	477	725	940	1012	865	635
In Water at 30 to 60 °C	NA	NA	NA	370	NA	850	925	780	454
Centerline-to-Wall ΔT, (c) °C									
In Air-Cooled Furnace	NA	235	220	290 (d)	453 (d)	NA	730	557	338
In Air at ~40 °C	70	NA	NA	312	495	700	753	604	370
In Water at 30 to 60 °C	NA	NA	NA	340	NA	800	895	750	424
Effective Thermal Conductivity, W/(m ²) (°C/m) (f)									
In Air-Cooled Furnace	NA	0.32	0.36	0.39 (d)	0.42 (d)	NA	0.33	0.37	1.36
In Air at ~40 °C	0.37	NA	NA	0.36	0.38	0.32	0.32	0.35	1.25
In Water at 30 to 60 °C	NA	NA	NA	0.35	NA	0.26	0.27	0.28	1.09

- a. PC-9(RLG) pot was 310 SS. All others were 304L.
b. Estimated from pot temperatures. The fill height was approximately 6 feet, except PC-9(RLG) = 3 feet.
c. Based on Zone 4 and/or Zone 5 pot temperatures.
d. No cooling air on to furnace.
e. Fission product content was predominantly ¹⁴⁴CePr.
f. W/(m²) (°C/m) × 0.578 = Btu/hr(ft²) (°F/ft).
NA Not Available

partial furnace temperature reduction may precede this step.

- Turn on cooling air when the pot centerline temperature reached 800 °C.

The manual reduction of temperature in individual furnace zones was both practical and satisfactory but not totally optimized. It did not allow a direct comparison with the more automated approach suggested by Holmes and Jury.^(8,9) Comparisons made in Reference 2 showed that temperature transitions (the "thermal heat wave") within the cake were not as severe as predicted by their analyses (possibly because the heats of dehydration and decomposition of the salts were neglected in computing the power required to raise the temperature of the solids to 900 °C). Reference 10 summarizes the development work performed at ORNL for the pot calcination and rising level pot glass processes and also presents a mathematical treatment of the calcination process.

In actual practice, with fewer thermocouples in the pot, or none at all, the entire operation will require programming on the basis of the heat rate content of the feed delivered to the pot and the general heating power requirements of each furnace zone. If programmed properly, the calcining and cooling period for small diameter pots may be shortened to where the pot will be ready for removal from the furnace very shortly after the feed is shut off. This is probably not true with large diameter pots, since the drying-cooling cycle increases with pot diameter; see Section 4.1.1.

Run PC-7 is an example of temperature control with a high internal heat generation rate. A plot of Run PC-7 temperatures is shown in Figure 4.6. Zone 6 temperatures during Run PC-7 were typical and are described here. (Temperatures within ± 15 °C of one another are sometimes combined and shown as one line in Figure 4.6). During the first 16 hours the

FIGURE 4.6. Run PC-7 Pot and Furnace Temperatures

furnace was on, 4 kilowatts/hr were used in Zone 6 and the furnace temperature controller was set at 900 °C. After 2 to 4 hours, the calcine scale started to build up on the pot wall, and at 16 hours the pot wall temperature increased to 875 °C. At this time, the furnace control point was reduced to 700 °C. The first indication of a "heat wave" was apparent at 18 hours as the Zone 6 internal temperatures were rising rapidly. The Zone 6 furnace power was turned off at 18 hours and the cooling air was turned on, but the "heat wave" continued as expected and peaked 2 hours later at 980 °C. The rest of the zones experienced the same pattern, and the maximum temperature inside the pot occurred when Zone 4 reached its peak at approximately 1050 °C. The feed to the pot was shut off at 39 hours and at 48 hours the "heat wave" in all zones was completed and the pot was ready for removal from the furnace.

Temperature control for both of the maximum temperature and maximum heat generation rate runs (PC-6 and PC-7) was adequate, but the limit of the furnace cooling system was reached for a pot wall temperature of 275 to 300 °C while either one or two blowers rated at 275 scfm each was being used. Natural cooling of the pot (by natural convection in cell air) gave 50 and 35 °C lower pot wall temperatures than could be obtained by cooling the outside of the furnace susceptor with an air blast from one and two blowers, respectively.*

4.1.3 Waste Volume Reduction

Data for the solidified pot calcine are presented in Table 4.2. The final waste solids volume averaged 43, 48 and 46 liters/tonne for the PW-1, PW-2, and PW-4m calcines, respectively. This volume is equivalent to 1 and 2.3 liters/1000 MWd_t for fuel irradiated to 45,000 MWd/tonne at 30 MW/tonne (PW-4m waste) and 20,000 MWd/tonne at 15 MW/tonne (PW-1 and 2 waste), respectively.

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

The bulk density of the calcines ranged from 1.18 to 1.43 kg/liter for an average of 1.32 kg/liter with a maximum deviation of 10.6%. There was no apparent correlation with either waste type or pot size. In ORNL and WSEP DVT runs the density ranged from 1.1 to 1.5 kg/liter for Purex type waste. (6,7)

The volume of feed required for a pot was estimated from the known feed composition by assuming a calcine density and calculating the weight of oxides required to fill the pot. The overall volume reduction factor from feed to solid product varied from 8 to 10 for the calcines.

4.1.4 Volatilization and Entrainment

In the WSEP pot calcine runs, from 3 to 6% of the ruthenium in the feed to the pot (based on ^{106}Ru) was volatilized during the PW-1 runs, 13 to 31% during the PW-2 runs and 11% during the one PW-4m run. The amount volatilized varied with the type of aqueous waste. Furthermore, less evolution of ruthenium occurred with low sulfate (PW-1 and PW-4m), moderate to low sodium in the wastes, and with earlier scaling of the pot wall during processing.

The PW-1 waste was intended to be sulfate free and to contain little sodium; however, the feed for the first two PW-1 runs contained sulfate equal to 40 to 55% of that present in the PW-2 runs. The sodium content was also excessive in the same two PW-1 runs, since it was added to suppress sulfate volatilization. Nevertheless, there was a significant difference in the amount of ruthenium evolved; and as shown in Figure 4.7, the shape of the ruthenium evolution curves differed. For the low sodium and low sulfate feeds (PW-1 and PW-4m), with early pot wall scaling, the ruthenium evolved at a nearly constant rate while for the high sodium and high sulfate feed (PW-2), with delayed scaling, 80% of the ruthenium volatilized during the last 40% of the run.

FIGURE 4.7. Accumulation of Ruthenium
in the Pot Solidifier Condensate

In general, for the conditions of low (or zero) sulfate and low sodium in the feed and early scaling of the pot wall (before about 25% of the total feed is fed to the pot) the ruthenium volatilized was less than 10%.

The time of pot wall scaling is dependent on many factors, including waste composition (solubility of metal salts, and nitrate decomposition temperatures), internal heat rate density in the waste, power input to the pot from the furnace, (pot wall temperature) and method of operation. In WSEP, wall scaling was normally defined as the time when a sharp increase in wall temperature occurred in the lower pot zones.

Entrainment from the pot calciner, based on the accumulation of $^{144}\text{CePr}$ in the pot condensate, ranged from 0.04 to 1.2%, as shown in Table 4.1. Generally, entrainment is dependent on boiloff rate and freeboard in the pot. About 3 feet of freeboard was maintained during the constant boiloff portion of the run by balancing the feed rate and furnace power (this was established prior to the runs). Data on the accumulation of ^{137}Cs in the pot condensate^(1,2) were similar to the $^{144}\text{CePr}$ entrainment data, indicating that ^{137}Cs was not significantly volatilized.

Phosphoric acid was added to the calciner feed in the last two runs (to prevent volatilization of the alkali metals) in place of the sulfate used during the first six runs. Both sulfate and phosphate proved suitable for this purpose; however, excessive sulfate ($\approx 0.6\text{M}$) caused undesirable solids precipitation problems in the aqueous solutions in WSEP.⁽²⁾ Sulfate volatilization was visibly noted during Run PC-2 where it was determined that there was insufficient sodium in the feed to combine chemically with the sulfate. Less than 0.5% of the sulfate was evolved from the PC-2 pot.

The volatilization of technitium was determined during Run PC-6 to be 3% of that in the feed to the pot.

4.1.5 Performance of the Pot Calciner

Solidification Pot

The WSEP calcine pots as shown in Figure 4.2 were 8 feet long and were made from 6 and 8-inch Schedule 40 Type 304L stainless steel pipe.⁽³⁾ Twelve-inch diameter pots were made from rolled 0.310-inch thick stainless steel plate. The WSEP pots were highly instrumented with wall and internal thermocouples at the midplane of each zone for a total of 18 thermocouples for each pot. The internal thermocouples were located in thermowells at the pot centerline and midway between the wall and the centerline.

Two methods of pot liquid level detection and control were used.^(1,2) These included an ORNL developed thermocouple probe which detected liquid level by changes in temperature, and a standard pneumatic-type bubbler dip-tube (weight factor) with a continuous air and steam condensate purge to prevent plugging. Experience to date indicates that the temperature type of level probe is not sufficiently reliable to indicate the level in the pot calciner or to control the feed rate. Although the steam purged liquid level tube (weight factor) was reliable, it was not used for automatic control because it could not detect foaming and because most effort was given to making the thermal probe work. With antifoam addition to the pot calciner, the steam purged liquid level tube should work satisfactorily for automatic level control.

When using the weight factor system it is necessary to add the steam (condensate) to the liquid level tube directly above and near the pot so that the steam addition doesn't affect the instrument signal. Pot thermocouples provided additional level information.

The pots contained a small de-entrainment baffle and piping for the addition of feed and chemical additives. The off-gas exited through a 2-inch opening. It was necessary to provide water flushing of the feed and chemical addition lines immediately before and after use to prevent them from plugging with calcine.

Foaming normally gave no serious operating problems during calcination if rapid decreases in feed rate were avoided. However, severe foaming was encountered during DVT run CPC-2⁽⁶⁾ and WSEP Run PC-4.⁽²⁾ Foaming was so severe that expulsion of feed from the pot through the safety overflow system occurred in both cases. Occasional mild foaming was also observed in other WSEP pot calcination runs. Although the cause of the severe foaming in pot calcination was not specifically determined, it was found during the radioactive phosphate glass runs in WSEP that the presence of small (30 to 1600 ppm) quantities of dibutyl phosphate in the Purex 1WW waste used for feed makeup caused severe foaming in the denitrator evaporator when the wastes were concentrated.⁽¹¹⁾

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

During Run PC-6 it was necessary to restart feed to the pot after the calcine had been baked. No problems were encountered with the cold feed hitting the hot calcine during the restarts.

Vent Line and Fill Head

The calcine pot fill head (Figure 4.1) was essentially a single manifold fitted with off-gas, feed, chemical addition, pot pressure (alternately used as the weight factor tube), and vent connections for the pot head.⁽³⁾ When the pot was positioned for filling, the fill head connections were sealed to the gasketed pot head by a special vee-flange clamp. The pot was raised to mate with the fill head, and the clamp was closed to seal the joint. The fill head was adapted to WSEP piping by using a row of special semi-remote connectors.

During calcination, volatile material left the pot via the vent line, which was designed to condense and reflux about 10% of the vapors for self-cleaning. This reflux washed the line continuously and prevented the deposition of solids. The reflux rate was controlled manually by adjusting the off-gas line cooling water and by observing the drip rate in the sight glasses. Refluxing liquid was drawn off at the base of the vent line before it entered the pot. The reflux could be drained to several locations -a catch tank, an evaporator, or to the pot. The remainder of the vent line between the reflux drawoff point and the pot throat was washed by returning reflux to the pot once or twice during the feeding period and also at the end of the pot feeding period. Non-browning quartz glass view ports were provided in the vent line at two locations for viewing the off-gas and the liquid reflux. The off-gas line viewports were darkened by ruthenium over a period of three or four runs.

A clean vent line was assured by spraying 2 to 5 liters of water into the pot through a spray nozzle located in the upper part of the vent line after the feeding period of each run and by washing the line with 10 to 30 liters of water after a new pot was installed for the start of the next run.

4.1.6 Performance of the Rising-Level Glass Process

Overall Processing Rate

The average processing rate for the 6-inch RLG run was 10 liters/hr; however, the run was terminated after it was approximately 65% completed due to feeding difficulties and a partial (75%) calcine blockage of the pot throat prior to the vent line. The expected boiloff rate from conventional operating techniques using 6 to 8-inch diameter RLG pots at 900 °C is 2 to 5 liters/hr.⁽¹²⁾ Because the design of the WSEP feed system did not allow continuous operation at these low rates and because these rates were lower than desired for commercial operation, a method was devised to increase the overall feed rate by a factor of about 3. In this method the feed was directed to flow filmwise down the RLG pot centerline thermowell.⁽¹²⁾ With the feed flowing down the thermowell, the effective heat transfer area for liquid boiloff was substantially increased (by a factor of about 8 for an empty pot) so that an initial feed rate of nearly 15 liters/hr was possible. This rate decreases as the pot is filled because the heat transfer area decreases as the thermowell becomes submerged in the rising glass.

Although this technique produced excellent results during a DVT run,⁽¹³⁾ it became apparent shortly after the start of run PC-9(RLG) that, in addition to feed flowing down the centerline thermowell, some of the feed was flowing down the intermediate thermowell as indicated by a substantial decrease in the recorded intermediate pot temperatures above the melt. Although the film feeding increased the capacity as expected, the diverted feed flow and calcine entrainment led to an eventual calcine blockage in the top of the pot; and the feed flow down the intermediate thermowell made it difficult to determine the glass, calcine, and aqueous phase inventories in the pot.

Radionuclide Heating Effects

During RLG Run PC-9, a 310 W/liter heat-rate density produced a 685 °C pot centerline temperature in the 6 inch diameter pot. The effective thermal conductivity of the solids was $1.2 \text{ W/(m}^2)(\text{°C/m})$. The thermal conductivity varies with temperature and is discussed in Section 6.3.2.

Temperature control during the rising level glass run was adequate. Temperature control was provided by turning off the furnace zones directly below the melt level. Although the furnace temperature was maintained at 950 °C during processing for the RLG run, the maximum internal melt temperature attained was only 1015 °C despite the heat rate density of 310 W/liter. This indicates the high effective thermal conductivity [approximately $3 \text{ W/(m}^2)(\text{°C/m})$] for the molten borosilicate product.* Temperature and level control descriptions in Reference 12 for a nonradioactive RLG run may be useful for understanding the expected temperature behavior during filling of a RLG pot.

Waste Volume Reduction

The final waste solids volume for the borosilicate RLG product was 32 liters/tonne, equivalent to 0.7 liters/1000 MWd_t for the 45,000 MWd/tonne type waste. The density of the glass was 3.5 kg/liter and the overall volume reduction from feed to glass was 12. The volume reduction is very dependent on the percent of waste in the glass. For PC-9 (RLG) this was 50 wt%.

Volatilization and Entrainment

During the Rising Level Glass run, 15% of the ruthenium and approximately 0.6% of the cesium (1.0% total cesium,

* For those pots having molten cores, the effective thermal conductivity (Keff) would include any convective heat transfer within the molten solids.

including entrainment) in the feed to the pot was volatilized. Based on ^{106}Ru and ^{137}Cs . Since this was the only RLG run made in WSEP, there are no comparative data, however, for the similar FINGAL process approximately 30% of the ruthenium in the feed was volatilized.⁽¹⁴⁾ (The FINGAL process was operated at 1050 °C compared to 950 °C for the WSEP RLG run.)

Although the amount of entrainment from the RLG pot (based on $^{144}\text{CePr}$ activity) was only 0.38%, indications during the run (including partial plugging of the pot throat) indicated a much higher entrainment.

Solidification Pot

The RLG pot was similar to that shown in Figure 4.2. The pot was made from 6-inch Schedule 40, Type 310 stainless steel pipe. The thermocouples in the RLG pot were staggered so that no two thermocouples were at the same level in order to provide a maximum of process level information.⁽¹⁾

The modification to the RLG pot inlet piping so that the aqueous waste flowed as a film down the centerline thermowell for increased capacity achieved its purpose; however, as discussed above, problems were encountered which eventually terminated the run. The staggered heights of the pot thermocouples provided level information; however, for economical reasons it will be necessary to reduce the number of thermocouples to a minimum or to have them removable for reuse. Although the WSEP RLG pot design has desirable features, additional development is required in order for the RLG process to achieve the development status of the other WSEP solidifiers.

4.1.7 Related Equipment Performance

Seal Pot

A secondary vent line from the calciner was provided for relief of pressure if the pressure in the pot increased to atmospheric level during operation. In this event, a

water-seal pot connected to the pot vent line directed the pot vapors through the alternate vent and allowed overflow of liquids directly to a catch tank.⁽³⁾

The pot calciner safety-relief seal pot functioned normally during all runs. No instabilities in the calciner or seal pot pressure were observed. A short flush is required to avoid calcine restrictions in the inlet line after a run with excessive entrainment or shortly after any occurrence of an excessive pot operating level.^(1,3) Although the water-seal in WSEP was only 24 inches of water, the hydraulic seal used at ORNL in development tests was 20 feet.⁽¹⁵⁾

Pot Furnace

The six zone induction-heated calciner furnace which had a temperature controlled susceptor to transfer heat to or from the pot calciner wall by radiation gave exceptionally good performance. While heating all zones each zone could be controlled within ± 10 °C of the set point (except during the first several hours of a run when all power was being used for boilup) without gross influence from adjacent zones. During heating and cooling of adjacent zones, the heated zone could not always be maintained at the maximum temperature (usually 700 °C at this point) because the available power was set to restrict each zone to 3, 4 and 8 net kilowatts for 6, 8 and 12-inch pots, respectively. When 3 net kilowatts/zone was used during Run PC-8, the furnace temperature in a heated zone was reduced excessively when cooling air was on to an adjacent zone. It is estimated that about 4 net kilowatts/zone would have provided sufficient heat with this furnace for both 6 and 8-inch diameter pots. Because of furnace end losses, the top and bottom zones were set to deliver about 25% more power than the other zones.

Cooling by forced air around the outside of the susceptor was sufficient for the pot runs (see Section 4.1.2). The same furnace was used for the phosphate glass runs where cooling of up to 12 kilowatts in a glass receiver pot was satisfactory.

During the entire WSEP program the furnace was operated at 600 to 950 °C for about 2600 hours without a significant problem. Prior to placing the furnace in radioactive service (at 1025 hours service), delaminated Fiberfrax^{R-1} insulation around the susceptor was replaced with Ceroform^{R-2} insulation. The furnace was not inspected following the radioactive runs.

Solidifier Condenser

The same process condenser was used for the vapors from all solidification processes in WSEP. A 304L stainless steel sleeve was installed at the inlet of the titanium condenser to prevent corrosion to the condenser at this point after local sulfate corrosion occurred during early DVT runs. Corrosion coupons were installed in the liner prior to radioactive operation. These were made of A-55 titanium, 304L and 316L stainless steel, and Nionel. The coupons were inspected at the end of the first series of six pot calcination runs and again after the first six and the second five phosphate glass runs. Although no increase in corrosion to either the liner or the coupons was visible, some solid deposits (up to 1/8 inch thick) were found on the samples and in the liner. Laboratory analysis of the deposits indicated that they were probably entrained calcine rather than ruthenium which was suspected. This condenser was in service for about 3500 hours until it was replaced for test purposes with a modified condenser prior to spray solidifier Run SS-11. The new

R-1 Carborundum Corporation

R-2 Johns-Manville Corporation

condenser⁽¹⁶⁾ contained 1/2-inch diameter stainless steel Pall rings in the condenser tubes to improve the condenser scrubbing efficiency. This condenser was used for a total of 400 hours during the final spray and pot solidification runs.

4.2 SPRAY SOLIDIFICATION

Thirteen spray solidification runs were made in WSEP.^(16,17) Eleven runs were made using the spray calciner attached to a continuous melter and two runs were made using the spray in pot melting (IPM) process. Although the design of the spray solidification system in WSEP was certainly not optimized and a less expensive melter material is desirable, its performance indicates that both solidification techniques are adaptable to commercial operation.

The essential features of the WSEP spray solidification equipment^(3,16) are shown in Figures 4.8 through 4.10. The spray calciner was mounted above the melter so the calcine could fall directly into the melter. The melter, in turn, was mounted directly above the receiver pot to allow free fall of the melt into the receiver. With in-pot melting, the melter was removed and replaced by a spool piece which connected the calciner and pot. Solids addition systems for both solidification techniques are shown in Figure 4.9 and the stainless steel pot used for either melt receiving or in-pot melting is shown in Figure 4.10.

4.2.1 Overall Processing Rates

The primary factors which limit 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 14-inch diameter WSEP spray calciner drying capacity was established at 28 liters/hr during DVT run CSCM-6 with the calciner furnace temperature at 700 °C.⁽¹⁸⁾

NOTES: BOTH COOLING COILS CONSTRUCTED FROM 1/4" OD HASTELLOY-X TUBING; COOLING COIL ASSEMBLY INSULATED WITH 1/2" 1" CERAFELT AND LINED WITH Pt FOIL.

SHELL	
Heat Transfer Area	23 ft ²
Volume	
Drying Chamber	271 ℓ
Tapered Bottom	86 ℓ
Total Volume	433 ℓ
Filter Chamber	
Clean Side	24 ℓ
Dust Side	52 ℓ
Material	310 SST
Wall Thickness	0.375"
ATOM. NOZZLE	
Type - Pneumatic, Internal Mix	all Welded
Liquid Orifice	304L SST
0.100 in. I. D.	
Final Orifice	303 SST
0.125 in I. D.	
FURNACE	
Type - Electrical Resistance, 3 Zones,	3 Phase, 240V
Power	45 kW
Heating Elements	Nichrome V
0.12 in. diam	
Max. Temperature	1000 °C
Normal Temperature	600-800 °C
Insulation	Tipersul
FILTERS	
Total Number	15
Material	316L SST
Mean Pore Size	65 μ m
Total Surface	15 sq. ft.
Normal Pressure Drop	6 in. water at 1800 ℓ /min
FILTER BLOWBACK SYSTEM	
Gas	Air or Steam
Flow	270 ℓ /min at 60 psig
Pressure	20-100 psig
Nozzles	0.11 in. I. D.
Venturis	
End Diam.	2 in.
Cone Angles	30 degrees

VOLUME	
Maximum	19.4 ℓ
Normal Operating	4.5 ℓ
CAPACITY	
Melter	40 ℓ /day melt
CONSTRUCTION	
Type	All Welded
Material	99.95% Pt
NOZZLES	
6" O. D.	1 } Top
2" O. D.	5 }
0.5" O. D.	2 (discharge)
FURNACES	
Melter	
Type	Elec. Resistance
Power	3 Phase, 126V
Heating Elements	20 kW
Kanthal A-1	
0.18 in. diam.	
Insulation K-28	K-28 and Fiberfrax
OPERATING	
Temperature Max.	1300 °C
Temperature Normal	1000-1200 °C
Pressure Max.	24 in. H ₂ O Vac
Net Furn. Power	4 kW
Gross Furn. Power	12 kW
MELTER HEAT TRANSFER AREA	
Above Melt Level	1.7 ft ²
Below Melt Level	1.0 ft ²

FIGURE 4.8. Spray Calciner Melter and Furnace Assembly

FIGURE 4.9. Melter and In-Pot Melting Solids Addition Systems in WSEP

FIGURE 4.10. Thermocouple Arrangement of Spray Solidifier Receiver Pots (and Phosphate Glass Receiver Pot, Section 4.3) in WSEP

Tables 4.3 and 4.4 summarize the run data and system performance for the WSEP spray solidifier runs. The processing rate for PW-1, PW-4m, and LMFBR wastes was normally limited by the calciner and averaged 16.2, 14.4 and 14.9 liters/hr, respectively. From these tests, the capacity of the calciner (700 °C furnace) is believed to be about 16 to 18 liters/hr of feed to the calciner. The processing rate for PW-2 waste was limited by the melter capacity (925 °C furnace and 30 °C ΔT) at a melt formation rate of about 1.5 liter/hr, (equivalent to 13 liters/hr of feed to the calciner with waste at 570 liters/tonne).⁽¹⁷⁾

During the in-pot melting runs, melting in the pot kept up easily with the production of powder in the calciner at an average melt formation rate of 2.5 to 2.7 liters/hr, with rates as high as 3 liters/hr being attained at the start of Run SS-12 (IPM). The processing rate for PW-4m waste using the in-pot melting modification of the spray solidification process is probably limited by the 8-inch pot (900-950 °C furnace) at approximately 3 liters/hr of melt.

In-pot melting was demonstrated for solidification of PW-1, PW-2 and PW-4m waste during spray calciner development tests.⁽¹⁹⁻²³⁾ The tests demonstrated that the melt forming capacity during in-pot melting should be nearly identical for any waste type for a given pot size and pot operating temperature. The PW-2 waste (phosphate type melt) requires processing at a lower temperature (approximately 825 °C furnace) because higher temperatures can volatilize the sulfate in the waste. At this temperature the in-pot melting process will produce approximately 2.3 liters/hr of melt with an 8-inch diameter pot.

TABLE 4.3. Spray Solidifier Feed and Run Data

Solidified Run Number	SS-1	SS-2	SS-3	SS-4	SS-5	SS-6	SS-7	SS-8	SS-9	SS-10	SS-11	SS-12 (IPM)	SS-13 (IPM)
Operating Mode	A	B-modified	A	A	A	A	A	A	A	A and B	A	A	B-modified
Pot Size	12	8	12	8	8	8	8	8	8	8	8	8	8
Waste Type	PW-1	PW-1	PW-2	PW-2	PW-1	PW-1	PW-1	PW-1	PW-4m	PW-4m	LMFBR	PW-4m	PW-4m
Feed Volume, liters/tonne	455	455	582	560	446	520	452	473	630	611	1232	556	352
Feed Temperature, °C	50	30	40	30	25	20	30	25	30	30	24	32	25
Feed Consumed, liters	603	789	357	500	887	986	839	800	792	750	669	301	308
Solids Additive to Melter (m) or Pot (p), kg	-	-	25.4 (m)	40.4 (m)	-	-	-	-	-	-	-	109 (p)	106 (p)
Total Feed Time, hr	37	57.3	31.6	40.5	53.2	55.6	47	55	52	56	45	28	20
Total Feed Time Off, hr	0.1	2.8	23.6	1	3.5	21	4	0.5	7.0	3.5	0	4.4	0
Average Feed Rate, liter/hr	16.3	13.8	11.3	12.3	16.7	17.7	17.9	14.5	15.2	13.5	14.9	10.8	15.4
<u>Radioactivity</u>													
Total Radioactivity in Feed to Calciner, (e) kCi	83	420	420	1400	2500	3000	3620	1830	2030	2580	3110	1390	2830
Radioruthenium in Feed to Calciner, kCi	5.7	5.3	26	15.3	16.8	24.1	22	14.4	10.2	13.1	14.4	6.8	11
Feed Heat Rate Density, W/liter	0.55	2.5	4.8	11	9.3	11	11.3	8.4	8.0	11.1	16.4	16.2	33.8
Fission Product Heat to Pot, W	285	2100	1550	5100	8200	10,000	12,700	7200	7200	7900	10,500	4900	10,000
Ruthenium Volatilized, %	75	74	73	11	70	50	59	35	57	45 (a)	75	1.9	0.5
¹⁴⁴ CePr Entrainment from Solidifier, (f) %	0.053	0.019	10 (b)	0.16	0.064	0.071	NA	NA	0.023	0.079 (a)	0.013	0.014	0.0011
Equivalent Spent Fuel Waste Waste to Pot, tonne	1.1 (c)	1.7	0.61	0.89	2.0	1.9	1.85	1.7	1.26	1.07 (d)	0.54	0.54	0.88
Average Processing Rate, tonne/day	0.8	0.7	0.45	0.5	0.9	0.8	0.94	0.74	0.58	0.46	0.29	0.46	1.05
Equivalent Age of Waste, yr	45	3.6	1.7	0.8	1.2	0.8	0.67	1.2	2.3	1.9	2.2	1.3	1.0

NA- Not Available

a. Determined for mode A portion of run only.

b. Filters failed.

c. 14% of calcine held up in calciner.

d. 13% of calcine held up in calciner.

e. Radioactivity was predominately ¹⁴⁴CePr

f. Based on heat generation rate in pot and ISOGEN program.

See Section 8.8

TABLE 4.4. Spray Solidifier Systems Performance

Solidifier Run Number	SS-1	SS-2	SS-3	SS-4	SS-5	SS-6	SS-7	SS-8	SS-9	SS-10	SS-11	SS-12 (IPM)	SS-13 (IPM)
Waste Type	PW-1	PW-1	PW-2	PW-2	PW-1	PW-1	PW-1	PW-1	PW-4m	PW-4m	LMFBR	PW-4m	PW-4m
<u>Spray Calciner</u>													
Furnace Temperature, °C	700	700	670	680	695	700	670	690	690	700	700	720-740	670-700
Internal Temperatures, °C													
- Top(a)	475	490	370	410	375	325	420	400	450	400	430	380	350
- Bottom(b)	600	600	520	560	500	460	540	580	600	570	600	580	570
Pressure, in. of water -													
Normal/During Filter Blowback	-10/0	-8/4max	-12/5max	-8/-1	-11/-3	-10/-2	-10/-2	-8/-2	-11/-3	-10/-2	-10/-2	-8/-2	-10/-4
Average Furnace Power, kW -													
Feed on/Atomizing Air Only	NA	NA	20/10	12/26	13/26	12/21	12/30	NA/22	NA	12/23	14/27	13/20	13/27
<u>Melter</u> ^(c)												<u>Pot</u>	
Furnace Temperature, °C	1175	1150	910	930	1125	1150	1125	1140	1175	1190	1180	925-950	925-950
Melt Temperature, °C	1100	1100	880	900	1100	1130	1060	1050	1100	1150	1140	~900	~1000
Drain Freeze Valve Temperature, °C - While Frozen/													
While Draining	NA/980	NA/950	440/800	415/835	800/950	830/940	780/900	820/930	920/950	825/1030	840/1035	--	--
Melt Production Rate, liter/hr	1.2	0.8	1.2	1.4	1.2	1.2	1.3	1.1	1.3	1.0	1.3	1.9	2.5
Melt Discharge Rate, liter/hr	NA	NA	NA	NA	NA	NA	65	52	23	24	34	--	--
<u>Pot Furnace</u>													
Temperature, °C	780	860	640	640	60	840	60	60	60	60	60	900-950	900-950
<u>Atomizing Feed Nozzle</u> ^(d)													
Atomizing Air Flow, scfm	NA	6	6	6.8	8.6	8.5	6.5	7.0	6.3	6.2	7.3	7.8	6.8
Air Pressure, psig	49-62	40	43	45	40	45	44	44	45	43	45	45	45
Air Temperature, °C	350	30-320	30	30	30	30	30	30	30	30	30	30	30
<u>Calciner Vibrator</u>													
Cycle, min/pulse, sec	1/3-9	1/3	1/2	2/2	1/2	1/2	1/2	1/2	1/2	0.25-1/2-5	1/2	0.5-1/2-4	1/2
Air Supply Pressure, psig	60	60	60	60	55	55	45	50	50-55	50-60	50	50-80	50
<u>Off-Gas Filters</u>													
Blowback Gas	Steam	Steam	Steam	Air	Air	Air	Air	Air	Air	Air	Air	Air	Air
Blowback Gas Temperature, °C	345	350	350	315	350	350	350	350	350	350	350	350	350
Blowback Gas Pressure, psig	26	20-33	27	40	40	45	42	44	42	40 to 60	40	40	40
Blowback Cycle, min/pulse, sec	2/1.5	2/1.5	2/2	2/2	2/2	2/2	2/2	2/2	2/2	2/2	2/2	2/2	2/2
Filter Pressure Drop, in. of water													
Start of run/End of run	7/11	9/18	3/11 ^(e)	5.8/7.5 ^(f)	4.0/5.5	5.7/6.0	3.0/4.8	4.5/4.5	4.5/4.8	4.8/8.0	2.7/3.0	2.8/2.6	3.6/3.2
Atomizing Gas Only (feed off)	NA	NA	1	1.5	3	3	1.5	NA	NA	2.4	NA	NA	NA
Air Inleakage to Solidifier, scfm	~9	~4	~7	~4 ^(f)	~8	~11	5	5	5	5	8	8	10
Total Noncondensable Gas Flow to Filters, scfm	11	11	13	11 ^(f)	17	20	13	13	12	13	16	17	18
Filter Chamber Temperature, °C	300	320	350	300	340	300	330	340	350	350	360	330	340
Total Gas Flow to Filters (at chamber temp.), cfm	~42	~41	~45	~33	~60	~60	55	51	51	50	59	53	63
Filter Face Velocity (at chamber temp.), ft/min	2.7	2.7	3.0	2.2	3.8	3.8	3.7	3.4	3.4	3.3	3.9	3.5	4.2

NA - Not Available

- a. 2 in. down from top near wall.
b. 60 in. down from top near wall.
c. Batch discharge in all runs except SS-1, with a 5 to 6 liter holdup and 3 to 6 hr residence time.
d. An internal-mix, two-fluid nozzle (Spraying Systems Co. Setup No. 42) for all runs except SS-1 where an external mix nozzle was used.

- e. Broken calciner filters resulted in high calcine entrainment losses and loss of vent capacity.
f. Stuck open solenoid blowback valve resulted in about 45 CFM added to calciner off-gas flow and reduced vent capacity.

4.2.2 Radionuclide Heating Effects

Receiver and In-Pot Melting Pot

The temperatures caused by the internal heat generation rate in the WSEP spray solidifier pots and additional data for the spray solids are listed in Table 4.5. The highest internal heat-rate density was 204 W/liter and was attained in Run SS-7. For this PW-1 waste in an 8-inch diameter air cooled pot, the pot centerline and wall temperatures were 900 °C and 425 °C, respectively. The predicted maximum allowable heat-rate density to avoid exceeding these temperature limits in an 8-inch diameter pot stored in air was estimated to be in the range of 220 to 250 W/liter.⁽¹⁷⁾ The lower value attained in Run SS-7 was due to a lower than anticipated thermal emissivity (about 0.6) for the pot wall. The thermal emissivity of the pot wall could have been increased to approximately 0.8 had the pot been heat-treated at 800 to 900 °C prior to the run to oxidize the pot wall.

Temperature data from the spray system pots indicate that the effective thermal conductivity of the phosphate type solids (including the container wall) is $1.2 \text{ W/(m}^2) \text{ (}^\circ\text{C/m)}$ and is independent of temperature. (See Section 6.4.2)

During Runs SS-4 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 lower potential for stalagmite formation in the pot at the higher entering melt rates (approximate instantaneous batch rates of 23 to 65 liters/hr) and because it was not necessary to heat the receiver pot. This technique also permits the use of mild steel containers (as in Runs SS-4 and 10) and simplified the collection of solidified waste with a high heat-rate density such as that in Run SS-7. During Runs SS-1, SS-2, and SS-3 and part of SS-5, the receiver pot was heated to promote uniform filling during periods of continuous melt overflow from the

TABLE 4.5. Spray Solidifier Solidified Product Data

Solidifier Run Number	SS-1	SS-2	SS-3	SS-4	SS-5	SS-6	SS-7	SS-8	SS-9	SS-10	SS-11	SS-12 (IPM)	SS-13 (IPM)
Pot Size	12	8	12/8 ^(f)	8	8	8	8	8	8	8	8	8	8
Pot Material	304L	304L	304L	MS	304L	304L	304L	304L	310	MS	304L	304L	304L
Waste Type	PW-1	PW-1	PW-2	PW-2	PW-1	PW-1	PW-1	PW-1	PW-4m	PW-4m	LMFBR	PW-4m	PW-4m
Product Weight, kg	120 ^(a)	152	27/77	160	209	207	197	170	194	176	186	162	151
Product Volume, liter	38 ^(a)	48	10/29	56	66	65	62	59	68	56	60	54	50
Bulk Density, kg/liter	3.16	3.16	2.7/2.6	2.86	3.17	3.18	3.16	2.9	2.87	3.14	3.1	3.0	3.0
Laboratory Measured Density, kg/liter	3.15	3.19	2.7/2.7	2.80	3.24	3.18	3.30	3.30	3.31	NA	3.29	2.8	NA
Volume Reduction, Feed to Solid	13.6 ^(b)	16.4 ^(c)	9.6/9	8.9	13.4	15.2	13.5	13.6	11.7	11.7 ^(d)	11.2	5.6	6.2
Adjusted Volume Reduction (based on feed at 378 liter/tonne)	11.3 ^(b)	13.6 ^(c)	6.2/5.9	6.0	11.4	11.0	11.3	10.8	7.0	7.2 ^(d)	3.4	3.8	6.6
Product Unit Volume, liter/tonne	34 ^(b)	28	61/64	64	33	34	34	35	54	52	111	100	57
Fission Product Heat in Pot, W	285	2100	390/1150	5100	8200	11,000	12,700	7200	7200	7900	10,500	4900	10,000
Heat Generation Rate Density, W/liter	7.5 ^(b)	44	39/40	93	127	168	204	120	107	141	175	90	200
Pot Radiation Reading at 6-in, kR/hr	2.5	11	NA/14	20	28	51	NA	28	26	25	40	21	58
Pot Steady State Temperature Data													
Centerline Temperature ^(e) , °C													
In Air Cooled Furnace	190	285	NA/315	505	640	735	920	605	594	611	759	474	824
In Air	NA	NA	NA	340 ^(g)	630	710	900	NA	520	539	608	435	785
In Water	NA	NA	NA	265	345	330 ^(h)	547	285	283	337	378	278	563
Centerline-to-wall Δt , °C													
In Air Cooled Furnace	30	70	NA/80	220 ^(g)	270	305	453	210	242	262	353	197	404
In Air	NA	NA	NA	170 ^(g)	285	345 ^(h)	475	NA	235	260	320	207	441
In Water	NA	NA	NA	220	295	285 ^(h)	522	245	243	297	334	238	513
Effective Thermal Conductivity, W/(m ²)(°C/m) ⁽ⁱ⁾													
In Air Cooled Furnace	1.3 ^(b)	1.6	NA/1.1	1.1 ^(g)	1.2	1.4	1.16	1.4	1.14	1.39	1.28	1.18	1.28
In Air	NA	NA	NA	1.0 ^(g)	1.2	1.3 ^(h)	1.11	NA	1.14	1.40	1.41	1.12	1.17
In Water	NA	NA	NA	1.1	1.1	1.1 ^(h)	1.0	1.2	1.09	1.23	1.35	0.98	1.01

NA - Not Available

MS - Mild Steel

a. An additional 17 liter (73kg) of material accumulated in pot prior to SS-1.

b. Based on 44 liter of product, 6 liter (20kg) held up in calciner.

c. Feed contained below nominal sodium.

d. Assumes 13% holdup of calcine in calciner.

e. Based on zone 4 and/or 5 pot temperatures.

f. Switched from 12-inch to 8-inch pot during run.

g. Data obtained after decay to 3600 W.

h. Data obtained after decay to 8100 W.

i. $W/(m^2)(^{\circ}C/m) \times 0.578 = Btu/hr(ft^2)(^{\circ}F/ft)$

melting.⁽¹⁷⁾ Temperatures of 650 to 700 °C and 750 to 800 °C were used to promote slumping of PW-2 and PW-1 melts, respectively.

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 and indirect air cooling was used for the filled pot zones. However, some temporary surges of the internal pot temperatures occurred (increases in temperatures to 900-1000 °C for Run SS-7). Typical receiver pot temperatures during batch dumping of melt (in Run SS-7) are presented in Figure 4.11.

The maximum solids temperatures obtained with PW-2 sulfate containing product was a 505 °C centerline temperature during Run SS-4. The PW-2 melt has a remelt temperature of approximately 700 °C. Laboratory tests showed that PW-2 spray solids stored at 700 to 800 °C underwent melt segregation with the sulfate concentrated in the upper phase.^(17,24) Some segregation occurred at temperatures as low as 550 °C. Because of this sulfate instability and the possibility of sulfate volatilization from the molten phase, it is recommended that the stored PW-2 product using the WSEP formulation be limited to a maximum centerline temperature of 700 °C.

During in-pot melting Runs SS-12 and SS-13, PW-4m waste calcine was fused with a borosilicate glass 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 maximum internal melt temperature was only 1040 °C. The calculated effective thermal conductivity for the molten borosilicate product was 4 to 7 W/(m²) (°C/m). Consequently, pot cooling requirements for preventing excessive temperatures were reduced. During Run SS-13 (IPM) the heat rate density of the melt was 200 W/liter. The effective thermal conductivity of the IPM borosilicate solids is

FIGURE 4.11. Receiver Pot Temperatures During Run SS-7

dependent on temperature (Section 6.); however, at the average product temperature anticipated with heat generating wastes it is approximately $1.2 \text{ W/(m}^2) \text{ (}^\circ\text{C/m)}$.

The pot internal temperatures provided the best indication of the progress of pot filling during the IPM runs. The receiver pot furnace was started initially with the bottom three zones set at 925 to 950 $^\circ\text{C}$ and the top three zones at 850 $^\circ\text{C}$. As shown in Figure 4.12, the pot centerline temperatures would start dropping as the melt level entered a respective zone, reaching a minimum of 650 to 700 $^\circ\text{C}$, when the zone was about half full and then increasing as the zone completed filling. When each zone was filled (as indicated by a centerline temperature in excess of 900 $^\circ\text{C}$) the respective furnace zone temperature was reduced and eventually turned off. The upper furnace zone temperatures were increased to 925 to 950 $^\circ\text{C}$ as the level increased so that at least two zones above the melt level were at temperature.

Melter

The net energy input required to form a fluid melt from the calcine was about 2 to 3 kilowatt-hrs/liter of melt. The highest heat rate density of 204 W/liter was attained for a PW-1 melt in Run SS-7. This heat rate density accounted for approximately 50% of the net heat requirement in a melt volume of 6 liters. However, the effect of internal heat generation was not apparent because of the continuous variation of melt volume from 0 to 6 liters (during batch dumping) and because of the high heat losses from the melter furnace system (about 12 kilowatts).

4.2.3 Waste Volume Reduction

Data for the solidified spray product are presented in Table 4.5. The final waste solids volumes averaged 33, 64, 53, and 111 liters/tonne for the PW-1, PW-2, PW-4m and LMFBR

4.39

FIGURE 4.12. Receiver Pot Temperatures During Run SS-13(IPM)

products respectively. These values are equivalent to 1.7 and 3.3 liters/1000 MWd_t for the PW-1 and PW-2 waste (20,000 MWd/tonne at 15 MW/tonne), and 1.0 liters/1000 MWd_t for PW-4m waste (45,000 MWd/tonne at 30 MW/tonne). The borosilicate waste solids volume for the PW-4m in-pot melting runs ranged from 57 to 100 liters/tonne due to the different amounts of additives used, but could be as low as 30 liters/tonne if the solids were made at the satisfactory flowsheet which has 50 wt% waste oxides.

Overall volume reduction factors varied from 5.6 to 16.4 due to the wide variation in wastes. The volume of waste required to fill a pot was estimated for each run in the same manner as for the pot calciner. The predicted volume reductions differed from actual values by an average of 8% with a maximum deviation of 15% during Run SS-1.

The bulk density of the spray-melter phosphate product averaged 3.1, 2.7 and 3.0 kg/liter for the PW-1, PW-2, and PW-4m runs and was 3.1 for the one LMFBR melter run. The bulk density of the IPM borosilicate product averaged 3.0 kg/liter. There was only slight deviation from any of these values. Laboratory measured densities were nearly identical with bulk densities for the first six runs and were higher by an average of 9% during the final runs. These higher values indicate voids in the solidified product.

4.2.4 Volatilization and Entrainment

During the spray demonstration runs, ruthenium, cesium, and tellurium were the only fission products with detectable amounts of volatilization. Ruthenium volatilization ranged from 0.5 to 75% (Table 4.3); cesium volatilization was as high as 0.3%; and 0.1% of the tellurium was volatilized during the one run in which measurements were taken.

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 4.13 as a function of the fraction of feed processed during the runs.

While processing PW-1, PW-4m, and LMFBR wastes which contained phosphoric acid as an additive, (Runs SS-1 through SS-11), the ruthenium volatilized from the solidifier ranged from 35 to 75%, which was in agreement with nonradioactive tests. When processing PW-2 waste, 73% of the ruthenium was volatilized during Run SS-3 compared to only 11% during Run SS-4. No explanation has been found for this wide variation between the two PW-2 runs.

Nonradioactive tests indicated that ruthenium volatilization was substantially reduced with low acid feeds⁽¹⁶⁾ accordingly, the free acid concentrations of the wastes processed during Runs SS-8 and SS-10 were reduced prior to each run in an attempt to reduce the ruthenium volatilized during solidification. The PW-1 feed for Run SS-8 was pretreated by steam stripping the waste (which included the phosphoric acid additive) in the waste evaporator. After the steam stripping 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 6.3M to 1.3M. Despite the major reduction in feed acidity, 35% of the ruthenium in the feed to the solidifier was volatilized during Run SS-8. Although this represented a reduction from the 50 to 75% volatilization experienced in the preceding spray solidifier runs with the PW-1 flowsheet, the decrease was not as low as that predicted from the developmental spray solidifier runs. The PW-4m feed for Run SS-10 was also acid stripped to nearly the same degree, and 45% of the ruthenium was volatilized.

FIGURE 4.13. Accumulation of Ruthenium in Spray Solidifier Condensate

The free acid concentrations in the feed to the solidifier are shown on Figure 4.13 for comparison with the ruthenium volatilized during each run.

Although the ruthenium volatilization dependence on acid concentration has been demonstrated, the relationship is not straightforward and other factors are involved. Variables which do not appear to be significant are the concentrations of ruthenium, sodium, aluminum, iron, sulfate, nitrate, or total cations. Although phosphate affects ruthenium volatilization (see below), the range of phosphate concentrations during the WSEP spray-melter runs (1.04 to 1.78M) did not present any correlation.

Since the ruthenium volatilization during the WSEP runs (and during nonradioactive pilot scale runs) was considerably higher than the 15 to 20% reported in earlier laboratory-scale radioactive tests,⁽²⁵⁾ it appears that the higher volatilization in WSEP may have been partially due to lower calciner temperatures. The approximately 100 °C higher wall temperature and the higher ratio of heat transfer area relative to feed rate (factor of 3 to 4) used during the earlier tests are estimated to have resulted in internal calciner temperatures 100 to 200 °C higher than the 350 to 600 °C temperatures in the WSEP spray solidification runs. A significant reduction in ruthenium volatilization from fluid bed calcination was noted⁽²⁶⁾ as the operating temperature was increased from 350 to 550 °C and was attributed to the instability of ruthenium tetroxide at high temperatures. For the temperature ranges that occurred in the eleven spray-melter runs (350 to 570 °C range in SS-6 to 490 to 600 °C range in SS-8) there was no obvious correlation of internal temperature with ruthenium volatilization.

During the radioactive laboratory scale tests the ruthenium volatilization from the spray calciner was reduced from 20% to approximately 3% when 52 g/liter of sugar was added to the Purex 1WW waste. ⁽²⁵⁾

A significant reduction in the amount of ruthenium volatilized from the spray solidifier occurred during the conversion of the waste to borosilicate glass (in-pot melting runs) 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 tests with low-acid PW-4m waste without phosphoric acid. ⁽¹⁶⁾ 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 some cesium was volatilized. During Runs SS-1 through SS-11, cesium was volatilized in the range of 0.06 to 0.3%. The cesium volatilization was probably entirely from the melting step as indicated by laboratory data on cesium volatilization from phosphate melts. ⁽²⁷⁾ During the in-pot melting runs cesium volatilization ranged from 0.002 to 0.07%.

During Run SS-11, special analysis showed that 0.1% of the tellurium in the feed to the spray solidifier was volatilized. The results agreed with the nonradioactive data ⁽²⁸⁾ wherein from 0.1 to 0.5% of the tellurium volatilized from the spray solidifier.

Less than 2 and 7% of the sulfate in the feed was volatilized from the PW-2 melts during Runs SS-4 and SS-3, respectively. ⁽¹⁷⁾ These values agree with data from nonradioactive runs. ⁽¹⁸⁾

With the exception of Runs SS-3 and SS-4, entrainment (based on ¹⁴⁴CePr) from the spray solidifier averaged less than

0.04% of the nonvolatile feed to the calciner (Table 4.3). During Run SS-3, the entrainment was 10% due to failure of the filters;⁽¹⁷⁾ and during SS-4, 0.16% was entrained due probably to no filter precoat on the new filters and to residual calcine in the vent piping from Run SS-3. Filter performance is discussed in the next section.

4.2.5 Performance of the Spray Calciner

Overall the spray calciner performance was satisfactory. Although some process and equipment difficulties were encountered, they were readily resolved. Those items which influenced the performance of the process and equipment are discussed below. Pertinent overall spray calciner test parameters were presented in Tables 4.3 and 4.4.

Spray Calciner Feed System

The chemically adjusted waste was pumped through a two-fluid pneumatic atomizing nozzle and sprayed into the top of the calciner.⁽³⁾ Air was used as the atomizing gas during the WSEP tests because it proved to be more reliable than steam during design verification⁽¹⁸⁾ and nonradioactive development tests.⁽²⁹⁾

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/hours. 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 one minute period until only waste was being fed and the water was off. The aqueous waste was fed to the solidifier at rates ranging from 9 to 21 liters/hr while processing all wastes. Processing rates were presented in Table 4.3. Feed flow control during all of the spray 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 the 15 to 20 liters/hr feed flow rate (see Section 5.6.2). 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 can result if feed is turned on directly to the hot nozzle or if the nozzle is not adequately flushed when the feed is turned off.

Six internal-mix atomizing nozzles (Spraying Systems Company Setup No. 42) were used during Runs SS-2 through SS-13 (IPM). However, only one nozzle was changed due to inherent nozzle problems, and this occurred after 180 hours of use after calcining the erosive PW-2 feed. An external mix nozzle was used during Run SS-1 but gave inadequate atomization and calciner wall scaling occurred. The nozzle operating history and other pertinent spray solidifier equipment history are presented in Table 4.6. Excluding the nozzle used in SS-13(IPM) because it was not replaced, the 5 internal mix nozzle used during 11 runs had an average life of 110 hours with a maximum of 180 hours and a minimum of 47 hours. Two nozzles were changed because of inoperative cleanout needles. The nozzle used during Runs SS-3 through SS-6 was changed following Run SS-6 because of calcine deposition in the calciner cone following Run SS-6 and because of increased nozzle air consumption which indicated possible erosion of the nozzle orifice. Erosion of the orifice in internal mix nozzles had been noted during nonradioactive tests,⁽¹⁹⁾ particularly when processing the more abrasive PW-2 waste.

The other two nozzle changes resulted after calcine deposition occurred in the calciner. During Run SS-10 deposition occurred because of poor atomizing air flow control; during Run SS-12(IPM) calcine deposition occurred apparently due to a non-optimized feed flowsheet for the in-pot melting process. Atomizing nozzle life is probably reduced by

TABLE 4.6. 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	600 to 700	-20 to +5	Atomized liquid and calcined waste; water and HNO ₃ vapors; oxides of nitrogen; oxides of sulfur; air	900	Excellent operation. Cone should have been slightly steeper than 30° from vertical
Calciner furnace	Nichrome V elements and Tipersul insulation	650 to 750	0	Cell air	1000	Excellent operation
Off-gas filters No. 1	Sintered 316-L 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	426	Excellent operation until two filters failed. The assembly was replaced prior to Run SS-4
No. 2	Sintered 316-L SS powder metal filters (1/16 in. thick)	200 to 400	-20 to +5		450	Excellent operation
Feed nozzle No. 1	303 SS (external-mix)	80 to 200	0 (feed side)-50 psig (air side)		41	Replaced prior to Run SS-2 because of excessive deposition during Run SS-1
No. 2	303 SS (internal-mix)	80 to 200	20 to 30 psig	Liquid waste and air	106	Replaced prior to Run SS-3 because of malfunctioning cleanout needle
No. 3	303 SS (internal-mix)	50 to 130	20 to 30 psig		180	Replaced after Run SS-6 because of deposition in calciner
No. 4	303 SS (internal-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
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
No. 7	303 SS (Internal-mix)	50 to 130	20 to 30 psig		20	

TABLE 4.6. (contd)

Equipment	Construction Material	Temp, °C	Pressure, in. of Water	Chemical	Total Operating Time, hr	Comments
Calciner Vibrator No. 1	Mild Steel	50 to 100	30 to 40 psig	Air	138	Replaced prior to Run SS-3 due to a stuck piston
No. 2	Mild Steel	50 to 100	30 to 40 psig	Air	52	Replaced during Run SS-4 when mount broke loose from calciner
No. 3	Mild Steel	50 to 100	30 to 40 psig	Air	102	Replaced during Run SS-6 when it quit vibrating
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	
Calciner seal pot	304-L 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
Melter furnace	Kanthal A-1 elements, K-28 and Fiberfrax insulation	800 to 1250	0	Cell air and receiver pot vapors	730	Excellent operation. Internal furnace leads failed after 500 hr of operation prior to Run SS-3 and had to be replaced
Melter freeze-valve cooling coil assembly	Hastelloy-X coils	800 to 1100	0	Cell air and receiver pot vapors	420	Excellent Operation
Receiver pot furnace	Kanthal A-1 elements Tipersul insulation Hastelloy-X susceptor	600 to 950	0	Cell air	300	Excellent Operation

start-stop type operation, where scaling or plugging problems would be most likely to occur and a considerable increase in life should be expected with continuous operation. Nozzle life is expected to be greater than 200 hours when low abrasive type wastes are being atomized.

Proper atomization requires steady feed and atomizing air flows. Otherwise, the larger particles can scale on the calciner wall or cone. Nozzle screening tests indicated that the median drop size from a pneumatic atomizing nozzle increases directly with increasing liquid-to-air volume ratio.⁽³⁰⁾ Frequent fluctuations in atomizing air flow such as occurred in Run SS-10 will cause unwanted calcine deposition.

After Runs SS-6, SS-10 and SS-12(IPM), calcine scale that accumulated on either the calciner walls or bottom conical section was removed by mechanical scraping. Scraping was performed by removing the calciner atomizing nozzle and the continuous melter and rodding through these two calciner openings. Scraping was also done through a nozzle on the calciner cone. Mirrors and a portable television camera were used for viewing.

A new nozzle installed for Run SS-11 and an improved atomizing air control system gave the smoothest calciner temperature and calcine fall of any of the WSEP runs (Figure 4.14). The calciner wall scaling during SS-12(IPM) reduced the calcining capacity by approximately 40%. Calciner temperatures during SS-12(IPM) are shown in Figure 4.14. A new nozzle installed for Run SS-13(IPM) produced satisfactory operation. However, although the calciner internal temperatures were nearly as steady during SS-13(IPM) as for SS-11, they exhibited a decreasing trend throughout the run in a similar manner as during the early part of SS-12(IPM). An inspection of the calciner after SS-13(IPM) revealed that essentially no scaling of the calcining chamber walls had occurred. Although an early feed surge during SS-12(IPM) may have been the cause of the

FIGURE 4.14a. Spray Calciner Temperatures During Run SS-11

FIGURE 4.14b. Spray Calciner Temperatures During Run SS-12 (IPM)

unexplained difficulties, it is possible that some additional optimization of the flowsheet is required for in-pot melting since the feed to the calciner for these two runs was the only one tested without phosphate in the feed (see Section 3.3.3). Spray calciner development tests were normally less than 12 hours long and did not indicate a wall scaling problem.

Occasional plugs (about once a day) formed on the feed side of the nozzle 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). The formation of a plug was noted by a sudden drop in the feed flow rate to the calciner and sudden increases in the internal calciner temperatures. The nozzle cleanout needle proved thoroughly effective in removing these plug formations when used before a complete stoppage of feed flow occurred. Non-heated atomizing air was used during all of the later runs; heated air in early runs caused drying and subsequent plugging in the nozzle orifice.

On two occasions (during Runs SS-3 and 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 for Run SS-7 which allowed satisfactory flushing of the air side of the nozzle, while it remained on the solidifier, by adding 50 milliliter amounts of dilute nitric acid directly to the atomizing air.

Calcining 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 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 calcining chamber walls only occurred during Runs SS-1 and SS-12(IPM) as discussed above. Scaling was not observed 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 of the waste in the calcining chamber (6 to 10 seconds) the contribution of the internal heat generation of 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. These temperatures allowed early adjustments to the feed flow rate 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 internal temperatures in the top calciner zone ranged from 300 to 500 °C for the runs, a temperature of 350 to 400 °C was about optimum for a feed rate of approximately 16 liters/hr. Average calciner temperatures during processing were presented in Figure 4.14.

The free-piston, air-operated vibrator mounted on top of the calciner performed satisfactorily at dislodging calcine from the calcining chamber walls. However, mechanical difficulties were experienced with it and it was necessary to replace it a number of times. Some additional testing of vibrators under radioactive "hot cell" conditions is recommended. Vibrators used in nonradioactive testing were much more reliable. The vibrator was normally actuated for 2 seconds of every minute, with an air supply pressure ranging from 40 to 60 psig. Although operation without a vibrator was not tested, indications were that a vibrator is needed for proper operation of the calciner.

The steepness of the cone walls at the bottom of the calciner was 30° from the vertical axis. Indications were that this is an absolute minimum to assure that the calcine will slide down them. A cone with a 25 to 29° angle is recommended.

Off-Gas Filtration

The spray solidifier off-gases exited through 15 square feet of sintered-powder metal (316L stainless steel) filters. The filters were cleaned by periodically blowing heated air back through them. Filter performance was normally very good.

As discussed earlier, with the exception of Runs SS-3 and SS-4, an average of less than 0.04% of the nonvolatile radioactivity was entrained from the solidifier through the filters during the runs. The cumulative percent entrainment obtained from tank samples and tabulated in Table 4.3 was higher than the instantaneous values obtained from in-line condensate samples for most runs. This was apparently due to a burst of calcine passing through the filters at the start of the run while the filter coat was being established. This characteristic was especially true for Run SS-4 where 0.16% was entrained through a new set of filters.

During Run SS-3, 10% of the calcine was entrained from the solidifier when two of the 15 filters failed. Both failures occurred just below the top manufacturer's circumferential weld which joined the porous metal to a solid collar. The filters failed after approximately 400 hours of actual service and had been found in good condition during a visual inspection at 300 hours.

Metallographic examination of samples of the filters taken near the failure and 4 to 5 inches below the failure indicated no corrosion but a loss of ductility in the porous metal at the point of failure.⁽¹⁷⁾ It was concluded that the failure

probably occurred between Runs SS-2 and SS-3 and was primarily due to the filter chamber being struck by the crane boom.

A combination of mechanical fatigue and corrosion is suspected as the cause of this loss in ductility. Fatigue at the top of the filter is postulated to have resulted from a vibrational pivoting action about the porous metal-to-solid metal weld. Since the filters were installed, other filters have become available with reinforced perforated support plates inside of the filters to minimize the mechanical stressing of the porous metal.

During the first several runs difficulties were experienced in controlling the filter pressure drop (as shown in Table 4.4) because sufficient process vent capacity was not available to permit the use of adequate blowback gas without pressurizing the solidifier. To alleviate this problem, a parallel vent line was installed and the replacement filter assembly which was installed prior to Run SS-4 was modified in such a way that only two filters at a time were reverse blown instead of three as on the original set of filters. During Run SS-10, the filter pressure drop became excessive when considerable calcine deposition occurred 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 and effectively flushed prior to Run SS-11 by spraying nitric acid (2 to 6M) into the upper filter chamber while simultaneously blowing back the filters with saturated steam.

Teflon valve disks on the blowback solenoid valves failed and caused sticking after a 1.5 year period with only 380 hours of actual operation and with radiation exposure levels of approximately 10^8 R. All of the valves were replaced following Run SS-10.

Either superheated steam or heated air was used during the runs as a blowback gas, and both proved satisfactory. However, when using steam, one must make sure that condensate does not accumulate in the supply system (a continual blowdown was used in WSEP). During operation each bank of two filters was usually blown back for 2 seconds once every 2 minutes. During most runs a blowback gas pressure of 40 to 45 psig maintained the filter pressure drop between 2.5 and 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. The filter blowback system was usually turned off for 10 to 30 minutes during batch discharge of the melter (see Melt Drain System in next section). Having the blowback off 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 in-leakage through the flanged connections on the solidifier (particularly on the melter) were estimated at 5 to 10 scfm, and represented 20 to 50% of the total off-gas flow. This amount of in-leakage air is higher than desirable.

Nonradioactive off-gas filtration studies of several types of filter materials are summarized in Reference 16.

4.2.6 Performance of the Melter

The calcined waste powder dropped from the spray calciner directly into the platinum melter⁽³⁾ where it was converted to a melt. During Runs SS-2 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 because it allowed the filling of unheated pots without stalagmite formation in the receiver pot.

As shown in Table 4.4, 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 LMFBR wastes, and 880 to a 900 °C during processing of PW-2 waste. Figure 4.15 shows typical melter temperatures during processing of the wastes. The time at which to discharge the melter was determined by the amount of waste fed between batches, and the melter internal temperatures. The desired 5 to 6 liter volume in the melter was usually indicated when the internal melt temperature measured 5-1/2 inches above the melter bottom (I2 in Figure 4.15) increased to almost equal the temperature at the lower part of the melter (I3 in Figure 4.15).

Following Run SS-11, the platinum melter was removed from the melter furnace, and it was found to have four large indentations in its side with the diameter reduced as much as 2 inches. The melter 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 one slight indentation prior to Run SS-5 after approximately 220 hours of service.

A similar distortion of a platinum melter occurred at Brookhaven National Laboratory.⁽³¹⁾ This distortion was attributed to the negative melter operating pressure and to the reduced creep resistance of the platinum caused by the long process exposures. A subsequent melter was fabricated at Brookhaven with increased wall thickness and stiffener rings welded to the outside melter wall to increase the wall strength.

As discussed in Section 3.2.2, an earlier platinum-0.5 wt% rhodium spray solidifier melter underwent brittle fracture due to the accidental addition of stainless steel to the melter during nonradioactive tests.

4.58

FIGURE 4.15. Melter Temperatures During Run SS-7

BNWL-1667

New furnace lead wires were remotely installed on the melter furnace after the original wires failed due to oxidation. The original wires were enclosed inside a jacket on the furnace. The new wires were installed externally so they would remain cooler for reduced oxidation. See Section 4.3.6 for final evaluation of the platinum.

It is possible to make non-platinum melters that are suitable for use with phosphate melts at temperatures up to 1000 °C and for use with borosilicate melts at temperatures up to 1100 °C (e.g. 50% chromium-50% nickel or Corronel-230 alloys). Tests with a pilot scale ceramic, chromium oxide melter produced satisfactory corrosion resistance results with phosphate melts at 1050 °C; however, the melter failed due to thermal cycling. Conceptual designs of nonplatinum melters are discussed in Section 8.3.

Solids Addition

To increase sulfate retention in melts with PW-2 waste, the melting point of the calcine was reduced to about 700 °C during Runs SS-3 and SS-4 by adding sodium metaphosphate (NaPO_3) as a solid directly to the melter. The NaPO_3 was not added to the feed because the low melting point of the mixture would have caused melting in the calciner at the operating temperature used and it would have reduced the calciner capacity at lower operating temperatures. Sodium metaphosphate glass particles (-6+10 mesh Tyler series) were added in small batches (400 to 600 grams every half hour) to the suction side of an air-operated jet. From there they were conveyed pneumatically into the cell and discharged into a screen-covered hopper on the solids feeder (Figure 4.9). The solids feeder consisted of a piece of pipe attached to a nozzle on the lower part of the calciner (conical section), with two air operated ball valves which served as an air lock so that the solids could be added without disrupting the solidifier vacuum. A vibrator aided transport of the solids.

The solids additions were closely monitored to maintain the correct addition rates of NaPO_3 . Nonradioactive development studies showed that 50 to 100% excess NaPO_3 increased sulfate evolution from the melt which caused the melt to foam in a heated receiver pot.⁽²⁰⁾ It was necessary to add a heated air purge (1 scfm at 250 °C) to the solids feeder to minimize condensation and subsequent plugging at the entry point to the solidifier, such as occurred during the early portion of Run SS-3.

Melt Drain Systems

Initially both the melter drain and weir tubes terminated inside separate electrically-heated chambers where heat could be applied to thaw the melt plug in the tubes to initiate melt flow. The weir was used during the first 60% of Run SS-1 to discharge the melter until the weir became frozen and could not be thawed.

During the remainder of Run SS-1 and all of Run SS-2, the melter was successfully batch-discharged using the drain freeze-valve heating system. After failure of new electrical freeze valve heaters (installed after Run SS-2), the melter was batch-discharged through the drain tube during Runs SS-3 and SS-4 with heating being supplied by a manipulator held propane torch. Tests on propane heating of platinum in contact with PW-2 melt indicated that no appreciable attack or embrittlement of the platinum would occur if the propane flame was not a reducing flame and if propane heating was used sparingly.⁽³²⁾

Due to the difficulties experienced with the previous electrical heating system and the potential for platinum embrittlement while using direct propane heating, a modified method to control the discharge of melt from the melter was developed prior to Run SS-5.^(17,33) The method consisted of freezing the melt in the tubes by air cooling coils surrounding each tube (Figure 4.8). To batch discharge the melter, the

air to the cooling coil of the drain freeze-valve was turned off to allow heat from the melter furnace to thaw the frozen plug. 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 minimize spattering of the melt stream and to avoid pressurizing the solidifier due to the reduced vacuum. 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 4 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.

It was difficult to seal the drain tube if the melter was not completely empty before trying to seal it. Sometimes it was necessary to reduce the melter furnace temperature approximately 100 °C in order to stop the melter from dripping. It was essential to seal the drain to prevent back-sparging of air through the unsealed tube such as occurred during SS-6 where splattered melt partially sealed off the powder inlet to the melter. A melter sight glass (non browning quartz) was used as an operating aid to observe such items as calcine powder fall, melter internal color, and backsparging. A sight glass is believed essential for the WSEP size melter and is recommended, at least initially, for any size of melter.

The cooling air flow rates to the drain-valve coil and the weir coil were 4 to 8 and 2 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 and PW-2

melts were normally batch discharged from the melter at instantaneous rates of 40 to 65 liters/hr. The PW-4m melts were considerably more viscous and discharged at rates of about 23 liters/hr. 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, an instantaneous batch filling rate of 23 liters/hr represents about the minimum rate at which an unheated 8-inch diameter pot can be filled with PW-4m melt without stalagmite formation problems. Batch discharge rates as low as about 15 liters/hr are sufficient for the more fluid melts.

Overall, the operating performance of the spray calciner-melter system was good. A properly operating system required only a minimum amount of surveillance to assure a continued smooth operation.

4.2.7 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 replaced with a transition spool-piece which coupled the spray calciner directly to the receiver pot.

The insulated spool-piece was provided with 1) a removable quartz glass window to allow viewing down into the pot with the aid of a mirror, 2) two 2-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 and 4) an air-operated vibrator to vibrate the spool-piece when desired. A solids addition system identical to that used during Runs SS-3 and SS-4 was installed (Figure 4.9) to add the required flux directly to the pot.

The -6 to +10 mesh borosilicate frit was added in 1 kilogram batches with the number of batches added per hour determined by the feed rate to the calciner to give the desired ratio of calcine to frit. The batch addition rate ranged from 4 to 6 batches/hr during the runs. The solids feeder system performed satisfactorily, with over 100 kilograms of frit being added to each in-pot melting run.

The progress of the in-pot melting runs was followed by observing the pot internal temperatures (Section 4.2.2) and by viewing through the spool piece window. The presence of a red glow in the pot gave assurance that the melting was progressing satisfactorily. Viewing was somewhat limited as the result of streaking of the window with calcine and deterioration of the hypolon rubber wiper blade due to the high spool piece temperatures (200 to 300 °C).

The feed to the calciner was discontinued at the end of each run when the decrease in the pot Zone 1 centerline temperature was sustained and 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 about 1 to 3 hours after the feed had been turned off and cooling air was turned on to all furnace zones using one blower (275 scfm).

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 hoped for level of 72 inches but was expected in view of high heat losses at the top of the pot, which was only heated to the 78 inch level. Although the top surface of the products was somewhat irregular, all of the material appeared to have been molten. There was a light film of calcine dust on the upper internal pot surfaces, but no accumulation of calcine was apparent.

4.2.8 Related Equipment Performance

Seal Pot

A secondary vent line from the solidifier provided for relief of solidifier pressure if it exceeded atmospheric pressure during operation. A water-seal pot in the line overflowed directly into a condensate receiver tank.

The calciner seal pot was an 8-inch diameter by 36-inch long section of pipe closed at each end and containing inlet and outlet piping arranged in such a way that pressure differentials of 20 inches of water were required to allow gas to flow from the calciner to the condensate tank. Backward flow of seal water to the solidifier was not possible by design. The use of the emergency vent system was not required in the WSEP tests. However, during operation the solidifier was occasionally vented through the seal pot during filter blow-back as the result of a decrease in venting capacity of the solidifier off-gas system, which sometimes occurred when the system vacuum was not properly adjusted.

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 operated at 800 to 850 °C and 650 to 700 °C to slump PW-1 and PW-2 melts, respectively, in the receiver during all of Runs SS-1, SS-2, SS-3, and the first half of Run SS-5. While filling the receivers during these runs, the zones below the melt level were unheated and sometimes cooled. The receiver pots were unheated for the rest of the spray-melter runs, and the furnace-cooler provided a cooling function only. Indirect cooling by 275 scfm of forced air around the outside of the furnace susceptor, coupled with 50 scfm of direct air cooling around the pot, 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 WSEP runs. A test of the 50 scfm of internal susceptor cooling air during Run SS-6 indicated that this added cooling decreased the average pot wall temperature 35 °C (from 430 to 395 °C) below that attained with external susceptor cooling only.

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 4.2.2.

Solidifier Condenser

See pot calcination (Section 4.1.5). The same condenser was used for all solidifiers.

4.3 PHOSPHATE GLASS SOLIDIFICATION

Eleven radioactive phosphate glass solidification runs were made in WSEP.^(11,34) Some improvement in the denitrator evaporator and melter feed systems, and a less expensive melter material or assurance of adequate reliability of melters are desirable to make the system more suitable for commercial use.

The essential features of the phosphate glass solidification system in WSEP are shown in Figures 4.16 and 4.17. The denitrator evaporator was mounted above the continuous melter so that concentrated liquid could flow directly down and into the melter through a solution feeder. The concentrate was lifted out of the denitrator with either an airlift or a screw.^(3,34) The melter was mounted directly above the receiver pot in the same manner as for the spray solidifier (Section 4.2). The receiver pot is identical to that used with

GLASS MELTER CONDENSER (E-117)	
CAPACITY	Condensing Vapor at 900 °C to 100 °C at 5 g/hr
CONSTRUCTION (EXTERNAL)	Welded 304-L
CONSTRUCTION (INTERNAL)	Welded Nionel
OPERATING Temperature	100 °C
Pressure	13-15 psia
HEAT TRANSFER AREA	54 ft ²
AUXILIARIES	Spray - Wide Angle Cone

DENITRATOR EVAPORATOR (TK-120)	
VOLUME	30L
Minimum Operating	40-50L
Maximum	70L
CAPACITY	35 g/hr
Boilup	8 hr
Folding Time	1-1/2 HP
AGITATOR	4 Blade Turbine
Power	0-200 RPM
Type	600-900 RPM
Speed	2 in. Dia.
Shaft	
CONSTRUCTION	Welded Titanium
Operating Temperature	100-160 °C
Pressure	13-15 psia
HEAT TRANSFER AREA	11 ft ²
TK Tube Bundle	8 ft ²
TK Jacket	
AUXILIARIES	Feed Out Two 10 GPM

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FIGURE 4.16. Denitrator Evaporator and Melter Condenser for Phosphate Glass Solidifier in WSEP

FIGURE 4.17. Continuous Melter and Furnace Assembly, Phosphate Glass Solidifier in WSEP

the spray-melter process (Figure 4.10) except 6-inch diameter pots with only 5 fill zones were also used with the phosphate glass process. (The top fill zone was expanded to 8 inches in diameter for the 6-inch pots.)

4.3.1 Overall Processing Rates

The platinum melter limited the WSEP processing rate to approximately 1.4 liters/hr of melt at a 1225 °C melter furnace temperature and a melt temperature of 1050 to 1200 °C. As with the platinum melter for the spray calciner, the low emissivity of platinum restricted the transmission of heat into the melter.

The melt making capacity of the development melter at BNL was approximately 2.0 liters/hr.⁽³⁵⁾ While not fully established, this increased capacity was primarily attributed to higher operating temperatures with the BNL melter and furnace. Although the BNL melter contained no internal heat generation, the melter wall and melt temperature were 1290 and 1250 °C, respectively, at an indicated furnace temperature of 1250 °C during a test with PW-4m waste.⁽³⁵⁾ The heat transfer area of the BNL melter (about 8-inch diameter by 18-inch heated height) was about 10% greater than the WSEP melter (about 10-inch diameter by 14-inch heated height). The BNL melter also had a more favorable geometry for radiation heat transfer.

The processing rate was not limited by the denitrator-evaporator since it could evaporate more than 35 liters/hr of distillate to provide a three-fold greater melter feed rate than the melter could handle.

Tables 4.7 and 4.8 summarize the feeding data and system performance for the WSEP phosphate glass solidifier runs. The 1.4 liter/hr melt forming rate should be expected with all of the flowsheets tested in WSEP. The processing rate was limited in the early runs by operating difficulties (foaming)

TABLE 4.7. Phosphate Glass Solidifier Feed and Run Data

Solidifier Run Number	PG-1 (a)		PG-2		PG-3		PG-4		PG-5 (a)		PG-6		PG-7		PG-8		PG-9		PG-10		PG-11	
	A/B		A		A		A		A/B		A		A		A/B		A		A		A	
Operating Mode	12		8		8		8		12		8		8		8		6		6		8	
Pot Size	PW-2		PW-2		PW-2		PW-2		PW-1		PW-1		PW-2		PW-4m		PW-4m		PW-4m		LMFBR	
Feed Volume, liter/tonne	480/580		586		458		540		666/1143		889		644		722		1023		1198		1916	
Total Feed to Denitrator, liter	964/431		873		697		725		420/842		616		806		660		579(c)		580		907(d)	
Total Feed to Melter, liter	709/394		520		318		669		271/728		584		675		610		423		414		726	
Startup Time (Concentration Period), hr	9/5		10		13		12		6/6		7		7.3		7.5		5.3		6.5		4.9	
Steady State Operation, hr	52.4/26		32		16		65		32/60		43		36.9		42		16.7		17.5		42	
Shutdown Time (Dilution Period), hr	11.7/15		14		14.4		13		2/10		14		13.5		5.7		5.4		6		11.8	
Avg. Feed Rate, liter/hr	15.7/13.9		18		11		9.4		11.1/12.8		12.3		18.2		13.3		26.3		24.2		19.3	
Avg. Feed Rate During Startup, liter/hr	21.6/19		22		11		20		25/25.8		23.6		25		16		31		31		35	
Avg. Feed Rate During Steady State, liter/hr	14.6/13		14		16		7.5		10/11.5		10.5		17		13		25		22		18	
Radioactivity																						
Total Radioactivity in Feed to Denitrator, kCi(f)	438		670		1540		1200		1290/1500		2560		3390		2500		1300		3600		3720	
Total Radioactivity to Melter, kCi(f)	349		419		604		1100		2200		2430		2800		2300		1025		2600		3275	
Radioruthenium in Feed to Denitrator, kCi	19.7		33		30		34		23.6/32.6		8		15.5		10.1		11		None		33	
Radioruthenium to Melter, kCi	13		20.3		10.2		30.9		42.2		7.5		13		9.8		9		None		30	
Feed Heat Rate Density, W/liter	1.3		3.9		10		7		13/8		16.8		17		14		11		24		14.5	
Fission Product Heat to Pot, W	1600		1700		3300		4200		8800		9600		9800		8800		4200		9300		11,900	
Ruthenium Volatilized from Solidifier, %	4.5(b)		~9		0.8(b)		1.5		11.4		4.7		8.8		4.6		6.6		(e)		7.9	
¹⁴⁴ CePr Entrainment from Solidifier, %	<0.1 (b)		0.02 (b)		0.003 (b)		0.23		0.25		0.22		0.05		0.07		0.12		0.08		0.05	
Equivalent Spent Fuel Waste																						
Waste to Pot, tonne	2.16		0.89		0.69		1.24		1.04		0.66		1.05		0.84		0.41		0.35		0.38	
Average Steady State Processing Rate, tonne/day	0.61/0.44		0.38		0.21		0.34		0.28/0.20		0.28		0.58		0.39		0.47		0.34		0.2	
Equivalent Age of Waste, yr (g)	7.5		2.5		1.0		1.45		0.53		0.22		0.46		1.0		0.9		0.25		1.5	

a. Run was performed as two separate parts.

b. Does not include loss from melter and substantial foamover losses that occurred during Runs PG-1, PG-2 and PG-3.

c. Consists of 481 liters at 1023 liter/tonne and 98 liters at 1970 liter/tonne.

d. Consists of 708 liters at 1961 liter/tonne and 199 liters at 3832 liter/tonne.

e. No radioruthenium in feed.

f. Radioactivity was predominantly ¹⁴⁴CePr.

g. Based on heat generation rate in pot and ISOGEN program. See Section 7.

TABLE 4.8. Phosphate Glass Systems Performance

Solidifier Run Number	PG-1 ^(a)	PG-2	PG-3	PG-4	PG-5 ^(a)	PG-6	PG-7	PG-8	PG-9	PG-10	PG-11
Waste Type	PW-2	PW-2	PW-2	PW-2	PW-1	PW-1	PW-2	PW-4m	PW-4m	PW-4m	LMFBR
<u>Denitrator Evaporator</u>											
Avg. Liquid Temperature, °C	137/138	137	136	137	134/132	132	136	123	126	123	121
Avg. Vapor Temperature, °C	135/136	135	136	110	110	109	116	111	110	112	108
Avg. Specific Gravity	1.8	1.8	1.8	1.9	1.8	1.8	1.9	1.7	1.7	1.7	1.7
Avg. Holdup Volume, liter	48/42	47	47	55	51/45	45	44	47	40	48	47
Feed Concentration Factor	4.5/6.0	5.0	4.0	3.1	3.5/5.5	4.2	4.6	2.7	3.7	4.6	3.6
Adjusted Concentration Factor (if feed were 378 liter/tonne)	3.5/4.7	3.2	4.0	2.2	2.0/1.8	1.8	2.7	1.4	1.4	1.5	0.7
Agitator	200	200	600	200	200	200	200	200(d)	Not Used	Not Used	Not Used
Avg. Tube Bundle Steam Pressure, psig	52/51	58	67	45-60	45-70	65	62	47	56	43	46
Nitric Acid Spray (6M) Added, liter	65/82	31	20	57	58/32	102	16.5	25	29	30	23
Antifoam B Solution Added, liter/hr	0	0	0	3.9(b)	2.6/1.2(c)	0	2.8	2.8	2.7	None Added	3.2
Ruthenium Volatilized from Denitrator, %	NA	0.9	0.8	0.2	0.5/0.5	0.4	0.8	0.62	0.88	(e)	0.48
Entrainment from Denitrator, %	<0.1	0.02	0.003	0.001	0.01/NA	0.03	0.001	0.029	0.063	0.036	0.001
<u>Airlift-Solution Feeder</u>											
Avg. Air Supply Rate, scfh	1.6/3.5	1.7	2.3	2.3	2.4/1.7	1.7	0.7	1.3	0.9	2.1	2.3
Avg. Air Supply Pressure, psig	7.4/8.8	13	6.0	8.3	9.6/6.1	8.0	6.2	5	5.2	5.6	6
Avg. Airlift Jacket Steam Pressure, psig	12/15	10	11	14	10/15	17	17	13.7	15.3	9.6	9.5
<u>Melter</u>											
Furnace Temperature, °C	1230	1230	1230	1220	1220	1220	1225	1230	1225	1250	1215
Melt Control Temperature (1/2 in. above Weir Overflow), °C	940	750-900	850	800-900	825	880	990	970	950	975	995
Melt Temperature (Bottom of Melter), °C	1075	1080	1100	1100	1050	1090	1150	1150	1135	1200	NA
Weir Temperature, °C	750	740	760	750	NA	NA	850	845	835	855	805
Freeze Valve Temperature (frozen), °C	460	460	330	640	570	690	545	580	600	615	525
Melter-Receiver ΔP, in. of water(f)	3.3	2-6	3	6-10	6-10	6-10	--	3-4	2.7	3.5	5
Sparge Nitrogen Flow, scfh	0.2	0.2-0.8	0.2-0.5	0.2-0.5	0.2-0.8	0.8	0.2	0.2	0.2	0.2	0.2
Steady State Melt Production Rate, liter/hr	1.2/0.87	0.62	0.44	0.8	1.2/0.86	1.08	1.54	1.29	1.29	1.21	1.33
Ruthenium Volatilized from Melter, %	NA ^(f)	~8 ^(f)	NA ^(f)	1.3	10.4	4.3	8	4	5.7	(e)	7.4
Entrainment from Melter, %	NA ^(f)	NA ^(f)	NA ^(f)	0.23	0.25	0.19	0.05	0.04	0.07	0.04	0.05
<u>Pot Furnace</u>											
Temperature, °C	590	580	310	600	600	600	600	620	600	615	600
<u>Melter Condenser</u>											
Inlet Gas Temperature, °C	390/370	300-420	370	320-360	450	425	400	475	400	440	470
Outlet Gas Temperature, °C	48	30	45	30	42	40	50	50	53	55	53
Steam Spray Rate, liter/hr	6.5	8.4	8.0	6.2	6.3/5.5	6.3	7.8	Not Used	Not Used	Not Used	Not Used
<u>Process Vent</u>											
Vacuum, in. of water	2-6	2-6	2-6	2-6	2-6	2-6	4.4	3.7	3.6	3.2	4.2
Noncondensable Off-gas Flow, 5	5	6	NA	NA	9	5	<6	<5	<10	<10	<5

NA - Not Available

- a. Run was made in two parts.
b. Contains 0.22 wt% Antifoam B.
c. Contains 0.67 wt% Antifoam B.

- d. Discontinued after 13 hr use.
e. No radioruthenium present in the feed.
f. Differential pressure between the melter and the melt receiver.

which were later overcome. Because of the high capacity of the denitrator, the concentration of the waste fed to it was not too important as long as it was not excessively diluted. However, because of the melter capacity limitation, the waste had to be concentrated to a maximum in the denitrator before it was fed to the melter. (See denitrator performance, Section 4.3.5).

Nitrogen sparge tests of the melter at an average sparge rate of about 0.5 scfh through 2 to 3 sparge tubes had no apparent effect on processing rates; however, erratic feeding of the melter occurred during the tests.

4.3.2 Radionuclide Heating Effects

The temperatures caused by the internal heat generation in the WSEP phosphate glass receiver pots are listed in Table 4.9. The highest internal heat rate densities attained were 198 and 317 W/liter in 8 and 6-inch diameter pots, respectively. The 317 W/liter heat rate density in Run PG-10 caused the average internal centerline temperature to reach 776 °C and the wall temperature to reach 375 °C while stored in air. In no cases were restrictions limiting centerline and wall temperatures to 900 and 427 °C respectively, exceeded during the phosphate glass runs.

Because the phosphate glass product has an approximate 700 °C remelt temperature, the maximum heat rate density was limited in WSEP by the molten core radius restriction that the frozen product thickness at the pot wall should not be less than one-half the pot radius. The heat rate density of 198 W/liter in the 8-inch diameter receiver pot of Run PG-11 produced an average intermediate (midway between the pot centerline and wall) zone temperature of 796 °C while stored in air. Consequently, the molten core restriction was definitely surpassed in this receiver. There were no adverse effects noted in the PG-10 and PG-11 receivers with respect to filling,

TABLE 4.9. Phosphate Glass Solidifier Product Data

Solidifier Run Number	PG-1	PG-2	PG-3	PG-4	PG-5	PG-6	PG-7	PG-8	PG-9	PG-10	PG-11
Pot Size	12	8	8	8	12	8	8	8	6	6	8
Pot Material	MS	304L	MS	MS	MS	304L	310	MS	304L	304L	304L
Waste Type	PW-2	PW-2	PW-2	PW-2	PW-1	PW-1	PW-2	PW-4m	PW-4m	PW-4m	LMFBR
Product Weight, kg	257(a)	101(a)	98	194	119/187	174	182	196	76	85	172
Product Volume, liter	92(a)	35(a)	35	73	44/69	62	67.3	66.7	26.6	29.3	60.0
Bulk Density, kg/liter	2.7	NA	NA	NA	2.8	NA	2.7	2.93	2.84	2.91	2.87
Laboratory Measured Density, kg/liter	2.8	2.9	2.8	2.9	2.7	2.8	2.9	2.9	2.8	3.0	2.9
Volume Reduction, Feed to Solid	11.2/13.5	14.1	9.1	9.1	6.2/10.6	9.4	10	9.2	15.9	14.1	11.9
Adjusted Volume Reduction (based on feed at 378 liter/tonne)	8.8	9.1	7.5	6.4	3.5	4.0	5.9	4.8	5.9	4.5	2.4
Product Unit Volume, liter/tonne	42	40	51	59	108	94	64	79	65	84	158
Fission Product Heat in Pot, W	1600	1700	3300	4200	8800	9600	9800	8800	4200	9300	11,900
Heat Generation Rate Density, W/liter	17	49	95	57	78	155	146	132	158	317	198
Pot Radiation Reading at 6-in, kR/hr	9.5	48	41	37	47	NA	34	38	30	59	68
<u>Pot Steady State Temperature Data</u>											
Centerline Temperature, °C											
In Warm Furnace (no cooling air)	316	NA	655	510	NA	NA	853	820	NA	NA	NA
In Air-Cooled Furnace	NA	355	NA	NA	712	780	782	710	566	827	834
In Air (@ ~38°C)	NA	NA	570	NA	NA	NA	749	660	NA	776	NA
In Water (@ ~30°C)	NA	NA	255	NA	NA	NA	548	475	307	540	622
Centerline-to-wall Δt, °C											
In Warm Furnace (no cooling air)	89	NA	255	175	NA	NA	202	220	NA	NA	NA
In Air Cooled Furnace	NA	135	NA	NA	352	380	401	350	204	369	417
In Air	NA	NA	320	NA	NA	NA	418	360	NA	401	NA
In Water	NA	NA	370	NA	NA	NA	502	433	282	520	590
Effective Thermal Conductivity, W/(m ²)(°C/m)											
In Warm Furnace (no cooling air)	1.03	NA	0.98	0.94	NA	NA	1.78	1.52	NA	NA	NA
In Air-Cooled Furnace	NA	0.94	NA	NA	1.13	1.07	0.9	0.97	1.22	1.22	1.18
In Air	NA	NA	0.78	NA	NA	NA	0.86	0.94	NA	1.12	NA
In Water	NA	NA	0.68	NA	NA	NA	0.72	0.77	0.88	0.87	0.86

NA - Not Available

MS - Mild Steel

a. An additional 17 kg (6 liter) of nonradioactive startup glass was accumulated in pot at start of PG-1 and PG-2.

storage or handling. The effective thermal conductivity of the phosphate glass solids varies with temperature (see Section 6.6.2); but at the average temperature anticipated with heat generating solids, the thermal conductivity should be about $1.0 \text{ W/(M}^2) \text{ (}^\circ\text{C/m)}$. Equations for molten core calculations are derived in Reference 36 and are summarized in Section 8.8.

The molten core restriction is obviously arbitrary and might be relaxed, especially in large diameter pots where one-half the radius would give a sizeable frozen wall thickness. Also, even if the molten product contacted the pot wall, the anticipated corrosion rate is less than 0.007 and less than 0.002 in./year for mild and stainless steel, respectively, at 700°C .⁽³⁷⁾ Before relaxing the molten core restriction, the possibility of phase segregation in the product should be considered (see Section 6.6.1).

Except in Run PG-3, the receiver pot furnace was held at about 600°C . This furnace temperature was essential during continuous melt discharge to assure that the pot wall temperature remained sufficiently high so that the steady drip of melt entering the receiver pot, at rates as low as 1 liter/hr, would not form stalagmites. This was confirmed during Run PG-3, where a 300°C receiver pot furnace temperature allowed glass stalagmites to form in the product receiver. Pot wall temperatures of 300°C allowed the entering melt to cool too rapidly to permit the melt to slump, thereby causing a buildup of melt on the pot thermowells. Batch dumping of the melt at rates of 60 to 120 liters/hr through the drain freeze-valve produced no stalagmites at a pot temperature of 300°C . During two other runs, stalagmites formed in the top of the pot above the heated portion of the furnace.

Continuous melt discharge was used in all runs except the later part of Run PG-3 and during Run PG-11. A typical receiver pot temperature profile for a continuous drain

operation, using data from Run PG-8, is shown in Figure 4.18. The heat rate density of 132 W/liter in the 8-inch diameter pot was not sufficient to require cooling of the pot during the run. One air blower rated at 275 scfm was sufficient to control the receiver pot centerline temperature below 900 °C and the pot wall below 425 °C in the filled PG-10 and PG-11 pots which contained the highest heat rate densities tested: 317 and 198 W/liter in 6 and 8-inch diameter pots, respectively.

During Run PG-11, it was necessary to use batch draining to prevent formation of stalagmites when the melter became tilted and allowed the continuous melt drip to strike near the top of the pot. Receiver wall temperature increases due to the batch drains were reduced by turning heat off to the zone being filled or by turning cooling air on or by combinations of both. The receiver temperature profiles for the PG-11 batch drain operation are shown in Figure 4.19.

Temperature control with the phosphate glass product is assisted by the rapid increase in effective thermal conductivity (k_{eff}) that occurs when the glass remelts at temperatures above 700 °C. The k_{eff} increases from about 1.2 W/(m²) (°C/m) at an average product (solid + melt + pot wall) temperature of 650 °C to 1.8 W/(m²) (°C/m) at 750 °C. The high thermal conductivity of the melt makes it easier to avoid exceeding a 900 °C centerline temperature except at high wall temperatures or excessively thin frozen wall thicknesses.

Melter

The net energy input requirement to form a fluid melt in the phosphate glass melter was about 1.5 to 3 kilowatt-hour/liter of melt. The maximum heat generation rate in the melter occurred during Run PG-10 and was about 1.9 kilowatts. The maximum steady state melt production rate occurred during Run SS-7 when the melt inventory gave a heat generation rate

FIGURE 4.18. Receiver Pot Temperatures During Continuous Drain from Melter in Run PG-8

FIGURE 4.19. Receiver Pot Temperatures During Batch Drain Operation from Melter During Run PG-11

of 0.9 kilowatts. There was no apparent correlation of melt production rate with internal heating within the melter. This was mainly due to the large heat losses in the melter furnace system. However, for larger melters with large melt inventories and lower relative furnace heat losses the fission product heat inventory should contribute to the melter processing rate. Furthermore, the large melt and fission product heat inventory in some cases may require forced cooling during non-operating periods.

Denitrator

The energy input requirement to denitrate and concentrate the waste entering the denitrator was about 0.8 kilowatt-hr/liter of feed. Concentrating the waste, which contained up to 22 W/liter for PW-4m waste, increased the heat rate density in the denitrator until in Run PG-10 the heat rate density was 104 W/liter. This maximum heat rate density accounted for about 40% of the calculated net process heat requirement. The quantitative effects of this available heat was not readily apparent since the denitrator-evaporator steam usage was only indirectly measured. However, the internal heat was sufficient to maintain the concentrate at near its boiling point without external heating.

4.3.3 Waste Volume Reduction

Data for the solidified phosphate glass product are presented in Table 4.9. The final waste solids volume averaged 101, 51, 76 and 158 liters/tonne for the PW-1, PW-2, PW-4m and LMFBR products respectively. These values are equivalent to 5 and 2.7 liters/1000 MWd_t for the PW-1 and PW-2 waste (20,000 MWd/tonne at 15 MW/tonne), and 1.7 liters/100 MWd_t for the PW-4m waste (45,000 MWd/tonne at 30 MW/tonne).

Overall volume reduction factors varied from 6.2 to 15.9 based on actual feed concentrations. This range was due to the wide variation in the waste compositions that were tested and also reflects the large range in fuel burnup that was covered. The volume reduction that took place in the denitrator is presented in Table 4.8. The remaining volume reduction occurred in the melter. The volume of waste required to fill a pot was estimated for each run in the same manner as for the pot and spray solidifiers. This predicted volume reduction differed from actual by an average of 8%. Maximum deviation was 14% in Run PG-5, the first run with PW-1 waste.

The laboratory measured density of the phosphate glass product averaged 2.9 kg/liter for the PW-2, PW-4m and LMFBR products and 2.75 kg/liter for PW-1. The bulk density in the WSEP pots was generally slightly lower than the laboratory value. The maximum difference of 7% occurred in Run PG-7. Differences are believed to be caused primarily by voids which can form in either slow cooling or extra viscous melts. Errors in measuring the volume and weight of the solid product may also contribute to the differences.

4.3.4 Volatilization and Entrainment

During the demonstration runs with PW-1, PW-2 and PW-4m wastes, ruthenium was found to be the only fission product significantly volatilized. Cesium evolution from the melter was slightly higher than could be accounted for by entrainment. Its volatilization ranged from 0.05 to 0.1%. During the run with simulated LMFBR waste, 2.6% of the ^{129m}Te in the feed to the melter was volatilized. Analysis of the effluents from a nonradioactive run made at BNL indicated that from 1 to 10% of the tellurium and 50 to 100% of the selenium could be expected to volatilize from the melter.⁽²⁸⁾ The quantity of selenium in the waste will be insufficient for its volatility to be a significant problem as long as less than 100% of it is volatilized. 2

Most of the ruthenium that was volatilized and entrained from the denitrator-evaporator was collected in the WSEP auxiliary evaporator; that which was volatilized and entrained from the melter was collected in the melter condensate receiving tank. When processing nonsulfate type wastes, the melter condensate can be combined with condensate from the denitrator or recycled to the denitrator.

Volatilization of ruthenium from the denitrator is shown in Table 4.8 along with similar data for the melter. Volatilization and entrainment of ruthenium from the denitrator-evaporator was typical of that from boiling concentrated nitric acid systems and ranged from about 0.2% to 0.9%. Entrainment from the denitrator ranged from 0.001 to 0.06%. The boiloff rates tested did not affect the entrainment markedly because the rates were below the capacity of the denitrator (viz., 35 liters/hr boiloff capacity). However, severe foaming that occurred during Runs PG-1, PG-2, and PG-3 caused a considerable loss of denitrator feed into the melter condensate. The foam-over losses were not included as part of the entrainment losses because the foaming problem was later solved (Section 4.3.5).

Ruthenium volatilization from the melter agreed with previously determined results. Design verification tests indicated that about 10% of the ruthenium feed to the melter would volatilize from the melter and that entrainment of non-volatiles would be less than 0.1%.⁽³⁸⁾ In a bench scale test at BNL, less than 2% of the ruthenium was volatilized from the melter.⁽³⁹⁾ Ruthenium volatilization results in WSEP are shown graphically in Figure 4.20. From 4 to 10% of the total ruthenium entering the melter was volatilized except during Run PG-4 where only 1.3% volatilized. The amount of volatilization was independent of the type of waste. Entrainment based on ¹⁴⁴CePr analysis ranged from 0.04 to 0.25%. Essentially, no ruthenium volatilization or entrainment data were

FIGURE 4.20. Accumulation of Ruthenium in the Phosphate Glass Solidifier Condensate

obtained during the first three phosphate glass runs because of the foam-over from the denitrator to the melter condensate.

If sulfate is present in the waste, it will be quantitatively volatilized from the melter (greater than 98%) and the melter condensate must be treated as a separate intermediate to high level waste stream. Cleanup and disposal of the sulfate-containing condensate is best handled by vacuum distillation^(3,40,41) with recycle of the nitric acid distillate and the bottoms to the solidification process and disposal of that portion of the distillate containing the sulfate by a method such as incorporation in asphalt. Additional references for handling the sulfate condensate are given in WSEP Volume 1.⁽⁴²⁾

If excessive phosphate is present in the waste (metal equivalents/mole phosphate less than 1.0), the excess phosphate will slowly volatilize from the melter.

4.3.5 Performance of the Denitrator Evaporator

Most of the process and equipment difficulties that were encountered in WSEP with the phosphate glass system were resolved, and the demonstration runs were satisfactorily completed. Those items which influenced the performance of the process and equipment are discussed below. Pertinent overall phosphate glass solidifier run parameters were presented in Tables 4.7 and 4.8.

Denitrator Evaporator

The desired melter feed concentration in the denitrator was attained on startup by continuously adding feed to an initial charge of boiling 6M HNO_3 . The volume was held constant at 35 liters during this period and no material was fed to the melter. During this concentration period, the feed rate to the denitrator averaged almost 25 liters/hr for all wastes and ranged from 11 to 35 liters/hr, depending primarily on the feed concentration. The startup period required from

about 5 to 7.5 hours in the final series of demonstration runs and was as high as 13 hours during the early runs when foaming problems were encountered. At the end of each run the shut-down period involved continual dilution of the contents of the denitrator-evaporator with either 6M nitric acid or water. No waste was fed to the denitrator during this period.

The denitrator concentrate boiling temperature was held at approximately 132, 137, 126, and 121 °C for the PW-1, PW-2, PW-4m and LMFBR wastes, respectively. These temperatures produced the maximum concentration that was reasonably handled in the WSEP system. Because of the higher fission product content in the waste from the higher burnup PW-4m and LMFBR fuels, lower temperatures were required to prevent the concentrate from becoming too dense and viscous. Flowsheets for the various wastes were generally optimized during a series of development runs at BNL to give the best operating behavior in the denitrator evaporator.

Significant denitration of the waste solutions occurs in the denitrator-evaporator. During PW-1 demonstration runs, 60 to 70% of the nitrogen in the feed to the denitrator was driven off and condensed in the solidifier condenser; during PW-2 runs 90 to 95% was driven off. Both denitration ranges for PW-1 and PW-2 wastes agree with those from previous Design Verification tests and BNL pilot plant studies at the same boiling temperatures. The extent of denitration was not determined with either PW-4m or LMFBR waste in the WSEP phosphate glass runs. The lower concentrate boiling point for these latter two wastes (less than 126 °C) results in less denitration but about 60% of the nitrate should be removed under WSEP conditions, based on unpublished data obtained at BNL.

Plugging of the specific gravity and liquid level (weight factor) tubes was a continual problem during the processing of PW-1 waste and occasionally occurred with other wastes.

The plugging was significantly minimized during the later runs by incorporation of a dip-tube self-cleaning operating technique. The technique consisted of venting the tubes to the denitrator-evaporator periodically to allow solution to rise inside the tubes and cleanse them. Venting the tubes for a 10 minute period of every 15 minutes of operation proved satisfactory for this purpose.

During the first three WSEP runs, foaming in the denitrator-evaporator was the most severe problem encountered. The primary indication of foaming during the runs occurred when the denitrator liquid and vapor temperature became equal. The vapor thermocouple was located 16 inches above the normal liquid level. Other indications of foaming were abnormal increases of specific gravity and liquid level (weight factor) when the foam was collapsed by spraying 6M nitric acid into the vapor space or by turning on denitrator jacket cooling water; increased weight factor readings in the denitrator overflow seal pot as foam entered; and abnormal increases in the weight factor, specific gravity, and temperature readings in the melter condensate receiver which received the overflow from the denitrator seal pot.

The use of cooling water in the denitrator jacket was partially successful in suppressing the foam. There was no evidence that agitator speed had any effect on the foaming.

After Run PG-3, laboratory studies conducted with non-radioactive and radioactive PW-2 feed established that dibutyl phosphate (DBP) in the Purex Waste was the main foaming agent and that commercial silicone antifoam agents would successfully counteract the DBP-induced foaming.⁽⁴³⁾ It was concluded from these tests that the concentration of antifoam in the denitrator-evaporator bottoms should be kept at about 100 ppm to adequately suppress foaming during the denitration-concentration of the phosphate glass feed.

Antifoam addition was first tested during Run PG-4; prior to the addition of antifoam, foaming was encountered as in previous runs. The foam was then successfully held to non-detectable levels for the first time by continuous addition of Dow Corning Antifoam B at a rate of 10 g/hr per liter of solution in the denitrator. The continuous addition was necessary because the antifoam decomposed in nitric acid solutions. Changing the feed entry point from below to above the liquid level may have helped to suppress the foam for 13 hours during startup, but excessive foaming still occurred with accumulation of DBP prior to the antifoam addition. Since the above addition rate was adequate, it was maintained at this level for all subsequent runs except for a short period at the beginning of Run PG-5 and during all of Run PG-10. Foaming in the denitrator was suppressed to undetectable levels during all subsequent runs, except during the first part of Run PG-7 when stale antifoam was inadvertently used.

The feed used in Run PG-10 was made only from a radio-rare earth solution and did not contain DBP. Because of this, no antifoam agent was added during this run and foaming did not occur.

Operational parameters in the denitrator-evaporator, (liquid and vapor temperatures, liquid volume, and specific gravity) are shown in detail in Figure 4.21 for Runs PG-7 (where mild foaming occurred) and PG-8. The vapor temperature surges during Run PG-7 were typical of mild foaming. During severe foaming the vapor temperature became equal to the liquid temperature.

Agitator

The denitrator-evaporator agitator was used during all portions of the first seven WSEP runs to assist in keeping the concentrated solution well mixed and to prevent settling of solids during the shutdown portion of the runs. Sluggish

FIGURE 4.21. Denitrator-Evaporator Operating Parameters During Run PG-7 (PW-2 Waste) and PG-8 (PW-4m Waste)

operation of the agitator was first noted in Run PG-8 which required its use to be curtailed during a major portion of Run PG-8 and in all subsequent runs. From that time its use was discontinued except during startup and dilution periods when boiling was not occurring. No obvious deleterious effects were noted during the runs when the agitator was not used nor were any obvious differences evident. The erratic operation of the agitator appeared to be due to dragging of the agitator shaft. This was believed to be due to failure of the shaft bearing lubricant from irradiation. The agitator operating history and other pertinent phosphate glass equipment history is presented in Table 4.10.

Melter Feed System

The transfer of concentrated waste from the denitrator-evaporator to the melter was achieved using an airlift pot during Runs PG-1 through PG-4, a modified airlift pot during Runs PG-5 through PG-11 and by a screw slurry pump for a short period during Run PG-11. With the airlift, the concentrated waste was airlifted from near the bottom of the denitrator to the airlift pot from which most of the hot concentrate recirculated back to the denitrator and part flowed over a weir into the melter feed line. The screw type slurry pump lifted the waste from the bottom of the evaporator with an auger which rotated within a snug fitting tubular casing. The amount of solution lifted was controlled by the screw rotation speed. All of the pumped solution overflowed into the melter feed line. Both of these systems are shown in Figure 4.17.

The transfer of concentrated waste from the denitrator-evaporator to the melter was limited to an average of about 3 liters/hr during the first six runs and 4 liters/hr during the last five runs because of the limited melt formation capacity of the melter. Because of this extremely low feed rate of a thick slurry, it was impossible to maintain a flow rate to

TABLE 4.10. Phosphate Glass Equipment Operating History

Equipment	Construction Material	Temp, °C	Pressure In-Water or Flow	Chemical	Operating Hours	Remarks
Phosphate Glass (5C) Rack	SS, Nionel	~50	-2 to -10	Liquid Nitrates, Sulfates, and Phosphate Slurries	1125	--- --- --- --- ---
Melter	Platinum	800-1270	-2 to -10	Phosphate Melts	1035	After 110 hr of CPG operation, the inadequately heated melter vent nozzle corroded and partially collapsed because of expansion stresses. It was replaced.
Melter Sparger No. 1	Platinum	800-1200	0 to 1.2 scfh	N ₂	1	Used only on trial basis during CPG-7.
No. 2	Platinum	800-1200	0 to 0.8 scfh	N ₂	445	Used only during in-cell hot operation.
Melter Level Dip Tube	Platinum	800-1200	0 to 0.5 scfh	Air	725	Used only during in-cell hot operation.
Melter Furnace No. 1	Hevi-Duty Kanthal A-1 Elements	800-1270	Trace Vacuum	N ₂ Purge in Jacket	861	N ₂ purge is to prevent oxidation of electrical wiring in furnace jacket. Elements failed at this time.
Melter Furnace No. 2	Hevi-Duty Kanthal A-1 Elements	800-1270	Trace Vacuum	N ₂ Purge in Jacket	252	--- --- --- --- ---
Melter Weir Heater	Kanthal A-1 Elements	600-1000	---	---	260	The weir heater burned out but was not required.
Melter Freeze Valve Heater	Kanthal A-1 Elements	600-1000	---	---	48	The F.V. heater burned out periodically and during PG-5 it failed and was not replaced.
Melter Off Gas Line	Platinum-5% Iridium	150-600	-2 to -10	Sulfate and Nitrate Vapors	1035	Excellent operation.
Melter Off Gas Line Heater	Nichrome Heating Wire	200-600	---	---	763	Excellent operation. A hand wrapped heater was used for CPG-7, the present heater was installed for radioactive operation. (a)
Melter Condenser (E-117)	Inner Shell, Tubes Drain-Nionel Outer Shell-SS	40-180	-2 to -10	Sulfate and Nitrate Vapors	1035	Excellent operation. After 200 hr service, the SS line on the 5C rack was changed to Nionel.
Melter Solution Feeder	Platinum	100-120	---	Purex Type Wastes	1035	Satisfactory operation
Denitrator Airlift Pot No. 1a	304L SS	120-140	-5 to +5	Purex Type Wastes	310	Removed and replaced after CPG-7 due to excessive corrosion caused by adding 5 liters of 17.5M H ₂ SO ₄ to the denitrator via the pot.
No. 1b	304L SS	120-140	-5 to +5	Purex Type Wastes	319	Removed and replaced after PG-4 due to inadequate removable features. (b)
No. 2	304L SS (Ti-Airlift Air Line	120-140	-5 to +5	Purex Type Wastes	393	Satisfactory operation. Installed prior to PG-5 to provide removable feature.

TABLE 4.10. (Contd)

Equipment	Construction Material	Temp, °C	Pressure In-Water or Flow	Chemical	Operating Hours	Remarks
Denitrator Evaporator (TK-121)	A-55 Ti	40-140	-2 to -10	Purex Type Wastes	1125	Evaporator airlift return line was corroded through following CPG-7 when 5 liters of 17.5M H ₂ SO ₄ was added to the denitrator via the airlift pot.
Denitrator Tube Bundle	A-55 Ti	40-140	0 to 100 psig steam	Purex Type Wastes	1125	Excellent operation.
Denitrator Agitator	SS Shaft, SS and Ti Impellers	40-140	---	Purex Type Wastes	914	After 330 hr the SS impeller was changed to A-55 Ti. The agitator ran backwards for PG-1 to 3. Used only intermittently after 914 hr due to partial failure.
Denitrator Over Flow Pot	304L SS	30-50	-2 to -10	Dilute HNO ₃	1125	---
Denitrator Seal Pot	304L SS	30-50	-2 to -10	Dilute HNO ₃	1125	---
Denitrator Vacuum Breaker	304L SS	30-50	-2 to -10	H ₂ O	300	Removed from the racks after CPG-7.
Melt Receiver Pots	304L SS 310 SS	100-900	Trace	Solidified Melt	380	Excellent operation. No visible warping or bending. No detectable corrosion of stainless steel pots.
	Mild Steel				375	Excellent operation. Mild Steel pots became externally corroded during water storage when reductants were not added to the water.
Receiver Furnace	Hastelloy X	100-900	---		2348	Excellent operation. Also used as pot calciner furnace. Delaminated insulation was completely replaced with Ceroform at 1025 hr just before radioactive service.
Screw Feeder	304L SS	115-125	---	Purex Type Wastes	63	Use discontinued after 13 hr run when drive motor failed.
Screw Feeder Motor		~50 °C	0 to 90 ^(c)	Cell air	138	Failed after 13 hr in hot cell.

a. CPG = "Cold" phosphate glass runs; or Design Verification Test (DVT) runs.

b. PG = "Hot" phosphate glass runs.

c. Air pressure, psig

the melter which did not cycle from about 0 to 5 liters/hr when using the airlifts. The airlifts were also susceptible to level and density changes in the denitrator and to the type of waste being concentrated.

The first airlift which had a fixed orifice in the recirculation return line, was quite suitable for use with the PW-2 sulfate-containing waste.⁽¹¹⁾ Prior to the runs with PW-1 waste (PG-5 and PG-6), a new airlift was installed with an adjustable plug valve in the recirculation line and several features for remote cleaning out of solids.⁽¹¹⁾ This was necessary because the increased solids plugging tendencies with PW-1 concentrate (encountered in development tests) would not permit satisfactory operation with the original unit.

The many remote features of the new airlift proved necessary to solve plugging problems during the two runs with PW-1 waste. In addition to the adjustable plug valve which could be used to clear solids in the return line to the denitrator, remote features included a rod through the plug valve which was used to clean out the recirculation line; provisions for chemical additions through the plug valve, the melter feed line, and a spray nozzle; and the ability to adjust or clean the air line which ran nearly to the bottom of the denitrator.

The melter feed line plugged during Run PG-5 after nearly 40 hours of operation. The concentrate plug in the melter feed line was removed by first rodding the solution feeder in the melter and then by gently tapping the melter feed line while it was heated with 25 psig jacket steam. This was followed with 6M nitric acid flushes through the line to insure that the line was clean. Other plugging problems during both PG-5 and PG-6 with PW-1 waste occurred with the airlift air supply line, airlift pot weight factor dip tube, and the airlift pot recirculation line.

The airlift pot was vented to the melter via the melter feed line during Runs PG-1 through PG-6. This procedure was changed midway through Run PG-7 and in the remainder of the runs by venting the airlift to the denitrator-evaporator. Smoother operation resulted from the change.

A screw feeder, developed at BNL, was installed for transferring feed to the melter in Run PG-11. The screw pump was in operation for 8 hours when its air driven motor failed, causing the use of the pump to be terminated. (The run was completed by using the airlift feed system)

During its brief performance, several advantages of the use of a pump of this type were apparent. These advantages included: a more stable melter operation as indicated by stable temperatures in the melter; higher than average temperatures in the melter at a melter feed rate of 3.5 liters/hr which indicated that an increased feed rate could be accommodated; less sensitivity to changes within the denitrator; and more positive flow control with less likelihood of fluctuations.

The melter feed line terminated in the melter in a cold finger called a solution feeder. The solution feeder absorbed heat from the melter and was cooled by a jacket containing 100 to 200 milliliters of boiling water. The boiling water was condensed and refluxed by a small coil of water cooled tubing. This system prevented plugging of the line from excessive heating of the concentrate while discharging the concentrate within a few inches of the melt to minimize spattering. The system worked reliably except for plugging with the PW-1 type waste as discussed previously.

The entire melter feed line and airlift pot was jacketed and kept hot by using low pressure steam. This system kept the concentrate just below its boiling point to maintain a

low viscosity and to minimize solids from settling or crystallizing during the transfer to the melter.

4.3.6 Performance of the Melter

In the melter, denitrator concentrate at 120 to 135 °C and at a nominal flowrate of about 4 liters/hr was converted to a melt at temperatures up to 1200 °C. During normal operation, the melt continuously overflowed from the melter via an internal melter weir at an average rate of about 1.3 liters/hr. At the end of each run, the contents of the melter were batch discharged through the drain freeze-valve. Throughout most of the runs, feed from the denitrator entered the melter as a gummy and bubbly material but caused no major difficulties. Melter operation during most runs proceeded smoothly except during short periods of foaming which sometimes followed excessive surges of feed to the melter.

Some foaming occurred in the melter during all the runs, but was usually held to inconsequential levels. In all cases, the foam level depended largely upon the feed rate to the melter. When a prolonged surge (on the order of 1 liter in about 5 minutes) of feed entered the melter, a surge of foam followed, such as in Runs PG-4 and PG-7. Successful control of foaming and melt level was normally accomplished by manually maintaining as steady a feed rate to the melter as possible and by always keeping some feed entering the melter. Entering feed would knock down the foam. There were no marked differences in foaming tendencies among the various wastes processed in these runs.

During the first runs, the melter internal weir was sealed with nonradioactive glass. In later runs the melter vacuum was reduced to 2 inches of water to minimize sucking air through the unsealed weir tube while concentrate was fed to the melter. When the weir tube sealed, as shown by melt dripping from the weir, the vacuum was increased to the normal 6 inches

of water. Excessive vacuum during steady state operation (greater than 10 inches of water) would cause air to be drawn into the melter through the weir tube, which resulted in foaming in the melter.

The melter furnace was operated at an average temperature of 1225 °C during all runs, and the resulting average internal melt temperature ranged from 1050 to 1200 °C as measured near the bottom of the melter. Figure 4.22 shows typical melter temperature profiles during the initial part of Run PG-11 where the screw feeder and airlift were used. Melt temperatures were similar for the four wastes tested, except that the melt temperature increased from about 150 °C below the furnace temperature to about 50 °C below the furnace temperature as the internal heat rate density increased.

The average melt level in the melter was about 6 inches. Manual melt level control was attempted by controlling the feed rate to the melter as a function of temperature readings within the melt. An upper thermocouple (1/2 inch above the weir overflow) was monitored to detect only sudden large changes in feed rate to the melter. The temperature 1/2 inch below the weir overflow level was used to estimate the melt level and the magnitude of the feed rate changes necessary to restore the melt to the proper temperature. The upper melt temperature averaged between 825 and 1000 °C during the runs. An optimum would have been about 850 °C for steady continuous operation and maximum capacity.

The installation of a new furnace prior to the start of Run PG-7 became necessary when several heating elements (made of Kanthal A-1) of the old furnace burned out. The elements were visibly distorted and severely bowed outward toward the center of the furnace.⁽³⁴⁾ The elements also sagged and may have made contact with neighboring elements. The furnace had been in use for 861 hours. The furnace was removed and

FIGURE 4.2. Typical WSEP Phosphate Glass Melter Temperatures

replaced with a nearly identical, but modified furnace that had been used briefly in nonradioactive spray solidifier development tests. Inspection of the old furnace was limited to remote viewing with a mirror. The second series of five phosphate glass demonstration runs was completed with the new modified furnace with no difficulty. The furnace was modified by installing vertical ceramic rods in front of each of the sets of Kanthal A-1 elements to limit their bowing. The effects of thermal cycling of the new furnace was lessened in these last runs by limiting the furnace heating and cooling cycles to 200 °C/hr. The higher melt making capacity during the last runs was partially attributed to the new furnace (possible higher actual temperatures).

The platinum melter was examined at the time of the furnace was being replaced. The sides of the melter were slightly concave. The lower two-thirds of the melter appeared to have larger grain growth than the upper portion. Both of these conditions have been noted in a melter used for over 2800 hours under similar, but nonradioactive, conditions at BNL.⁽³¹⁾

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

At the completion of the WSEP runs the spray and phosphate glass melters were cut up to permit recovery of the platinum. Samples that had been exposed to both the vapor and melt phase were taken from both melters for metallographic evaluation.

Figures 4.23 and 4.24 show photographs of the samples from the phosphate glass and spray melters, respectively, for comparison purposes. Both samples have large grain structures, with the spray melter grains somewhat larger than those from the phosphate glass melter.

The autoradiographs of the etched surfaces indicate only surface contamination with no radioactivity within the metal or grain boundaries. The autoradiographs show that the phosphate glass melter appears to have more surface contamination. However, this characteristic may only reflect differences in the decontamination and etching preparation steps. The larger amount of contamination on the phosphate glass melter sample may also indicate some penetration of contamination (ruthenium) into the platinum surface. After extensive decontamination of a separate melter sample the activity which remained was found to be greater than 90% ^{106}Ru . In studies initiated at BNL⁽⁴⁴⁾ on a melter in use there, ruthenium, rhodium, and palladium had penetrated the platinum to a greater extent than any other elements.

Unpublished BNL creep test results (performed at Battelle Memorial Institute, Columbus) revealed that the phosphate glass pilot plant platinum melter had undergone a loss of creep resistance*. A sample of the melter ruptured after 3972 hours with an elongation of 12.3% at test conditions of 100 psi and 1250 °C. The second stage creep rate was 0.5% per 1000 hours between 200 and 1400 hours. The tertiary stage creep rates were 1.4% at 2000 hours, 2.0% at 2500 hours, 2.9% at 3000 hours, and 4.7%

*The BNL pilot plant melter had been in service for 3.3 years and the walls had partially collapsed to an inward concave shape at the end of this time. The melter had been at 1250 °C (under glass-forming conditions) for 2808 hours. Collapse of the crucible occurred at an accelerating rate during the last two 100 hour runs after it apparently became out of round under the prolonged negative operating pressure (5 inches of water maximum). (31)

Neg F8011 2.375X
Macroetched Samples

Neg 2066 2.375X
Autoradiograph
- 30 min Exposure

Neg F8013 37.5X
Microstructure of Vapor
Phase Sample

Neg F8014 37.5X
Microstructure of Melt
Phase Sample

FIGURE 4.23. Samples of Platinum Taken from the
Phosphate Glass Melter

Neg F8012 2.375X
Macroetched Samples

Neg 2064 2.375X
Autoradiograph
- 18 hr Exposure

Neg F8015 37.5X
Microstructure of Vapor
Phase Sample

Neg F8016 37.5X
Microstructure of Melt
Phase Sample

FIGURE 4.24. Samples of Platinum Taken from the Spray-Melter

at 3500 hours. Previous tests with virgin platinum gave 1.5% elongation in 2000 hours and showed zero creep from 2000 to 6000 hours when the test was concluded.

Melter Drain System

Melt was discharged to the receiver pot via the internal overflow weir during all of the demonstrations with the exception of the latter parts of Runs PG-3 and PG-11. At the end of each run, the melter was emptied through the drain freeze-valve to minimize the potential for breaking loose the internal weir in the melter due to different coefficients of thermal expansion of the glass and the platinum melter.* During Run PG-11, a tilted melter made it necessary to drain the melter in batches for a large portion of the run to prevent melt from striking the receiver pot walls in the top of the pot.

The electrical drain-freeze valve heater burned out during Run PG-5. A propane-air torch was then used to heat the drain freeze-valve to drain the melter after Runs PG-5 through PG-8. The batch drains during PG-11, and the final drains in PG-9 and PG-10, were affected by turning off the direct air blast cooling air and allowing the frozen products in the drain valve to thaw. The valve was sealed by turning cooling air on again.

The air cooled drain system that worked so well for the spray calciner-melter was not installed in the phosphate glass system, but should have performed equally well.

Off-Gas Line, Melter Condenser and Steam Spray

Off-gases generated in the melter consisted mainly of water, nitric acid, nitrogen oxides, and sulfuric acid (when present in the waste) and, to a lesser extent, phosphoric acid. In

*Differential thermal expansion data obtained with melt samples indicated that no problem would exist in storing these melts in mild steel, 304L or 310 stainless steel if the pots were not subjected to repeated temperature cycling.(45)

addition, some volatilized ruthenium, selenium and tellurium and entrained materials were present. This stream was routed through a platinum-5% irridium off-gas line to the melter-condenser. The temperatures of the gases passing through this line into the condenser were maintained at 300 to 475 °C in the WSEP runs to prevent condensation and thereby minimize corrosion in the line.

The gas temperatures at the inlet of the melter condenser were essentially the same as those of the off-gas line. The gas temperatures at the outlet of the condenser ranged from 30 °C to 55 °C. Typical temperatures of the collected condensate were 30 °C. Steam spray additions to the bottom chamber of the condenser during PW-2 runs produced higher condensate temperatures. The steam spray additions were made (through a modified, full-cone, Nionel spray nozzle) to recover and dilute the sulfuric acid volatilized from the PW-2 melt. Dilution was necessary to inhibit corrosion of the stainless steel melter condensate drain line. Sulfate was not present in significant quantities in the other wastes; consequently, it was not necessary to use steam additions in those runs. The drain line on the melter condenser was cooled with a water cooling jacket to further reduce corrosion in the line.

Recovery of volatilized sulfuric acid and sulfur oxides in the melter condensate from PW-2 waste ranged from 90 to 99%, except in Run PG-4 where it decreased to 72%. This low recovery in Run PG-4 was directly attributable to the plug which developed in the melter off-gas line. Because of the plug, much of the melter off-gas was vented directly through the melter emergency vent (seal pot) and the melter condensate tank to the denitrator-evaporator process condenser.

Average melter condensate rates were 2.7 liters/hr for PW-1 waste, 2.0 liters/hr for the runs with PW-2 waste where denitrator foamover to the melter condensate did not occur,

and 2.7 liters/hr for the PW-4m and LMFBR wastes. Steam spray addition to the melter condenser added approximately 7 liters/hr to the melter condensate during the runs with PW-2 waste.

4.3.7 Related Equipment Performance

Seal Pots

Emergency vent lines from the denitrator-evaporator and melter were provided for relief of pressure if it exceeded atmospheric pressure during operation. Water-seal pots in each of the two lines permitted the pots to vent and overflow directly into the melter condensate tanks.

The melter seal pot was an 8-inch diameter by 22-inch long section of pipe which was closed at each end and contained inlet and outlet piping designed so that pressure differentials of 8 inches of water would allow gas to flow from the melter to the condensate tank. Seal water could not flow backwards to the melter. The melter seal pot was required during Run PG-4 when the melter vent line plugged.

The denitrator-evaporator overflow seal pot was a 6-inch diameter by 17-inch long section of pipe which was closed at each end and contained inlet and outlet piping designed so that pressure differentials of 12 inches of water would allow gas to flow to the condensate tank. The overflow seal pot was never needed for emergency venting of the denitrator during the runs but did provide a path for foamover flow during the early runs in WSEP.

Receiver Pot Furnace and Solidifier Condenser

See Pot Calcination (Section 4.1.5). The same furnace and solidifier condenser were used for both processes.

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5.0 AUXILIARY PROCESS SYSTEMS PERFORMANCE

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5.0 AUXILIARY PROCESS SYSTEMS PERFORMANCE

Conversion of high-level aqueous wastes to solids generates radioactive effluent streams which must be decontaminated before disposal to the environment. The radioactivity content of the immediate effluent from the WSEP solidifier was a factor of 10 to 1000 less than the original aqueous waste. Demonstration of the effluent cleanup (decontamination) was a significant part of the WSEP program for which the objectives were:

- To provide data on decontamination of solidifier off-gas prior to its discharge to the atmosphere.
- To characterize the secondary aqueous effluent streams from waste solidification.
- To evaluate the performance characteristics of the individual auxiliary equipment, i.e., condensers, evaporator, acid fractionator, filters, scrubber, tanks, pumps, agitators, etc.

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

Flowsheet studies have indicated that the recovered nitric acid and water streams from the solidification process in WSEP could be reasonably recycled to a fuel reprocessing plant.⁽¹⁾ The recovered nitric acid, which is slightly contaminated with radionuclides, could be recycled to the separations process head end (fuel dissolution, etc.) while the less contaminated recovered water could be used for chemical makeup for the head end and for certain streams in the first cycle solvent extraction operation.

The data regarding the effluents resulting from solidification in WSEP can be generalized as follows:

- The immediate effluent from the solidifiers was decontaminated by factors of 1.3 to 200 for radioruthenium and 100 to 100,000 for radiocerium (representing nonvolatiles)* but it still remained as a highly contaminated waste.
- The radioactivity removed from the solidifier off-gases was distributed to three aqueous streams. The bulk of it remained in the evaporator bottoms where it could be recycled to the solidifier feed. About 0.1% of the ruthenium was found in the fractionator bottoms (recovered HNO_3) and less than 0.0001% in the fractionator distillate. Also about 0.0001% of the cerium was found in the fractionator bottoms and about 0.0000001% in the fractionator distillate. The radioactivity in the fractionator distillate exceeded 10CFR20 Table II, Column 2 values⁽²⁾ by factors of 1000 to 100,000.
- The cleanup of solidifier effluents by the WSEP effluent treatment system was adequate for the final gaseous effluent stream with decontamination factors from the solidifier feed to the stack of 10^{10} for radioruthenium and 10^{12} for radiocerium representing nonvolatiles.

A summary of information on typical effluents resulting from waste solidification in WSEP is presented in Table 5.1.

* In WSEP, $^{144}\text{CePr}$ was used as a measure of the behavior of all nonvolatile material in the effluent treatment system.

TABLE 5.1. Typical Effluents Resulting from Solidification of High-Level Radioactive Waste(a)

Stream	Major Constituent	Radium Ruthenium Ci/Ci in Feed ^(b)			Radiocesium Ci/Ci in Feed ^(b)			Potential Disposal
		PC	SS	PG	PC	SS	PG	
Solidifier Condensate	1 to 6M HNO_3	2×10^{-1}	6×10^{-1} (1×10^{-2}) ^(c)	8×10^{-2}	6×10^{-3}	7×10^{-4}	2×10^{-3}	Recycle to solidifier feed or to fuel reprocessing plant waste concentrator.
Fractionator Bottoms	7 to 10M HNO_3	1×10^{-3}	4×10^{-3}	2×10^{-3}	2×10^{-6}	5×10^{-6}	8×10^{-7}	Recycle for reuse in fuel reprocessing plant.
Accumulated Fractionator Distillate	0.01 to 0.1M HNO_3	1×10^{-6} (4×10^{-4}) ^(d)	1×10^{-5}	4×10^{-6}	1×10^{-8}	1×10^{-9}	1×10^{-8}	Recycle for reuse in fuel reprocessing plant or provide further contamination.
Scrubber Bottoms	0 to 2M NaOH	1×10^{-5}	4×10^{-5}	3×10^{-6}	$\sim 10^{-8}$	$\sim 10^{-8}$	$\sim 10^{-8}$	Intermediate level waste treatment or combine with high level aqueous waste.
Final Off-Gas from Scrubber	Air	$\sim 10^{-8}$	$\sim 10^{-8}$	$\sim 10^{-8}$	$\sim 10^{-9}$ ^(d)	$\sim 10^{-11}$	$\sim 10^{-11}$	To building ventilation filters.
Final Off-Gas to Stack	Air	$\sim 10^{-10}$	$\sim 10^{-10}$	$\sim 10^{-10}$	$\sim 10^{-12}$	$\sim 10^{-12}$	$\sim 10^{-12}$	To atmosphere.

a. Based primarily on average of typical values for all WSEP runs.

b. Total curies of radionuclide accumulated in auxiliary tank during entire run/total curies of radionuclide in feed to solidifier during entire run.

c. For in-pot melting runs SS-12 and SS-13.

d. Average value for last three pot calciner runs.

PC=pot calcination, SS=spray solidification, PG=phosphate glass solidification

5.1 AUXILIARY PROCESS SYSTEMS

Process auxiliaries 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 and water.

In the WSEP auxiliary system, vapors from the solidification system for primary off-gas decontamination were condensed and the resulting condensate was re-evaporated in the evaporator (while concentrating solidifier feed in some cases). The vapors from the evaporator were decontaminated from entrained aerosols in the evaporator tower by impingement plates, bubble caps, and a mist eliminator before being vented to the evaporator condenser. The evaporator condensate was routed to an acid fractionator where nitric acid was recovered. The vapors from the fractionator were again condensed and about 80% of the fractionator distillate was recycled to the evaporator as nitric acid strip water. The remaining 20% was collected as an intermediate level waste stream. The uncondensed gases were treated by high efficiency filtration, caustic scrubbing, and additional filtration before discharge to the atmosphere. Figure 5.1 illustrates the WSEP auxiliary process system. A detailed description of the auxiliary equipment and their design criteria can be found in Reference 3.

5.1.1 Operating Modes

Three different auxiliary operating modes were demonstrated in WSEP. These were designated as Modes A, B, and C as shown in Figure 5.2. Complete descriptions of the operating modes can be found in Reference 4. Mode C was only demonstrated during pot calcination Runs PC-4 and PC-5.

Operating mode applications in a fuel reprocessing plant are visualized as shown in Figure 5.3. In all cases, the condensed solidifier vapors are concentrated in an evaporator. During Mode A operation, the evaporator concentrate is an additional effluent stream which must be recycled back to the

FIGURE 5.1. WSEP Auxiliary Process System

FIGURE 5.2. WSEP Process Mode Options

FIGURE 5.3. Operating Mode Applications in a Fuel Reprocessing Plant

solidifier feed or to the waste concentrator in a fuel reprocessing plant. In Mode B and C operation condensed solidifier effluents are mixed with incoming waste before being re-evaporated.

The ruthenium concentration in the evaporator was substantially greater with Mode B and C operation, but ruthenium in the evaporator distillate was primarily dependent on the acid concentration in the evaporator bottoms, evaporator boil-off, the fraction of ruthenium volatilized from the solidifier and the noncondensable gas flow rate. Thus, in WSEP the difference in the ruthenium concentration in the evaporator and fractionator distillate streams with different operating modes was generally less than the difference between the ruthenium concentration in the evaporator during the different modes.

5.2 SOLIDIFICATION EFFLUENT TREATMENT IN WSEP

The effectiveness of solidification effluent treatment in WSEP is discussed in the following sections.

5.2.1 Effluent Characteristics

The effluents from solidification processes consist of volatilized material from the feed, entrained liquid or solid aerosols, and process air. The volatilized materials consisted primarily of water, nitric acid, various oxides of nitrogen, and a small amount of ruthenium tetroxide (RuO_4). The small amount of noncondensable constituents in the solidifier off-gases were discharged to the atmosphere after treatment.

5.2.2 Control of Ruthenium

Minimizing the amount of ruthenium volatilized is one of the major concerns in solidification and evaporation of radioactive wastes. Ruthenium behavior in waste processing is extremely complex and is further complicated by being directly related to nitrogen-oxide chemistry, which is also complex.

Ruthenium volatilization is caused by oxidation of ruthenium compounds to volatile RuO_4 .⁽⁴⁾ Therefore, it should be possible to suppress volatilization by the addition of suitable chemical reducing agents, such as sugar, phosphite, hypophosphite, organic phosphates, etc., to boiling nitric acid solutions.^(5,6,7,9) Other ways of minimizing ruthenium volatilization are to maintain a low concentration of nitrates and nitric acid in the evaporator bottoms and resulting overheads,^(5,7) and lowering the distillation temperature by means of vacuum distillation. A combination of these methods may be advantageous.

Ruthenium tetroxide is readily decomposed to particulate RuO_2 . Gas phase decomposition results in formation of fine particles of RuO_2 which are very difficult to scrub from the gas. Deposition is accelerated on surfaces of stainless steel, glass, nonfluorinated plastics, and especially on reducing surfaces such as formaldehyde saturated silica gel, and on ferric oxide granules.^(8,9) However, the decomposition of RuO_4 is retarded by the presence of nitrogen oxides.⁽¹⁰⁾

The performance of the WSEP auxiliary system was primarily dependent upon its ability to remove radionuclides from the solidifier off-gas. Therefore, to assess the performance, the accumulation of radioactivity in each auxiliary tank was determined at the end of each run and is summarized in Table 5.2. Decontamination factors (DF's) at each stage in the system were also determined to help evaluate the performance of each individual unit such as the evaporator, fractionator, condensers, filters and scrubber. Ruthenium decontamination performance in WSEP is summarized in the following subsections.

Pot Calcination

During the pot calcination runs, from 3 to 31% of the ruthenium (^{106}Ru) present in the feed to the pot was

TABLE 5.2 Radionuclide Distribution in WSEP Auxiliaries

Ruthenium Emitted (a)										Nonvolatiles Emitted (b)									
Fraction (c)										Fraction (c)									
Run No.	Mode	From Solidifier	To Fractionator, to 10-3	To Fractionator Receiver, to 10-7	To Scrubber, to 10-6	To Scrubber Off-Gas, (d) to 10-9	Fractionator Distillate Ratio to 10CFR20 (e)	Scrubber Off-Gas Ratio to 10CFR20 (f)	Stack Off-Gas Ratio to 10CFR20, to 10-4 (f)	From Solidifier	Fractionator, to 10-7	To Fractionator Receiver, to 10-9	To Scrubber, to 10-9	To Scrubber Off-Gas, (d) to 10-12	Fractionator Distillate Ratio to 10CFR20 (e)	Scrubber Off-Gas Ratio to 10CFR20 (f)	Stack Off-Gas Ratio to 10CFR20, to 10-4 (f)		
PG-1	A	0.14	0.074	<0.13	0.88	-	<16	-	<150	0.004	10	<1.6	1.6	-	-	-	-	-	
PG-2	B	0.30	1.42	40	11	-	6,400	-	<71	0.004	900	40	1,400	-	<1.1	350	-	7	
PG-3	A Mod.	0.31	0.12	1.2	1.7	-	350	-	<71	0.003	<15	3.2	100	-	<1.7	70	-	4.3	
PG-4	C	0.05	1.70	2.8	0.05	-	1,000	-	<71	-	70	9.6	3.1	-	<1.3	1,800	-	63	
PG-5	A	0.03	0.31	170	-	-	40,000	-	<4	-	3.2	25	-	-	<0.7	2,200	-	8.6	
PG-6	A	0.13	0.35	1.7	1.0	-	1,600	-	<4	0.012	1.0	<0.1	10	-	0.6	20	-	8.2	
PG-7	A	0.06	2.6	4,600	23	1.2	430,000	50	<4	0.002	4.60	NDG	NDG	-	0.9	75	-	8.5	
PG-8	A	0.11	1.4	3,000	20	13	200,000	400	220	0.012	23.0	0.4	NDG	1,100	6,900	250	17		
PG-9	A	0.15	2.3	3,600	740	170	180,000	250	4.1	0.004	41.0	0.96	NDG	1,300	150	250	10		
(RLG)																			
PG-1	A, B	<0.1	10.0	170	-	-	15,000	-	<4	<0.001	NA	1,800	NDG	-	4.1	17,000	-	8.5	
PG-2	A	0.9	1.0	13	9.0	-	10,000	-	<4	<0.001	<1.2	11	40	-	5.8	770	-	8.9	
PG-3	A	<0.1	0.39	140	9.3	-	66,000	-	<4	<0.001	7.9	9.6	NDG	-	0.5	1,100	-	8.1	
PG-4	A	<0.02	0.85	20	0.8	-	7,800	-	<4	0.003	3.1	2	4	-	2	400	-	23	
PG-5	A, B	0.11	2.1	6.7	1.3	-	1,800	-	<4	0.003	2.8	35	0.8	-	1	1,800	-	21	
PG-6	A	0.05	1.0	29	0.7	-	3,200	-	<4	0.002	15	3.3	NDG	-	4	550	-	26	
PG-7	A	0.14	1.6	10	0.001	110	2,500	5,000	<4	0.004	17	28	440	710	1	55	-	<0.06	
PG-8	A, B	0.046	1.4	28	12.0	-	5,600	400	<4	<0.001	NDG	0.4	163	27	4.8	89	2,000	2.8	
PG-9	A	0.056	0.076	6.5	NDG	3.5	1,600	100	<4	0.001	8.0	28	NDG	6.9	0.1	3,500	10	1.4	
PG-10	A	NA (g)	NA (g)	NA (g)	NA (g)	NA (g)	NA (g)	100	<4	0.0007	4.9	3.2	NDG	3.5	0.05	2,150	10	1.4	
PG-11	A	0.071	0.52	2.2	0.63	1.4	2,200	100	<4	0.0004	13	2.6	NDG	2.3	<0.23	1,500	10	<7.7	
SS-1	A	0.75	0.82	4	0.33	-	16	-	<150	0.0005	<10	630	290	-	<10	140	-	16	
SS-2	B Mod.	0.74	4.0	30	2.5	-	45	-	<71	0.0002	63	2.4	<1	-	3.6	1.5	-	15	
SS-3	A	0.73	2.4	80	25	-	37,000	-	<4	0.10 (h)	40	31	22	-	11	940	-	3	
SS-4	A	0.11	1.4	270	36	-	140,000	-	<4	0.002	9.6	3.5	68	-	<1.2	870	-	<16	
SS-5	A	0.70	6.4	600	85	-	180,000	-	<4	0.0006	4.8	0.3	17	-	<0.9	1,100	-	<21	
SS-6	A	0.50	6.5	200	36	-	22,000	-	<4	0.0007	7.9	6.2	5.7	-	<16	510	-	<16	
SS-7	A	0.59	12.0	29	51	-	10,000	-	<4	0.001	270	0.47	NDG	-	<0.3	220	-	<11	
SS-8	A	0.35	3.6	48	29	-	14,000	-	<4	<0.001	120	1.1	50	-	<0.5	180	-	<8	
SS-9	A	0.57	6.5	23	18	-	4,600	50	<4	<0.0002	NDG	NDG	NDG	9.9	2.3	-	50	51	
SS-10	A, B	0.45	5.3	47	32	1.3	41,000	1,000	<4	0.0008	3.9	0.1	NDG	22	1.5	12	2,000	34	
SS-11	A	0.75	2.1	52	19	18	16,000	500	<4	0.0001	3.9	0.80	7.7	14	3.0	220	50	78	
SS-12	A	0.019	1.4	19	31	10	11,000	200	<4	0.0001	24	NDG	NDG	32	2.0	150	50	24	
(IPM)																			
SS-13	B Mod.	0.005	0.62	23	6.7	11	8,000	400	4	0.00001	NDG	NDG	NDG	150	<0.74	3,000	50	<18	
IPM																			

NA	Not Available.
NDG	No detectable gain in radioactivity.
a.	Ruthenium represented by ^{106}Ru .
b.	Nonvolatiles represented by $^{144}\text{CePr}$.
c.	Total curies of component gained in auxiliary tank/total curies of component in feed to the solidifier.
d.	Total curies of component in off-gas/total curies of component fed to solidifier for entire run.
e.	10CFR20 Table II, Column 2.
f.	10CFR20 Table II, Column 1.
g.	No radioruthenium in feed to solidifier.
h.	High value due to failure of solidifier off-gas filters.

volatilized from the solidifier and was condensed and accumulated in the auxiliary evaporator. Figure 5.4 presents the accumulation of ruthenium in the auxiliary tanks as a function of fraction of waste fed to the solidifier during the pot runs.⁽¹¹⁾

The evaporator was operated with a bottoms acidity ranging from 3 to 8M HNO_3 and an overhead acidity of less than 1M HNO_3 to reduce the potential for ruthenium volatilization. Typical evaporator and fractionator operating parameters are presented in Figure 5.5, while additional operating data are summarized in Table 5.3.

Decontamination factors across the evaporator and fractionator are presented in Table 5.4. Cumulative ruthenium DF's* across the evaporator ranged from 350 to 4700 during the first six runs but decreased to 30 to 80 during the last series of runs. The decrease in DF's is believed to be primarily from internal contamination of the system, (buildup of ruthenium during the intervening WSEP runs)** since the operating conditions were not significantly different during the two periods.

Ruthenium volatilization from the WSEP auxiliary evaporator was correlated by instantaneous DF's (DF_i 's).*** Generally, the DF_i 's for the first series of pot solidification runs varied inversely with the nitric acid concentration in the evaporator bottoms and resulting distillate as shown in Figure 5.6. This indicated that ruthenium volatility increased with increasing acidity in the evaporator bottoms. However, during the last series of three pot runs, there was considerable scatter in data points and a consistent correlation was

-
- * Total curies in evaporator bottoms at end of run from any source/total curies gained in the fractionator.
 - ** This was true, even though the entire auxiliary system (except for some off-gas piping) was thoroughly flushed with combinations of water, nitric acid, and caustic prior to each WSEP run.
 - *** Instantaneous concentration of component in evaporator bottoms/instantaneous concentration of component in evaporator distillate.

FIGURE 5.4. Accumulation of Ruthenium in WSEP Auxiliaries During the Pot Solidification Runs

FIGURE 5.5. Typical Auxiliary Evaporator Operating Parameters During the Pot Calcination Runs

TABLE 5.3. WSEP Auxiliary Operating Parameters During the Pot Calcination Runs

Solidification Run	PC-1	PC-2	PC-3	PC-4	PC-5	PC-6	PC-7	PC-8	PC-9 (RLG)
Operating Mode	A	B	A-modified	C	C	A	A	A	A
<u>Evaporator (TK-113) Average Operating Conditions</u>									
Bottoms, M HNO ₃	4.5	(PW-2)	5.5	(PW-1)	(PW-1)	7.0	5.0	5.5	4.8
Distillate, M HNO ₃	0.5	0.5	0.5	0.6	0.6	0.6	0.3	0.4	0.3
Boiloff Rate, liter/hr	105	179	112	108	138	61	122	42	39
Stripwater Addition Rate, liter/hr	90	152	85	94	102	48	105	30	23
Volume, liters - Start	143	445	1307	63	54	186	504	232	432
- End	232	51	156	504	215	251	287	198	280
Sugar Addition (@ 0.085M), g moles	5.53	5.18	7.48	---	---	---	---	---	---
Waste Addition, liters	0	968	543	1307	758	0	0	0	0
<u>Fractionator (TK-115) Average Operating Conditions</u>									
Bottoms, M HNO ₃	10	7.5	9.5	9.6	10.4	7.8	9.6	8.3	7.5
Distillate, M HNO ₃	0.04	0.03	0.02	0.03	0.07	0.02	0.04	0.06	0.04
Boiloff Rate, liters/hr	100	197	112	105	121	56	116	36	33
Reflux Ratio	0.1-0.2	0.1-0.2	0.1-0.2	0.1-0.2	0.1-0.2	0.1-0.2	0.24	0.71	0.78
Volume, liters - Start	412	296	454	390	419	393	342	434	416
- End	944	940	551	1000	644	618	589	625	621
4M NaOH Addition to Tower, liters @ 5 l/hr	---	---	---	361	---	---	---	---	---
<u>Fractionator Distillate Receiver (TK-116)</u>									
Bottoms, M HNO ₃ - Start	0	0	0	0	0	0	0.02	0.02	0.29
- End	0.04	0.03	0.02	0.03	0.07	0.02	0.03	0.02	0.16
Volume, liters - Start	166	180	197	212	194	212	284	540	384
- End	907	1007	931	900	786	424	692	768	751
<u>Off-Gas Scrubber (TK-118)</u>									
Recirculation Rate, liters/hr	40	40	40	20	20	20	20	20	20
Bottoms, M NaOH - Start	--	--	--	--	--	--	3.6	2.4	2.0
- End	1.5	0.9	1.2	0.9	1.5	1.1	3.1	2.0	1.8
Volume, liters - Start	409	405	489	510	482	491	425	475	450
- End	218	267	398	380	453	401	417	438	388

TABLE 5.4. Decontamination Factors Across the WSEP Auxiliary Evaporator and Fractionator for the Pot Solidification Runs

PC 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)	Final Ci/liter		Average Acidity, M HNO ₃		Cumulative Ruthenium DF(c)	Cumulative Cerium DF(c)	Instantaneous Cerium DF(d)
				Bottoms	Distillate				¹⁰⁶ Ru	¹⁴⁴ CePr	Bottoms	Distillate			
1	A	Nitric Acid plus Pot Condensate ^(e)	Sugar and Stripwater (Fractionator Distillate)	4.5	0.5	1.2×10^3	2×10^2	2×10^4	3.4	---	10	0.04	5.7×10^3	NA	NA
2	B	Batch Waste plus Pot Condensate	Sugar and Stripwater	---	0.5	5.6×10^2	7.7×10^3	3×10^5	32	590	7.5	0.03	4.2×10^2	NA	NA
3	A ^(f)	Nitric Acid plus Aged Pot Condensate	Sugar and Stripwater	5.5	0.5	2.6×10^3	$>5.9 \times 10^4$ (g)	6×10^4	2.7	54	9.5	0.02	6.9×10^3	NA	NA
4	C	Continuous Feed of Waste plus Pot Condensate	Stripwater	---	0.6	7×10^2	1.5×10^5	7×10^5	11	234	9.6	0.03	6.0×10^3	NA	NA
5	C	Continuous Feed of Waste plus Pot Condensate	Stripwater	---	0.6	4.7×10^3	3.4×10^5	2×10^6	29	2209	10.4	0.07	2×10^2	NA	NA
6 ^(h)	A	Nitric Acid plus Pot Condensate	Stripwater	7.0	0.6	3.5×10^2	1.3×10^5	---	3.7	54	7.8	0.02	2.1×10^3	NA	NA
7	A	Nitric Acid plus Pot Condensate	Stripwater	5.0	0.3	2.9×10^1	3.5×10^3	$10^2 - 10^4$	1.0	8.9	9.6	0.04	7.8	NA	NA
8	A	Nitric Acid plus Pot Condensate	Stripwater	5.5	0.4	8.2×10^1	5.4×10^3	$10^2 - 10^4$	1.2	64	8.3	0.06	10	3.2×10^2	$10^2 - 10^3$
9(RLG)	A	Nitric Acid plus Pot Condensate	Stripwater	4.8	0.3	5.9×10^1	8.4×10^2	$10^2 - 10^4$	0.95	19	7.5	0.04	9.9	2.0×10^3	$10^3 - 10^4$

NA Not Available

- Total curies of component in evaporator at end of run/total curies of component gained in the fractionator.
- Instantaneous concentration of component in evaporator/instantaneous concentration of component in evaporator distillate.
- Total curies of component in fractionator at end of run/total curies of component gained in fractionator distillate receiver.
- Instantaneous concentration of component in fractionator/instantaneous concentration of component in fractionator distillate.
- Part of pot condensate (vent line reflux) was collected in separate tank.
- Modified Mode A. Aged batch of Ru in nitric acid was fed to evaporator and pot condensate from the run was collected in a separate tank so only noncondensibles from the pot were going to the evaporator.
- Value assumes gain in fractionator to be 0.1 Ci. No gain detected.
- Data through first shutdown period only, but includes a complete pot calcining and cooling cycle.

FIGURE 5.6. Volatilization of Ruthenium from WSEP Auxiliary Evaporator During the Pot Calcination Runs

not obtained. A modified solidifier condenser and condenser off-gas filtering system, described in Section 5.6, was used during the last series of runs.

Sugar addition (5 to 8 gram moles per run) to the evaporator during each of Runs PC-1, 2 and 3 did not decrease ruthenium volatilization.⁽¹²⁾ Ruthenium volatilization was typically below 1% of that present in the evaporator bottoms without reductant addition; however, larger reductant additions should decrease ruthenium volatilization.

Average radionuclide activities in gas samples taken during the last 3 runs are presented in Table 5.5. The solidifier condenser off-gas during these runs contained greater than 10^{-4} $\mu\text{Ci}/\text{cm}^3$ of ^{106}Ru . During Run PC-8, the solidifier condenser off-gas passed through a HEPA filter before it entered the evaporator. This resulted in a 5-fold lower concentration of ruthenium in the evaporator condenser off-gas during PC-8 than during PC-7. This difference showed that removal of particulate ruthenium from the solidifier off-gas decreased the ruthenium accumulation in the auxiliary system downstream of the evaporator. The ruthenium DF's across the solidifier condenser were 300 to 1000 during the last three runs while the ruthenium DF across the solidifier condenser off-gas filter for PC-8 was 200. DF's across the WSEP process condensers and process off-gas filters during the last three pot runs are summarized in Table 5.6.

Most of the ruthenium that volatilizes from the evaporator is condensed and accumulated in the fractionator. The average concentration of ^{106}Ru in the evaporator condenser off-gas ranged from about 10^{-5} to 10^{-6} $\mu\text{Ci}/\text{cm}^3$ in the last three pot runs. Ruthenium DF's across the evaporator condenser ranged from 100 to 3000. These were generally comparable to the solidifier condenser DF's.

Ruthenium equivalent to about 0.01 to 0.1% of the ruthenium fed to the solidifier accumulated in the fractionator bottoms.

TABLE 5.5. Average Concentration of Radionuclides in the Process Off-Gas During Runs PC-7 Through PC-9 (RLG) (a)

PC Run Number	Solidifier Condenser Off-Gas, $\mu\text{Ci}/\text{cm}^3$		Off-Gas from Condenser Filter, $\mu\text{Ci}/\text{cm}^3$		Evaporator Condenser Off-Gas, $\mu\text{Ci}/\text{cm}^3$		Fractionator Condenser 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	$^{144}\text{CePr}$
7	1×10^{-4}	8×10^{-5}	(b)	(b)	1×10^{-5}	3×10^{-5}	2×10^{-5}	$>10^{-8}$
8	8×10^{-4}	6×10^{-3}	4×10^{-6}	9×10^{-5}	2×10^{-6}	2×10^{-5}	7×10^{-6}	5×10^{-8}
9	4×10^{-4}	8×10^{-4}	4×10^{-4} (b)	1×10^{-3} (b)	5×10^{-6}	2×10^{-5}	2×10^{-6}	1×10^{-7}

PC Run Number	Off-Gas from High Efficiency Pre-Scrubber Filter, $\mu\text{Ci}/\text{cm}^3$		Final Off-Gas from Scrubber $\mu\text{Ci}/\text{cm}^3$ Ratio to 10CFR20 (c)			
	^{106}Ru	$^{144}\text{CePr}$	^{106}Ru	$^{144}\text{CePr}$	^{106}Ru	$^{144}\text{CePr}$
7	3×10^{-6}	3×10^{-5}	1×10^{-8}	$>10^{-8}$	50	25
8	2×10^{-5}	1×10^{-5}	8×10^{-8}	1×10^{-7}	400	250
9	6×10^{-6}	4×10^{-6}	5×10^{-8}	1×10^{-7}	250	250

a. Average values for entire run

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

c. 10CFR20 Table II, Column 1.

TABLE 5.6. Decontamination Factors Across Process Condensers and Process Filters During Runs PC-7 Through PC-9

PC Run	Average DF (a)					
	^{106}Ru			$^{144}\text{CePr}$		
	PC-7	PC-8	PC-9(RLG)	PC-7	PC-8	PC-9(RLG)
Solidifier Condenser (E-111) (a)	3×10^2	7×10^2	1×10^3	4×10^3	5×10^3	1×10^4
Solidifier Condenser Off-Gas Filter (b)	(c)	2×10^2	(c)	(c)	9×10^2	(c)
Evaporator Condenser (E-113) (a)	1×10^2	3×10^3	2×10^3	(d)	4×10^2	6×10^2
Fractionator Condenser (E-115) (a)	(d)	1×10^3	2×10^3	NA	6×10^3	(d)
Pre-Scrubber High Efficiency Filter (F-112) (b)	NA	2×10^2	(d)	NA	3×10^2	(d)

NA Not Available

a. DF = Total curies of component to the condenser/total curies of component in noncondensable gas stream leaving the condenser.

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

c. The solidifier condenser off-gas filter was bypassed.

d. Data Unreliable

The cumulative ruthenium DF's across the fractionator were generally greater than 10^3 during the first series of runs and averaged about 10 during the last three runs. This difference in DF's is again attributed to a contaminated system. The ruthenium DF_i's across the fractionator ranged from less than 100 to greater than 1000 but were typically greater than 100.

Average stripwater rates to and boiloff rates from the evaporator were listed in Table 5.3. The amount of fractionator distillate recycled to the evaporator is inversely proportional to the evaporator overhead acidity. The distillate receiver accumulated an average of 0.0004% of the ruthenium fed to the solidifier during the first six pot runs while 0.04% accumulated during the last three runs. The accumulated fractionator distillate (final aqueous process effluent) contained a concentration of radionuclides which was above 10CFR20 Table II Column 2 values by factors as high as 400,000.

The off-gas leaving the fractionator condenser contained from 10^{-5} to 10^{-6} $\mu\text{Ci}/\text{cm}^3$ of ruthenium during the last three runs. Ruthenium DF's across the fractionator condenser were greater than 1000 for the last two pot runs.

Approximately 2 to 5 scfm to noncondensable gases (Table 4.1) leaving the fractionator condenser were filtered through a high efficiency filter before entering the off-gas scrubber. The filter DF for radioruthenium was 210 during Run PC-8. Approximately 99% of the remaining radioruthenium in the process off-gas was removed in the off-gas scrubber. Typically about 0.001% of the radioruthenium fed to the solidifier accumulated in the scrubber bottoms.

The final process off-gas leaving the off-gas scrubber contained concentrations of radioruthenium that were factors of 50 to 400 above 10CFR20 Table II Column 1 values. However, the final process off-gases were filtered twice more and mixed

with about 120,000 scfm of building ventilation air before entering the stack. This additional filtration and dilution reduced the ruthenium concentration to below detection limits. The radioruthenium in the stack gases was typically 1/1000 of the $2 \times 10^{-10} \mu\text{Ci}/\text{cm}^3$ 10CFR20 Table II Column 1 value. This value includes all radioruthenium emitted to the off-gas from the facility. Other sources of radionuclides in the facility are ventilation air from eight other high-level radioactivity cells and process vent effluents from other radioactive cell activities.

Spray Solidification

During the spray solidification runs with the phosphate melt system, from 11 to 75% of the radioruthenium fed to the solidifier was volatilized from the solidifier and accumulated in the auxiliary evaporator. Ruthenium volatilization from the solidifier during runs with the in-pot melting borosilicate system was only 1.9 and 0.05%. Figure 5.7 presents the average and range of accumulation of ruthenium in the WSEP auxiliaries as a function of fraction of waste fed to the spray solidifier.

The auxiliary evaporator was operated with a bottoms acidity of 2 to 6M HNO_3 and an overhead acidity of less than 1M HNO_3 to keep the ruthenium volatilization typically below 1% of that present in the evaporator bottoms. Typical evaporator and fractionator operating conditions are shown in Figure 5.8 and in Table 5.7.

Decontamination factors across the evaporator and fractionator are presented in Table 5.8. Cumulative ruthenium DF's across the evaporator varied from 14 to 3700. The lowest DF_c occurred in Run SS-12(IPM). During Run SS-12 the low DF was due to the method used to calculate DF's. Although the ruthenium accumulation in the evaporator decreased by a factor of about 50 (decreased volatilization from the

FIGURE 5.7. Accumulation of Ruthenium in WSEP Auxiliaries During the Spray Solidification Runs

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FIGURE 5.8. Typical Auxiliary Evaporator Operating Parameters During Spray Solidification Runs

TABLE 5.7. WSEP Auxiliary Operating Parameters During the WSEP Spray Solidification Runs

Solidification Run	SS-1	SS-2	SS-3	SS-4	SS-5	SS-6	SS-7	SS-8	SS-9	SS-9	SS-9	SS-9	SS-10	SS-10	(c) SS-11	(c) SS-12	(c) SS-13
Operating Mode	A	B-mod ^(a)	A	A	A	A	A	A	Acid Run 1 ^(b)	PW-4m Run ^(b)	Acid Run 2 ^(b)	Evap. Run ^(b)	A	B	A	A	(a) 8-mod
Evaporator (TK-113) Average Operating Conditions																	
Bottoms, M HNO ₃	3	1.5	4.6	5.0	5.0	4.9	4.3	4.0	4.0	4.3	4.7	3.4	4.0	3.0	5.1	4.1	3.2
Distillate, M HNO ₃	0.1	0.03	0.4	0.4	0.5	0.5	0.3	0.2	0.2	0.2	0.2	0.04	0.2	0.4	0.4	0.2	0.4
Boiloff Rate, liter/hr	50	65	60	70	55	65	70	77	91	93	110	160	70	130	58	46	78
Stripwater Addition Rate, liter/hr	36	50	50	55	50	30	60	61	96	79	99	170	60	90	45	40	60
Volume, liters - Start	195	350	365	340	290	475	415	342	212	321	301	271	312	450	756	414	390
- End	155	235	220	270	450	310	418	330	321	301	271	284	450	320	87	329	350
Sugar Addition, moles/hr (d)	0.13	0.17	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Process Condenser Water Spray - liters/hr	---	---	---	---	---	---	---	60	---	53	---	---	---	---	---	40	---
Fractionator (TK-115) Average Operating Conditions																	
Bottoms, M HNO ₃	7.7	10	6.0	9.3	8.7	8.7	7.9	8.7	6.7	8.1	7.6	8.5	7.4	7.0	9.1	8.2	8.0
Distillate, M HNO ₃	0.06	0.06	0.01	0.09	0.05	0.10	0.07	0.04	<0.07	0.06	0.04	<0.01	0.04	0.03	0.1	0.01	0.01
Boiloff Rate, liters/hr	45	60	50	65	55	60	66	77	89	88	95	170	65	140	56	42	64
Reflux Ratio	0.63	0.48	0.57	0.44	0.52	0.48	0.20	0.20	0.28	0.28	0.26	0.15	0.40	0.20	0.28	0.3	0.40
Volume, liters - Start	400	275	310	525	520	605	389	540	530	555	779	975	428	635	570	410	371
- End	705	710	865	560	640	805	652	547	555	779	975	876	635	678	637	556	646
Fractionator Distillate Receiver (TK-116)																	
Bottoms, M HNO ₃ - Start	0	0	0	0	0	0	0.03	0.03	5.6	5.2	0.17	5.7	0.25	0.29	<0.01	<0.001	<0.001
- End	0.09	0.06	0.05	0.05	0.05	0.09	0.05	0.04	5.2	0.2	5.7	6.1	0.29	0.05	0.06	0.01	0.006
Volume, liters - Start	185	210	190	220	220	215	246	290	463	276	441	261	226	178	206	414	771
- End	365	895	740	490	430	995	344	822	276	857	216	257	178	555	719	473	841
Off-Gas Scrubber (TK-118)																	
Recirculation Rate, liters/hr	40	40	30	30	30	30	<30	30	30	30	30	30	30	30	30	30	30
Bottoms, M NaOH - Start	2.1	0.7	1.5	1.3	2.0	2.2	2.0	0.06	2.0	1.4	0.01	<0.001	1.9	1.4	0.4	1.58	2.06
- End	1.1	0	1.4	0	0.04	0.07	0.04	0.09	1.4	0.01	<0.001	<0.001	1.4	0.8	<0.01	0.42	1.39
Volume, liters - Start	475	480	370	415	470	565	397	732	476	533	733	771	484	448	423	441	459
- End	360	270	310	335	475	395	466	806	533	714	771	810	448	477	419	559	450
Solidifier Condensate (TK-117)																	
Bottoms, M HNO ₃ - Start	---	0.05	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
- End	---	2.1	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Volume, liters - Start	---	85	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
- End	---	1185	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---

- a. B-mod=modified Mode B operation. The solidifier condensate was routed to a separate receiver (TK-117). During Run SS-13, 2M nitric acid was added to the evaporator at approximately the same rate as condensate was produced to simulate the condensate.
- b. Special runs were made to help analyze radionuclide distribution in the auxiliaries
- c. A modified solidifier condenser and condenser off-gas filter were used during these runs. (See Section 5.6.4.)
- d. Recycled from the fractionator distillate tank and used as stripwater.

TABLE 5.8. Decontamination Factors Across the WSEP Auxiliary Evaporator and Fractionator for the Spray Solidification Runs

SS Run	Mode	Solution in Evaporator	Additive	Evaporator				Instantaneous Ce-rium DF ^(b)	Final Ci/liter		Fractionator				
				Average Acidity, M HNO ₃		Cumulative Ruthenium DF ^(a)	Cumulative Cerium DF ^(a)				Average Acidity, M HNO ₃		Cumulative Ruthenium DF ^(c)	Cumulative Cerium DF ^(c)	Instantaneous Ce-rium DF ^(d)
				Bottoms	Distillate				Bottoms	Distillate					
1 ^(e)	A	Nitric acid, solidifier condensate and sugar solution	0.13 moles/hr sugar and stripwater	3.0	0.1	8.4 x 10 ²	NA	NA	15	0.2	7.7	0.06	2 x 10 ³	NA	NA
2	B-Mod. (f)	Raw waste plus sugar solution	0.17 moles/hr sugar and stripwater	1.5	0.03	6.3 x 10 ²	NA	NA	54	540	10	0.06	1.3 x 10 ³	NA	NA
3	A	Nitric acid plus solidifier condensate	Stripwater	4.6	0.4	3.2 x 10 ²	2.5 x 10 ⁴	10 ³ - 10 ⁴	37	68	6.0	0.05	2 x 10 ²	1.1 x 10 ²	NA
4	A	Nitric acid plus solidifier condensate	Stripwater	5.0	0.4	7.6 x 10 ¹	1.7 x 10 ³	10 ⁴	5	7.0	9.3	0.09	4.7 x 10 ¹	3.7 x 10 ²	NA
5	A	Nitric acid plus solidifier condensate	Stripwater	5.0	0.5	1.1 x 10 ²	1.5 x 10 ³	10 ³	23	3.2	8.7	0.05	1.2 x 10 ²	3.2 x 10 ²	NA
6	A	Nitric acid, solidifier condensate and sugar solution	0.77 moles/hr sugar last 38% of run and stripwater	4.9	0.5	7.3 x 10 ¹	1.6 x 10 ³	10 ⁴	35	8.4	8.7	0.10	3.1 x 10 ²	<5 x 10 ²	NA
7	A	Nitric acid plus solidifier condensate	Stripwater	4.3	0.3	5.2 x 10 ¹	9.8 x 10 ²	10 ³ - 10 ⁴	29	190	7.9	0.07	4.3 x 10 ³	5.8 x 10 ⁴	NA
8	A	Nitric acid plus solidifier condensate	Stripwater	4.0	0.02	1.1 x 10 ²	2.4 x 10 ⁴	10 ³ - 10 ⁶	18	2400	8.7	0.04	7.3 x 10 ²	2.3 x 10 ³	NA
9	A	Nitric acid plus solidifier condensate	Stripwater	4.3	0.2	8.7 x 10 ¹	1.5 x 10 ³	10 ³ - 10 ⁴	19	4.9	8.1	0.06	>6.5 x 10 ²	NA	NA
10	A	Nitric acid plus solidifier condensate	Stripwater	4.0	0.2	1.2 x 10 ²	1.7 x 10 ⁴	10 ⁴	---	---	7.4	0.04	NA	NA	NA
10	B	Nitric acid, solidifier condensate plus HL waste	Stripwater	3.0	0.2 to 0.6	3.7 x 10 ³	3.3 x 10 ⁵	10 ⁴ - 10 ⁶	17	2100	7.0	0.03	1.2x10 ^{3(e)}	NA	NA
11	A	Nitric acid plus solidifier condensate	Stripwater	5.7	0.4	3.5 x 10 ²	7.3 x 10 ³	10 ² - 10 ³	61	2.3	9.1	0.1	6.3 x 10 ²	1.3 x 10 ³	10 ² - 10 ⁴
12	A	Nitric acid plus solidifier condensate	Stripwater	4.1	0.2	1.4 x 10 ¹	74	10 ² - 10 ³	0.7	1.5	8.2	0.01	7.5 x 10 ²	7.1 x 10 ³	10 ² - 10 ⁴
13	B-mod (f)	Nitric acid plus HL waste	Stripwater	3.2	0.4	3.6 x 10 ³	2.2 x 10 ⁴	10 ⁴ - 10 ⁶	59	830	8.0	0.01	3.7 x 10 ²	8.6 x 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 evaporator distillate.

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 fractionator distillate.

e. Total run including both Mode A and B.

f. A modified Mode B operation - solidifier condensate was accumulated in a separate receiver.

NA Not Available.

solidifier), the ruthenium accumulation in the fractionator only decreased by a factor of about 6 compared to previous spray runs. The modified solidifier condenser and condenser off-gas filtering system was used during Runs SS-11, SS-12(IPM), and SS-13(IPM).

Sugar was added to the evaporator at 0.13 and 0.17 moles/hr during Runs SS-1 and SS-2 respectively in an attempt to reduce ruthenium volatilization. Also during Run SS-6, 0.77 moles/hr of sugar was added during the last 38% of the run. The sugar addition apparently did not decrease ruthenium losses from the auxiliary evaporator, since the accumulation rate of ruthenium in the fractionator remained constant with or without sugar addition.⁽¹³⁾

Steam was added to the solidifier condenser during Run SS-6 at about 15 kg/hr to provide a greater condensate flow for scrubbing ruthenium vapor from the solidifier off-gas. It was apparently ineffective, since ruthenium carryover to the fractionator bottoms was about the same as in the other runs (0.65% of the solidifier feed ruthenium).

Ruthenium carryover to the fractionator was nearly independent of the evaporator acidity as shown by the plot of ruthenium DF's versus distillate acidity in Figure 5.9. However, a correlation did exist between the DF's and evaporator distillate acidity during acid stripping operations carried out prior to Runs SS-8 and SS-10, as shown in Figure 5.10.

The presence of nitrogen oxides from the spray solidifier increased the evaporator overhead acidity stepwise by approximately $0.2M\ H^+$ when the solidifier feed was started. This increase also occurred with the pot and phosphate glass solidifiers but to a lesser degree. Thus the nitric acid concentration in the evaporator distillate may have been slightly higher than the concentration in equilibrium with the evaporator bottoms. The nonequilibrium acidity may partially account for the scatter in ruthenium DF's shown in Figure 5.9.

FIGURE 5.9. Ruthenium Volatilization from WSEP Auxiliary Evaporator During the Spray Solidification Runs

FIGURE 5.10. Comparative Ruthenium Volatilization from WSEP Auxiliary Evaporator During Feed Acid Stripping and During Operation of Spray Solidifier

Finally, the accumulation of ruthenium in the fractionator did not follow ruthenium increases in the evaporator. These observations suggest that gas phase carryover of ruthenium from the solidifier condenser off-gas to the fractionator was as important as, if not more important than, volatilization from the evaporator. Gas phase flow of ruthenium apparently occurred but has less effect on DF's during the phosphate glass and pot calcination runs, possibly because of the smaller noncondensable gas flow and lower ruthenium volatilization from the solidifier.

The use of the modified solidifier condenser and condenser off-gas filtering system in Runs SS-11, 12, and 13 apparently reduced the carryover of ruthenium in the noncondensable gas stream. The solidifier condenser off-gas contained about $6 \times 10^{-2} \mu\text{Ci}/\text{cm}^3$ of ^{106}Ru during Run SS-10 using the original condenser and about $6 \times 10^{-3} \mu\text{Ci}/\text{cm}^3$ of ^{106}Ru during Run SS-11 where the modified solidifier condenser was used. Lower levels of radioactivity were also found in the fractionator bottoms; however, as shown in Figure 5.11, the accumulation in the fractionator during Run SS-11 where the solidifier filter was used was not linear with time as was the case in previous spray solidification runs. There was a factor of about 2 to 6 decrease in ruthenium accumulation compared with Runs SS-7 through SS-10.⁽¹⁴⁾ This decrease indicates that gas phase flow of ruthenium previously experienced in the spray solidification runs contributed significantly to the ruthenium accumulation in the fractionator. The decrease in ruthenium accumulation during Runs SS-12(IPM) and SS-13(IPM) is also attributed to the reduction in ruthenium volatilization from the solidifier.

Recycling the evaporator stripwater at 60 liters/hr through a spray nozzle into the solidifier condenser during the first 37 hours of Run SS-8 did not apparently reduce

FIGURE 5.11.

Comparative Accumulation of Ruthenium in Fractionator in Selected WSEP Spray Solidification Runs.

ruthenium accumulation in the fractionator. During Run SS-12(IPM), using the new modified solidifier condenser, stripwater 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(IPM) was 10-fold lower than in SS-13(IPM) and 200-fold lower than in Run SS-11. Much of the improvement over Run SS-11 was attributed to the decrease in ruthenium volatilization from the solidifier using the in-pot melting technique.

The average concentrations of radionuclides in the process off-gas are summarized in Table 5.9 while DF's across the WSEP process condensers and process off-gas filters are summarized in Table 5.10. The ruthenium DF's across the solidifier condenser were greater than 1000 based on data from Runs SS-11, SS-12(IPM), and SS-13(IPM). The ruthenium DF's across the solidifier condenser off-gas filter varied from a high of 2000 during Run SS-11 to a low of 15 during Run SS-12(IPM). Ruthenium DF's across the evaporator condenser averaged about 10,000.

Ruthenium equivalent to 0.03 to 1.2% of the ruthenium fed to the solidifier accumulated in the fractionator. The cumulative ruthenium DF across the fractionator varied from a low of 47 to 4.8×10^3 . The instantaneous ruthenium DF's across the fractionator were typically greater than 100.

Typically, 90% of the fractionator distillate was recycled back to the evaporator as stripwater while the remaining 10% was accumulated in the fractionator distillate receiver. Average evaporator stripwater and boiloff rates are listed in Table 5.7. The distillate receiver accumulated ruthenium equivalent to about 0.001 to 0.0001% of the ruthenium fed to the solidifier. The fractionator distillate (final aqueous process effluent) contained a concentration of radionuclides which was above 10CFR20 Table II Column 2 values by a factor as high as 100,000.

TABLE 5.9. Average Concentration of Radionuclides in the Process Off-Gas During Runs SS-9 Through SS-13

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	6×10^{-2}	1×10^{-3}	(a)	(a)	NA	NA	NA	NA
11	6×10^{-3}	4×10^{-5}	3×10^{-6}	3×10^{-6}	3×10^{-7}	9×10^{-7}	5×10^{-6}	3×10^{-7}
12(IPM)	3×10^{-5}	7×10^{-5}	2×10^{-6}	4×10^{-5}	9×10^{-7}	5×10^{-5}	5×10^{-7}	7×10^{-7}
13(IPM)	3×10^{-4}	5×10^{-4}	3×10^{-6}	4×10^{-4}	8×10^{-6}	7×10^{-4}	2×10^{-7}	4×10^{-8}

SS Run Number	Off-Gas from High Efficiency Prescrubber Filter, $\mu\text{Ci}/\text{cm}^3$		Final Off-Gas from Scrubber			
			$\mu\text{Ci}/\text{cm}^3$		Ratio to 10CFR20 ^(b)	
	^{106}Ru	$^{144}\text{CePr}$	^{106}Ru	$^{144}\text{CePr}$	^{106}Ru	$^{144}\text{CePr}$
9	NA	NA	1×10^{-8}	2×10^{-9}	5×10^1	5
10	NA	NA	2×10^{-7}	9×10^{-7}	1×10^3	2×10^3
11	4×10^{-8}	1×10^{-8}	1×10^{-7}	2×10^{-8}	5×10^2	5×10^1
12(IPM)	-	2×10^{-9}	4×10^{-8}	2×10^{-8}	2×10^2	5×10^1
13(IPM)	2×10^{-8}	2×10^{-8}	8×10^{-8}	2×10^{-8}	4×10^2	5×10^1

NA Not Available

a. Filter not installed

b. 10CFR20 Table II Column 1

TABLE 5.10. Decontamination Factors Across the Process Condensers and Process Off-Gas Filters During Spray Solidification Runs SS-11 through SS-13(IPM)

SS Run	Average DF ^(a)					
	¹⁰⁶ Ru			¹⁴⁴ CePr		
	11	12(IPM)	13(IPM)	11	12(IPM)	13(IPM)
Solidifier Condenser (E-111)	1×10^3	6×10^3	5×10^3	6×10^2	3×10^3	2×10^4
Solidifier Condenser Off-Gas Filter ^(b)	2×10^3	20	95 ^(c)	10	2	1 ^(c)
Evaporator Condenser (E-113)	6×10^4	1×10^4	1×10^3	8×10^2	(d)	(d)
Fractionator Condenser (E-115)	60	6×10^2	1×10^2	50	NA	5×10^3
High Efficiency ^(b) Filter (F-112)	1×10^2	1×10^2	(d)	(d)	4×10^2	(d)

NA Not Available.

- DF = Total curies of component to condenser/total curies of component in noncondensable off-gas leaving condenser.
- DF = Average concentration of component in off-gas to filter/average concentration of component in off-gas leaving filter.
- Filter failed.
- Data are unreliable.

The off-gas leaving the fractionator condenser contained less than 10^{-5} $\mu\text{Ci}/\text{cm}^3$ of ^{106}Ru , which was also typical of the evaporator condenser. Ruthenium DF's across the fractionator condenser varied from about 60 to 600.

Approximately 10 to 20 scfm of noncondensable gases leaving the fractionator condenser were filtered through a high efficiency filter before entering the off-gas scrubber. The ruthenium DF across the process filter prior to the scrubber was about 100. Most of the remaining radioruthenium in the process off-gas was removed in the off-gas scrubber where ruthenium equivalent to an average of 0.004% of the radioruthenium fed to the solidifier accumulated in the scrubber bottoms.

The final process off-gas leaving the off-gas scrubber contained concentrations of radioruthenium that were factors of 50 to 1000 above 10CFR20 Table II Column 1 values. However, after final filtering and mixing with the 120,000 scfm of building ventilation air, the ruthenium in the stack gases was no greater than 1/1200 of the 2×10^{-10} $\mu\text{Ci}/\text{cm}^3$ 10CFR20 Table II Column 1 value.

Phosphate Glass Solidification

During the phosphate glass solidification runs, from 0.2 to 3.0% of the radioruthenium fed to the solidifier was volatilized from the denitrator and accumulated in the auxiliary evaporator. Figure 5.12 presents the accumulation of radioruthenium in the WSEP auxiliaries as a function of the fraction of feed to the phosphate glass solidifier.

The auxiliary evaporator was operated with a bottoms acidity of 4 to 7M HNO_3 . Stripwater (fractionator distillate) was recycled back to the evaporator to strip nitric acid while maintaining the average evaporator overheads from 0.2 to 0.6M HNO_3 . Typical auxiliary evaporator operating conditions

FIGURE 5.12. Accumulation of Ruthenium in WSEP Auxiliaries During the Phosphate Glass Solidification Runs

are shown in the Figure 5.13. Other operating data for the evaporator, as well as other auxiliaries, are presented in Table 5.11.

Data on DF's across the evaporator and fractionator are presented in Table 5.12 to show the effects of evaporator bottoms and overhead acid concentration on ruthenium DF's. Cumulative ruthenium DF's across the evaporator varied from a low of 11 to a high of 580 and averaged about 50. In general, these values were typical of other WSEP runs. The lowest DF_c occurred in Run PG-3 where sugar was added to the evaporator in an attempt to improve ruthenium retention,⁽¹⁵⁾ thereby showing no improved ruthenium retention in the evaporator by the sugar addition as tested.

Most of the ruthenium that escaped from the evaporator to the overhead condensate was condensed and accumulated in the fractionator where additional decontamination occurred. About 10^{-5} $\mu\text{Ci}/\text{cm}^3$ of ^{106}Ru were present in the evaporator condenser off-gas to the fractionator tower, indicating an average DF across the evaporator condenser of 330. The ruthenium DF_c across the fractionator varied from 15 in the Mode A portion of Run PG-8 to 8000 in Run PG-10 where no radioruthenium was fed to the solidifier. The ruthenium DF_i 's across the fractionator were typically greater than $10^{2.1}$.

Evaporator DF_i 's again correlated poorly with distillate acidity, as shown in Figure 5.14. The generally low DF_i 's for ruthenium are again attributed to contamination and gas phase carryover of ruthenium from the solidifier.

Average concentrations of radionuclides in the process off-gas for the last five runs are summarized in Table 5.13 while DF's across the WSEP process condensers and process off-gas filter are summarized in Table 5.14. The DF's across the solidifier condenser for radioruthenium were generally about 40 (about 2.5% of the ruthenium in the solidifier off-gas remained in the condenser off-gas).

FIGURE 5.13. Typical WSEP Auxiliary Evaporator Operating Parameters During the Phosphate Glass Solidification Runs

TABLE 5.11. WSEP Auxiliary Operating Parameters During the Phosphate Glass Solidification Runs

Solidification Run	PG-1		PG-2	PG-3	PG-4	PG-5		PG-6	PG-7	PG-8		PG-9	PG-10	PG-11
	Part 1	Part 2				Part 1	Part 2			Part 1	Part 2			
Operating Mode	A	B	A	A	A	A	B	A	A	A	B	A	A	A
<u>Evaporator (TK-113) Average Operating Conditions</u>														
Bottoms, M HNO ₃	6	6	4	4	5	3	7	5	5.4	5.0	4.8	5.3	5.0	4.5
Distillate, M HNO ₃	0.6	0.6	0.4	0.5	0.4	<0.2	0.7	0.3	0.3	0.4	0.4	0.2	0.2	0.2
Boiloff Rate, liter/hr	70	160	53	70	50	20	88	68	65	77	110	82	93	167
Stripwater Addition Rate, liter/hr	60	125	41	65	40	12	61	56	50	71	80	62	56	155
Volume, liters - Start	662	244	340	361	166	213	132	320	511	223	492	499	320	494
- End	244	428	177	217	340	132	326	290	310	492	500	408	370	391
Sugar Addition, liters/hr (0.13M)	--	--	--	3	--	--	--	--	--	--	--	--	--	--
waste Addition, liters	--	1140	--	--	--	--	--	--	--	--	677	--	--	--
<u>Fractionator (TK-115) Average Operating Conditions</u>														
Bottoms, M HNO ₃	11	14	10	12	10	9	11	8	7.9	9.2	7.9	8.1	9.0	9.3
Distillate, M HNO ₃	0.02	0.09	0.02	0.04	0.02	0.02	0.02	0.02	0.01	0.03	0.03	0.01	0.01	0.03
Boiloff Rate, liters/hr	70	150	47	70	45	20	83	69	60	75	108	77	88	161
Reflux Ratio	0.1	0.1	0.1-0.2	0.25	0.1-0.2	0.1-0.2	0.1-0.2	0.2	0.44	0.36	0.25	0.35	0.32	0.17
Volume, liters - Start	438	460	440	386	343	424	493	420	324	369	576	412	540	411
- End	460	826	779	421	696	493	893	500	706	579	714	470	676	618
<u>Fractionator Distillate Receiver (TK-116)</u>														
Bottoms, M HNO ₃ - Start	0	0	0	0	0	0	0	0	0.01	0.01	0.01	0.01	0.01	0.02
- End	0.02	0.09	0.02	0.04	0.02	0.02	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.03
Volume, liters - Start	210	365	212	226	214	256	636	195	220	286	482	263	689	211
- End	1247	1276	590	644	764	670	2038	800	851	482	833	695	921	688
<u>Off-Gas Scrubber (TK-118)</u>														
Recirculation Rate, liters/hr	20	20	20	20	20	20	20	20	30	30	30	30	30	20
Bottoms, M NaOH - Start	0.82	0.45	1.0	1.1	0.9	0.5	0.3	1.0	1.6	2.0	2.0	2.0	2.0	2.0
- End	0.82	0.45	1.0	1.1	0.9	0.5	.03	1.0	1.6	2.0	2.0	2.1	2.2	2.0
Volume, liters - Start	495	338	361	473	544	503	453	533	521	463	474	453	393	415
- End	338	280	276	444	226	453	325	483	464	474	479	407	344	438

TABLE 5.12. Decontamination Factors Across WSEP Auxiliary Evaporator and Fractionator for the Phosphate Glass Solidification Runs

PG Run	Mode	Evaporator									Fractionator			
		Solution in Evaporator	Additive	Average Acidity, M HNO ₃		Cumulative Radioruthenium DF(a)	Cumulative Radiocerium DF(a)	Instantaneous Radiocerium DF(b)	Final Ci/liter		Average Acidity, M HNO ₃		Cumulative Radioruthenium DF(c)	Cumulative Radiocerium DF(c)
				Bottoms	Distillate				¹⁰⁶ Ru	¹⁴⁴ CePr	Bottoms	Distillate		
1	A	Nitric acid plus denitrator condensate	Strip-water	6	0.6	3.6 x 10 ¹	NA	10 ⁴	2.0	9.5	11	0.02	2.1 x 10 ²	NA
1	B	Batch waste plus denitrator condensate	Strip-water	6	0.6	4.2 x 10 ²	3.3 x 10 ⁶	NA	160	1800	14	0.09	7.2 x 10 ²	NA
2	A	Nitric acid plus denitrator condensate	Strip-water	4	0.4	3.7 x 10 ¹	1 x 10 ⁵	10 ⁵	4.3	270	10	0.02	8.0 x 10 ²	1.1 x 10 ¹
3	A	Nitric acid plus denitrator condensate	Strip-water	4	0.5	1.1 x 10 ¹	2.7 x 10 ³	10 ⁴	0.7	16	12	0.04	5.5 x 10 ¹	8.5 x 10 ¹
4	A	Nitric acid plus denitrator condensate	Strip-water	5	0.4	3.2 x 10 ¹	3.1 x 10 ⁵	10 ⁶	2.5	310	10	0.02	4.3 x 10 ²	3.3 x 10 ³
5	A	Nitric acid plus denitrator condensate	Strip-water	3	<0.2	9.7 x 10 ¹	9.4 x 10 ⁴	10 ⁶	3.2	60	9	0.02	1 x 10 ³	NA
5	B	Batch waste plus denitrator condensate 0.13M sugar solution	Strip-water	7	0.7	3.9 x 10 ¹	2.1 x 10 ⁵	10 ⁶	14	5400	11	0.02	6 x 10 ³	3.3 x 10 ³
6	A	Nitric acid plus denitrator condensate	Strip-water	5	0.3	1.7 x 10 ¹	8.3 x 10 ³	10 ⁴	0.5	150	8	0.02	3.5 x 10 ²	4.8 x 10 ²
7	A	Nitric acid plus denitrator condensate	Strip-water	5	0.3	4.9 x 10 ¹	2.7 x 10 ⁴	10 ⁵	3.4	400	8	0.01	1.5 x 10 ³	8.3 x 10 ³
8	A	Nitric acid plus denitrator condensate	Strip-water	5	0.4	1.5 x 10 ¹	NA	10 ² to 10 ³	0.2	3.6	9	0.03	1.5 x 10 ¹	>2.4 x 10 ³
8	B	Nitric acid, denitrator condensate and HL waste	Strip-water	5	0.4	5.8 x 10 ²	1 x 10 ⁵	10 ²	19	430	8	0.03	5.8 x 10 ²	9.5 x 10 ⁴
9	A	Nitric acid plus denitrator condensate	Strip-water	5	0.2	1.4 x 10 ²	1.9 x 10 ³	10 ² to 10 ³	0.2	4.5	8	0.01	2.0 x 10 ³	NA
10	A	Nitric acid plus denitrator condensate	Strip-water	5	0.2	2.9 x 10 ²	1.9 x 10 ³	10 ² to 10 ³	0.3	8.0	9	0.01	8.0 x 10 ³	NA
11	A	Nitric acid plus denitrator condensate	Strip-water	4	0.2	4.8 x 10 ¹	1.9 x 10 ⁴	10 ⁴ to 10 ⁵	1.6	190	9	0.03	2.7 x 10 ³	9.1 x 10 ²

NA Not available.

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

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

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

FIGURE 5.14. Ruthenium Volatilization from the WSEP Auxiliary Evaporator During the Phosphate Glass Solidification Runs

TABLE 5.13. Average Concentration of Radionuclides in the Process Off-Gas
During WSEP Phosphate Glass Solidification Runs PG-7 through PG-11

No.	Mode	Denitrator Condenser (E-111) Off-Gas, $\mu\text{Ci}/\text{cm}^3$			Evaporator Condenser (E-113) Off-Gas, $\mu\text{Ci}/\text{cm}^3$			Fractionator Condenser (E-115) Off-Gas, $\mu\text{Ci}/\text{cm}^3$		
		^{106}Ru	^{137}Cs	$^{144}\text{CePr}$	^{106}Ru	^{137}Cs	$^{144}\text{CePr}$	^{106}Ru	^{137}Cs	$^{144}\text{CePr}$
7	A	3×10^{-3}	2×10^{-5}	1×10^{-4}	3×10^{-5}	1×10^{-6}	4×10^{-4}	NA	NA	NA
8	A,B	2×10^{-2}	3×10^{-4}	1×10^{-3}	2×10^{-5}	4×10^{-7}	1×10^{-5}	2×10^{-7}	8×10^{-8}	2×10^{-6}
9	A	3×10^{-3}	3×10^{-5}	1×10^{-4}	6×10^{-6}	2×10^{-6}	2×10^{-5}	9×10^{-8}	7×10^{-8}	1×10^{-5}
10(a)	A	2×10^{-4}	9×10^{-5}	2×10^{-3}	5×10^{-6}	3×10^{-7}	2×10^{-5}	9×10^{-8}	8×10^{-8}	4×10^{-5}
11	A	2×10^{-2}	1×10^{-4}	4×10^{-4}	2×10^{-5}	8×10^{-7}	2×10^{-4}	1×10^{-6}	1×10^{-7}	2×10^{-5}

No.	Mode	Off-Gas from Filter (F-112) to Scrubber, $\mu\text{Ci}/\text{cm}^3$			Final Process Off-Gas From Scrubber					
		^{106}Ru	^{137}Cs	$^{144}\text{CePr}$	$\mu\text{Ci}/\text{cm}^3$			Ratio to 10CFR20(b)		
		^{106}Ru	^{137}Cs	$^{144}\text{CePr}$	^{106}Ru	^{137}Cs	$^{144}\text{CePr}$	^{106}Ru	^{137}Cs	$^{144}\text{CePr}$
7	A	NA	NA	NA	1×10^{-6}	1×10^{-6}	1×10^{-6}	5×10^3	2×10^3	2×10^3
8	A,B	NA	NA	NA	7×10^{-8}	4×10^{-8}	4×10^{-8}	4×10^2	80	1×10^2
9	A	2×10^{-8}	3×10^{-8}	2×10^{-7}	3×10^{-8}	1×10^{-8}	6×10^{-9}	1×10^2	20	10
10(a)	A	6×10^{-8}	4×10^{-8}	5×10^{-8}	2×10^{-8}	8×10^{-9}	6×10^{-9}	1×10^2	20	10
11	A	NA	NA	2×10^{-8}	3×10^{-8}	5×10^{-8}	4×10^{-9}	1×10^2	1×10^2	10

NA Not Available.

a. No radoruthenium in feed to solidifier.

b. 10CFR20 Table II Column 1.

TABLE 5.14. Decontamination Factors Across the Process Condensers and Off-Gas Filters During WSEP Phosphate Glass Solidification Runs PG-7 Through PG-11

PG Run	Average DF									
	^{106}Ru					$^{144}\text{CePr}$				
	7	8	9	10	11	7	8	9	10	11
Denitrator Condenser (E-111)(a)	40	40	40	40	2000	60	60	1800	450	10
Auxiliary Evaporator Condenser (E-113)(a)	200	200	150	320	800	70	70	440	390	30
Fractionator Condenser (E-115)(a)	NA	NA	370	NA	200	NA	NA	380	NA	NA
High Efficiency ^(b) Filter (F-112)	NA	NA	2-9	2-7	NA	NA	NA	130-800	330-1700	4000

a. DF = Total curies of component to condenser/total curies of component in noncondensable off-gas from the condenser.

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

NA Not Available

Ruthenium accumulation in the fractionator was directly related to the ruthenium present in the evaporator, thus indicating that gas phase carryover of ruthenium from the solidifier condenser off-gas and through the evaporator without scrubbing was not as important as the volatilization of ruthenium from the evaporator. As shown in Figure 5.15, this was confirmed during the Mode B portion of Run PG-8 when the accumulation of radioruthenium in the fractionator increased on switching from Mode A to Mode B operation. The increase was caused by the increase in ruthenium concentration in the evaporator bottoms and by the increased amount of boiloff required to strip the acid from both the waste and the incoming phosphate glass condensate during Mode B.⁽¹⁶⁾ However, the final accumulation of ruthenium was still in the range of that with Mode A.

Typically 90% of the fractionator distillate was recycled back to the evaporator while the remaining 10% was accumulated in the fractionator distillate receiver. The distillate receiver accumulated ruthenium equivalent to 0.00002 to 0.002% of the ruthenium fed to the solidifier during the last five runs. The fractionator distillate (final aqueous process effluent) was above the 10CFR20 Table II Column 2 value by factors as high as 66,000.

Approximately 5 to 10 scfm of noncondensable gases leaving the fractionator condenser were filtered through the high efficiency filter before entering the off-gas scrubber. The filter DF's for radioruthenium were quite low and ranged from about 2 to 9 during Runs PG-9 and PG-10. Most of the remaining radioruthenium in the process off-gas was removed in the off-gas scrubber where from $7 \times 10^{-7}\%$ of the equivalent radioruthenium fed to the solidifier during Run PG-7 to 0.0013% during Run PG-8 accumulated in the scrubber bottoms.

The final process off-gas leaving the off-gas scrubber contained concentrations of radioruthenium that were factors

FIGURE 5.15. Comparative Accumulation of Ruthenium in the Fractionator During WSEP Phosphate Glass Runs

of 100 to 5000 above 10CFR20 Table II Column 1 value. However, after the final process off-gases were filtered and mixed with about 120,000 scfm of building ventilation air, the ruthenium in the stack gases was no greater than 1/2500 of the $2 \times 10^{-10} \mu\text{Ci}/\text{cm}^3$ 10CFR20 Table II Column 1 value.

5.2.3 Control of Other Radionuclides

Entrainment of nonvolatile constituents in liquid vapor systems is affected by many variables. These variables include boilup rates, vapor velocities, depth of submergence, geometry, and liquid-vapor physical properties. These factors were considered in the design of the WSEP auxiliaries.⁽³⁾

A mathematical model of the WSEP auxiliaries has been made, with particular emphasis on control of ruthenium volatilization and particulate entrainment. Calculated decontamination factors for the caustic scrubber acting on particles and gaseous RuO_4 vapor showed that the WSEP scrubber would adequately scrub particles greater than about 0.1 microns in diameter.⁽¹⁷⁾ Therefore, for good entrainment control, it is important to use high efficiency filters to remove radionuclide particles. Removal of the particles from the solidification off-gas streams in WSEP is discussed in the following subsections.

Pot Calcination

Solidification of high level waste by the pot calcination process in WSEP resulted in 0.3 to 1.2% entrainment of non-volatile constituents from the pot. The entrained material was accumulated in the WSEP auxiliary evaporator as shown in Figure 5.16 for the last series of pot runs.

Cumulative and instantaneous DF's for nonvolatiles ($^{144}\text{CePr}$) across the evaporator were typically about 10^3 to 10^5 , as shown in Table 5.4. The overall DF's for nonvolatiles from the original aqueous waste through the auxiliary system

FIGURE 5.16. Accumulation of Cerium in WSEP Auxiliaries During Pot Calcination Runs PC-7 through PC-9

to the recovered acid in the fractionator (Table 5.2) ranged from about 10^5 to 10^7 . Comparable DF's to the fractionator distillate were typically 10^9 . Analysis of gas phase samples, and condenser and filter DF's were included in Tables 5.5 and 5.6. Inconsistency and low DF's observed in some runs are believed to have been caused by system or sampling contamination.

The accumulation of nonvolatile $^{144}\text{CePr}$ in the off-gas scrubber solution was generally nondetectable. The off-gas leaving the scrubber contained a concentration of radiocerium that was above the 10CFR20 Table II Column 1 value by a factor of approximately 200 for the final three pot solidification runs.

Spray Solidification

With spray solidification, 0.001 to 0.1% of nonvolatile constituents were typically entrained from the solidifier and accumulated in the auxiliary evaporator. Cumulative DF's for nonvolatiles across the evaporator ranged from 74 for Run SS-12(IPM) to 3.3×10^5 during the Mode B portion of Run SS-10. Instantaneous DF_i 's for nonvolatiles across the evaporator typically ranged from about 10^3 to 10^5 . For all three WSEP solidifiers, the evaporator DF's were generally highest when evaporating high level waste as opposed to evaporating only solidifier condensate. Thus the higher DF's are probably more typical of the actual evaporator performance, while the lower DF's indicate some contamination or limitations of the sampling systems.

The overall DF's for nonvolatiles from the original aqueous waste through the auxiliary system to the recovered acid in the fractionator ranged from about 10^6 to 10^7 . Comparable DF's to the fractionator distillate were typically 10^9 . Typical accumulation of nonvolatile radioactive nuclides in the WSEP auxiliaries during spray solidification is shown

in Figure 5.17. Gas phase analysis and DF's were presented earlier in Tables 5.9 and 5.10. The $^{144}\text{CePr}$ results were comparable with those obtained in the pot and phosphate glass solidification runs.

The accumulation of nonvolatiles in the off-gas scrubber was generally nondetectable (at most the fraction of feed radiocerium was less than 10^{-9}). The off-gas leaving the scrubber contained a concentration of radiocerium that was above the 10CFR20 Table II Column 1 value by factors of about 50.

Phosphate Glass Solidification

With phosphate glass solidification, 0.07 to 0.4% of non-volatile constituents were entrained from the denitrator-evaporator* and accumulated in the auxiliary evaporator. Cumulative DF's for nonvolatiles ($^{144}\text{CePr}$) across the evaporator ranged from about 10^3 to 10^6 while typical instantaneous DF's ranged from about 10^3 to 10^5 . The overall DF's for $^{144}\text{CePr}$ from the original aqueous waste through the auxiliary system to the recovered acid in the fractionator were typically 10^6 . Comparable DF's to the fractionator distillate were typically 10^9 . Accumulation of nonvolatile radionuclides in the WSEP auxiliaries during phosphate glass solidification is shown in Figure 5.18 for several runs. Gas phase $^{144}\text{CePr}$ analysis and DF's were presented in Tables 5.13 and 5.14.

Filtering efficiencies for nonvolatiles by the pre-scrubber filter ranged from about 98 to 99.9%. This efficiency generally reduced accumulation of nonvolatiles in the off-gas scrubber to less than detectable. As with ruthenium, the nonvolatile radioactive constituents entering the atmosphere were well

* The melter condensate was collected separately and thereby did not have an effect on the effluent cleanup system. (See Section 4.3.4)

FIGURE 5.17. Accumulation of Cerium in WSEP Auxiliaries During Spray Solidification Runs

FIGURE 5.18. Accumulation of Cerium in WSEP Auxiliaries
During Phosphate Glass Solidification Runs

below the 10CFR20 Table II Column 1 value after the scrubber off-gas was filtered twice more and mixed with other building and process air. This was true for all three WSEP solidifiers.

5.2.4 Nitric Acid and Condensate Recovery

The vapors leaving the auxiliary evaporator contained nearly all of the nitrogen present as nitric acid and nitrates in the solidifier feed. Most of the nitrogen was recovered as 6 to 14M nitric acid in the fractionator. The fractionator distillate typically contained about 0.02M HNO_3 . Generally 10 to 20% of the nitrogen in the original waste was recovered in the caustic scrubber.

Pot Calcination

The modified solidifier condenser used during the last three pot solidification runs removed 39 to 56% of the nitrogen that volatilized from the solidifier. The remaining nitrogen is believed to have been present as oxides of nitrogen which were carried through the condenser in the gas phase without scrubbing contact. The nitrogen oxides were partially converted to nitric acid in the evaporator tower and condenser. Thus the nitric acid concentration in the evaporator distillate may have been slightly higher than the concentration in equilibrium with the evaporator bottoms nitric acid concentration. On the other hand some nitric acid rectification probably occurred in the evaporator tower, thus compensating somewhat for the absorption of NO_x .

During these runs the fractionator accumulated essentially all of the nitric acid leaving the evaporator plus the nitric oxides which were converted to nitric acid upstream of the fractionator. The amount of nitrogen lost to the caustic scrubber and that lost to the stack gas (estimated by material balance between feed and cumulative liquid effluent analysis) are shown in Table 5.15 for all three solidification processes.

TABLE 5.15. Nitrogen Behavior in WSEP Solidification Runs

Solidifier Run	Total System Nitrogen Recovered, %	Average Instantaneous Recovery, % In Solidifier Condensate	Feed Nitrogen Recovered, % In Scrubber	Nitrogen Lost to Stack % ^(c)
Pot				
7	98	56	8	2
8	103	50	13	0
9 (RLG)	79	39	17	21
Spray				
1	88	NA	NA	12
2	94	NA	NA	6
3	93	NA	12	7
4	94	55	27	6
5	91	60	17	9
6	91	35	20	9
7	104	64	18	0
8	95	50 (60) (a)	10	5
9	85	73	27	15
10	86	50	21	14
11	48	37 (a)	8 (b)	52
12 (IPM)	68	46 (a)	39	32
13 (IPM)	95	33	26	5
Phosphate Glass				
1	114	NA	4	0
2	116	NA	7	0
3	96	NA	14	4
4	117	>70	NA	0
5	101	>90	4	0
6	105	>90	9	0
7	94	>70	5	6
8	104	>80	7	0
9	93	>80	4	7
10	95	>80	5	5
11	92	>70	6	8

- a. During fractionator distillate spray addition to solidifier condenser.
- b. The scrubber became neutralized after 30% of the feed was fed to the solidifier.
- c. Obtained by difference.

Nitrogen data were not obtained during the first six pot calcination runs; but the off-gas scrubber, which started with 2 to 4M NaOH at the beginning of each run, absorbed up to 17% of the nitrogen fed to the solidifier during Runs PC-7, PC-8 and PC-9(RLG). The neutralization of the scrubber caustic that occurred was linear with feed input to the solidifier and in direct proportion to the accumulation of nitrogen in the scrubber.

The only nitrogen losses from the WSEP system during this last series of runs occurred during PC-9(RLG) where only 79% of the feed nitrogen was recovered. This loss is believed to be primarily due to the larger degree of nitrate decomposition in the solidifier during the rising level glass run.

Spray Solidification

From 33 to 73% of the nitrogen that volatilized from the spray solidifier was condensed from the off-gases by the solidifier condenser and accumulated in the auxiliary evaporator. Increased absorption of nitrogen oxides did not occur in the solidifier condenser during Run SS-6 when approximately 15 kg/hr of steam were sprayed into the condenser, or when 40 kg/hr of fractionator distillate was sprayed into the condenser during Run SS-12(IPM), but did occur during Run SS-8 when 60 kg/hr of fractionator distillate was sprayed into the condenser.

Nonequilibrium between the evaporator distillate and bottoms nitric acid concentrations was more pronounced than with the pot or phosphate glass solidifiers because of the increased nitrogen oxides in the off-gas from the spray solidifier. Generally, the indicated evaporator distillate acidity would increase by as much as 0.2M when feed was started to the spray solidifier.

The off-gas scrubber, which started with 0.5 to 2M NaOH at the beginning of each run, absorbed from 8 to 39% of the nitrogen fed to the solidifier at a rate proportional to the

solidifier feed rate. Five to 50% of the feed nitrogen was lost to the stack (from material balances), but generally nitrogen losses were less than 15%. The higher losses for spray solidification were attributed in part to the greater inert gas dilution from the atomizing air, inleakage, and the process vent jet motive air. Also, a greater fraction of the nitric acid in the solidifier feed was decomposed to nitrogen oxides at the high solidifier operating temperatures.

Phosphate Glass Solidification

From about 70 to 90% of the nitrogen that volatilized from the denitrator was removed from the solidifier off-gas in the denitrator condenser.

The off-gas scrubber absorbed from about 1 to 8% of the nitrogen fed to the denitrator; less than 10% was lost or unaccounted for. During the phosphate glass solidification runs, the caustic scrubber solutions were not significantly neutralized by oxides of nitrogen as occurred during the spray solidification runs. These data indicate that less nitrate was converted to nitric oxide (NO) in phosphate glass solidification than with the other two solidifiers in WSEP. This result is expected since most of the feed nitrogen is evolved during the relatively low temperature (120 to 140 °C) denitration-evaporation step.

5.3 PROCESS CONTROL OF THE WSEP AUXILIARY SYSTEM

Nitric acid and water recovery and decontamination from the solidifier off-gases are highly dependent on steady-state operation in the evaporator and acid fractionator.

During most runs in WSEP the operation of the evaporator and fractionator was controlled manually by three control loops. The volume of the evaporator bottoms was maintained constant by regulating the steam flow to the evaporator tube bundle as a function of the weight factor and/or specific gravity in the

evaporator. The evaporator acid concentration was maintained constant by measuring the acidity of the evaporator condensate and controlling the rate of recycle stripwater to the evaporator. When the overhead vapors from the evaporator were in equilibrium with the evaporator bottoms, the conductivity of the distillate was an indirect measure of the bottoms acidity. Boilup in the fractionator was controlled to maintain the weight factor and/or specific gravity of the fractionator bottoms. Early attempts to automatically control the evaporator and fractionator were unsuccessful because the primary sensing elements did not function suitably for automatic control. The liquid temperatures in these tanks had lags, and both specific gravity signals were affected by the boilup rate.

Automatic control of the auxiliaries was again initiated during the later runs (during short periods of phosphate glass solidification Run PG-11, during spray solidification Run SS-13 and during the last three pot solidification runs).⁽¹⁸⁾ Six standard three-mode controllers were used in three interacting cascade control loops as shown in Figure 5.19.

Automatic control tests and analog simulation studies of the auxiliaries prior to the last three pot runs showed that to avoid overshoot in the stream control loops it was necessary to operate the weight factor controllers with zero reset. However, it was found that the controllers could not be operated as proportional-only instruments, and some long-term cycling resulted. Therefore, to eliminate this problem, the General Electric 412 analog computer, normally used for data logging, was programmed to function as a controller with zero reset. The process computer established the set points for the steam flow controllers of the evaporator and fractionator as functions of the weight factor of the contents of the two respective vessels. In addition, the computer was programmed to provide 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 by excessive boilup.

FIGURE 5.19. Basic Instrumentation for Automatic Control of WSEP Auxiliaries

Overall, automatic control of the auxiliaries with zero reset in the controllers worked satisfactorily except during equipment failures.*

During Run PC-9 automatic control performed quite well except for three periods when the acid concentration and specific gravity in the evaporator overshot the set points because of too great a change in the set points, as shown in Figure 5.20. Weight factor control of the evaporator boilup was very satisfactory, except for the three periods, while specific gravity control worked well for the fractionator boilup during Run PC-9. However, during Run SS-13, it was again verified that the specific gravity measurement in the fractionator was affected by the boilup rate, resulting in poor control. Therefore, specific gravity control could not be used for controlling the steam flow without compensating provisions for the boilup rate effect.** When the control system was then based on the weight factor measurement, adequate stable operating conditions were maintained; but the primary function of maintaining the fractionator bottoms at 10M HNO_3 was not performed well. Manual set point inputs were also required as the level in the fractionator increased during the run.

5.4 AUXILIARY HANDLING OF PUREX WASTE

High level waste solutions contain precipitates which may interfere with liquid transfer, storage or concentration.

* During Run PC-7 blown fuses in the computer and during Run PC-8 a faulty start-up procedure compromised control of the system. Also, a partial failure of the conductivity sensor during Run PC-8 interrupted stable control.

** For this same reason, evaporator specific gravity could not be used as a control signal.

FIGURE 5.20. Typical Auxiliary Evaporator and Fractionator Operating Parameters During Automatic Control

While amorphous, noncaking precipitates could be handled at concentrations up to about 50 vol%, relatively small quantities of heavy, caking precipitates caused plugging of pipes and equipment in WSEP.

The precipitates present in a given waste solution depend largely upon the chemical additive used in the reprocessing plant and during the subsequent treatment of the waste. The PW-1, PW-2, PW-4m and LMFBR waste solutions used in the demonstration tests were believed to be representative of typical Purex plant wastes. That is, they contained the full gamut of expected precipitate types, although the comparative amounts of precipitate varied somewhat with each run because compositions were never identical.

The volume of settled solids in samples of the feed solutions used in the WSEP solidification tests ranged from 2 to 65%, and were typically 20 to 30%. The majority of the solids encountered in the solidification feeds contained molybdenum, phosphorous, and zirconium and were believed to be zirconium phosphomolybdate compounds. The solids were 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 wastes, the phosphomolybdate compound is predominant and the solids are gelatinous and noncrystalline.

The predominant solids in PW-2 waste are sodium rare-earth sulfates which form a very hard cake that is nearly impossible to resuspend and which can cause plugging of piping systems if it is not handled properly.⁽¹²⁾ When phosphoric acid is added to PW-2 waste, the precipitate becomes gelatinous; but on close inspection, small needleshaped crystals (believed to be sodium rare-earth sulfates) are also present.

When the PW-1, PW-4m and LMFBR wastes are continuously boiled, the precipitates lose their gelatinous characteristics and become a very loose, easily-suspended precipitate (even after prolonged settling). PW-4m waste was concentrated to

less than 110 liters/tonne in a laboratory test, and the 37 vol% precipitate was readily suspended after 5 days of settling. Continuous boiling of the PW-2 waste was not attempted. Some plugging of evaporator dip tubes occurred during continuous boiling of all waste types in WSEP. (See Section 5.6.4.)

Wastes containing boron and/or silicon additives are much more difficult to handle than either the initial wastes or the phosphate containing wastes. The in-pot melting flow-sheet used for Run PC-9 (RLG) required adding boron (as B_2O_3) to the PW-4m liquid waste. The solution with 0.84M B_2O_3 and 0.84M $NaNO_3$ additives required dilution to 700 liters/tonne and heating to 60 °C to avoid precipitation of the boric acid. The addition of silica to the feed tank was not considered since failure of centrifugal feed pumps of the type used in WSEP had been experienced in past tests with silica-containing feeds.

5.5 SAMPLING

5.5.1 Aqueous Samples

During the earlier WSEP runs, sampling of low level radioactive samples, primarily fractionator distillate and scrubber solution samples, within the hot cell resulted in samples which were contaminated from cell air or remote handling devices.⁽¹²⁾ However, after the eighth run in WSEP, contamination of the low level radioactive aqueous samples (i.e., those of the fractionator distillate and scrubber solutions) within the hot cell was eliminated by routing the sample lines outside of the cell to a new sampling station.

Because of the relatively high lift for the sampling jets, well-circulated and representative samples of the WSEP evaporator and acid fractionator were difficult to obtain unless the two tanks were boiling. Consequently, all samples for these two tanks, including start and end of run samples, were obtained when the tanks were boiling. Incorporation of the above improvements led to improved data from all aqueous samples.

Relatively little difficulty was experienced in plugging of the sampling system.⁽³⁾ The full-flow systems used, in conjunction with minimum apertures of 0.1 inches in diameter, provided for relatively troublefree aqueous sampling.

5.5.2 Process Off-Gas Sampling

Gas sampling techniques were initiated prior to the last series of phosphate glass runs to provide better definition of the type, form, and extent of radioactivity present in the process off-gas. Process off-gases leaving the solidifier condenser, the evaporator condenser, the fractionator condenser, the high efficiency process filter prior to the scrubber and prior to the stock were sampled for both particulate and gaseous forms of radioactivity. This sampling was accomplished by routing a side stream of the process gases through first a glass fiber filter* and then a scrubber containing 2M KOH. The off-gas sampling systems are described in References 14 and 18.

Gas samples were believed to be reasonably representative of the process off-gases. However, samples were routed through 20 to 30 feet of sampling line before reaching the sampler, and particle disposition in these lines probably influenced the data somewhat. The sample lines which used polyethylene tubing were changed every two or three runs while the stainless steel lines were thoroughly flushed before each run to minimize this problem. Tests were made using two scrubbers and two sets of filters to confirm that one set was sufficient to remove the radioactivity.

5.6 GENERAL PERFORMANCE OF AUXILIARY EQUIPMENT

Overall performance of the auxiliary equipment during the WSEP runs was satisfactory. Exceptions were some feed pump

* Gelman Type A

failures, occasional plugging of specific gravity dip tubes and other pipes, and gradual deterioration of the insulation on the electrical and instrument wiring within the hot cell. The general operating experience of the specific WSEP auxiliary equipment is presented in Table 5.16 and discussed in the following sections.

5.6.1 Pumps and Agitators

Overall performance of pumps for moving high level waste solutions was poor. The feed pumps used during Runs SS-1 and 2, PC-1 through PC-6, and PG-1 were canned-rotor inline pumps with boron carbide seals and boron carbide bearings with graphite thrust faces.⁽³⁾ Water lubricant to the bearings was recirculated through a small reservoir and a jacketed cooler but was separated from the process fluid by a mechanical seal. Several pump failures occurred by the shaft becoming bound and by electrical connector failures. A modified inline pump assembly was then used more successfully. It consisted of two conventional Deanline® centrifugal pumps. The pumps contained double mechanical, pumped-fluid-lubricated seals with graphite rotating rings.⁽³⁾ Isolation ball valves were installed on the pump assembly to prevent drainage of waste from the solidifier feed tank if the pump seals failed and to allow remote change-out in approximately four hours without the need to transfer the feed out of the feed tank. Some pump failures resulted with this new pump because of seal and bearing failures; however, the pumps have a considerably longer life expectancy than the canned-rotor pumps if they are thoroughly flushed after shutdown.

Feed pump operating experience is summarized in Table 5.17. Pump life is decreased by start and stop operation (some pump failures occurred because of the seals drying out between runs). In an extended pump operating test with nonradioactive feed,

® RTM Dean Brothers Pumps, Inc.

TABLE 5.16. WSEP Auxiliary Equipment Operating Summary

Equipment	Construction Material	Temp., °C	Avg. Press., in. Water	Chemical	Operating Time, hr	Remarks
Feed Tanks	304L SS	25 to 100	-5	Darex, Purex, TBP-25 Type Waste	4480	Satisfactory Operation. Agitators used approximately 3536 hr in each tank.
Condensate Tanks	304L SS	25	-10 to 20	H ₂ O, Dilute HNO ₃	3900	Submerged pump used 1954 hr.
Caustic Scrubber	304L SS	25 to 40	-10 to 20	Dilute NaOH	3900	Excellent Operation. Circulation pump used 1954 hr.
Evaporator	A-55 Ti	110	-10 to 20	Boiling Waste	3650	Minor titanium corrosion caused by fluoride ion during early DVT runs.
Fractionator	A-55 Ti	115	-10 to 20	8 to 14M HNO ₃	3650	Excellent Operation
Solidifier Condenser No. 1	A-55 Ti	100 to 200	-10 to 20	HNO ₃ Vapors	3500	Localized vapor entry corrosion (up to 0.06 in.) caused by volatilized sulfate during early DVT Runs 3 and 4.
Solidifier Condenser No. 2	A-55 Ti	100 to 200	-10 to 20	HNO ₃ Vapors	400	
Evaporator Condenser	A-55 Ti	100 to 110	-10 to 20	Dilute HNO ₃	3650	
Fractionator Condenser	304L SS	100 to 110	-10 to 20	H ₂ O, Dilute HNO ₃	3650	
Feed Pumps	304L SS	60		Adjusted Waste	See Table 5.17	Relatively Poor Operation. Changed from the original inline pump to conventional pump prior to Run PG-3.
Flowmeters:						
Feed, magnetic	Vitreous enamel liner. Platinum sealed electrodes. Inconel flowtubes.	30 to 80	~100	Concentrated Wastes	2840	Relatively Poor Operation. Occasional intermittent readings due to lead wire failures. Also frequent shifts in calibration and loss of sensitivity, partially attributed to low WSEP flow rates.
Condensate, electronic rotameter		30 to 80	10 to 30	Dilute Acid, Water	3510	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	30,000	Was changed after the first six pot runs after the second series of phosphate glass runs, and after the last series of spray solidification runs.

TABLE 5.17. WSEP Feed Pump Experience

Pump No.	Service ⁽¹⁾ (Runs)	Feed Type	Hours	Date	Remarks
P-3	RLG-2	PW-1	29	8-22-66	Installed on feed tank prior to RLG-2 Connector was corroded away during PC-1 Sampler leaked on connector clamp during SS-1
	PC-1	PW-2	44	2-03-67	
	SS-1	PW-1	37		
	CSCM-10	PW-2	15		Reinstalled on feed tank prior to SS-2 Pump shaft froze during PC-6
	SS-2	PW-1	57	3-30-67	
	PC-6(Part 1)	PW-2	23	8-22-67	
			205 Total		
P-6	PC-2	PW-2	42	2-06-67	Installed on feed tank Pump failed electrically (not during run)
	PC-3	PW-2	31	3-29-67	
			73 Total		
P-2	PC-4	PW-1	42	8-1-66	Installed on evaporator prior to PC-4 Removed pump from evaporator due to suction nozzle leak during PC-5 Replaced gaskets and reinstalled on evaporator
	PC-5	PW-1	28	7-12-67	
				7-14-67	
	PC-6(Part 2)	PW-2	5	8-24-67	Pump shorted out and failed during PC-6
			75 Total		
P-4	PC-6(Part 3)	PW-2	20	9-08-67	Installed on feed tank prior to Part 3 of PC-6 (Bearing water temperature ran high approximately 80°C during 20 hr of operation of PC-6) Pump failed 2/3 through run PG-1
	PG-1(Part 1)	PW-2	64	11-16-67	
			84 Total		
P-7	PG-1(Part 2)	PW-2	34	11-22-67	P-7 is the first of the Deanline R Pump to be used(C) After run PG-2, P-7 was removed
	PG-2	PW-2	64	12-12-67	
			98 Total		
P-8	PG-3	PW-2	79	1-24-68	A new design dual pump jumper was in- stalled with one Deanline Pump as primary and the second as secondary - P-8 is primary. P-9 was secondary
	PG-4	PW-2	90	2-27-68	
	PG-5	PW-1	83	4-16-68	
			252 Total		
P-9	PG-5	PW-1	33 Total	4-23-68	P-8 started leaking feed during PG-5, switched over to pump P-9. P-8 was changed out after the run
P-10	PG-6	PW-1	64 Total	5-13-68	
P-11	SS-3	PW-2	36 Total	7-7-68	New pump installed prior to SS-3
P-12	SS-4	PW-2	42	9-12-68	P-12 failed 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	
			297 Total		
P-14	SS-9	PW-4m	61	2-25-69	Pump failed prior to start of PG-7
	SS-10	PW-4m	65	3-25-69	
	PG-7	PW-2	0	6-9-69	
			126 Total		
P-15	PG-7	PW-2	53	6-9-69	Pump P-15 failed prior to PG-10
	PG-8	PW-4m	76	8-6-69	
	PG-9	PW-4m	28	9-22-69	
			157 Total		
P-16	PG-10	PW-4m	26	9-24-69	Pump P-16 failed during PG-11
	PG-11	LMFBR	1	12-1-69	
			27 Total		
P-17	PG-11	LMFBR	68	12-1-69	P-17 was not used after run SS-12. Pump did not fail but was replaced prior to SS-13
	SS-11	LMFBR	50	2-24-70	
	SS-12	PW-4m	36		
			154 Total		
P-18	SS-13	PW-4m	36	5-11-70	Pump did not fail but was replaced for PC-9 (RLG)
	PC-7	PW-1	43	8-3-70	
	PC-8	PW-4m	40	9-8-70	
			119 Total		
P-19	PC-9 (RLG)	PW-4m (borosilicate)	60	10-12-70	

a. Pumps P-1, P-5, and P-13 were not used.

b. RLG = Rising level glass, PC = Pot calciner, SS = Spray solidifier, CSCM = "Cold" spray calciner melter,
PG = Phosphate glass.

c. Deanline Centrifugal Pump, Type 3/40L, Deanalloy Class 50, 316 SST Construction. 5 gpm at 130 ft head.

a similar centrifugal pump was operated continuously for 553 hours before the seals failed.

Submerged canned-rotor inline pumps were used in the caustic scrubber for recirculating the caustic to the top of the scrubber tower and in the final condensate tank for providing a continuous source of flush water. Part of the pumped stream was routed through a hydroclone where solids were removed and returned to the tank, and the cleaned stream was routed to the bearings and motor coolant channel. Performance of these pumps was excellent, however the lead wires failed and required changing (see Section 5.6.6).

Top entering agitators with double mechanical seals were used on both feed tanks and on the solidifier condensate tank. (3) Except for lead wire failures their performance was excellent.

5.6.2 Feed Control System and Flow Measurement

Operation of the recirculating feed system controls over the range of about 2 to 60 liters/hr was only fair to good because the normal feed rates were below the lower range of the recommended operating range of the flowmeter. The flowmeter tube diameter was limited to 3/16 inches to minimize plugging with waste solids and the resultant fluid velocity was insufficient for good operation. The automatic feed controller received an input signal from the magnetic flowmeter and delivered an output signal to the feed control valve. Difficulties experienced with magnetic flowmeters 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 periodically changing the electrical wires.

A 1/2-inch Hammel Dahl valve with a No. 5 spline trim was used satisfactorily to control the feed to the solidifier. Solids in the feed readily passed through the control valve. Special flushing procedures were used prior to and after feeding to keep the feed line satisfactorily free of solids deposition.

Performance of magnetic flowmeters in the solidifier and evaporator condensate lines was only partially satisfactory because of oscillating flow which was caused by the system vacuum acting on the fluid in the pipes. An electronic rotometer in the stripwater line performed very satisfactorily during the entire WSEP program.

5.6.3 Evaporator and Fractionator

Overall performance of the WSEP evaporator and fractionator was satisfactory. Some scheme for steady-state operation such as the automatic control discussed in Section 5.3 would normally be used on a production basis to maintain a constant concentration and volume of acid in the fractionator. During the majority of the WSEP runs, manual control was used with minimum adequacy. It is believed, however, that in a production solidification scheme where operations are more continuous, and where normal liquid hold-ups are greater (especially in the evaporator), improved control will result.

The specific gravity and liquid level dip tubes of the evaporator would occasionally plug. Flushing the dip tubes with alternate solutions of nitric acid and caustic between runs eliminated most of the plugging; however, special design and operating practices for the dip tubes should be made for more reliability in continuous operation. Semi-continuous wetting of the inside of the dip tubes substantially reduced the solids plugging. In WSEP, this wetting was done by venting the tubes to the cell for about 10 out of every 15 minutes to allow the waste solution to rise into the tubes and wash out the tubes.

Chemical complexants were added to the titanium evaporator and fractionator vessels to minimize fluoride-induced corrosion. Eight liters of 2.6M $\text{Al}(\text{NO}_3)_3$ was added to each of the vessels

before every run. In WSEP, this was done when waste solutions were boiled in the evaporator, even though enough iron, zirconium, and aluminum complexants were normally present in the waste solution to inhibit corrosion. No leaks occurred during the program.

5.6.4 Solidifier Condenser

The original solidifier condenser (a vertical single-pass shell and tube heat exchanger with condensation inside the tubes) allowed considerable gas phase carryover of uncondensed ruthenium and nitrogen oxides to the evaporator. A modified solidifier condenser with improved scrubbing characteristics and a condenser off-gas filtering system, as described in Reference 14, were installed prior to Run SS-11 to improve decontamination of the solidifier off-gas. The new condenser was essentially like the original condenser except that the bottom halves of the condenser tubes were filled with crimped 5/8-inch stainless steel Pall rings.* The modified condenser was used during Runs SS-11, 12, and 13 and PC-7, 8 and 9. See Section 5.2.2 for performance results.

5.6.5 Filters

The high-efficiency (HEPA) process vent filters (F-111 or F-112) performed well (changed only three times in nearly four years, and one of these changes was to assure a clean filter for data purposes), but those in the secondary feed tank vent system (F-113) required several changeouts during early runs because of excessive pressure drops (greater than 10 inches of water). This was caused by the filters becoming wet with acid vapors because of inadequate pre-heating of the

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

moist gases upstream of the filter. The aluminum spacers between the filter material were also seriously deteriorated in all failed filters. Prior to Run SS-7 the secondary feed tank vent system was rerouted to ventilate through the WSEP waste vault vent system, and the original vessel vent filter location was no longer used. Prior to abandoning this routing, the vessel vent filter was changed six times, with 74 days the shortest duration between changes.

5.6.6 Electrical and Instrument Wiring

The original wiring was insulated primarily with linear polyethylene, a moderately radiation-resistant material. This material became brittle after as short a time as 6 months of radioactive operation and broke, thereby causing wire breakage or insulation failure. Less expensive neoprene rubber proved much more satisfactory for wire insulation in WSEP. The neoprene remained considerably more pliable, and a useful life of at least 2 or 3 years in a radiation field of 1000 to 5000 R/hr can be expected. Life expectancy is shortened if the wiring has to be handled frequently.

5.7 INTEGRATION OF A WASTE SOLIDIFICATION SYSTEM WITH A FUEL REPROCESSING PLANT

The flowsheets developed in Section 7 specify recycle of the recovered nitric acid and fractionator distillate streams to the reprocessing plant. A conceptual reprocessing flowsheet using these recycled streams has been prepared and the key features are summarized in Figure 5.21. In this flowsheet, 80% of the recovered acid is used as dissolver acid and to adjust the 1AF stream (Purex 1A Column feed stream) composition, and 20% is used in the 1AS stream (1A Column scrub). Likewise, about 75% of the recovered water is used as nitric acid stripwater for a high level waste concentrator, 4% is used to prepare the 1AF stream, 12% is used in the 1AS stream, and the remaining 9% is used to prepare the 1BX stream (1BX Column plutonium strip).

FIGURE 5.21. Integration of Waste Solidification With a Conventional Purex Fuel Reprocessing Plant

The main contaminant in the recovered acid and water is radioruthenium. In order to reuse the recovered acid and water, the effect of recycling the radioruthenium must be determined. The calculated effect of various levels of radioruthenium contamination in recycled solidification effluent streams on the first solvent extraction cycle decontamination from fission products is illustrated in Figure 5.22. This shows that the fission product decontamination factor for plutonium (DF) from the 1AF to the 1BP is seriously lowered by a ruthenium content in the recycled acid as low as 0.01% of that in high level waste (HLW) (equivalent to a ruthenium DF from the HLW to the recovered acid of 10^4). The uranium product stream can tolerate about 10-fold more ruthenium in the recycled streams before its DF suffers correspondingly. To show the effect of actual WSEP effluents, the range of fuel ruthenium in the recovered acid and water are also shown in Figure 5.22. The data show that some improvement in ruthenium DF to the recovered acid stream is desirable to avoid excessive ruthenium contamination in the plutonium product.

The effect of ruthenium in the recycled water at the ruthenium levels expected is relatively minor. This is illustrated by the family of curves in Figure 5.22 for various ratios, N/W, of total ruthenium content in the recovered nitric acid to that in the recovered water (in effect, N/W is the corresponding ratio of cumulative ruthenium DF's to the recovered acid and water streams).

FIGURE 5.22. Effect of Ruthenium in Recycled Acid and Water on First Solvent Extraction Cycle Decontamination Factors

REFERENCES FOR SECTION 5

BNWL quarterly and WSEP reports referenced below are listed in a report bibliography at the end of Section 3.

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16. WSEP Report, Volume 7, BNWL-1541.
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19. Quarterly Report, BNWL-1263, pp 22-29.

6.0 EVALUATION OF SOLIDIFIED WASTE
PRODUCTS PRODUCED BY WSEP
PROCESSES

CONTENTS

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6.0 EVALUATION OF SOLIDIFIED WASTE PRODUCTS PRODUCED BY WSEP PROCESSES

6.1 SOLIDIFIED PRODUCT CHARACTERISTICS

The United States' concept for high level radioactive waste control requires that the wastes be solidified and placed in high-integrity steel pots. Interim storage is permitted at the reprocessing site; however, the pots of radioactive waste must ultimately be shipped by rail or truck to a Federal repository for safekeeping.⁽¹⁾ Characteristics of the wastes, and the changes in characteristics of the wastes which may result from long-term thermal and radiation exposure, will affect design and operation of interim storage, shipping, and Federal repository facilities and must be well defined.

The 33 WSEP pots are being held to serve as a demonstration of interim storage of prototypical high level solidified wastes. Product properties are being measured during this period which are pertinent not only to interim storage but also to shipping and handling at the Federal repository. Air-cooled or water-cooled interim storage of solidified high level waste is possible and both are being demonstrated with the WSEP pots. Immediately after processing, most of the pots were placed in a water storage facility described on page 4.46 in Reference 2. The pots were transferred to an adjoining cell for the interim storage demonstration. In this cell, ten of the WSEP pots are being held in special pods in the Solids Storage Engineering Test Facility (SSETF)⁽³⁾ wherein the storage environment of these selected pots is carefully controlled. The SSETF pods are designed so that pot pressure and temperature profiles can be monitored continuously. Four of the SSETF pots are stored in water at about 50°C, the remaining six are stored in air at about 425°C. The remaining 23 WSEP pots are stored in open racks in the SSETF cell. Ambient cell temperature averages about 35°C. The storage history of each WSEP pot is shown in Figure 6.1.

FIGURE 6.1. WSEP Pot Interim Storage Program Schedule

Data collected during the interim storage period are being correlated with measurements made on nonradioactive solidified waste specimens prepared in the laboratory and on "grab" samples of the melt taken during processing. Core drilled samples are being taken from each WSEP pot to determine the effects of interim storage conditions and irradiation upon solidified waste characteristics. The core drilling technique is described in Reference 3. As of March, 1972, 11 WSEP pots have been sampled by core drilling. The proposed core drilling schedule for the remaining interim storage period is included in the data shown in Figure 6.1.

A tabulation of the characteristics of the solidified waste products from the WSEP processes, based on information gained from measurements on core drilled pot samples, grab samples, and laboratory-prepared nonradioactive samples, is given in Table 6.1. This table attempts an overall view of a complex subject. Detailed discussions of measurement techniques and individual properties can be found in References 4, 5 and 6. Summary discussions of the product properties, as related to each process, are presented below.

6.2 POT CALCINATION PRODUCT

6.2.1 Density and Homogeneity

The bulk density of the product obtained in the 8 WSEP pot calcination runs averaged 1.3 g/cc, ranging from a low of 1.18 to a high of 1.43. These densities are average densities obtained from the total weight of product and the estimated fill height in the pots.

The pot calcine product is present in the pot as a porous cake of friable calcine containing an irregular cylindrical or cone-shaped void at the top center. Due to the way the process is operated, the calcine is formed in a somewhat laminar fashion

TABLE 6.1 Characteristics of Solidified High Level Waste

	<u>Pot Calcine</u>	<u>Spray Melt</u>	<u>Phosphate Glass</u>	<u>Borosilicate Glass (a)</u>
Form	Scale	Monolithic	Monolithic	Monolithic
Description	Calcine Cake, Friable	Ceramic Hard, Tough	Glass Hard, Brittle	Glass Hard, Brittle
Bulk Density g/ml	1.2 to 1.4	2.7 to 3.3	2.7 to 3.0	3.0 to 3.5
Wt% Fission Product Oxides (Max.)	90	30	25	50
Thermal Conductivity, W/(m ²) (°C/m)	0.3 to 0.4	1.0 to 1.4	0.8 to 1.2	1.0 to 1.4
Leachability in Cold Water, g/cm ² -Day	10 ⁻¹ to 10 ⁻²	10 ⁻³ to 10 ⁻⁵	10 ⁻⁴ to 10 ⁻⁶ (b)	10 ⁻⁴ to 10 ⁻⁵

a. Produced by either in-pot melting or rising level glass processing.

b. Much of the phosphate glass in the WSEP radioactive pots is devitrified and exhibits increased leachability (leach rates = 10⁻² to 10⁻³ g/cm²-day).

on the pot walls and bottom as the run progresses. The central void results because the liquid feed to the pot is discontinued when the boil-off reaches a certain minimum rate.

6.2.2 Thermal Conductivity

The effective thermal conductivities (K_{eff}) measured on the WSEP pot calcine products are plotted as a function of average calcine temperature in Figure 6.2. The K_{eff} of individual pots increased with temperature. The data do not indicate any difference resulting from waste type. Generally thermal conductivity increased with increased bulk density. The three runs with the highest heat rate density (PC-6, 7 and 8) had the lowest K_{eff} and bulk density (see also Table 3.3).

6.2.3 Pressurization

No significant pressurization (greater than 1 psig) has been detected in any of the WSEP pot calcine pots. Two of the pots, from runs PC-6 and 8, are being stored in SSETF with wall

FIGURE 6.2. Variation Effective Thermal Conductivity of Pot Calcination Product with Temperature

temperatures of 425-450°C. The pressure in most of the pots tested has actually decreased below atmospheric because the pots were welded closed when there was high radioactive heat generation.

It should be noted that, although no significant pressurization of pot calcination pots has been detected, some volatiles (predominantly nitrates) are present in the product. This is indicated by the outgassing that occurs under vacuum. Leak testing with a helium leak test meter, as performed on the pots from the other WSEP processes, was generally not done on the pot calcination pots because outgassing prevented achieving the low system pressures required without prolonged vacuum pumping. A satisfactory leak rate of 5×10^{-8} atm/cc/sec was obtained on one pot calcine pot (PC-6) after a semicontinuous 3-week period of vacuum pumping.

6.2.4 Corrosion

All of the WSEP pot calcination pots were checked for pot wall corrosion as part of the afterfill measurements. No corrosion has been found within the limits of the ultrasonic technique being utilized. It is concluded that wall corrosion is less than 20 mils during processing and after up to 4 years of interim storage, the longest period for which data are available (PC-1). Inspection of the pot wall samples from the one pot that has been core drilled (PC-7) corroborated this conclusion. It is probable that a process control device such as a thermowell would be required at the centerline of each process pot in a commercial plant. Corrosion of the WSEP pot thermowells has not been measured but the corrosion was negligible in nonradioactive tests.

6.2.5 Dispersibility

The pot calcine product is given some degree of coherence by the sulfate or phosphate which is added in small quantities to the feed solution if not initially present. Compounds are formed with sodium which melt at the processing temperatures and form

a binder. The product, however, remains quite friable in comparison to the melt-formed products and presents a greater potential for spread of contamination if its containment is accidentally breached.

6.2.6 Leachability

The leachability of a calcine can be conveniently described by measuring the fraction of a given constituent which is leached. The fraction of ^{137}Cs that was leached from a WSEP pot calcine product is shown as a function of time in Figure 6.3. Comparable data for zirconia calcine from the WCF fluid bed calciner⁽⁸⁾ and for WSEP spray and phosphate glass PW-1 ceramic products are included in the Figure 6.3.

6.3 RISING-LEVEL GLASS (RLG) MODIFICATION OF THE POT CALCINATION PROCESS

Discussion is limited to the specific borosilicate formulation demonstrated in the WSEP program.

6.3.1 Density and Homogeneity

The density of the RLG product is quite high, approximately 3.5 g/cc, reflecting the high proportion of fission products in this product. The product is a glass that may contain particles of undissolved oxide suspended in the glassy matrix.

6.3.2 Thermal Conductivity

The effective thermal conductivity of the RLG product is presented as a function of average product temperature in Figure 6.4. The K_{eff} of the borosilicate waste is dependent on temperature. Over the range of 200 to 600°C the thermal conductivity fits the equation:

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

Above approximately 650°C the product is in a softened or molten state and the effective thermal conductivity of the product in

FIGURE 6.3. Comparative Leachability of Pot Calcine Product at 25 °C

FIGURE 6.4. Variation of Thermal Conductivity of RLG Product with Temperature

the pot increases rapidly. The effective thermal conductivity of the WSEP RLG product was almost a factor of two higher than the thermal conductivity measured on nonradioactive material of the same chemical composition.

6.3.3 Pressurization

The WSEP RLG pot has been stored at elevated temperature (wall temperature = 450°C) since 4-21-71 in a SSETF pod. As of this writing there has been no indication of pot pressurization.

6.3.4 Corrosion

Pot corrosion during RLG processing at 900°C is quite low. Laboratory-measured corrosion rates are shown below:

	Corrosion Rates, mils/month	
	<u>310 SS</u>	<u>304L SS</u>
900°C	2-105	13-235
950°C	200	425
1000°C	6-400	223-808

Severe pitting of the 304L surfaces was reported; pitting of the 310 surfaces was much less marked. Because of its superior corrosion resistance, 310 stainless steel was used in the WSEP RLG run.

Ultrasonic wall thickness measurements and examination of wall discs obtained during core drilling of the WSEP pot corroborated the low corrosion predicted by nonradioactive tests.

6.3.5 Dispersibility

The RLG product samples shattered into many pieces, none over 0.75 in their longest dimension, during core-drilling. For this reason standard dispersibility test data (the standard dispersibility test is described in Reference 4) have not been obtained on the RLG product.

6.3.6 Leachability

Leach rates measured on the WSEP RLG product are shown in Figure 6.5. Measurements made on laboratory-prepared nonradioactive samples are included for comparison.

FIGURE 6.5. Leachability of RLG Product at 25 °C

6.4 SPRAY CALCINER-MELTER PROCESS

6.4.1 Density and Homogeneity

The average density of spray calciner-melter phosphate-based products as a function of waste type is shown below:

	Bulk Density in WSEP Pots, g/cm ²	Density ^(a) of Lab-prepared Samples, g/cm ²	Porosity ^(a) of Lab-prepared Samples, vol%
PW-1	3.2	3.51	3.9
PW-2	2.8	2.99	0.5
PW-4m	3.0	3.46	3.9

a. Determined by mercury porosimetry.

The spray solidification process produces a solid which fills the pot uniformly and homogeneously. For the radioactive runs this was indicated by the generally consistent radial temperature differences along the length of each pot, indicating the heat generation in the solid waste was essentially uniform at the time the pots were filled. The relative distributions of ^{137}Cs and ^{144}Ce in samples from different positions in the WSEP pots are being measured as an additional means of determining product homogeneity and detecting possible fission product migration or segregation. Preliminary analyses indicate some migration of cesium from the hottest central zone toward cooler portions of the pot.⁽⁶⁾

Spray solidified product will separate into two phases when held in the molten or semi-molten state for prolonged periods. Two month tests showed detectable phase separation occurring above the following temperatures:

<u>Waste Type</u>	<u>Maximum Stable Melt Temperature, °C</u>
PW-1	Approx. 900
PW-2	Approx. 600
PW-4m, LMFBR	Approx. 800

The phase separation results in the product splitting into two layers, the upper layer usually amounting to 20-40 percent of the whole volume. The upper layer becomes somewhat richer in phosphate than was the original melt; in some cases sufficient phosphate segregation occurs to produce a glass in the upper layer. The melting point of the lower layer increases by as much as 200°C over that of the original melt.

Considerable fission product segregation between the two phases occurs. In general the mono- and di-valent cations tend to concentrate in the upper layer and the higher valence cations in the lower layer, as shown by the following data:

<u>Melt Constituent</u>	<u>Concentration Ratio, Upper Layer/Lower Layer</u>	
	<u>PW-2 Melt ^(a)</u>	<u>PW-4m Melt ^(b)</u>
Cs	--	1.8
Sr	1.3	--
Ni	1.5	--
Fe	0.9	--
Cr	0.5	--
Rare Earths	0.1	0.3
Zr	0.4	--
Ru	--	0.06

a. 8 weeks at 750°C.

b. 8 weeks at 950°C.

Although a thorough analysis has not been made, the potential for marked fission product segregation may mitigate against "molten core" storage of phosphate-based spray solidified product. Molten core storage would imply a pot centerline temperature of greater than approximately 900, 700, and 900°C, for PW-1, PW-2 and PW-4m solids, respectively.

6.4.2 Thermal Conductivity

The effective thermal conductivity of the spray calciner-melter product as determined in the WSEP pots is plotted in Figure 6.6. The thermal conductivity of laboratory prepared non-radioactive specimens of similar chemical composition is also shown. In contrast to the calcine and glass products, the thermal conductivity of the ceramic spray products is independent of temperature up to 600°C. The thermal conductivity of nonradioactive melts increased by approximately 15% when they were held 8 weeks at 600°C. The effective thermal conductivity of the WSEP products averaged slightly higher than the thermal conductivity of the non-radioactive material, even after the nonradioactive thermal conductivity had been enhanced by thermal treatment. In one pot,

FIGURE 6.6. Effective Thermal Conductivity of Spray Calciner-Melter Phosphate Ceramic Waste

SS-6, the K_{eff} was much higher. The increased K_{eff} resulted from an inadvertent 24-hour high temperature treatment (centerline temperature of 900 to 950°C) about one month after the run was completed. It is possible that the partially fused melt filled the void spaces during this high temperature period to produce a less porous solid.

6.4.3 Pressurization

No significant pressurization has been measured on any pot of sulfate-free spray solidifier product. This includes pots of both PW-1 and PW-4m waste which have been held with wall temperatures of 430°C for over 18 months as of this writing.

The spray solidifier flowsheet for processing the PW-2 waste composition produced a solidified product which contained 14 wt% SO_3 and 41 wt% P_2O_5 . The flowsheet provided for the addition of sodium and calcium, both of which form sulfates that are stable to temperatures in excess of 900°C. In the presence of phosphate, however, the stability of the sulfates is decreased. Laboratory tests indicated an appreciable rate of sulfate decomposition even below the melting point of the product ($\sim 725^\circ\text{C}$).⁽¹⁰⁾ The decomposition reaction produces SO_3 which remains gaseous down to 44.6°C and may cause pot pressurization. No pot pressurization has been observed in either of the WSEP sulfate-bearing spray solidifier pots (SS-3 and 4); however, once processing was completed, the centerline temperature was maintained below 500°C in both pots.

A more severe test was conducted in the laboratory. Non-radioactive spray solidifier PW-2 product was held for 120 days in an 11.5-in long platinum cylinder contained within a sealed evacuated vessel. A temperature gradient ranging from 800°C at the bottom to 350°C at the top was applied to the cylinder of product. Although the bottom 3 inches of product was molten, no SO_3 was released at the top, as indicated by the lack of any

increase in pressure. Severe melt segregation, of the type described in Section 6.4.1, occurred in that portion of the melt held above 700°C. It was concluded that the maximum permissible core temperature of spray solidified PW-2 wastes during storage is probably more limited by phase segregation than by pressurization.

6.4.4 Corrosion

Mild steel and Type 304L and 310 stainless steel were demonstrated to have satisfactory corrosion resistance for spray calciner-melter pots. Afterfill ultrasonic wall thickness measurements indicated negligible pot wall corrosion (less than 20 mils) occurred during filling of the WSEP spray solidifier pots, and no pot wall corrosion has been detected during interim storage.

6.4.5 Dispersibility

The spray calciner-melter product is a rugged, rock-like substance which is difficult to fracture. When fractured by the force of a sharp blow, as in the standard dispersibility test, the product tends to break into a few large chunks with only a comparatively small amount of dispersible fines. Dispersibility tests performed on core drilled samples of WSEP spray product indicate that this desirable characteristic is not adversely affected by radiation (See Table 6.2).

6.4.6 Leachability

Leach rates measured on spray calciner-melter products are shown in Figures 6.7, 6.8, and 6.9. The leach rate data are presented as smoothed curves even though the leach rate data generally exhibit considerable scatter (see Reference 6 for more details).

The leachabilities of the radioactive spray solidified products from the processing of PW-1, PW-2 and PW-4m wastes

FIGURE 6.7. Leachability of Spray Calciner-Melter PW-1 Product at 25 °C

FIGURE 6.8. Leachability of Spray Calciner-Melter PW-2 Product at 25 °C

FIGURE 6.9. Leachability of Spray Calciner-Melter PW-4m Product at 25 °C

TABLE 6.2. Spray Solidifier Product Dispersibility, (a)
Comparison of Radioactive and Nonradioactive
Products

Waste Type	Specimen	Crushed Sample Particle Size Distribution, wt%		
		>0.1 inch	0.02-0.1 inch	<0.02 inch
PW-1	SS-6 Core drill	70.0	20.0	10.0
PW-1	Nonradioactive, 100°C storage	86.4	7.9	5.7
PW-1	Nonradioactive, 600°C storage	95.7	2.6	1.7
PW-4m	SS-10 Core drill	98.4	0.8	0.8
PW-4m	Nonradioactive, 100°C storage	78.7	11.0	10.3
PW-4m	Nonradioactive, 600°C storage	70.4	20.1	9.4

- a. The dispersibility test procedure is described in Reference 4.

were all somewhat higher than the leachabilities of corresponding nonradioactive spray solidified products. Studies of the effect of storage temperature were made in which nonradioactive spray solidified products were stored at 100°C and 600°C. The leachability of PW-1 and PW-2 products was unaffected, however the leachability of the PW-4m product held at 600°C was significantly higher than that of the product held at 100°C.⁽⁵⁾

6.5 IN-POT MELTING

6.5.1 Density and Homogeneity

The in-pot melting product is a black glass containing relatively small amounts of occluded and dispersed material and a small quantity of slag at the top surface. The density of laboratory-prepared samples was 3.10 g/cm². Bulk density measured in the two WSEP in-pot melting runs was 3.0. The in-pot melting borosilicate product is difficult to devitrify and has good

high temperature stability. Samples held in the laboratory at 950°C for 8 weeks showed no tendency to separate into layers as did many of the phosphate-based melts.

6.5.2 Thermal Conductivity

The effective thermal conductivities measured on the products from the two WSEP in-pot melting runs were very similar and are plotted in Figure 6.10. The K_{eff} , unlike that for the spray calciner-melter ceramic product, is temperature dependent. The K_{eff} also increases sharply when the product melting temperature is exceeded.

6.5.3 Pressurization

No significant pressurization of the SS-13(IPM) pot being stored in the SSETF has been observed.

6.5.4 Corrosion

Corrosion rates, as shown below, were measured to determine the maximum allowable operating temperature.

In-pot Melting Corrosion of Stainless Steel

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

Corrosion rates at typical storage temperatures (<425°C wall temperature) have not been measured but should be negligible. The corrosion rates above are for surfaces immersed in melt; approximately fifty percent 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.

FIGURE 6.10. Effective Thermal Conductivity of In-pot Melting Process Borosilicate Glass

After-fill ultrasonic wall thickness measurements made on the WSEP in-pot melting pots indicated corrosion during processing was negligible (<20 mils). Tests of SS-13(IPM) after 6 months, including examination of wall samples and ultrasonic wall thickness measurements, indicated no corrosion was

occurring during storage. A SS-12(IPM) ultrasonic wall thickness scan produced similar findings.

6.5.5 Dispersibility

The in-pot melting product samples shattered into many pieces, none over 0.75-in. in their longest dimension, during core-drilling. For this reason standard dispersibility test data have not been obtained on the in-pot melting product.

6.5.6 Leachability

Leach rates which have been measured on in-pot melting products are shown in Figure 6.11.

6.6 PHOSPHATE GLASS

6.6.1 Density and Homogeneity

The average density of phosphate glass products as a function of waste type, and storage temperature, is shown below:

	Bulk Density in WSEP Pots	Density ^(a) of Lab-prepared Samples, g/cm ²		Porosity ^(a) of Lab-prepared Samples, vol%	
		<u>Glassy</u>	<u>Devitrified^(b)</u>	<u>Glassy</u>	<u>Devitrified^(b)</u>
PW-1	2.8	2.74	2.81	0.26	2.7
PW-2	2.8	2.91	2.93	0.76	1.5
PW-4m	2.9	2.98	3.00	0.11	1.6

a. Determined by mercury porosimetry.

b. Devitrified by holding at 600°C for 8 weeks.

The phosphate glass product is a black glass which devitrifies at temperatures above about 550°C. The molecular realignment which occurs upon devitrification results in an increase in absolute density and an increase in porosity of the bulk sample. As will be seen below, devitrification also changes other properties of the phosphate glass product. Of the first four WSEP

FIGURE 6.11. Leachability of In-pot Melting PW-4m Product at 25 °C

phosphate glass pots core-drilled (PG-6, 7, 8 and 10), all but PG-8 were found to be almost completely devitrified. The central core of PG-8 was devitrified, but about 1.5 inches of the product next to the wall remained glassy. Most of the devitrification of the WSEP phosphate glass process products occurred during the initial cool-down period after processing (detectable devitrification occurs in less than two hours at 650°C).

The phosphate glass process produces a solid which fills the pot uniformly and homogeneously. Tests for fission product segregation or migration in the WSEP pots by 1) examination of radial and longitudinal temperature profiles for anomalies and 2) analysis of core-drilled samples, have been negative except for one pot, PG-6, where a small amount of cesium migration to cooler areas of the pot is indicated.⁽⁶⁾

Phosphate glass product exhibits a tendency to separate into two phases when held in the molten state for prolonged periods. Two month tests showed phase separation occurring as follows:

<u>Waste Type</u>	<u>Maximum Stable Melt Temperature</u>
PW-1	Undefined, less than 850°C
PW-2	Above 950°C
PW-4m, LMFBR	Approx. 900°C

Phase separation was most marked in the phosphate glass PW-1 formulation, however this melt formulation also exhibited poor processing characteristics. In future processing of PW-1 waste by the phosphate glass process the melt formulation would probably be changed to more closely resemble that used for PW-4m processing.

Phase separation in the phosphate glass melts is apparently a precipitation phenomenon. Finely divided crystals (coarse crystals in the case of PW-1 melts) collect in the lower portions of the melt. The rather slight degree of fission product segregation which occurs is shown by analysis of a phosphate glass PW-4m melt after 8 weeks storage at 950°C:

	<u>Concentration Ratio, Upper Phase/Precipitate Phase</u>
Cs	1.1
Sr	1.5
Ru	0.4
Rare Earths	0.7

Phosphate glass products exhibit viscous flow above about 550°C and may be considered molten at about 650°C. Indications are that "molten core" storage of all phosphate glass products, except PW-1, at temperatures up to 900°C should be satisfactory.

6.6.2 Thermal Conductivity

The effective thermal conductivity of the phosphate glass product is presented as a function of average product temperature in Figure 6.12. The range of thermal conductivities measured on 21 nonradioactive PW-1, PW-2 and PW-4m phosphate glass samples is included in the figure for comparison. Ten of the nonradioactive samples were devitrified by holding at 600°C for 2 months. The devitrified phosphate glass samples exhibited a small, but significant, increase in thermal conductivity compared to the nondevitrified samples. The effective thermal conductivity of the phosphate glass products in the WSEP pots (which was measured immediately after processing) corresponds closely to that of the devitrified nonradioactive samples. While this may serve as an indication that the phosphate glass products in the WSEP pots devitrified rapidly, it should be noted that the effective thermal conductivity measured in the spray solidified WSEP pots also tended to be higher than the thermal conductivity measured on nonradioactive spray solidifier products (see Section 6.4.2).

6.6.3 Pressurization

Two WSEP phosphate glass pots (PG 7 and 8) are being stored in the SSETF with wall temperatures of 425-460°C. No significant pressurization (>1 psig) has been observed in PG-8. Pressure is not being monitored in PG-7 due to a small leak in the thermowell (see below). Sulfate-containing PW-2 waste was processed in Run PG-7. During processing, sulfate is driven out of the melt quantitatively, thus the potential for pressurization due to release of SO_3 in the pots does not exist in the phosphate glass process.

6.6.4 Corrosion

The corrosion rates of three WSEP pot materials in phosphate glass PW-1 product are given below:

FIGURE 6.12. Effective Thermal Conductivity of Phosphate Glass

	Corrosion Rate, mils/year		
	<u>304L SS</u>	<u>310 SS</u>	<u>Mild Steel</u>
600°C	0.4	0.4	10
700°C	2	2	68

Corrosion of the pot walls at the proposed maximum 425°C storage temperature should not be of concern.

The corrosion rates of stainless steel in phosphate glass melts increase gradually with temperature until about 950°C, above which temperature the corrosion rates increase very rapidly.⁽¹¹⁾ A different corrosion mechanism, perhaps involving depassivation, apparently becomes predominant above 950°C. After-fill ultrasonic wall thickness measurements indicate that corrosion of the WSEP pots was negligible (<20 mils) during processing. Subsequent ultrasonic wall thickness measurements and examination of wall samples from the four phosphate glass pots which have been core-drilled (PG-6, 7, 8 and 10) indicate no further wall corrosion has occurred during storage for periods up to 2.6 years. However, the thermowells in two pots (PG-6 and 7) were found to have developed leaks, as shown by tests in which it was possible to pressurize the vapor space within the pot by applying air pressure to the thermowells.⁽¹²⁾ The thermowell failure is very localized in PG-6. Several sample sections of thermowell were retrieved from the pot by core-drilling and none of the sample sections were corroded significantly. The failure in the PG-7 pot has not yet been investigated thoroughly. Thermowell failure is not considered a serious problem since the wells can be easily capped and welded.

6.6.5 Dispersibility

Devitrification of the phosphate glass products has a marked effect upon their dispersibility characteristics. The devitrified products tend to be tougher and, when broken, to break into larger pieces than the nondevitrified glasses which tend to

shatter into large number of relatively smaller pieces. The dispersibility characteristics of radioactive phosphate glass samples core-drilled from WSEP pots closely resemble those of nonradioactive phosphate glass samples which have been devitrified by thermal treatments (see Table 6.3).

TABLE 6.3. Phosphate Glass Product Dispersibility, ^(a)
Comparison of Radioactive and Nonradioactive
Products

Waste Type	Specimen	Crushed Sample Particle Size Distribution, wt%		
		>0.1 inch	0.02-0.1 inch	<0.02 inch
PW-1	PG-6 Core Drill	95.7	1.1	3.2
	PG-6 Core Drill	91.0	6.7	2.3
	Nonradioactive, 100°C storage	34.6	41.1	24.6
	Nonradioactive, 600°C storage ^(b)	91.7	5.1	3.2
PW-2	PG-7 Core Drill	90.9	5.4	3.6
	PG-7 Core Drill	95.2	2.3	1.2
	PG-7 Core Drill	93.2	4.2	1.4
	Nonradioactive, 100°C storage	46.8	36.2	16.9
	Nonradioactive, 600°C storage ^(b)	97.4	1.5	1.1
PW-4m	PG-10 Core Drill	92.5	5.3	2.1
	Nonradioactive, 100°C storage	58.8	28.6	12.6
	Nonradioactive, 600°C storage ^(b)	94.6	3.7	1.7

a. The dispersibility test procedure is described in Reference 4.

b. Devitrified.

6.6.6 Leachability

Devitrification of the phosphate glass products results in a very significant increase in leachability as is shown by the leach rate measurements plotted in Figures 6.13, 6.14 and 6.15. In general, the leach rates of core-drilled samples from the WSEP phosphate glass pots are of the same magnitude as the leach rates of the thermally devitrified nonradioactive samples and about a factor of 1,000 higher than the nondevitrified products.

FIGURE 6.13. Leachability of Phosphate Glass PW-1 Product at 25 °C

FIGURE 6.14. Leachability of Phosphate Glass PW-2 Product at 25 °C

FIGURE 6.15. Leachability of Phosphate Glass PW-4m Product at 25 °C

REFERENCES FOR SECTION 6

BNWL quarterly and WSEP Reports referenced below are listed in a report bibliography at the end of Section 3.

1. U. S. Federal Register, Title 10, Part 50, "Licensing of Production and Utilization Facilities," 35 222 (1970) 17530.
2. WSEP Report, Volume 2, BNWL-968.
3. WSEP Report, Volume 3, BNWL-832.
4. R. J. Thompson, J. E. Mendel, C. Hampton, Jr. and H. H. Irby, Sr., Waste Solidification Demonstration Program; Experimental Techniques for Characterization of High-Level Radioactive Solidified Waste, BNWL-1425. Pacific Northwest Laboratory, June 1970.
5. R. J. Thompson, J. E. Mendel and J. H. Kleinpeter. Waste Solidification Demonstration Program: Characterization of Nonradioactive Samples of Solidified High-Level Waste, BNWL-1393. Pacific Northwest Laboratory, June 1970.
6. J. E. Mendel and J. L. McElroy, Waste Solidification Program, Volume 10, Evaluation of Solidified Waste Products, BNWL-1666. Pacific Northwest Laboratory, July 1972.
7. H. W. Godbee and J. T. Roberts. Laboratory Development of a Pot Calcination Process for Converting Liquid Wastes to Solids, USAEC Report ORNL-2986. Oak Ridge National Laboratory, Oak Ridge, Tennessee, August 30, 1961.
8. M. W. Wilding and D. W. Rhodes. Characteristics of Radioactive Zirconia Calcine After Heating to High Temperature, IN-1486. Idaho Nuclear Corporation, June 1971.
9. Chemical Technology Division Annual Progress Report, Period Ending March 31, 1971. ORNL-4682, page 103. Oak Ridge National Laboratory.
10. Quarterly Report, BNWL-1003, pp. 43-45.
11. E. J. Tuthill, G. Strickland and G. G. Weth. "Platinum for High Temperature Crucibles Used in Processing Radioactive Wastes," I&EC Process Design and Development (8), 36-43 (1969).
12. J. L. McElroy, J. E. Mendel and F. P. Roberts. Summary Report on Analysis of the Semi-Fluid Condition in the PG-6 Phosphate Glass Solids Container, BNWL-B-112. Pacific Northwest Laboratory, May 1971 (Unpublished).

7.0 PROJECTED FLOWSHEETS FOR
A 5 TONNE PER DAY
COMMERCIAL PLANT

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7.0 PROJECTED FLOWSHEETS FOR A 5 TONNE PER DAY COMMERCIAL PLANT

Material balance flowsheets are presented in this section to serve as a basis for comparison of the four major solidification processes studied in WSEP. The four processes--pot calcination, phosphate glass, spray calcination with melter, and spray calcination with in-pot melting--are illustrated by two flowsheets each in Figures 7.1 through 7.8. The first flowsheet in each set describes the solidification of a high-salt waste (PW-2) containing considerable amounts of iron, sodium, and sulfate process additives; the second flowsheet treats a low-salt waste (PW-4m) containing essentially only fission product nitrate salts.

Only one of several possible processing modes is described. In this mode, the incoming dilute waste is concentrated to a minimum volume suitable for short-term interim storage, the chemicals required for the individual solidification process are added, and the waste is solidified. Off-gases from the solidification process, if essentially sulfate-free, are condensed, scrubbed and returned to the plant waste evaporator along with sufficient "strip" water to maintain the acidity in the evaporator overheads at or below 0.5M. The condensed evaporator overheads are sent to the plant acid fractionator for recovery of a slightly contaminated, concentrated nitric acid stream suitable for recycle to the separations process head end (fuel dissolution, etc.) and a much less contaminated, dilute acid stream suitable for use in chemical makeups for the head end and first cycle solvent extraction operations. A major portion of the fractionator overhead stream is used in a quench scrubber to scrub ruthenium and entrained solids from the solidifier off-gas before being routed to the waste evaporator for use as strip water.

FIGURE 7.2 Pot Calcination Flowsheet for PW-4m Type Waste

FIGURE 7.3 Spray-Melter Solidification Flowsheet for PW-2 Type Waste

FIGURE 7.4. Spray-Melter Solidification Flowsheet for PW-4m Type Waste

FIGURE 7.6. Spray-Inpot Melting Solidification Flowsheet for PW-4m Type Waste

FIGURE 7.7. Phosphate Glass Solidification Flowsheet for PW-2 Type Feed

FIGURE 7.8. Phosphate Glass Solidification Flowsheet for PW-4m Type Waste

The compositions, weights, and volumes given in the flowsheets for each stream are expressed as gram moles, kilograms, and liters, respectively, per metric ton (tonne) of reactor fuel processed. A discussion of the major factors involved in specifying the flowsheets is presented below.

7.1 WASTE TYPES AND COMPOSITIONS

Most of the WSEP development work was done with four waste types, designated PW-1, PW-2, PW-4m and LMFBR. The PW-1 and PW-2 waste compositions were representative of those generated from relatively low burn-up fuels reprocessed by conventional solvent extraction techniques, such as those used by the Nuclear Fuel Services (NFS) reprocessing plant at West Valley, New York.⁽¹⁾ The PW-1 waste composition was comparable to the NFS first solvent extraction cycle waste and contained considerable ferric nitrate to correspond with that derived from dissolution of chopped-fuel dissolver basket liners. The PW-2 waste simulated a combined first and second cycle waste containing ferric, sulfate, and sodium ions from plutonium valence adjustment steps. It differed from the actual NFS combined waste in that it did not include the iron from the dissolvable fuel basket liners. The PW-4m waste composition was that derived from high burnup fuels reprocessed by "clean" techniques of the future (e.g., no metal salt additives). The LMFBR waste was representative of that from clean processing of LMFBR fuel, but it was diluted before use to approximately the same composition as the PW-4m waste.

The PW-2 and PW-4m waste compositions were chosen for the preceding flowsheets because they illustrate the unique problems encountered in solidifying sulfate-containing and high fission-product content wastes. Detailed chemical compositions of the two wastes used in the flowsheet calculations are presented in Table 7.1; the activities of major radioisotopes as a function of time are presented in Table 7.2; and heat generation rates versus cooling time are tabulated in Table 7.3 and plotted in

TABLE 7.1. Chemical Composition of High-Level Liquid Wastes

Basis: 1 metric ton (tonne) of thermal reactor fuel at 6 months out of the reactor after removal of 99.9% of the uranium and 99.7% of the plutonium by TBP extraction.

A. Major Constituents from the Irradiated Fuel

Constituent	Average Atomic wt.	Assumed Ionic Form		Assumed Oxide Formula	PW-2 Waste 20,400 MWd/tonne at 15 MW/tonne		PW-4m Waste 46,600 MWd/tonne at 31 MW/tonne	
		Aqueous Solution	Phosphate Melt		G-Moles of		G-Moles of	
					Element	Kg Oxide	Element	Kg Oxide
Se	81.1	SeO ₂ ⁻²	SeO ₂ ⁻²	SeO ₂	0.38	0.04	0.84	0.10
Rb	86.4	Rb ⁺²	Rb ⁺²	Rb ₂ O	2.46	0.23	5.34	0.50
Sr	89.2	Sr ⁺²	Sr ⁺²	SrO	6.24	0.66	13.47	1.42
Y	89.0	Y ⁺³	Y ⁺³	Y ₂ O ₃	3.24	0.37	7.01	0.79
Zr	93.3	Zr ⁺⁴	ZrO ₂ ⁺²	ZrO ₂	24.31	3.05	54.05	6.77
Nb	95.0	--	NbO ₃ ⁻	Nb ₂ O ₅	0.05	0.01	0.09	0.01
Mo	97.6	MoO ₄ ⁻²	MoO ₂ ⁺²	MoO ₃	21.82	3.18	49.60	7.22
Tc	99.0	TcO ₄ ⁻	TcO ₄ ⁻	Tc ₂ O ₇	5.33	0.83	11.64	1.84
Ru	102.2	Ru ⁺⁴	RuO ₂ ⁺²	RuO ₂	12.95	1.74	30.86	4.14
Rh	103.0	Rh ⁺³	Rh ⁺³	Rh ₂ O ₃	2.77	0.35	5.04	0.64
Pd	105.8	Pd ⁺²	Pd ⁺²	PdO	5.63	0.69	16.00	1.95
Ag	109.0	Ag ⁺	Ag ⁺	Ag ₂ O	0.29	0.03	0.62	0.07
Cd	111.6	Cd ⁺²	Cd ⁺²	CdO	0.28	0.04	0.93	0.12
Sn	122.6	SnO ₃ ⁻²	SnO ₂ ⁺²	SnO ₂	0.25	0.04	0.64	0.10
Sb	123.3	SbO ₃ ⁻	Sb ₂ O ₄ ⁻²	Sb ₂ O ₃	0.08	0.01	0.18	0.03
Te	129.5	TeOOH ⁺	TeO ₂ ⁻²	TeO ₂	2.30	0.37	5.44	0.88
Cs	135.0	Cs ⁺	Cs ⁺	Cs ₂ O	14.13	2.02	29.64	4.24
Ba	137.7	Ba ⁺²	Ba ⁺²	BaO	6.45	0.99	15.51	2.38
La-Dy	143.3	RE ⁺³	RE ⁺³	RE ₂ O ₃	42.65	7.13	96.71	16.18
U	238.0	UO ₂ ⁺²	UO ₂ ⁺²	UO ₃	4.07	1.16	3.92	1.06
Np	237.0	NpO ₂ ⁺	NpO ₂ ⁺	NpO ₂	1.42	0.38	4.37	1.18
Pu	239.5	Pu ⁺⁴	PuO ₂ ⁺²	PuO ₂	0.07	0.02	0.11	0.03
Am	241.7	Am ⁺³	Am ⁺³	Am ₂ O ₃	0.41	0.11	1.59	0.42
Cm	243.4	Cm ⁺³	Cm ⁺³	Cm ₂ O ₃	0.03	0.01	0.41	0.11
Total Fuel Constituents					157.6	23.45	354.0	52.21

B. Major Separations Process Additives

Constituent	Atomic wt.	Assumed Ionic Form		Assumed Oxide Formula	PW-2 Waste 20,400 MWd/tonne at 15 MW/tonne		PW-4m Waste 46,600 MWd/tonne at 31 MW/tonne	
		Aqueous Solution	Phosphate Melt		G-Moles of		G-Moles of	
					Element	Kg Oxide	Element	Kg Oxide
H	1.008	H ⁺	H ⁺	--	13,010	0	10,400	0
Na	23.00	Na ⁺³	Na ⁺	Na ₂ O	390	12.09	~ 0	0
Fe	55.85	Fe ⁻	Fe ⁺³	Fe ₂ O ₃	185	14.77	~ 0	0
NO ₃ ⁻	--	NO ₃ ⁻	--	--	13,500	0	11,090	0
SO ₄ ⁻²	--	SO ₄ ⁻²	SO ₄ ⁻²	SO ₃	370	29.62	0	0
PO ₄ ⁻³	--	PO ₄ ⁻³	PO ₃ ⁻	P ₂ O ₅	9.0	0.64	4.4	0.31
Total Process Additives					27,464	57.12	21,495	0.31

C. Combined Waste Characteristics (Before Addition of Solidification Process Chemicals)**Non-Volatile Constituents in Solution:**

	PW-2 Waste		PW-4m Waste	
	Fuel Only	Total	Fuel Only	Total
Total Cation Equivalents, EM ⁺	362.66	1,307.66	817.59	817.59
Total Anion Equiv. (SO ₄ ⁻ Not Included) EM ⁻	50.24	77.24	113.81	127.01
Net M ⁺ Equivalents = EM ⁺ - EM ⁻	312.42	1,230.42	703.78	690.58

Non-Volatile Constituents in Melts:

	PW-2 Waste		PW-4m Waste	
	Fuel Only	Total	Fuel Only	Total
Total Cation Equivalents, EM ⁺	331.17	1,276.17	746.77	746.77
Total Anion Equiv. (SO ₄ ⁻ Not Included) EM ⁻	10.91	19.90	24.67	29.07
Net M ⁺ Equivalents = EM ⁺ - EM ⁻	320.26	1,256.27	722.10	717.70
Total Alkali Metal Equivalents	16.6	406.6	35.0	35.0
Total Alkali + Alkaline Earth Equivalents	42.0	432.0	92.9	92.9
Total Multivalent Cation Equivalents	314.3	869.3	711.2	711.2

Net Melt Equivalents/mole	2.03	---	2.04	---
Net Melt Equivalents/MWd	0.0157	---	0.0155	---

TABLE 7.2. Activity of Major Radioactive Fission Products as a Function of Cooling Time

Fission Product	Curies/tonne							
	20,400 MWd/tonne @ 15 MW/tonne				46,600 MWd/tonne @ 31 MW/tonne			
	0.5 yr.	1 yr.	4 yr.	10 yr.	0.5 yr.	1 yr.	5 yr.	10 yr.
⁹⁰ Sr (a)	4.76×10^4	4.70×10^4	4.37×10^4	3.76×10^{-4}	1.02×10^5	1.01×10^5	9.16×10^4	8.09×10^4
⁹¹ Y	6.00×10^4	6.77×10^3	--	--	9.79×10^4	1.10×10^4	--	--
⁹⁵ Zr	1.03×10^5	1.47×10^4	--	--	1.80×10^5	2.56×10^4	--	--
⁹⁵ Nb	2.01×10^5	3.12×10^4	--	--	3.50×10^5	5.45×10^4	--	--
¹⁰³ Ru	2.34×10^4	9.58×10^2	--	--	4.56×10^4	1.86×10^3	--	--
¹⁰⁶ Ru (a)	1.69×10^5	1.19×10^5	1.49×10^4	2.33×10^2	4.00×10^5	2.83×10^5	1.77×10^4	5.52×10^5
¹³⁴ Cs	6.47×10^4	5.49×10^4	2.04×10^4	2.81×10^3	2.64×10^5	2.24×10^5	5.97×10^4	1.15×10^4
¹³⁷ Cs	6.39×10^4	6.32×10^4	5.90×10^4	5.13×10^4	1.46×10^5	1.44×10^5	1.31×10^5	1.17×10^5
¹⁴¹ Ce	1.46×10^4	2.97×10^2	--	--	2.62×10^4	5.32×10^2	--	--
¹⁴⁴ Ce (a)	3.70×10^5	2.37×10^5	1.65×10^4	7.99×10^1	6.87×10^5	4.41×10^5	1.26×10^4	1.49×10^2
¹⁴⁷ Pm	8.57×10^4	7.51×10^4	3.39×10^4	6.94×10^3	1.18×10^5	1.03×10^5	3.58×10^4	9.53×10^3
Total Fission Product (b)	1.87×10^6	1.07×10^6	2.73×10^5	1.42×10^5	3.76×10^6	2.26×10^6	4.94×10^5	3.16×10^5

a. Does not include short-lived daughter isotopes

b. Includes short-lived daughter isotopes and small contributions not listed above.
Does not include activity from actinide elements.

TABLE 7.3. Heat Generation Rates in Fuel Reprocessing Plant Waste as a Function of Cooling Time. Fuel reprocessed at 6 months from reactor discharge.

Years From Reactor Discharge	Watts/tonne of Fuel Processed*	
	20,400 MWd/tonne	46,600 MWd/tonne
0.5	8,380	19,210
1	4,800	11,680
2	2,490	6,370
3	1,550	4,150
4	1,120	3,000
5	890	2,440
6	760	2,100
7	670	1,870
8	630	1,700
9	600	1,580
10	570	1,480
15	490	1,200
20	420	1,060
35	290	720

* Includes heat generation rate from actinide elements not removed by separations processing (100% of the americium, curium, and neptunium radioactivity plus 0.3% of the plutonium radioactivity.)

Figure 7.9. Fission product and actinide compositions were calculated by the ISOGEN computer program⁽²⁾ for 3.4% enriched uranium fuels irradiated in thermal reactors to fuel burnups of 20,400 MWd/tonne at 15 MW/tonne for the PW-2 waste and 46,600 MWd/tonne at 31 MW/tonne for the PW-4m waste. At a given cooling time, the combined fission product mass and heat contents of irradiated fuels vary nearly linearly with burnup for fuels aged six months or more; thus the data in these tables and in Figure 7.9 may be used to estimate the fission product composition and heat content of fuels with different burnup histories.

FIGURE 7.9. Heat Generation Rates in Fuel Reprocessing Plant Waste as a Function of Cooling Time

For improved accuracy, the plutonium content of the irradiated fuels was taken from Reference 3, a compilation of yield data calculated by the ALTHAEA computer code for varying fuel designs and enrichments for typical pressurized and boiling water power reactors. A plot of typical plutonium content versus fuel burnup for 4% enriched uranium fuel is presented in Figure 7.10 for a Diablo Canyon-type pressurized water reactor.

The data in Figure 7.10 were used to estimate the amount of chemical additives required for plutonium valence adjustment in the PW-2 waste composition calculations. Typically, 5 to 10 moles of ferrous sulfamate are used to reduce Pu(IV) to Pu(III) in the Purex process partition cycle, and an amount of sodium nitrite slightly in excess of that required to destroy the sulfamate is added to the second cycle plutonium feed to react with the sulfamate and to initiate the autocatalytic reoxidation of Fe(II) and Pu(III). For the purposes of this flowsheet study, the required ferrous sulfamate/plutonium mole ratio was assumed to decrease linearly from 8 to 4 as the plutonium content of the fuel increased from 0 to 70 moles/tonne. The sulfamate decomposes to sulfate at the ratio of 2 moles/mole iron. The sodium nitrite requirement was assumed to be 1.05 moles/mole sulfamate or 2.1 moles/mole iron. These relationships are used later in Subsection 8.8.1 to calculate the volume of solidified PW-2 type waste as a function of fuel burnup for the various solidification processes. The acidity and volume of the incoming, dilute PW-2 waste were calculated by assuming that the second-cycle waste had been preconcentrated to remove most of the water and some of the nitric acid before combining it with the unconcentrated first cycle waste. Thus the volume and acidity do not differ much from that of the PW-4m waste, which is assumed to consist only of unconcentrated first cycle waste.

Both the PW-2 and PW-4m waste contain a small amount of phosphate derived from entrained and dissolved tributyl phosphate solvent. In actual practice, these wastes would also

FIGURE 7.10. Typical Plutonium Content of ^{235}U -Enriched LWR Fuel as a Function of Burnup

contain a small amount of dissolved stainless steel corrosion products; but in most cases the contribution of the corrosion products to the solid content of the waste should be negligible.

The calculated total equivalents of cations and anions in the waste are included in Table 7.1 for use in material balance and solidification-additive calculations. Both the spray calciner and phosphate glass processes require the addition of phosphoric acid and certain metal cations to prepare melts with desired viscosities and chemical stability. As discussed in Section 3, the properties of these melts are conveniently correlated in terms of the M^+/P ratio (the ratio of metal cation equivalents to the metaphosphate ion equivalents). For many metals, such as sodium or calcium, determining the metal ion equivalents in the phosphate melt is a straightforward process. However, for metals such as ruthenium, zirconium, and molybdenum, calculation of the metal equivalents per mole is at best an educated guess. Ruthenium, for example, can exist in aqueous solutions in valences ranging from +2 to +8 but most normally exists in nitric acid solutions as nitrosylruthenium nitrate complexes. Zirconium can exist both as Zr^{+4} and ZrO^{+2} (hydrolyzed zirconium) ions in acidic solutions. Molybdenum exists as molybdate anions ($MoO_4^{=}$) in nitric acid solutions, but there is evidence from melting point and leachability data that molybdenum may exist as cations, perhaps MoO_2^{++} or MoO_2^{+} , in phosphate glass melts.*

Generally, in the absence of conflicting data, the more metallic elements of plus 4 valence or greater were assumed to be present in melts as partially hydrolyzed cations (zirconyl, molybdyl, etc.) while the less metallic elements (Se, Te, Sb,

* Data in Reference 4 indicate that the most stable potassium-molybdenum-phosphate glasses are formed at molybdenum/phosphate mole ratios of 1/1 to 2/1, where the phosphate content is that remaining after subtracting that used to form potassium metaphosphate.

Tc) were assumed to be present in melts as anions (M^-). The assumed ionic forms are included in Table 7.1. For all practical purposes, these assumptions result in about two net M^+ equivalents of fission products per mole of total fission products in both aqueous solutions and phosphate glass melts, or about 0.015 net M^+ equivalents of fission products/tonne per MWd/tonne of burnup. Actinides in the waste, including an estimated 0.1% of the uranium and 0.25% of the plutonium in the fuel, will add about 3 to 5 percent to the fission product equivalent total.

7.2 WASTE EVAPORATOR OPERATING MODES

Waste evaporator operating modes A, B, and C have been described in Section 5 and in earlier volumes of this series in conjunction with operation of the WSEP. The operating mode selected for flowsheet illustration most closely resembles Mode B, in which condensate from the waste solidifier is combined with incoming waste in the waste evaporator and the concentrated waste is held in separate storage, feed makeup, and solidifier feed tanks to provide lag storage, accountability sampling, and chemical adjustment capabilities prior to solidification.

An alternate mode, comparable to WSEP Mode A, was briefly considered but not evaluated in detail. In this mode, the solidifier condensate would be evaporated in a second concentrator and the bottoms would be recycled to the concentrated waste solidifier feed. This mode would avoid a potential large recycle of volatile ruthenium from the solidifier to the main waste evaporator. The second evaporator would have a relatively small evaporative load, and its operation could be specifically tailored to minimize ruthenium volatilization. The advantage of this mode would depend mainly on the volatility of the ruthenium species in the waste solidifier condensate.

If it is no more volatile than that in the original waste, there would be little or no advantage in the separate evaporation of the two streams. There are insufficient data at this time to indicate whether or not this is the case.

The main considerations in either operating mode are the volatility of ruthenium from the evaporator and the solution stability of the concentrated waste. Solution stability is achieved by restricting the acid and salt content of the concentrated waste to that indicated in the flowsheets. Formation of cement-like rare earth sulfate precipitates limits the PW-2 waste concentration to about four times the volume of the PW-4m waste concentrate. The indicated PW-2 concentrate volume of 500 liters/tonne should be increased to about 820 liters per tonne (0.45M sulfate) for prolonged aqueous storage to provide added safety. Likewise, the PW-4m concentrated waste volume should be increased from 130 to about 300 liters/tonne to avoid potential solids problems during storage. With this option, a small auxiliary feed evaporator such as that described above would be recommended to reduce the heat load on the solidifier equipment.

Ruthenium volatility is dependent on the formation of volatile RuO_4 in the evaporator by the oxidizing strength of the boiling nitric acid waste. Both ORNL workers⁽⁵⁾ and WSEP have correlated ruthenium volatility as a function of the evaporator distillate acidity. The validity of such a correlation depends on a number of factors, including the temperature of distillation, the relationship between the nitric acid concentration in the evaporator overheads and the nitrate concentration in the bottoms, and the presence of ruthenium reductants in either the bottoms (sugar, phosphites, organic phosphates, etc.) or in the overhead vapors (e.g., NO or NO_2)

In WSEP, ruthenium volatilization was significantly lower at distillate acidities below 0.5M, and this concentration was used as the basis of the flowsheet design. The

desired overhead acidity is maintained by operating the evaporator as a steam stripper, using a portion of the overhead condensate from the acid fractionator to supply the necessary strip water. The nitric acid vapor-liquid equilibrium data used to estimate the flowsheet equilibrium evaporator bottoms acidities is shown in Figure 7.11. The correlation was developed from Gillespie equilibrium still data presented in Reference 5 for boiling, simulated TBP-25, Darex, and Purex high level wastes. The use of the hydrogen ion-nitrate ion product as a correlation parameter has a semi-theoretical basis in that the volatility of nitric acid should be dependent on the concentration of undissociated nitric acid in the liquid phase, which by the mass action law should be proportional to the product of the hydrogen and nitrate ion concentrations and to the ionic strength--in this case represented approximately by the dissolved metal cation equivalent concentration. WSEP nitric acid equilibrium data for PW-1 waste containing phosphoric acid⁽⁶⁾ was also correlated reasonably well by this technique. In the latter case, it was assumed that the total hydrogen ion concentration in the evaporator bottoms was equal to the nitric acid concentration plus twice the phosphoric acid concentration.

Some rectification of the nitric acid overheads can occur in the waste evaporator and should be compensated for by lowering the allowable overhead acidity accordingly to maintain control of ruthenium volatilization. The WSEP ruthenium-overhead acidity correlation was not corrected for a probable small amount of acid rectification, and the specified 0.5M HNO_3 in the overheads should thereby include some safety margin with respect to ruthenium volatility.

7.3 SOLIDIFIER FEED MAKEUP ADDITIVES

Each of the waste solidification processes requires certain additives to give desired melt properties or to prevent the volatilization of sulfate or fission products. The amount of

FIGURE 7.11. Nitric Acid Vapor-Liquid Equilibrium Data Correlation for Boiling, High Level Waste Solutions

additives used in the example flowsheets was derived from the general rules presented in Section 3. In most cases, the additives can be added directly to the concentrated waste; but in some instances, addition directly to the solidifier melter or pot is specified. Calcium nitrate, for example, is added directly to the pot in the PW-2 flowsheet during pot calcination to avoid calcium sulfate precipitation in the solidifier feed tank;* sodium metaphosphate is added directly to the spray solidifier melter in the PW-2 flowsheet to minimize sulfate volatilization due to phosphate displacement of sulfate from its salts and to avoid lowering the "stick-point" temperature in the spray chamber; and sodium borosilicate frit is added directly to the pot in the PW-4m spray calciner in-pot melting flowsheet to avoid erosion of the spray feed system.

Feed makeup could be either continuous or batchwise. The latter technique is recommended to permit laboratory confirmation of the desired feed compositions. Continuous makeup or feed-line blending may be preferred where undesirable precipitates are formed by feed additives.

7.4 SOLIDIFIER OPERATION

Typical temperature operating limits are included in the solidifier blocks of the flowsheets. These correspond to the optimum temperatures determined in WSEP for the two feed types. The indicated densities of the solidified products also correspond to typical values obtained in WSEP and were used, together with the weight of solidified product oxides, to obtain the solidified product volume. A further discussion relating product volume, heat content, and pot size to irradiation and cooling history is presented in Section 8.8.

* Where significant feed solids already exist, $\text{Ca}(\text{NO}_3)_2$ may be added directly to the concentrated waste without significantly increasing the solids volume or changing the character of the solids. (7)

WSEP experience has shown that periodic addition of flush water or anti-foam agents to the solidifier may be required in some flowsheet applications to prevent off-gas line plugging, to clean fouled heat transfer surfaces, or to counter foaming tendencies of wastes containing tributyl phosphate solvent degradation products. The volumes of these streams, if used, would be small and highly dependent on the equipment design and feed stream characteristics.

7.5 SOLIDIFIER OFF-GAS TREATMENT AND RECOVERY

The weight and composition of gaseous effluents from the solidifiers were determined from nitrogen and total weight balances over the solidifier unit. A portion of the nitric acid and nitrate entering the solidifier is decomposed to nitric oxide and nitrogen dioxide. Nitrogen dioxide and nitric acid vapors will be readily absorbed in the quench scrubber-condenser to produce nitric acid and additional nitric oxide. The quench-scrubber liquid is obtained from the nitric acid fractionator overheads and is routed from the quench scrubber to the waste evaporator to serve as nitric acid strip water. Nitric oxide is slowly oxidized to nitrogen dioxide, and a major fraction of it can be absorbed and recovered as nitric acid in the ensuing off-gas treatment steps by careful equipment design and operation. Rough estimates (based on WSEP auxiliary performance) of nitrogen oxide losses to the off-gas system following the various scrubbing and nitric acid recovery steps are included in the flowsheets. Estimated nitrate losses range from about 5 to 10 mole % for the pot calciner and phosphate glass processes to about 25 mole % for the spray calciner processes, based on the nitrate entering the solidifier.

In addition to nitric acid and nitrogen oxides, the solidifier off-gases will contain small amounts of volatile fission products and volatile chemical additives. The only volatile fission product of concern is ruthenium. Measured ruthenium

volatilized in WSEP ranged from about 10 to 20% of the input ruthenium for the pot calciner and phosphate glass processes to about 40 to 80% for the spray calciner process with phosphate melts. The lowest ruthenium volatilization observed was about 1 to 2% for the borosilicate-based spray-in-pot melting process using PW-4m waste. Over 99% of the volatilized ruthenium is expected to be removed from the solidifier off-gas by the quench-scrubber and returned to the high level waste evaporator bottoms. The net effect of the ruthenium volatilization from the solidifier will be an increase in the ruthenium content of the solidifier feed by this reflux mechanism. At steady state, the ruthenium content of the concentrated high level waste will be increased by a factor of $1/(1-f)$, where f represents the fraction of solidifier feed ruthenium volatilized by the solidifier. For example, if 75% of the ruthenium in the feed is volatilized in the spray calciner, the ruthenium content of the waste evaporator bottoms will eventually increase by a factor of $1/(1-0.75) = 4$ times the amount brought in by the incoming high level waste. Similar calculations can be made for the partially volatile fission products Se, Te, Tc, Mo, Sb, and Sn; however none of these present the radiological hazard of ruthenium, and only the volatility of selenium (and possibly technetium) approaches that of ruthenium.⁽⁸⁾ Little, if any, fission product iodine or bromine is expected to reach the solidification process; if present, they would be almost totally volatilized.

Of the chemical additives shown, only sulfate presents a volatility problem. For most of the solidification processes, sulfate volatility is adequately suppressed by the addition of alkali or alkaline earth cations to the feed (less than 5% sulfate volatilized in the WSEP pot and spray calciners). However, the high phosphate content in the melter of the phosphate glass process completely displaces the sulfate from the melt and results in the generation of a highly contaminated side stream containing all of the sulfate as sulfuric acid. This stream also contains

nitric acid from the nitrate not removed by the denitrator-evaporator and a small amount of phosphoric acid distilled from the melter. The vapor is highly corrosive to stainless steel and must be diluted with water (or steam) in the melter condenser to avoid excessive corrosion. Although the generation of this sidestream is a drawback of the phosphate glass process when solidifying PW-2 type feeds, a vacuum distillation technique has been developed for recovering decontaminated nitric and sulfuric acids as separate streams suitable for recycle or disposal as intermediate level wastes.^(9,10) The bottoms from this distillation process would contain phosphoric acid and entrained and volatilized fission products, including most of the volatilized ruthenium, and would be returned to the solidifier feed tank as a very small volume recycle stream.

Several other volatile chemical additives have been considered or are occasionally used in AEC and commercial reprocessing plants. These include mercury salts for control of radio-iodine evolution and fluoride or HF for improved dissolution of refractory thorium or plutonium oxides or for vessel decontamination purposes. Mercury, if present, is completely volatile in all of the WSEP waste solidification processes and must be removed from the high level waste before solidification to avoid off-gas plugging problems. Fluoride is partially volatile as HF, but it is believed that most of it can be retained by chemical complexing. Cadmium, proposed as a criticality poison, may be slightly volatile unless retained by sulfate or phosphate complexing.

7.6 NITRIC ACID FRACTIONATION

The dilute nitric acid overheads leaving the high level waste evaporator pass through a deentrainment device, such as a high-efficiency mist eliminator, and a condenser before being fed to an atmospheric pressure nitric acid fractionator for recovery of a concentrated (50%) nitric acid product stream

suitable for recycle to the head-end of the reprocessing plant. Careful design to provide good deentrainment and vapor-liquid scrubbing contact in the upper portion of the fractionating tower should provide sufficient ruthenium decontamination of the fractionator distillate to permit it to be used as makeup water in the head-end and first solvent extraction cycle of the reprocessing plant, as indicated in Section 5. For the widest utility in recycle applications, the acid concentration in the distillate should be held at or below $0.01M$ by appropriate tower design and internal reflux ratio in the exhausting section of the tower.

WSEP experience, which may not be typical in all cases due to contamination of the off-gas system with radio-ruthenium deposits, showed that fractionator distillates containing as little as 0.0001% of the ruthenium activity fed to the solidifier could be obtained for all processes. Under optimum conditions, the WSEP concentrated acid product contained about 0.1% of the solidifier feed ruthenium. However, representative fractionator product streams derived from the spray calciner runs averaged about five times these levels of ruthenium, as might be anticipated from the greater ruthenium volatility from the spray calciner.

The final off-gas disposition from the fractionator is not shown in the flowsheets. The composition and volume should be fully compatible with the process off-gases generated in other sections of the plant (e.g., fuel dissolver off-gases), and they would most probably be combined for ultimate acid scrubbing, iodine removal, and filtration steps prior to stack release.

REFERENCES FOR SECTION 7

BNWL quarterly and WSEP reports referenced below are listed in a report bibliography at the end of Section 3.

1. Safety Analysis Spent Fuel Reprocessing Plant, GEH-26407 (Docket No. 50-201), Nuclear Fuel Services, Inc., New York, July 1962.
2. H. H. Van Tuyl. "ISOGEN--A Computer Code for Radioisotope Generation Calculations," USAEC Report HW-83785. General Electric Co., September 1964.
3. Final Report on Agency Research Contract 513/RB: Theoretical Analysis of Plutonium Buildup and Uranium Depletion in Pressurized Water and Boiling Water Power Reactors, Battelle Pacific Northwest Laboratories, Research Report to International Atomic Energy Agency, Vienna, Austria, August 1968.
4. J. D. Provance and D. C. Wood. "Molybdenum Phosphate Glasses Containing Ag_2O or K_2O ," J. Am. Ceram. Soc., 50, 511-520, 1960.
5. W. E. Clark, J. C. Suddath, C. W. Hancher, R. E. Blanco, H. W. Godbee, J. M. Holmes, and C. L. Fitzgerald. "Development of Processes for Solidification of High Level Radioactive Waste: Summary for Pot Calcination and Rising Level Potglass Processes," ORNL-TM-1584, August 12, 1966.
6. J. E. Mendel, Unpublished Data, November 1966.
7. WSEP Report, Volume 4, BNWL-814, p. 5.19.
8. Quarterly Report, BNWL-1311, p. 27.
9. R. F. Drager, R. W. Johnson, and L. P. Hatch. "Decontamination of Melter Off-Gas Condensates from the Phosphate Glass Process by Distillation," BNL-50184, March 1969.
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8.0 DESIGN CONSIDERATIONS FOR A
5 TONNE PER DAY WASTE
SOLIDIFICATION FACILITY

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8.0 DESIGN CONSIDERATIONS FOR A 5 TONNE PER DAY WASTE SOLIDIFICATION FACILITY

The WSEP equipment was designed to process the waste from approximately 0.3 to 1.0 tonne/day of fuel, depending upon waste composition, solidification scheme, and process flowsheet. In addition, WSEP equipment was designed to obtain a large amount of data in a relatively few short-time tests. Currently, two commercial fuel reprocessing plants are in operation in the USA with nominal capacities of approximately 1 tonne/day. One of these plants has announced tentative plans for expansion to approximately 3 tonnes/day. The next commercial plant scheduled for operation in the USA in 1974 will have a capacity of approximately 5 tonnes/day. Because of these larger planned capacities in the relatively near future, the results from the WSEP tests have been analyzed for application to commercial fuel reprocessing plants having the nominal capacity of 5 tonnes per day of fuel. Another major factor in this analysis is that commercial equipment need not provide much data but must operate reliably for many years on a routine production basis.

Application to reprocessing plants larger than 5 tonnes/day, which may exist in the more distant future, is not studied specifically in this report, but in most cases, extrapolation by additional factors of 2 to 4 should not be difficult.

8.1 PRIMARY BASES AND ASSUMPTIONS

The basic assumptions for the design considerations are that the reprocessing plant operates at the instantaneous rate of 5 tonnes/day of LWR fuel material, and generates either of the two alternative waste compositions selected in Section 7 (WSEP waste designations PW-2 and PW-4m). Relatively straightforward interpolation to conditions for other fuel exposures and for most other waste compositions can be performed for other cases by the methods used in Sections 7 and 8.

8.1.1 Regulatory Requirements

The primary regulation for controls relating to the solidification scheme is Reference 1, which requires that

- a. high level waste must be converted to an approved solid within 5 years after reprocessing of the fuel,
- b. the solidified high level waste must be shipped to a Federal repository within 10 years after reprocessing of the fuel,
- c. no high level waste may be shipped from the reprocessing plant site which has not been converted to an approved solid form, and
- d. ultimate disposal of high level waste will not be permitted on any land other than that controlled by the Federal Government.

It is further required that the solidified waste be thermally, chemically, and radiolytically stable, with internal pressure buildup to be less than the maximum safe level. The outside surfaces of the container must have only low levels of smearable radioactive contamination.

Upon receipt of the solidified high level waste at the Federal repository, the reprocessor will pay the Federal Government a one-time fee for disposal of the waste and for perpetual surveillance as required. The fee is presently proposed to increase with the amount of radioactive decay heat in the waste (up to an approximate maximum allowable heat rate of 5 kilowatts/container), and to increase with the age of the waste (up to a maximum allowable age of approximately 10 years) per unit of heat content.⁽²⁾ The containers of waste are expected to be limited to an overall length of no more than 10 feet and an overall diameter no greater than 2 feet.

At the present time, no direct specifications exist for the solidified waste. However, requirements will most likely be

controlled by considerations regarding interim storage, transportation, and final disposal. Transportation requirements would likely be similar to those for transportation and handling of other highly radioactive materials.^(3,4) These requirements allow for control of release of radionuclides by the total packaged system, that is, the container plus the shipping cask. At the present time, the main regulatory requirements which the cask-plus-container-plus waste must meet are to:

- withstand a 30-foot free fall onto a solid, unyielding surface, followed by,
- a 40-inch drop into an unyielding 6-inch-diameter piston, followed by,
- exposure to the equivalent of a fire at 1475 °F for 30 minutes followed by no artificial cooling for an additional 3 hours, followed by,
- submergence in water for 24 hours.

After exposure to this situation, the maximum amount of radionuclides that can be released within the regulations is:

- 0.1% of the total radioactivity of the package, or
- 0.01 curies of Group I, 0.5 curies of Group II, and 10 curies of Group III and IV radionuclides, except inert gases are limited to a release of 1000 curies.*

In addition, the accessible surface area of the package (in this case, the cask) must be less than 180 °F, the surface of the container must have low radioactivity contamination, and the container package must have two lines of containment to restrict release of radioactive materials.

Most of these transportation regulations pertain to the mechanical integrity of the package, and are primarily accommodated by design of the cask more than the contents. However, the requirement of withstanding a fire will impose additional

* See References 3 and 4 for group designations.

restrictions on the thermal and radiolytic stability of the solidified waste. It is believed that all of the solidified wastes from the four processes which were developed in the USA meet the existing transportation regulations when packaged in reasonable containers and shipped in casks similar to those used for shipment of spent fuels. Requirements for interim storage and final disposal should include thermal, chemical radiolytic stability, but specific requirements will depend upon the characteristics of the two facilities.

8.1.2 Waste Compositions

The waste compositions used as the basis for design considerations are those designated PW-2 and PW-4m in the WSEP demonstrations.* The discussions regarding waste compositions and the description of the waste compositions plus the chemical additions required for each solidifier were given for the reference flow-sheets presented in Section 7.

8.1.3 Effluent Treatment

Conversion of high level aqueous wastes to solids results in an effluent stream that contains lower levels of radioactivity than the original liquid waste by a factor of 10 to 500. The radionuclide content of this stream must be reduced to a level that can be satisfactorily managed. The radionuclides in the high level waste must be decontaminated by factors of up to about 10^{10} to meet the proposed AEC release requirements (nominally 10^{-5} times concentrations in 10CFR20 for the public at large for gaseous effluents at the site boundary, and 1 to 10^{-3} times 10CFR20 concentrations for liquid effluents in the total plant outfall.)⁽¹⁾ The primary contaminant in the immediate

* The PW-2 and PW-4m wastes have exposures of 20,000 MWd/tonne at 15 MW/tonne and 45,000 MWd/tonne at 30 MW/tonne respectively. However, the wastes used in the economic evaluation in Section 9 were exposed to 33,000 MWd/tonne at 30 MW/tonne.

effluent stream from all three processes is radioruthenium followed by radiocerium, radiocesium, and radiostrontium.

Auxiliary off-gas processing equipment for waste solidification must be designed to provide decontamination to assure that the effluent stream when combined with the other similar reprocessing plant waste streams will be acceptable for recycle to the fuel reprocessing plant or for final release to the environment. Initial studies have indicated that the portion of the plant waste streams from waste solidification can be recycled after a reasonable amount of treatment in the main auxiliaries of the reprocessing plant.

Process auxiliaries required for a solidification system consist of (1) equipment for preparing the aqueous waste as feed for a solidifier, and (2) equipment for initial decontamination of the solidifier off-gas. Process auxiliaries which are assumed to be shared with those usually present in a fuel reprocessing plant are an evaporator for concentrating the dilute high level waste raffinate from solvent extraction, equipment for further decontamination of the solidifier and waste evaporator off-gases, and equipment for separation of water, nitric acid and nitrogen oxides in the off-gases into concentrated nitric acid, water and clean gas streams. For this study, only the incremental additions for waste solidification to the capabilities of the process auxiliaries normally used in fuel reprocessing are included as waste solidification items. These incremental auxiliary additions include feed systems to the solidifiers, solidifier off-gas scrubbers and condensers, waste re-evaporator systems when interim aqueous storage is used, and interim solid storage requirements.

If a reprocessor chooses to have a waste solidification plant which is separate from the main plant, process auxiliaries could also include a waste concentrator, an acid recovery system, and additional off-gas clean-up equipment.

8.1.4 Bases for Conceptual Design

The major design bases for a waste solidification system are basically similar to those for the high radioactivity areas of an aqueous fuel reprocessing plant. Some of the major bases used in this conceptual design are listed below.

- The waste solidification system is an integral part of the fuel reprocessing plant, with appropriate sharing of facilities, services, and manpower.
- Shielding for all parts of the high level waste system is that equivalent to 6 feet of ordinary concrete.
- Operation of the system is from a remote control room where reasonably possible. Where not reasonably possible, operations are supplemented by using combinations of mechanical or master slave manipulators, cranes, or mechanical motion devices. Viewing for these latter activities is by use of large shielding windows.
- The waste solidification system is remotely maintained, using a remotely-operated crane and remote connectors. Where manipulation and viewing are available, they are used to supplement remote maintenance.
- The solidification system is designed with sufficient flexibility to handle plant wastes with normal variations in compositions.
- Double-containment within the process cell is used where practicable for added safety for solidification equipment exposed to a potentially severe environment.
- High quality fabrication and materials of construction are used in all equipment.
- Receiver-storage pots for solidified waste are fabricated with high quality but with minimum cost materials, complexity and appurtenances.
- Sizes of receiver-storage pots are controlled to limit the maximum internal centerline temperature to no greater than

about 425 °C during storage. Temperatures during processing may exceed these limits by about 100 °C for time periods no more than a few days.

8.1.5 Operating Assumptions

An operating efficiency of 75 percent is assumed for the conceptual design of the reprocessing plant and for the waste solidification system. The plant and the waste solidification system will be operated 24 hr/day and 7 days/week using 3 shifts/day. These bases result in 274 days of operation during the year at the rate of 5 tonnes/day for a total fuel reprocessing load of 1370 tonnes/yr.

8.2 POT CALCINATION

Of the two pot solidification processes, only pot calcination is used for design considerations since appreciably more development is needed for the Rising Level Glass process to have it in a comparable state of development. Information discussed in this section is primarily based upon that developed in Sections 4 through 7 and 8.8.

The basic equipment required for pot calcination^(5,6) is (a) a pot for calcining the waste, (b) a multiple-zone furnace for heating and cooling the pot, (c) a fill head, and (d) a special off-gas line from the pot which can be continually cleaned of accumulated deposition of entrained material.

8.2.1 Conceptual Design*

A design concept for the pot calciner is shown in Figure 8.1. The primary features of the design include: retractable fill head; a swivel vent line with cooling jacket; stationary pot furnace with heating and cooling, and pot with centerline thermowell using removable thermocouples.

* The design concepts received significant contributions by and were drawn by D. H. Siemens, Battelle-Northwest.

POT CALCINATION SYSTEM

Off Gas Line	PW-2	PW-4m
Diameter, In.	3	3
Material	304 L SST	
Fill Head Material	304 L SST	

Pot Furnace*				
Heat Transfer Area, ft ²	50	25		
I.D., in.	18	~ 8	12	~ 3
Internal Height, ft	10	furn-	10	furn-
Type - Resistance or Induction Heated, 6 zones	aces			aces
Total Power, kW	150 (ea)	100	100	(ea)
Max. Temp., °C	1000		1000	
Normal Temp., °C	900		900	

*The actual furnace size and the number of furnaces depends on the pot size.

FIGURE 8.1. Conceptual Design of Pot Calciner

Process Pot

The 304L stainless steel pot contains a 3/4-inch stainless steel pipe as a centerline thermowell for three removable thermocouples. (It may even be possible, through sufficient operating experience, to operate by procedure only without thermocouples. A considerable amount of long-term operation would be required, however, before such a decision could be made.) A baffle is provided (near the top of the pot) for gross separation of entrainment from passing vapors. Other features within the pot are removable and are part of the fill head.

Pot Fill Head

The fill head connects the pot to the process feed system and the vent system (off-gas line). Feed enters and the off-gases leave the pot through the calciner fill head. An air-steam purged dip tube and a thermocouple enter the pot as part of the fill head for measurement of liquid level. A chemical addition line and an air-purged pressure measuring dip tube enter the pot as part of the fill head. The feed and chemical addition pipes and the liquid level measuring devices extend to below the baffle in the pot; the other devices terminate at the fill head.

The entire fill head and attached piping retract about two feet using swivels, to permit removal of the fill head. When the pot is filled with calcine, the fill head is retracted and placed in its adjacent cleaning station where it may be sprayed with water or other chemicals for cleaning if desired. While the fill head is in the retracted position, the pot has a cap placed on it and is removed to the weld and test station. A new pot is then installed and the process is continued.

Off-Gas Vent Line

The off-gas vent line between the pot fill head and the next piece of off-gas processing equipment (a scrubber in this

study) includes a jacket for partial reflux, on-stream cleaning. The reflux is normally drained to the high level waste concentration system to prevent extra boil-up duty in the pot. The reflux must also be drained back into the pot to wash the off-gas line at the fill head and the neck of the pot for about 15 minutes every 12 hours during a batch and near the end of the feeding to the pot. A spray is included for optional cleaning use, and a valve is included for sealing the system when the fill head is removed.

Pot Furnace

A six-zone, stationary electric furnace with both heating and cooling is used. Each zone is separately controlled by individual furnace thermocouples. A zone divider is used for controlling air flow around the pot during cooling. The divider is made removable to allow for many different pot sizes or for possible furnace repair. Cooling air in each zone is directed onto the pot via a hollow-cone spray nozzle and is vented to the cell on the opposite side of the pot. Approximately 50 cfm of air should be provided per zone for cooling, for a maximum of 300 cfm per pot.

No furnace susceptor is believed to be necessary if a resistance type furnace is used; if induction heating is used, a susceptor is desirable for added safety. A drain in the bottom of the furnace to a sump or equivalent is shown to minimize furnace damage in case of a pot failure.

8.2.2 Conceptual Cell Layout*

A conceptual cell arrangement for the pot calcining equipment is shown in Figure 8.2. Up to six pot furnaces and six pot fill heads are included in one cell; for cases requiring more

* The design concepts received significant contributions by and were drawn by D. H. Siemens, Battelle-Northwest.

FIGURE 8.2. Conceptual Cell Arrangement for Pot Calciner

pot lines, another cell would be desirable. In addition, a single calciner vapor scrubber in the waste evaporator cell serves all the pot lines. A pot welding and testing station is included in each cell which contains calciners. Primary control during feeding, calcination and cooling is from a control room remote from the cell. Several viewing windows and manipulators are used for direct in-cell manipulation.

New pots are transferred into the cell through a transfer mechanism and are then handled with an in-cell crane. The pots are remotely lowered into the pot furnaces and the fill heads are positioned and sealed to the pots. After filling, calcining, and cooling, the pots are capped and then transferred to the pot test station. (See Section 8.5.) A stainless steel lined partition between the calcination and pot testing area provides for minimized contamination of the pot testing area. The pot testing equipment, in turn, is located in a semi-hood in the cell to further minimize contamination within that area.

The pot calciner feed tanks and vapor scrubber are in the same cell as the high level waste concentrator. For calcining, one feed makeup and one feed tank are shown. Each of these tanks is arbitrarily sized for about two days' holdup. Chemical adjustments to the feed are added to the feed makeup tank.

Where interim aqueous storage is used, an additional waste concentrator, condenser, and calciner feed tank are required (but are not shown in the design concept.) For interim aqueous storage, three or more large tanks are required in a separate vault area (one tank for filling, one tank for emptying, one for a spare, and possibly one or more tanks for "dead" storage).

8.2.3 Equipment Scale-Up

Scale-up information for the two reference wastes is presented in Table 8.1.

TABLE 8.1. Pot Calciner Conceptual Design Scale-Up Information

Pot Diameter, In. (Std Pipe)	PW-2 Waste (Nominally, 20,000 Mwd/tonne at 15 MW/tonne)							PW-4m Waste (Nominally, 45,000 Mwd/tonne at 30 MW/tonne)		
	6	8	10	12	16	20	24	6	8	10
Feed to pot, l/Te	550	550	550	550	550	550	550	132.5	132.5	132.5
Total feed calcined, l/day	2750	2750	2750	2750	2750	2750	2750	662.5	662.5	662.5
Overall average feed rate, l/hr	114.6	114.6	114.6	114.6	114.6	114.6	114.6	27.6	27.6	27.6
Volume solid waste in pot, l	45.4	78.7	124.1	177.9	278.0	437.2	632.4	454	78.7	124.1
Unit volume solid waste, l/Te	70.6	70.6	70.6	70.6	70.6	70.6	70.6	42.0	42.0	42.0
Tonnes/pot	0.64	1.11	1.76	2.52	3.94	6.19	8.95	1.08	1.87	2.95
Pots/day	7.77	4.49	2.85	1.98	1.27	0.81	0.56	4.62	2.67	1.69
Feed per pot, liters	354	613	966	1386	2166	3406	4927	143	248	391
Initial feed rate per pot, l/hr	17.3	30.0	47.3	67.8	106	167	241	17.3	30.0	47.3
Average feed rate per pot, l/hr ^(c)	14.3	18.8	21.7	23.1	24.4	25.2	25.7	12.9	16.0	17.1
<u>Time Cycle/Pot: (g)</u>										
Pot preparation time, hr	2	2	2	2	2	2	2	2	2	2
Time at initial rate, hr ^(c)	16	14	12	11	9	8	8	6	5	5
Time at reduced rate, hr ^(c)	9	19	33	49	79	127	184	5	10	18
Calcining and cooling time, hr ^(d)	6	10	15	20	31	48	68	5	8	12
Pot removal time, hr	2	2	2	2	2	2	2	2	2	2
Total time, hr/pot	35	47	64	84	123	187	264	20	27	39
Overall processing rate, Te/day/pot	0.44	0.57	0.66	0.72	0.77	0.79	0.81	1.3	1.7	1.8
Total pot lines required	12	9	8	7	7	7	7	4	3	3
<u>Heat Generation and Dissipation</u>										
<u>Air-Cooled Pot Storage: (a)</u>										
Max. heat rate at solidification, kW/pot	6.60	7.00	7.24	7.41	7.60	7.78	7.93	6.60	7.00	7.24
Min. age at solidification, yr ^(f)	0.4	0.7	1.2	1.7	2.5	3.6	5.1	2.1	3.3	5.0
Maximum T _C , °C	900	900	900	900	900	900	900	900	900	900
Maximum T _w , °C	280	250	228	210	187	168	154	280	250	228
<u>Water-Cooled Pot Storage (b)</u>										
Max. heat rate at solidification, kW	6.60	7.00	7.24	7.41	7.60	7.78	7.93	8.58	8.58	8.58
Min. age at solidification, yr ^(f)	0.4	0.7	1.2	1.7	2.5	3.6	5.1	1.6	2.8	4.2
Maximum T _C , °C	715	753	775	791	809	825	839	900	900	900
Maximum T _w , °C	100	100	100	100	100	100	100	100	100	100
<u>Air or Water-Cooled Storage</u>										
Heat rate at 5 yr, kW/pot	0.58	1.0	1.6	2.3	3.5	5.5	8.0	2.6	4.6	7.2
Heat rate at 10 yr, kW/pot	0.37	0.63	1.0	1.4	2.2	3.5	5.1	1.6	2.8	4.4
Age at 4 kW/pot, yr ^(e,f)	0.75	1.4	2.2	2.9	4.4	7.5	18	3.3	5.9	11.7

Shaded area presents data for pots containing greater heat generation rates at 10 years' cooling than the proposed limit for salt mine storage.

- For air cooling using natural convection and radiation, the maximum centerline temperature is limited to 900 °C.
- For water cooling where the maximum wall temperature is 100 °C and the maximum centerline temperature does not exceed 900 °C. The air cooled limit, above, is used for PW-2 (sulfate containing) waste to avoid exceeding 900 °C during the time the pot must be handled in air and during processing.
- Obtained by correlation presented in Appendix A.
- From Figure 8.3.
- Limit for proposed salt mine storage is 500 W/ft or 4 kilowatts total for an 8-ft fill.
- Total time out-of-reactor.
- For water-cooled cases.

Process Pot

The pot size is limited by the capacity for cooling the self-generating heat in the pot after calcination is completed. As waste is concentrated, salts precipitate from the solution and form a deposit on the walls and the bottom of pots. As this deposit (scale) increases inward and upward, the heat transfer rate to the boiling sludge is reduced, the pot wall temperature approaches the furnace operating temperature (900 °C), and boilup rate decreases. Therefore, the feed rate must be continually reduced to a point where it is no longer practical to continue feeding (in the range of 3 to 10 liters/hr).

The overall processing rate for pot calcination is inversely proportional to the total salts in the waste and is proportional to pot diameter up to diameters of about 16 inches (see Figure 4.3.) Consequently, the system in general can be scaled up by reducing the salt content in the waste through changes in the reprocessing scheme, or for any given waste by adding additional pot lines, or by adding interim aqueous storage which permits the use of larger pots.

If foaming occurs it would further limit the throughput to the pot. Therefore, if foaming agents are present in the waste (e.g., dibutyl phosphate), an antifoam agent should be added to subdue foaming and to maintain the capacity. Dow Corning Antifoam B was used effectively for this purpose in WSEP.⁽⁶⁾

Allowable pot sizes and minimum pre-solidification cooling time for the waste are dependent on the heat dissipation characteristics of the solidified waste, as discussed in Section 8.8. The maximum heat rate, for salt mine disposal based on a center-line temperature of 900 °C in air or water storage,* for PW-2

* The maximum pot temperature with PW-2 waste should not exceed about 900 °C, even for relatively short time periods, because of the potential for decomposition of sulfates above that temperature.

waste is 7.8 kilowatts for an 8-foot fill height in a 20-inch pot at 3.6 years out-of-reactor. To solidify at 0.4 years out-of-reactor requires a 6-inch pot which can contain 6.6 kilowatts. To process 5 tonnes/day, seven pot lines are needed for 12 to 24-inch pots and 12 pot lines are needed for 6-inch pots.

To solidify the PW-4m waste with air-cooled interim pot storage, out-of-reactor times of 2.1, 3.3, and 5.0 years are required for 6, 8, and 10-inch pots, respectively; however, the heat in the 10-inch pot exceeds the proposed salt mine limit. For interim storage in water in which the centerline temperature might be allowed to reach 1150 °C for a short period during processing or while the pot is temporarily hanging in air, 8.6 kilowatts can be put into a pot. (This maximum temperature can be reduced, if desired, by designs using forced air cooling both in air and in the processing furnace.) This higher amount of heat in a pot allows reduction of aging time before solidification to 1.6 years for a 6-inch pot, 2.8 years for an 8-inch pot, and 4.2 years for a 10-inch pot. The number of pot lines required for processing PW-4m waste are four for 6-inch pots and three for 8- and 10-inch pots.

Feeding times for the pot calciner for PW-2 and PW-4m wastes were calculated from a mathematical model which simulates the WSEP pot operating technique. The derivation of this model is presented in the Appendix. For the model it is assumed that there is an initial constant feed rate period where heat transfer is through the pot wall into the concentrated solution until the time that scale forms on the pot wall. During the falling feed rate period, heat transfer is through the thickening calcine scale on the pot wall.

The rate during the constant feed rate period was determined by the vapor velocity in the upper part of the pot which is equivalent to a boilup rate of approximately 85 liters/hr per square foot of cross-sectional area in the pot. The volume in

the pot was controlled to reach the maximum pot operating volume at the end of the constant feed rate period. This boilup rate is for nonfoaming wastes, and for an 8-inch-diameter pot this represents a boil-off rate of about 30 liters/hr. This rate varies linearly with the cross-sectional area of the pot, so that for a 12-inch-diameter pot, the maximum initial boilup rate is about 68 liters/hr.

The pot feeding times are calculated to give a pot that contains the equivalent of 8 feet of calcine with a bulk density of 1.3 kg/liter in a 10-foot-long pot. These bases give a feed rate at the time the feed is stopped of less than approximately 10 liters/hr. For the large diameter pots used for the PW-2 waste, the feed could be cut off earlier (i.e., at about 90% of the feed into the pot) to reduce the feeding time considerably. See Figure 4.3 for an example of how the percent of pot fill affects the average feed rate.

Pot calcining and cooling times are taken from either Figure 8.3 or from the straight line portion of Figure 4.5: at the point on the line of $\frac{850}{\text{watts/liter}}$, the hours are read from the other ordinate. (The watts/liter value for the calcine in each pot size is obtained from the data in Table 8.1)

Pot preparation time (time for installation of the pot, initial half-filling of the pot, and initial furnace heat-up) and pot removal times were estimated directly from WSEP experience.

Pot Furnace

A multiple-zoned furnace is required because the heating and cooling needs vary with pot height at any given time in the filling cycle. Some of the solids from the feed and sludge and scale formed during calcination fall to the bottom of the pot; thus, solids accumulation progresses faster from the bottom upward than it progresses from the walls inward. As a result,

FIGURE 8.3. Estimated Pot Calcining and Cooling Times After Feed Is Off to Pot

the progress of concentration or calcination of the waste is different for each vertical segment of the pot, and therefore, heat requirements vary with pot height at any given time. In fact, cooling of the bottom segments is normally required at the same time that the upper pot segments still require heating. The actual number of furnace zones required is not definitely known, but six zones for a pot to be filled with 6 feet of calcine is definitely adequate. From WSEP data, six zones should be sufficient for 8 to 9 feet of calcine, but the use of fewer zones for that height appears doubtful.

Maximum furnace heating requirements are based on pot diameter which, in turn, determines the maximum boiling rate. Heating requirements are maximum during the initial or concentration stage, before the onset of calcination. At this time, the maximum heating requirements are limited by stable, non-foaming boiling conditions in the pot. Approximately one kilowatt of heat rate is required for each liter/hour of aqueous feed rate to the pot. This heat should be distributed approximately uniformly within each heating zone, and allowances should be made for end losses from the furnace. The normal operating temperature of the furnace should be about 900 °C.

Cooling is also required in the furnace to remove the heat of radioactive decay from the calcine after the material has been calcined. Zone cooling is required for the same reasons zone heating is needed. Design of furnaces with zone heating is relatively straightforward, while design for zone cooling is considerably more difficult. Design of a system for zone cooling of pots by direct contact with water (or with an equivalent volatile liquid coolant) would be a difficult design problem. In addition, the small additional heat load that a pot of calcine can dissipate with water cooling in storage is nearly the same as with direct forced air cooling of the pot. For these reasons, the concept used in this study

with the pot calciner uses air cooling. Cooling loads for the furnace are based on the capability to cool the pot, its contents, and the furnace to the desired temperature in the desired time, plus removing the heat of radioactive decay. These cooling requirements in WSEP were about 10 kilowatts for sensible heat and 5 kilowatts for heat of radioactive decay for the pot calciner. For pots with 8 feet of calcine, the cooling requirements would be about 12 and 6 to 8 kilowatts for these respective needs.

8.2.4 Materials of Construction

In pot calcination, the pots serve as the processing vessels as well as the storage containers. Consequently, they are exposed to severe corrosive conditions during calcination and must be made of corrosion-resistant material.

Stainless steel Type 304L is satisfactory as a material of construction for the pots, with corrosion rates less than 0.1 inch per year during processing and negligible after processing.⁽⁷⁾ Similarly, the use of 304L stainless steel for the pot fill head, off-gas line, and other process piping provides satisfactory corrosion resistance.

8.3 SPRAY SOLIDIFICATION

Design considerations for spray solidification using a continuous melter and using the in-pot melting technique are presented in this section, and are based on information developed in Sections 4 through 7 and 8.8.

The basic equipment required for the spray solidification process when a continuous melter^(8,9) is used includes: (a) a feed atomization system, (b) a heated calcining chamber and its furnace, (c) an off-gas de-entrainment system, (d) a melter and its furnace, and (e) a receiver-storage pot. When in-pot melting is used, item (d) is deleted and item (e) must also serve as

a melt pot and requires a furnace. When sulfate-containing PW-2 waste is being processed or when using a nonplatinum continuous melter, a system for adding melt-making solids is required.

8.3.1 Conceptual Design*

The design concept for the spray solidifier with a continuous melter is shown in Figure 8.4, and the spray solidifier with in-pot melting is shown in Figure 8.5.

Feed Atomization System

The solidifier feed is atomized by an internal-mixing pneumatic atomizing nozzle using air as the atomizing gas. This nozzle is removable and may be replaced in event of failure. Two or more nozzles may be necessary. An in-line cleaning needle which is remotely operated is used to remove plugs in the nozzle if they should occur.

Heated Calcining Chamber and Furnace

The calcining chamber concept for the spray calciner is that of a vertical cylinder which is heated externally through the walls with a surrounding resistance-heated electrical furnace which contains three or four heating zones. The waste is sprayed downward through the chamber from the atomizing feed nozzle(s) at the top of the calcining chamber. A free-piston type of vibrator mounted on top of the calciner is used to dislodge deposits from the upper section of the calciner.

Off-Gas De-entrainment System

The fine, powdered calcine produced in the calcining chamber is separated from the process off-gas by a bank of cylindrical sintered stainless steel filters in a chamber

* The design concepts received significant contributions by and were drawn by D. H. Siemens, Battelle-Northwest.

SPRAY MELTER SYSTEM

Spray Calciner	PW-2	PW-4m	PW-2	PW-4m
Heat transfer area, ft ²	190	120	190	36
Diameter, in.	36	30	36	18
Height, ft	20	15	20	8
Material	310 SST		310 SST	
Atomizing Nozzle	Pneumatic, internal mix		Pneumatic, internal mix	
Type	304L SST		304L SST	
Material	304L SST		304L SST	
Furnace				
Type - Electrical resistance, 3 zones				
Power, kW	300	200	300	70
Max. Temp., °C	900		900	
Normal Temp., °C	700		700	
Filters				
Total surface, ft ²	150	90	150	30
Material	304L Sintered SST		304L Sintered SST	
Mean Pore Size	65 μm		65 μm	
Melter	Platinum		Melter (non-Platinum)	
Heat transfer area, ft ²	20	12	5	3
Diameter, in.	26	21	12	10
Height, in.	36	29	20	14
Material (melter & nozzles)	99.5% Pt, 0.5% Rh		Corronel-230	
Thickness, in.	~0.10		0.5	
Furnace (melter & freeze valves)				
Type, Electrical Resistance				
Power, kW	~ 70	~ 50	30	20
Max. Temp., °C	1000	1250	1000	1100
Normal Temp., °C	950	1150	900	1050

FIGURE 8.4. Spray Solidifier with Continuous Melter Conceptual Design

SPRAY IN-POT MELTING SYSTEM

<u>Spray Calciner</u>	<u>PW-2</u>	<u>PW-4m</u>
Heat Transfer Area, ft ²	190	36
Diameter, in.	36	18
Height, ft	20	8
Furnace Power, kW	300	70
Filters		
Total Surface, ft ²	150	30

See Figure 8.4 for additional calciner features

Pot Furnace*

Heat Transfer Area, ft ²	50	25
I.D., in.	18	12
Internal height, ft	10	10
Type - Resistance or Induction Heated, 6 Zones	<div style="display: flex; align-items: center;"> <div style="margin-right: 10px;"> $\left. \begin{array}{l} \sim 3 \\ \text{furnaces} \end{array} \right\}$ </div> </div>	
Total Power, kW	100 (ea)	75 (ea)
Max. Temp., °C	950	1000
Normal Temp., °C	825	950

*The actual furnace size and the number of furnaces will depend on the pot size. See Table 8.2

FIGURE 8.5. Spray Solidifier with In-Pot Melting Conceptual Design

adjacent to the calcining chamber. The filters are periodically cleaned by short pulses of preheated air directed backwards through the filters. Control of the pulses of filter blowback air is accomplished through a bank of solenoid valves near the filter chamber. Only 20% of the filters are cleaned at a time to minimize reduction of process vacuum during the blowback pulses.

Continuous Melter and Furnace

The powdered calcine falls from the calcining and filter chambers into a continuous melter, or into the final pot when in-pot melting is used. The continuous melter is made of Corronel-230 when making phosphate ceramics with PW-2 type wastes or borosilicate glasses with other wastes, such as the reference PW-4m waste. Platinum is used for the continuous melter when making phosphate ceramics with PW-4m waste. Because of the weak structural strength of the melter materials at the processing temperatures, the melter is supported by a ceramic skeleton within the melter furnace.

The melter contains internal thermocouples for temperature and melt level information, and a sight glass for direct viewing. The melter is discharged batchwise through a bottom outlet freeze-valve tube to the receiver-pot below whenever the melt level reaches about half the heated height of the melter.

The melter is heated by an electrical resistance-heated furnace which contains the ceramic skeleton for supporting the melter. The freeze valve tube is heated by a separate, small electrically heated zone at the bottom of the furnace. Cooling of the freeze valve is done using air around the freeze valve tube within the freeze valve furnace.

Receiver-Storage Pots

The pots for continuous spray melting are the same as those used for pot calcination except they are made of mild steel and

have no baffle. The removable thermocouples in the stainless steel pot thermowell are used to measure the level of the solid (although with sufficient operating experience, operation without thermocouples is possible).

The pot is mounted in a rotating storage rack which is part of a water-cooled, water-filled tank for cooling the pots. The rack is rotated as new pots are needed and filled pots are removed to the test and weld station (see Section 8.5).

In-Pot Melting Pots and Furnaces

When in-pot-melting is used, the continuous melter is deleted and the powdered calcine and granular melt-making flux is fed directly into the pot. Because of melting capacity limitations, a conceptual design has been produced in which several in-pot melting pots are used for one calciner, with the calcine and melt-making flux being distributed to each pot through the rotating valve assembly shown. The rotating valve may be operated by stopping for programmed time periods at each port, or by continuous rotation using varying rpm for part or all of each rotation. Isolation valves at each port maintain the system sealed during pot change-out.

Stainless steel pots are used for in-pot melting. The pots are placed in multiple, retractable furnaces arranged in a circle below the single calciner. To allow for pot cooling and change-out time requirements, one more pot system is desired than is needed for in-pot melting only. Each furnace moves outwardly away from the circle of furnaces during pot change-out time. The five furnaces and pot shown in the design concept are believed to be about the maximum number which can practically be associated with one calciner. Each furnace is electrically heated and air cooled in six zones as with pot calcination.

Solids Addition System

When in-pot-melting is used, or when a nonplatinum, continuous melter is used, or when sulfate-containing PW-2 waste is being processed, a system for continuous addition of granular melt-making solid flux is needed. Designs for this system are not shown in the design concept, but it is assumed that conventional, commercially available systems which are modified for this service, can be used.

8.3.2 Conceptual Cell Layout*

The conceptual cell arrangement for the spray solidification equipment using continuous melting is shown in Figure 8.6. One spray solidifier, one fill rack holding four pots, and one pot welding and testing station are included in one cell. Several viewing windows and manipulators are used for control. Primary control is from a control room remote from the cell.

New pots are transferred into the cell through a transfer mechanism and are then handled with an in-cell crane. Pots are stored in a storage rack while waiting to be used. Pots are placed in the water-cooled, four-pot rack for filling.

After filling, the pots are covered and are capped and removed to the adjacent pot weld and test station. The partition between the pot test station and the solidifier, and the pot testing area are similar to those for the pot calciner.

The solidifier feed tanks and vapor scrubber are in the same cell as the high level waste concentrator. Where interim aqueous storage is used, an additional waste concentrator, condenser, and calciner feed tank are required (but are not shown in the design concept). Also, for interim aqueous storage, three or more large tanks are required (one for receiving,

* The design concepts received significant contributions by and were drawn by D. H. Siemens, Battelle-Northwest.

FIGURE 8.6. Conceptual Cell Arrangement for Spray Solidifier with Continuous Melter

possibly one or more which are full of waste, one being emptied for waste solidification, and one spare). For solidification, one feed makeup and one feed tank are shown. Each of these tanks is arbitrarily sized for about two days' holdup. Chemical adjustments to the waste are added to the feed makeup tank.

The conceptual cell arrangement for the spray solidification equipment using in-pot melting is shown in Figure 8.7. The concept is shown with five heating and cooling furnaces which have the total melting capacity of four furnaces on a full-time basis.

8.3.3 Equipment Scale-Up

Scale-up and other related considerations for the spray solidification processes with the two reference waste compositions are presented in the following discussions.

Feed Atomization System

The high level aqueous waste which is fed to the spray calciner must be atomized into fine particles. Atomization by internal-mixing pneumatic atomizing nozzles is satisfactory, whereas atomization by external-mixing pneumatic atomizing nozzles has not been satisfactory.⁽¹⁰⁾ (See Section 4.2.5) The pattern of the spray relative to the geometry of the calciner should be such that the spray pattern should not contact the calciner walls before the spray has travelled approximately two feet or more. Proper performance of the atomizing nozzle is one of the key factors in satisfactory operation of the calciner. The atomizing nozzle, which is relatively inexpensive should therefore be made removable (removable by means of remote maintenance) in event of failure. In addition, because solids in the waste may plug the atomizing nozzle, provisions for in-line nozzle cleaning are required, such as the remotely operated clean-out needle used in the WSEP.

Atomization has been successfully accomplished using air. Although atomization with steam has not been done successfully

FIGURE 8.7. Conceptual Cell Arrangement for Spray Solidifier with In-Pot Melting

(due to calcining at the nozzle tip and to pulsing flow caused by condensation), and requires additional development, the use of steam would decrease the noncondensable gases in the off-gas system. Other gases, such as oxygen or nitrogen, could also be considered for atomization if some benefit resulted.

Because the pneumatic atomizing nozzle would normally be the internal mixing type, a plug in the nozzle could result in backup of radioactive waste into the "cold-side" of the atomization system. Consequently, some safety features must be built into the nozzle and feed system to prevent such an occurrence. In WSEP, controls were provided to automatically shut off the feed pump if the atomizing gas pressure exceeded a preset value.

The quality of atomization affects significantly the capacity of a spray calciner for two reasons: (1) the diameter of the atomized mist particles strongly controls the amount of vaporization and calcining accomplished in a given system, and (2) the amount of turbulence in the calciner as caused by the atomizing nozzle significantly affects the convective heat transfer from the chamber walls. With external-mixing nozzles, the central core of the spray pattern (which contains most of the liquid flow) is composed of particles too coarse to be completely calcined in 7 feet of calcining chamber length. The added length required to accomplish the calcining capacity with external-mixing nozzles has not been determined. The overall gas flow rate through the calciner chamber has a nonturbulent Reynolds number (in the order of 1000). However, eddy currents caused by the ejector-like action of the atomizing nozzle are sufficient to cause a high degree of turbulence and therefore relatively high heat transfer rates, at least in the vicinity of the feed nozzle. For distances three to six diameters (of the calcining chamber) downstream from the feed nozzle, the heat transfer rates have been shown to be about 70% of those in the first three diameters. (15)

A key limitation to the ultimate capacity of the spray calciner may well be with scale-up of the atomizing nozzle. Kaser⁽¹⁶⁾ found that larger nozzles required a significantly higher ratio of atomizing gas flow to liquid flow than smaller nozzles for the same quality of atomization. With the size of nozzle used in WSEP, a volumetric ratio of air (at room conditions) to waste of about 750 gave satisfactory atomization for operation of the calciner. Under these conditions the mass median particle size was approximately 60 micrometers and the maximum particle size was about twice that diameter.⁽¹⁰⁾ Although it is not fully established, this quality of atomization appeared to be necessary for satisfactory operation of the calciner. On the other hand, a larger-sized calciner should be operable with lower quality atomization. Alternatively, designs which incorporate the use of multiple small nozzles might be considered for development. Nozzle and calciner designs should be checked for more precise determination of capacity characteristics with full scale testing before radioactive operations.

Heated Calcining Chamber and Furnace

The capacity of a given calcining chamber depends upon waste composition, atomization quality, and furnace operating temperature. The ultimate capacity in WSEP was defined as the feed rate above which deposits of undried waste adhered to and built up on the chamber walls. This ultimate capacity represented an exit temperature of the vapors and calcine of about 150 to 200 °C. However, a preferred design basis is a minimum exit temperature of about 250 °C.

Because the heat load varies somewhat with vertical position of the calcining chamber, the furnace surrounding the chamber should have a separate heating zone for at least the top two to three feet of the chamber. The furnace operating temperature can be at the highest practical temperature which will

not cause excessive corrosion, volatilization of normally "non-volatile" constituents, or sintering of the calcined waste to the chamber walls. For PW-4m waste with no melt-making additives as used with borosilicate flowsheets, this temperature is probably in the range of 900 to 1000 °C, and is likely limited by corrosion or by volatilization of alkali metal oxides. For the PW-4m waste, phosphate-based flowsheet and the PW-2 waste flowsheet with melt-making additives as used with a continuous melter, the maximum temperature would be about 720 °C as limited by the stick point (sintering point) of about 750 °C. Net heat rate requirements for the process are about 1 kilowatt for each liter per hour of aqueous feed rate.

Transfer of heat from the calciner walls to the atomized waste is primarily by convection, with some contribution from radiation. Consequently, the capacity of a calciner, with other factors constant, is approximately proportional to the heat transfer area and to the temperature difference between the chamber walls and the particles and vapors. In WSEP where the heat transfer area was 21 square feet, the wall temperature was 700 °C, and the average vapor temperature was about 300 °C, the normal operating capacity of the calciner was approximately 16 liters per hour of aqueous feed. From the WSEP information, the calciner sizes shown in Figures 8.4 and 8.5 were developed. The internal dimensions of the WSEP calcining chamber, 13 inches in diameter by 6 feet long, are believed to be the smallest practical for any low capacity.⁽¹¹⁾ As an option, the spray calciner could be operated at 900 °C wall temperature when converting the PW-4m waste to borosilicate glass, with the resultant heat transfer area requirement conservatively reduced to approximately 25 square feet, or just slightly greater than that in WSEP. However, operation of the larger sized calciner at a lower temperature was selected for this study.

The extent to which the diameter of the spray calciner can be increased with essentially no decrease in capacity/unit of heat transfer area is not known. Although it has not been demonstrated beyond a diameter of 1.5 feet,⁽¹⁵⁾ the capacity relationships are believed to hold at least up to a diameter of 3 feet.

A device for rapping the upper section of the calcining chamber every 1 to 10 minutes is required to dislodge calcine deposits. In WSEP, a free-piston, air-operated vibrator mounted on top of the calciner performed the function successfully, although frequent failures of the vibrator did occur.

Off-Gas De-entrainment System

The calcine from the heated calcining chamber is a powder with a mean particle diameter of about 60 micrometers. These particles are sufficiently fine that good de-entrainment must be performed to prevent most of the particles from entering the off-gas system. The de-entrainment can be performed by dry filtration or by other devices such as a cyclone. Sintered stainless steel filters are generally preferred over cyclones in that they provide a higher particle removal efficiency for the pressure drop incurred, and they permit ready discharge of the filtered solid back into the chamber where the dust originated. A total filter area of 1 to 2 square feet per liter/hr of aqueous feed to the calciner is required to keep the pressure drop at levels of 3 to 10 inches of water. Sintered stainless steel filters with a mean pore size of 65 micrometers were used satisfactorily in the WSEP. A backup reinforcing screen which is integral with the sintered metal filter is recommended for added structural strength. Filters of sintered fibrous stainless steel and tight, Dutch-twill weave wire mesh should also be satisfactory, based on pilot-scale tests.⁽⁹⁾

The filters must be cleaned on a frequent basis. In WSEP, cleaning was done by periodic (every 1 to 5 minutes) short

pulses (0.5 to 1.5 seconds) of air or superheated steam (at 20 to 50 psig) directed backwards through the filters. To minimize the reduction in vacuum in the calciner during blowback, the blowback should be done on one-fifth to one-tenth of the filters at any one time. If the geometry of the blowback system is similar to that of a gas ejector venturi such as used in WSEP and in the design concept in this study, more efficient use of the motive blowback gas can be accomplished by using the blowback to pump filtered off-gases backwards through the filters.

Continuous Melter and Furnace

The small amount of residual nitrate and water in the powdered calcine from the spray calciner must be volatilized and the powder must be heated to form a melt in the continuous melter. The capacity of a continuous melter is proportional to the heat transfer area of the melter walls, but specific scale-up factors have not been experimentally determined. The relative amount of heat transferred to the melt with the WSEP melter by conduction and convection to and through the melt, and that transferred by radiation from the upper walls of the melter to the surface of the melt are not known specifically. However, both transfer modes are believed to be significant. An increase in furnace temperature will increase the heat transferred by radiation more than by the other two modes because of the effect of the temperature to the 4th power with radiation.

In WSEP, the melter had 1.0 ft^2 of heat transfer surface below the melt level and 1.7 ft^2 above the melt level. Under WSEP operating conditions, the maximum melting capacity was 2.2 liter/hr of melt for PW-2 and 2.6 liter/hr of melt for PW-4m, as determined during design verification tests.⁽¹⁷⁾ During the WSEP demonstrations, these capacities were not obtained because the different conditions in the calcination step caused the calciner to be limiting at lower equivalent melting rates. For the

reference PW-2 waste, a melting capacity of 16 liters/hr of melt is needed, thereby requiring about 20 ft^2 of heat transfer surface. For PW-4m, a melting capacity of 12 liters/hr of melt is needed, therefore requiring 12 ft^2 of heat transfer area.

The sizes of the heat transfer area of the platinum melter selected for this study were shown in Figure 8.4. The maximum operating volume (taken at 50% of heated height) is 93 liters for PW-2 and 49 liters for PW-4m. Where the melter content can exceed the total usable volume in the pot (e.g., a 6-inch pot holds only 45 liters) the maximum operating volume in the melter should be limited to the pot volume during operation. The maximum volume of melt in the melter should also be no greater than that which can be cooled in an emergency if the melt must be held in the melter for an extended time period. This emergency cooling can be accomplished by air purging around the melter, or also possibly by the continuous addition of water into the melter.

For the continuous nonplatinum melter which can be used for processing PW-4m waste using the same glass composition as with the in-pot melting schemes, the emissivity of 0.8 (versus 0.15 for platinum) significantly improves the heat transfer from the furnace to the melter. The calculated radiant heat transfer coefficient (h_r) is about $17 \text{ Btu/hr}(\text{ft}^2)(^\circ\text{F})$ at 1175°C furnace temperature (and 75°C temperature difference) for the platinum melter, versus 65 for the nonplatinum melter at 1100°C furnace temperature (and 25°C temperature difference). The ratio of these calculated overall heat transfer coefficients is 3.8. The melting requirement for the nonplatinum melter processing PW-4m waste is 7.3 liters/hr of melt, which requires a heat transfer area of only 2 ft^2 , or less than that in WSEP. The size of the heat transfer area of the nonplatinum melter was selected to be 10 inches in diameter

by 14 inches high. This size will provide a heat transfer area of about 3 ft² (or about 50% greater than that calculated to be necessary), but the larger size is preferred to permit easier nozzle entry and manipulation around the melter. For processing PW-2 waste into a phosphate ceramic with a nonplatinum melter, the melter size selected was taken directly from the heat transfer area required. (See Figure 8.4)

Discharge from the melter can be continuous through an overflow weir system or batchwise through a freeze valve drain. In WSEP demonstrations, continuous discharge of melt at the slow rate of about 0.5 liter/hr required maintaining the receiver pot at temperatures near the melting point of the waste to eliminate buildup of stalagmites in the receiver pot. This technique, which requires zone heating of the pot, is not used in the conceptual design. Discharge of melt at the higher rates of 3 to 7 liters/hour (accomplished by thawing the frozen melt in a freeze valve drain which then permitted the batch of molten waste in the melter to drain rapidly) could be done in WSEP into pots which were unheated and uncooled.

The melter discharge system to the receiver pot must provide for nonspattering and nonwavering flow of melt into the pot without significant effects on process vacuum. A continuous slow flow of melt could be used but would require a zone-heated and cooled pot furnace. Batch discharge of melt eliminates the need for a pot furnace and is used in this design concept. At least some technique is needed to plug the drained melter to permit operating the melter and calciner while the pots are being changed. Nonmechanical schemes for batch discharging such as sealed syphons or overflows or freeze valves are recommended because they avoid the complexities associated with the structural and corrosion requirements with a mechanical shutoff control.

Net heat rate requirements into the process in the melter are approximately 3 kilowatts for each liter/hr of melt

formed.^(8,9) The furnace for heating the platinum melter and its freeze valve should have the capability of operating continuously (as well as with occasional shutdowns) at temperatures up to about 1250 °C. The furnace for heating the non-platinum melter and its freeze valve should have similar capability at temperatures up to about 1150 °C.

Receiver-Storage Pots and Pot Furnaces

Scale-up information for spray solidifier pots is presented in Table 8.2. The maximum allowable heat rate for the reference PW-2 waste based on a centerline temperature of 700 °C* in air storage is 16.5 kilowatts in a 20-inch diameter pot at 1.7 years out of the reactor to meet the proposed salt mine limits. To process waste from 5 tonnes/day of fuel, one pot is required per day. To solidify at 6 months, only 12-inch-diameter or smaller pots can be used. This information applies to using both the continuous melter and in-pot melting.

To solidify PW-4m waste using the continuous melter with the phosphate system, out-of-reactor ages of 0.5 to 2.0 years are permissible for 6- to 12-inch pots respectively. If the proposed salt mine limit were to be used, the maximum size pot that could be used is a 10-inch pot which contains 19.3 kilowatts at the time of solidification. Unless the wastes are made more dilute, the borosilicate melts used are smaller in volume than the phosphate melts, and pots for borosilicate melts must be smaller than those for phosphate melts if processing occurs at the same out-of-reactor time. For in-pot melting with the borosilicate system, five pot melting lines are required to provide the melting capacity for 6-inch diameter pots; only one line would be required for 14-inch diameter pots (not shown in Table 8.2).

* The 700 °C limit applies to PW-2 sulfate-containing wastes only. A limit of 900 °C is used for the PW-4 sulfate-free waste

TABLE 8.2. Spray Solidifier Conceptual Design Scale-Up of Pots

	Phosphate Melts										Borosilicate Melts					
	PW-2 Waste (Continuous Melter or IPM)					PW-4m Waste (Continuous Melter)					(Continuous Melter or IPM)					
	6	8	10	12	16	20	24	6	8	10	12	6	8	10	12	12
Feed to Solidifier, t/Te	694	694	694	694	694	694	694	446	446	446	446	130	130	130	130	130
Feed to Solidifier, t/hr	145	145	145	145	145	145	145	93	93	93	93	27	27	27	27	27
Total Melt to Pots, t/hr	16.4	16.4	16.4	16.4	16.4	16.4	16.4	11.9	11.9	11.9	11.9	7.3	7.3	7.3	7.3	7.3
Melt to Each IPM Pot, t/hr	1.7	3.0	4.7	6.8	10.6	(16.7)	(24.1)	--	--	--	--	1.7	3.0	4.7	6.8	6.8
Volume Solid Waste in Pot, t	45	79	124	178	278	437	632	45	79	124	178	45	79	124	178	178
Volume Solid Waste in Pot, t/T _{te}	78.5	78.5	78.5	78.5	78.5	78.5	78.5	57	57	57	57	35	35	35	35	35
Tonnes/Pot	0.58	1.00	1.58	2.27	3.54	5.57	8.06	0.80	1.38	2.18	3.12	1.30	2.25	3.54	5.09	5.09
Pot Fill Time, Continuous Melter, hr	2.8	4.8	7.6	10.9	17.0	26.7	38.7	3.8	6.6	10.4	15.0	4.79	10.8	17.0	24.4	24.4
Pot Fill Time, In-Pot Melting	26.2	26.2	26.2	26.2	26.2	26.2	26.2	--	--	--	--	26.2	26.2	26.2	26.2	26.2
Pots/day	8.6	5.0	3.2	2.2	1.4	0.90	0.62	6.3	3.6	2.3	1.6	3.8	2.2	1.4	0.98	0.98
Pot Lines In-Pot Melting	10	6	4	3	2	1	1	--	--	--	--	5	3	2	2	2
Air-Cooled Pot Storage (a)																
Max. Heat Rate at Solidification, kW/Pot	12.0	13.0	13.9	14.6	15.6	16.5	17.1	15.5	18.2	19.3	20.1	15.5	19.3	20.4	21.4	21.4
Min. Age at Solidification, yrs(d)	<0.3	<0.3	0.5	0.7	1.1	1.7	2.3	0.5	0.9	1.4	2.0	1.0	1.5	2.2	3.0	3.0
Maximum T _p , °C	700	700	700	700	700	700	700	850	900	900	900	820	900	900	900	900
Maximum T _w , °C	380	345	320	300	275	253	235	427	405	375	351	427	418	383	375	375
Water-Cooled Pot Storage (b)																
Max. Heat Rate at Solidification, kW/Pot	22.0	22.0	22.0	22.0	22.0	22.0	22.0	29.4	29.4	29.4	29.4	31.9(e)	31.9(e)	31.9(e)	31.9(e)	31.9(e)
Min. Age at Solidification, yrs. (d)	<0.3	<0.3	<0.3	0.4	0.8	1.2	1.8	<0.3	0.4	0.8	1.3	<0.3	0.8	1.4	2.0	2.0
Maximum T _p , °C	700	700	700	700	700	700	700	900	900	900	900	900	900	900	900	900
Maximum T _w , °C	100	100	100	100	100	100	100	100	100	100	100	100(g)	100(g)	100(g)	100(g)	100(g)
Air or Water-Cooled Storage																
Heat Rate at 5 yrs, kW/Pot	0.52	0.90	1.4	2.0	3.2	5.0	7.2	1.9	3.4	5.3	7.6	3.2	5.5	8.7	12.3	12.3
Heat Rate at 10 yrs, kW/Pot	0.33	0.57	0.90	1.3	2.0	3.2	4.6	1.2	2.0	3.2	4.6	1.9	3.3	5.3	7.6	7.6
Age at 4 kW/Pot, yrs (c,d)	0.7	1.2	2.0	2.7	4.0	6.5	14	2.5	4.2	7.3	13	3.9	7.5	17	31.5	31.5

Shaded area presents data for pots containing greater heat generation rates at 10 years cooling than the proposed limit for salt mine storage.

a. For air cooling using natural convection and radiation, limiting the molten core to half the pot radius.

b. For water cooling with batch melt dumping using the continuous melter. The molten core is limited to half the pot radius for PW-2 and PW-4m.

c. Limit for proposed salt mine is 500 W/ft of pot or 4 kilowatts total for an 8-ft fill.

d. Total time out-of-reactor.

e. A frozen wall will exist in the pot with air cooling in the pot furnace.

f. Platinum melter required here; for all other cases with continuous melters, platinum or nonplatinum melters may be used.

g. For the in-pot melting system, the wall temperatures could be as high as about 600 °C in ambient air until the pots are inserted into water.

The pots must be cooled during filling from the continuous melter to remove the sensible heat and heat of radioactive decay (12 to 20 kilowatts/pot) in the pot and its contents, to provide a wall temperature which is reasonably low for structural and handling purposes (to as high as about 425 °C), plus the 12 to 20 kilowatts of radioactive decay heat in the waste (up to about 300 W/liter of waste). Filling at high rates without heating could be done without internal pot thermocouples, except for a thermocouple near the top of the pots to determine when the pots were filled. Any obstructions such as thermocouples inside the top of the pots should be minimized to prevent premature buildup of waste at that point. A partial process seal which connects the pot to the continuous melter and controls the access by cell air is desirable to minimize exposure of the melt to cell air. A tight process-type sealed connection would also be desirable but is believed not to be necessary.

For in-pot melting, heat must be transferred to the solids on the surface of the melt by radiation from the pot walls and by conduction up through the melt. Therefore, the melting capacity for in-pot melting is proportional to the cross-sectional area of the pot plus the portion of the circumferential area of the pot below the melt level which provides heat into the melt. For 8-inch-diameter pots and the pot furnace at 900 to 950 °C, the melting capacity in WSEP was estimated to be about 3 liters/hr of borosilicate melt. Based on the relative cross-sectional areas, the melting capacity of various pot sizes ranges from 1.7 liters/hr of melt for a 6-inch-diameter pot to 24.1 liters/hr for a 24-inch-diameter pot. With these capacities, the numbers of pot lines shown in Table 8.2 were developed.

A multiple-zoned furnace is required to provide both heating and cooling for in-pot melting with six zones representing

an acceptable number of zones for a 10-foot long pot. The net process heating requirement in each zone is similar to that for a continuous melter, and the cooling requirement is the same as that for the pot when using a continuous melter with a heated pot. One internal pot thermocouple near the centerline of each zone is required to permit control of temperatures in individual furnace zones. A good process seal is required between the calciner and the pot to permit venting of the process gases generated in the pot through the calciner.

Flux Addition System

A system for adding melt-making flux to the pot is required for the in-pot melting technique, for the continuous nonplatinum melter when making borosilicate glass, and for the continuous melter when PW-2 waste is being processed. The borosilicate or phosphate fluxes should be in a nondusting, free-flowing form which is suitable for continuous or frequent batch metering into the pot. Also, the particle size should be small enough to provide rapid melting in the pot. In WSEP, a granular frit of particle size +10 to -4 mesh was used satisfactorily.

8.3.4 Materials of Construction

Materials of construction that can be considered for the spray calciner include Hastelloy X, 310 stainless steel, Corronel 230, and a special 50Cr-50Ni alloy. Spray chambers constructed of Hastelloy X and of 310 stainless steel performed satisfactorily during nonradioactive pilot plant operation and should be used when operating in the temperature range of 700 to 1000 °C. Type 310 stainless steel was used in the WSEP spray calciner at approximately 700 °C with no appreciable corrosion of the unit noted. The off-gas piping and filters associated with the calciner, which are exposed to temperatures less than 500 °C, should be made of 304L stainless steel. Type 316L stainless steel can be used in some places but is generally inferior to Type 304L.

Of all the metals tested, only platinum, platinum-gold or platinum-low-rhodium alloys (platinum and platinum-0,5 wt% rhodium was satisfactorily used in WSEP) have shown the necessary corrosion resistance to phosphate melts at temperatures up to 1300 °C. Corrosion rates for platinum are less than 0.001 in./yr as long as nonstandard reducing conditions are eliminated. Heating platinum in contact with silicates or phosphates under reducing conditions can lead to rapid failure. Although platinum has been operated for up to 16,000 hours in some tests,⁽¹²⁾ failure or serious damage due to corrosion or excessive creep rates has occurred in as short a time as less than 1000 hours of service.^(9,13) (See Section 4.3.6.) Therefore, the long-term suitability of platinum under high temperature conditions under stress remains to be confirmed.

For design purposes, indications are that at 1200 °C, the stress in the platinum should not exceed 50 to 100 psi.⁽¹⁴⁾ Platinum linings inside heat-resisting structural materials such as Hastelloy X or ceramics may be considered as melter materials for phosphate melts.

Less exotic materials can be used for continuous melters using low-temperature phosphate melts (e.g., with PW-2 waste) or borosilicate melts at temperatures up to about 1100 °C, although additional testing is recommended. Corronel 230, and possibly Type 310 stainless steel or an alloy of 50% chromium-50% nickel are suitable for the reference borosilicate glass formulation with PW-4m waste. Laboratory tests have shown corrosion rates at 1100 °C for the reference borosilicate formulation with PW-4m rates to be 0.0036 and 0.07 in./yr for Corronel 230 and Type 310 stainless steel, respectively; at 1050 °C, corrosion rates of Corronel 230, 50% chromium-50% nickel alloy, Type 310 stainless steel, and Nionel were 0.0024, 0.01, 0.032, and 0.034 in./yr, respectively.⁽²¹⁾ In general, maximum

corrosion rates occurred at the melt-vapor interface. Alloy Corronel-230 also appears to be suitable for the reference phosphate ceramic formulation with PW-2 waste up to about 1000 °C, with corrosion rates of 0.13 in./yr.⁽¹⁷⁾ In addition, Inconel is used in the French pot vitrification scheme and an alloy similar to Type 310 stainless steel was used in the English FINGAL process at 1050 °C. All of these materials are very weak at the required operating temperature, and require special designs for structural support.

Mild steels are suitable materials for melt receiver-storage pots when the wall temperature does not exceed about 650 °C for periods of a few days. The use of mild steel is not only limited by the corrosiveness of the molten or solidified waste at higher temperatures, but also by air oxidation. Air oxidation of a mild steel receiver during filling with melt product at 600 to 700 °C was reduced in WSEP by a factor of about 5 by purging the space between the pot and the furnace with nitrogen. Stainless steels of the 300 series (such as 304L) are suitable materials of construction when temperatures are as high as 950 °C for a few days. For in-pot melting where temperatures up to about 1050 °C are encountered, Type 310 stainless steel is suitable.

8.4 PHOSPHATE GLASS SOLIDIFICATION

Design considerations for phosphate glass solidification are presented in this section, and are based on information developed in Sections 4 through 7 and 8.8.

The basic equipment required for the phosphate glass solidification process^(13,18) includes: (a) a continuous evaporator, (b) a melter feed system, (c) a continuous melter and furnace, (d) a melter condenser and condensate receiving tank with PW-2 wastes, and (e) a receiver-storage pot.

8.4.1 Conceptual Design*

A design concept for the phosphate glass solidification equipment is shown in Figure 8.8 and discussed in the following sections.

Evaporator

A commercially-available, horizontal, cylindrical wiped film evaporator which tapers to a slightly smaller diameter at its outlet was chosen for this study. It is believed that other types of evaporators would also be suitable, but this type has had some testing for this service. A concentrically mounted shaft with four blades provides distribution and wiping of feed solution and concentrate onto a steam-heated surface. Off-gas vents are arranged to permit vapors to flow concurrently with the feed stream.

Liquid waste plus additives entering the evaporator are spread into a thin film; the concentrate flows axially, filmwise from the feed end "down-hill" to the concentrate product end. The concentrate end of the evaporator contains a bottom-discharge line and centrifugal de-entrainment discs from which the vapors flow to an overhead vapor vent.

Melter Feed System

The concentrate drain line from the wiped film evaporator (the melter feed line) has a steam-heated jacket to maintain the concentrate at the evaporator concentrate temperature ($\sim 140-160$ °C), thereby maintaining the concentrate in a fluid, semi-pastelike state for feeding the melter. A screw feeder inside the melter feed line is used to deliver concentrate to the melter. Although the screw feeder concept proposed here is simple in principle and is expected to perform satisfactorily,

* The design concepts received significant contributions by, and were drawn by D. H. Siemens, Battelle-Northwest.

Wiped Film Evaporator	PW-2	PW-4m
Heat Transfer Area, ft ²	18	14
Diameter, in.	18	15
Length, ft	4	3.5
Material	Tantalum	Tantalum
Operating Temp., °C	~ 160	~ 150

Melter

Heat Transfer Area, ft ²	10	18
Diameter, in.	18	24
Height, in.	25	34
Material (melter & nozzles)	99.5% Pt	0.5% Rh
Thickness, in.	~ 0.1	
Furnace (melter & freeze valve)		
Type-Electric Resistance Power, kW	50	70
Max. Temp., °C	1300	1300
Normal Temp., °C	1250	1250
Off Gas Line Material	95% Pt - 5% Ir	
Heater Temp., °C	500	500
Melter Condenser Area, ft ²	50	100
Material	Nionel	
Melter Feeder System	Titanium except parts exposed to melter vapors are 99.95% Pt	
Material

FIGURE 8.8. Phosphate Glass Solidifier Conceptual Design

more development is required for it and for the solution feeder (where the denitrated concentrate enters the melter). At the melter end of the melter feed line, the concentrate flows through a water-jacketed and shielded platinum tube into the heated zone of the melter. Boiling water surrounding the feed line at this point removes heat picked up from the melter while maintaining the feed in a fluid state. The boiling water is refluxed by a condenser above the melter.

Continuous Melter and Furnace

The concentrated aqueous slurry from the evaporator flows into a continuous melter where the remaining volatile constituents are drawn off and the remaining constituents are converted to a molten glass. The melter and its furnace are similar to those for the spray calcination continuous melting system described in Section 8.3.1. The melter is constructed of platinum and is supported by a ceramic skeleton to compensate for the weak strength of platinum at the process temperatures. The melt is discharged batchwise through a bottom-outlet-freeze valve tube into the pot below whenever the melt level reaches about half the heated height of the melter.

The melter is heated by an electrical resistance-heated furnace which contains the ceramic skeleton for supporting the melter. The freeze valve tube has a separate electric heater and an air-cooling coil at the bottom of the main melter furnace. The vapors from the melter are routed through a platinum-5% iridium alloy tube to a process condenser. For sulfate-containing PW-2 waste the condensate is collected separately; for PW-4m waste the condensate is recycled to the denitrator. The melter vapor tube is heated to prevent condensation which increases corrosion and the tendency for scale build-up in the line.

Melter Condensate System

A separate condensate receiver tank is required when processing sulfate-containing PW-2 waste, in order to recover the volatilized sulfate separately. The recovered melter condensate--sulfate, nitric acid, water, phosphoric acid and recovered fission products--is collected in a receiver. The melter condensate must then be treated and disposed of as a separate waste by systems not shown in the conceptual design.

Receiver Storage Pots

The receiver-storage pots and the associated system are the same as those for the spray solidifier continuous melting system (see Section 8.3.1).

8.4.2 Conceptual Cell Layout

A concept for a cell arrangement for the solidification equipment, shown in Figure 8.9, is similar to that previously shown for the spray calciner continuous melter system. The solidifier, solidifier condenser and pot welding and test station are included in one cell. Several viewing windows and manipulators are used for improved operations. Primary control is from a control room remote from the cell.

New pots are transferred into the cell through a transfer mechanism and then are stored in racks prior to use. The pots are placed in the four-position rotating rack in the in-cell water-cooled water tank, and one pot is remotely moved into position below the melter. After a pot is filled, it is rotated away from under the melter while the next empty pot is positioned below the melter. The filled pot is covered and removed to the adjacent pot weld and test station, which is similar to that for the spray solidifier.

The solidifier feed tanks and vapor scrubber are located in the same cell as the high level waste concentrator. Where

FIGURE 8.9. Conceptual Cell Arrangement for Phosphate Glass Solidifier

interim aqueous storage is used, an additional waste concentrator, condenser, and solidifier feed tank are required (but are not shown in the design concept) (see Section 8.3.2). Also, for interim aqueous storage, three or more large tanks are required in a vault area (one for receiving, one being emptied for waste solidification, one spare, and possibly one or more for "dead" storage). For solidification, one feed makeup, one feed tank and one melter condenser (and one sulfate-containing condensate tank for PW-2 wastes only) are needed. Each of these tanks is arbitrarily sized for two day's holdup. Chemical adjustments to the feed are added to the feed makeup tank.

8.4.3 Equipment Scale-Up

Scale-up and other related considerations for the phosphate glass solidification process for the design capacity with the two reference waste compositions are presented in the following discussions.

Evaporator

A continuous evaporator is needed to concentrate the feed to a thick slurry to reduce the evaporative load in the melter. The evaporator must be able to handle corrosive liquids with viscosities up to about 50 poise and boiling points up to about 160 °C. Designs should be aimed toward providing a low hold-up volume, for minimizing the foaming, and for maintaining suspension of solids. In WSEP, an evaporator using a removable short-tube calandria and an external jacket was used. This evaporator performed reasonably well but it was not capable of maximum concentration and it had a moderately high hold-up volume. Nonradioactive studies during the WSEP program* showed that a wiped film evaporator has more beneficial characteristics to concentrate

* Tests were made with simulated phosphate glass waste fed at 40 liters/hr using a horizontal wiped film evaporator with 5 square feet of heating surface.

and denitrate phosphate glass feeds to thick viscous slurries than the calandria type used in WSEP,⁽¹⁹⁾ and a wiped film evaporator is used in this study. Although other types of wiped film evaporators may perform equally well in this service, a horizontal evaporator with rigid but adjustable-clearance metal blades was selected in this study, based on tests with that type of unit.

Because the wiped film evaporator operates with turbulent flow, high heat transfer rates are obtainable. In general, increasing the blade speed will increase rate of heat transfer, but a point will be reached when gain in overall heat transfer does not justify the increased power input.

Concentration factors across the wiped film evaporator of up to approximately 8 for the reference PW-2 waste, and 3.5 for the reference PW-4m waste, are considered to be practical, and are used in the sizing presented in Figure 8.8. The concentrate temperature will range from about 140 up to 150 °C for PW-2 and up to 160 °C for PW-4m waste. Viscosities will range up to about 50 poise.

Melter Feed System

The method of feeding the melter must have the capability of reliably pumping and metering small flow rates as low as 4 liters/hr of the thick slurry from the evaporator. The feeding system must keep the slurry near its boiling point to prevent excessive precipitation in the feed line, and it must keep the temperature below calcination temperature (about 170 °C) as the material enters the melter. In WSEP, concentrate was air-lifted from near the bottom of the evaporator to an elevated airlift pot from which most of the hot concentrate recirculated back to the evaporator. Part of the concentrate overflowed into the melter feed line. The concentrate in the melter feed line flowed by gravity several feet through a steam-jacketed pipe

into the melter. In the melter the concentrate flowed out of the jacketed tube and into the melter through a "cold finger" extending into the melter far enough so that the concentrate would not free-fall more than 8 to 10 inches to minimize spattering. The platinum cold finger, which was cooled by boiling and refluxing water in its jacket, is necessary to prevent calcination and plugging at the point where the concentrate enters the melter.

The airlift scheme used in WSEP (see Section 4.3.5) is not suitable for production use because of frequent plugs which formed at several points in the system. In WSEP, these plugs were removed by frequent use of built-in clean-out devices, drain valves, and flushes. In addition, the airlift scheme poses a limit to the degree of concentration which can be tolerated in the evaporator. Brief testing of a simple Archimedes screw in WSEP⁽¹³⁾ showed much promise and is the basis for its use in this study. Use of the screw as conceived here with no lift requirements together with the wiped film evaporator should provide for more stable melter operation, less sensitivity to changes in the evaporator operation, and more positive control.

Continuous Melter and Furnace

The net heat transfer requirements for the phosphate glass melter are 30 to 100% higher than those for the spray calciner-melter, primarily because of the added evaporation and denitration load. The desired freeboard above the melt level is also somewhat higher because of the foaming tendency in the melter. The actual heat load in the melter and thus the size of the melter is strongly dependent upon the degree of concentration performed in the denitrator-evaporator.

As with the spray calciner-melter, the capacity of a continuous melter is proportional to the melter wall area, but specific scale-up factors have not been determined (see Section 8.3.3).

Melter capacity determined in WSEP and at BNL was about 1.7 liters/hr of melt. The concentration factors achievable in the wiped film evaporator reduce the evaporation-denitration heat load in the melter by about 80% compared to that in WSEP thereby increasing the capacity of a given size of melter by approximately 40%. In the WSEP melter, evaporation and denitration accounted for about 50% of the net heat requirements.

For the reference PW-2 waste the melter described in Figure 8.7 was designed for a capacity of 10 liters/hr of melt, with a concentration factor across the melter at 1.5. The maximum operating volume (taken at 50% of heated height) is 30 liters of melt. For the reference PW-4m waste, a melting capacity of 18 liters/hr is required. The conceptual melter in Figure 8.7 has a maximum operating volume of 73 liters of melt. Where melter contents can exceed the total volume in the pot (e.g., a 6-inch pot holds only 45 liters), the maximum operating volume in the melter should be limited to the pot volume during operation. See added discussion in Section 8.3.3.

The furnace for heating the melter should have the capability of operating continuously at temperatures up to 1300 °C, similar to the furnace for the spray calciner melter. The net heat rate requirement is 4 to 7 kilowatts for each liter/hr of melt formed, depending upon operating conditions in the denitrator-evaporator.

The system for discharging from the melter to the receiver pot requires considerable attention in design. The same concept is used here as with the spray calciner melter: batch draining of the melter is accomplished through a separately heated and cooled freeze valve at the bottom of the melter. (See Section 8.3.3.)

Melter Condensate System

During processing of PW-2 waste where sulfate is present, separate recovery of the totally volatilized sulfate from the

melter off-gas is necessary. Therefore, a separate system is required for collecting the condenser melter off-gas vapors. This system consists of an absorber-condenser (for any waste) and a condensate receiver tank (for sulfate-containing waste only).

The sulfate-containing melter condensate is another waste stream which must be disposed of. Although not shown in this conceptual design, the suggested method involves decontamination of the condensate by vacuum distillation,⁽¹¹⁾ followed by incorporation into asphalt for disposal. During vacuum distillation, water and nitric acid, and sulfuric acid are distilled into separate streams, leaving a residue of phosphoric acid, fission products, and other salts. Sufficient decontamination of radionuclides from the sulfate-containing distillate is provided (by factors of 200 to 1000), to permit incorporation of the decontaminated sulfuric acid into asphalt for final disposal.⁽²⁴⁾ The nitric acid-water fraction and phosphoric acid residue may be recycled back to the waste system.

Receiver-Storage Pots

The container for receiving the molten glass and the system for the pots are similar to that for spray solidification continuous melting. Similarly, since batch discharge of melt is used, no furnace is required, and the pots can be cooled with air or water while being filled (as in this study).

Scale-up information for receiver storage pots and related equipment performance data are presented in Table 8.3. By limiting the radius of the molten core to half the pot radius and limiting the temperature of the molten core-solid interface to 700 °C, a total of 18 kilowatts of heat in PW-2 waste can be put into a 16-inch-diameter air-cooled pot. For PW-4m waste, the limit is 16.6 kilowatts for 12-inch-diameter pots. Larger pots could only be used if the proposed salt mine limit were relaxed.

TABLE 8.3. Phosphate Glass Solidifier Conceptual Design Scale-Up of Pots^(a)

	PW-2 Waste (Nominally, 20,000 MWd/tonne at 15 MW/tonne)						PW-4m Waste (Nominally, 45,000 MWd/tonne at 30 MW/tonne)					
	Pot Diameter, Inches						Pot Diameter, Inches					
	6	8	10	12	16	20	6	8	10	12	16	20
Feed to Solidifier, $\ell/\text{Te}^{(e)}$	610	610	610	610	610	610	443	443	443	443	443	443
Feed to Solidifier, ℓ/hr	127	127	127	127	127	127	92	92	92	92	92	92
Feed to Solidifier, ℓ/d	3050	3050	3050	3050	3050	3050	2215	2215	2215	2215	2215	2215
Evap. Conc. Factor	8	8	8	8	8	8	3.5	3.5	3.5	3.5	3.5	3.5
Conc. to Melter, ℓ/Te	75	75	75	75	75	75	128	128	128	128	128	128
Melter Conc. Factor	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Melt to Pot, ℓ/hr	10.4	10.4	10.4	10.4	10.4	10.4	17.7	17.7	17.7	17.7	17.7	17.7
Volume Solid Waste in Pot, ℓ	45	79	124	178	278	436	45	79	124	178	278	436
Volume Solid Waste in Pot, ℓ/Te	50	50	50	50	50	50	85	85	85	85	85	85
Tonnes/Pot	0.9	1.6	2.5	3.6	5.6	8.7	0.5	0.93	1.5	2.1	3.3	5.1
Pot Fill Time, hr	4.3	7.6	11.9	17.1	26.7	41.9	2.5	4.5	7.0	10.1	15.7	24.6
Pots/day	5.6	3.2	2.0	1.4	0.9	0.6	9.4	5.4	3.4	2.4	1.5	1.0
Air-Cooled Pot Storage: ^(b)												
Max. Heat Rate at Solidification, kW/pot	13.6	14.6	15.5	16.6	18.0	19.0	13.6	14.6	15.5	16.6	18.0	19.0
Min. Age at Solidification, yrs	<0.2	0.4	0.8	1.0	1.7	2.2	<0.2	0.7	1.2	1.7	2.8	3.3
Max. Interim Air Storage, T_E , °C	~850	~850	~850	~850	~850	~850	~850	~850	~850	~850	~850	~850
Max. Interim Air Storage, T_W , °C	385	357	335	320	300	280	385	357	335	320	300	280
Water-Cooled Pot Storage:												
Heat Rate at Solidification, kW/pot	26.5	26.5	26.5	26.5	26.5	26.5	26.5	26.5	26.5	26.5	26.5	26.5
Age at Solidification yrs ^(f)	<0.1	<0.2	0.3	0.7	0.9	1.7	<0.1	<0.2	0.6	0.9	1.6	2.5
Interim Water Storage, T_E , °C	~850	~850	~850	~850	~850	~850	~850	~850	~850	~850	~850	~850
Interim Water Storage, T_W , °C	100	100	100	100	100	100	100	100	100	100	100	100
Air or Water-Cooled Storage												
Heat Rate at 5 yrs, kW/pot	0.81	1.4	2.3	3.2	5.0	7.8	1.2	2.2	3.6	5.0	8.0	12.3
Heat Rate at 10 yrs, kW/pot	0.52	0.92	1.4	2.1	3.1	5.0	0.74	1.4	2.2	3.1	4.8	7.6
Age of 4 kW/pot, yrs ^(d,f)	0.8	2.0	3.0	4.0	6.5	17.5	1.6	2.9	4.5	6.7	15	27

Shaded area presents data for pots containing greater heat generation rates after 10 years cooling than the proposed limit for salt mine storage.

- Based on flowsheets presented in Section 7.0.
- For air cooling using natural convection and radiation, limiting the molten core to half the pot radius.
- For water cooling, limiting the molten core to half the pot radius.
- Proposed salt mine limit is 500 W/ft of pot or 4 kilowatts total for an 8-ft fill.
- Does not include melter condensate recycle.
- Total time out-of-reactor.

To process PW-2 wastes at 0.5 year cooling time or less limits the pot size to 8 inches in diameter; for PW-4m waste, the same pot size limit is less than 8 inches in diameter. The advantages of using the larger pots are evident in Table 8.3, especially if the proposed salt mine storage limits can be exceeded.

8.4.4 Materials of Construction

The materials of construction for the denitrator-evaporator which can be considered because of their corrosion resistance to the concentrates are Zircaloy-2, titanium and tantalum. Corrosion was no more than 0.03 in./yr at 140 °C for Zircaloy, 0.05 in. per yr for titanium, and less than 0.01 in./yr for tantalum.⁽⁷⁾ Titanium was used for the WSEP denitrator. At higher temperatures, such as those used in this study, tantalum or tantalum-clad materials should be used. The primary corrosion variables in the denitrator are the phosphate concentration and temperature. The corrosion rates increase significantly as the M/P ratio decreases below 1.0.

Platinum or high platinum alloys are required for melter construction. Platinum-5% gold alloy was the only alloy found to be as corrosion resistant as pure platinum. Platinum and its alloys are relatively weak structurally at melter temperatures, and potential creep failure must be considered in design. Platinum-0.5% rhodium alloy has lower creep rates than pure platinum by a factor of about 2, with very little decrease in corrosion resistance; therefore, it was used in WSEP and is recommended for this study.

Alternative metallic materials that have been studied for construction of melters include tantalum, Inconel 825, Carpenter 20, Hatelloys B and D, and stainless steel Types 304 and 310. All showed good corrosion resistance below 900 °C, but all were destroyed after 1 hour at 1050 °C. Platinum can be corroded by reaction of platinum, phosphorus and another metal. Combined

contact of platinum, stainless steel, and phosphate glass melts can result in severe localized intergranular attack and embrittlement of the platinum from the free phosphorus formed by reaction with the metals. Therefore, designs should eliminate the possibility for this ternary system to exist.

The only ceramic substitute for the expensive plating that has been tested and has shown good corrosion resistance to phosphate glass melts was alumina. However, poor resistance to thermal shock severely restricts the use of alumina or other ceramics for a phosphate glass melter.

The melter off-gas line must be resistant to the highly corrosive nitric acid sulfuric-nitric acid mixtures at temperatures up to 600 °C. Platinum-5% iridium alloy showed the greatest resistance to corrosion by sulfuric-nitric acid solutions. Platinum-5% iridium was used in WSEP, but platinum-5% rhodium alloy could also be used. Although not confirmed, nionel may also be suitable.

As with the spray calciner continuous melting system, mild steel is suitable for receiver-storage pots for phosphate glass as long as the long-term pot wall temperature is less than about 400 °C to prevent excessive air oxidation. In general, the corrosion rates for mild steel in phosphate glass at 500 to 700 °C are about 100 times less than the air oxidation rates at the same temperatures. For higher temperatures, stainless steel Types 304L or 310 are suitable as long as the wall temperature remains less than about 900 °C for short periods of time or less than about 750 °C for extended time periods.

8.5 INTERIM AQUEOUS STORAGE

For interim storage of aqueous waste the concentration of the waste is limited to about 850 liters/tonne for reference

PW-2 waste, based on WSEP laboratory experience. This concentration reduces the potential for significant precipitation of rare earth sulfates which can cake in the bottom of the storage tanks even with continuous agitation. For PW-4m wastes, the aqueous storage volume was selected to be 300 liters/tonne; at this volume, the 10 volume % solids are relatively "friendly" and easily suspended. The nitric acid concentration should not exceed about 4M for PW-2 and 1.5M for PW-4m to minimize corrosion rates to stainless steel storage tanks at a temperature of about 70 °C.

Extensive cooling must be supplied to remove the heat of radioactive decay. At 0.5 year cooling time, the concentrated waste contains 9.4 W/liter and 67 W/liter for PW-2 and PW-4m wastes, respectively. The value for PW-4m waste is two times greater than the maximum used in the WSEP tests where cooling was done by a jacket or coil in a 3.5-foot diameter tank. It is believed that large quantities of the PW-4m aqueous wastes can be cooled with practical but extensive tank and cooling system designs. However, this must be confirmed. There should be no problem in cooling the PW-2 reference waste at the proposed concentration, but the storage volumes are quite large.

To maximize the capacity of the solidification equipment in the conceptual design, the interim stored waste is reconcentrated to smaller volumes before the waste is solidified. An additional evaporator similar to the high level waste evaporator is used to preconcentrate the waste before solidifier feed makeup. (However, this evaporator and its associated auxiliary equipment and tankage are not shown in the conceptual designs.) For this study the waste is reconcentrated to the same volume as without interim aqueous storage, or 500 liters/tonne for PW-2 waste and 130 liters/tonne for PW-4m waste.

For an example case with 2 years aqueous storage, six tanks might be selected with a capacity of 0.5 year each: one filling, one emptying, three in "dead" storage (i.e., tanks full of waste with no filling or emptying), and one spare. Interim storage time is taken as filling time plus dead time. Total volume of all tanks, allowing 20% freeboard, is 1,150,000 gallons for PW-2 and 410,000 gallons for PW-4m waste. For a similar example with 5 years storage, 13 tanks might be selected (including two spares) each with 0.5 year storage. The total volume of these tanks is 2,500,000 gallons for PW-2 and 880,000 gallons for PW-4m. The maximum cooling load for each tank is about 4 megawatts for the PW-2 and 10 megawatts for the PW-4m reference wastes. Total cooling load for PW-4m waste is about 34 megawatts for 2 years storage and 47 megawatts for 5 years storage. For PW-2 wastes, these values are about 15 and 21 megawatts, respectively.

The interim aqueous storage concept selected for use in the cost analysis is that developed at ORNL, using a modification of existing "permanent storage" techniques.⁽²⁵⁾ In this concept, the acid wastes are stored in tanks grouped around three sides of an operations building that contains many of the major equipment items of the cooling and ventilation systems. A cooling tower and pumps, an emergency water storage tank, a water surge tank, and a stack (and associated fans) are also provided.

The tanks are similar in design to those in use at the Savannah River Plant (Figure 8.10). These tanks are cylindrical in shape, with a diameter-to-height ratio of 3; are made of 1/4 to 2-inch-thick stainless steel plate; and are housed in stainless steel-lined, reinforced-concrete vaults, with 2 to 4-feet-thick walls that are buried under about 10 feet of earth.

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FIGURE 8.10. Conceptual Aqueous Waste Storage Tank

The occurrence and severity of leaks are determined by monitoring for both liquid and airborne radioactivity in the 2-1/2 foot, air-purged annulus. The tanks have stainless steel-lined, internal columns for support, and are equipped with water coils for cooling the tank contents to below 70 °C. A water-cooled condenser, used to handle the cooling load from the total tank farm, is located in the operations building (Figure 8.11) to provide a secondary means for heat removal. Steam produced from self-boiling wastes during emergencies is vented to this condenser through an off-gas header in the top of the tank. Air, which is swept through the vapor space in each tank during normal operation at the rate of about 600 cfm to remove electrolytic hydrogen, is likewise vented through the off-gas header and filtered before discharge. Temperature, density, and liquid level of the tank contents, the concentration of hydrogen in the vapor space above the liquid, and the pressure inside the tank are monitored.

The water from the cooling coils is passed through external heat exchangers, where the heat is transferred to a secondary water-cooling circuit and then recycled through a 250,000-gallon surge tank to the tank coils. Heat is removed from the secondary circuit by passing the water through an induced-draft cooling tower.

The waste is transferred through a diversion box from the processing plant to the tank farm for storage and back. Access ports in the tanks provide for introducing sluicing jets and pumps for transferring the wastes.

8.6 INTERIM SOLID WASTE STORAGE

The design concept used for storage of solidified waste is basically that developed at ORNL⁽²⁵⁾ and is shown in Figure 8.12. The solidified waste pots are stored in a water basin under

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FIGURE 8.11. Operations Building for Conceptual Aqueous Waste Storage System

FIGURE 8.12. Concept of Interim Solids Storage Facility

about 12 feet of water to provide shielding and cooling. The water from the basin is recirculated through an external heat exchanger which is cooled by secondary cooling water that is cooled in a cooling tower. A portion of the recirculating basin water is routed through filtration and ion exchange treatment. The pots are received in the central canal area by an underwater transfer mechanism between process cell (Sections 8.2, 8.3, and 8.4) and the canal. From here the pots are transferred underwater by 5-ton bridge cranes near the water level to one of the many storage areas which are separated by concrete walls or by aluminum partitions. The pots are stored upright in individual aluminum stands in the storage areas.

The required cross-sectional area of the storage areas is assumed to be three times the total cross-sectional area of the pots when the basin is full. The number of compartmented storage areas is determined by the total cross-sectional area of the pots, which in turn is dependent upon total interim storage time and the specific solidified waste. The basin is completely lined with stainless steel. The total basin and operating area is inside a building which can withstand the standard AEC basis tornado and earthquake.

After the interim storage period, the pots are transferred underwater to the final load-out and test facility (see Section 8.7). Typical cooling requirements for interim solid storage of PW-4m waste which is stored 8 years from 2 years out-of-reactor to 10 years are 32 megawatts; for 5 years storage from 5 years out-of-reactor to 10 years are about 19 megawatts.

8.7 WASTE CONTAINERS AND WASTE CONTAINER TESTING

A conceptual design of a simplified high level waste container is presented in Figure 8.13. The containers (pots) are fabricated of mild steel for use with the phosphate-glass or the

Diameter, in.	6	8	10	12	16	20
Wall Thickness*	Schedule 40 Pipe					
Internal Thermowell(1)	3/4" Sch. 80 Pipe					
	310 SST					

Material:

Spray Melter & Phosphate Glass Process	—Mild Steel, except— Thermowell is 304L SST**
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Pot Calciner and Spray-In-Pot Melting	—304L SST—
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X-Dimension

Spray Melter and Phosphate Glass Process	—0 to 4 ft—
Pot Calciner	—6 to 9 ft—
Spray In-Pot Melting	—4 to 9 ft—

*To a maximum wall thickness of 0.5 inches.

**310 SST may be preferred for more corrosive melts.

FIGURE 8.13. Waste Pot Conceptual Design

spray-continuous-melter processes, and Type 304L stainless steel for use with the pot calcination and spray-in-pot melting containers. The pots are constructed of standard Schedule 40 pipe up to a maximum wall thickness of 0.5 inch.

The need for stainless steel containers for the two batch type of processes is only required during processing. For storage, mild steel should be adequate.* Although not shown in this study, it should be possible to obtain a considerable cost savings in the stainless steel containers by fabricating them with only a thin layer of stainless steel on the inside of a mild steel shell. This could be done by methods such as explosive welding or conventional lining techniques.

The thermowell pipe in each pot is made from 304L stainless steel Schedule 80 pipe regardless of the material of the container. Thermocouples are inserted into the thermowell prior to pot use and removed for reuse after the pot is filled with solidified waste. The top end of the thermowell will then be welded shut.

Several shapes of thermowells are shown. For the phosphate glass or spray calciner-melter schemes, the upper part of the thermowell should be located to one side of the pot to prevent melt from striking the upper part of the thermowell. Melt striking the upper part of the thermowell could cause formation of stalagmites and could prevent the pot from filling completely. This characteristic is of special concern for unheated pots as used in the design concepts in this study. The internal thermocouples are used to measure melt level during filling. If some centerline temperatures are also desired, the lower bends in the thermowell would be used to extend the lower part of the thermowell into the centerline of the pot.

* Corrosion inhibitors are required in the water storage basin to prevent excessive external corrosion to mild steel pots.

With the pot calcine or in-pot melting pots, centerline temperatures are used for operation. For these cases the thermowell can be made with one bend to run down the entire centerline of the pot. In all cases, each thermowell bend should have a long radius to ease the thermocouple installation and removal, and to minimize flat top surfaces where powder or melt could build up.

The simplified pot has a flat plate bottom and a machined band around the top. The band serves as a seal surface for mating to the in-cell equipment, a welding surface for seal welding to the pot lid, and a provision for grasping, lifting, and transporting the pots with a caliper-type lifting device. The overall height of the pots is 10 feet, including the bail and the leak testing tube on the lid. The leak test tube is a piece of thick-wall tubing which serves as a leak test connection after filling.

For pot calcination, the pot contains a baffle with holes for the insertion of the pot filling and level detection tubes that are a part of the pot fill head. This pot design is a substantial departure from the ORNL and WSEP pot calciner design where all of these features were included as part of the pot and the pot head seal surface was only about 3 inches in diameter. The features on the conceptual pot are believed to provide for satisfactory operation at near-minimum cost.

After the pots are initially filled with solidified waste, they are moved to the pot welding and testing station where they are set in a water-cooled water bath (see Figures 8.2, 8.6, and 8.9). There, a lid is welded on and the thermocouple well is seal welded shut. The tube on the pot lid is then connected to a pressure measuring device and/or vacuum-type leak tester to test the sealed pots for leaks. When the pot has been tested and found to be satisfactorily leak-free, the tube is crimped shut and a seal weld is made along the crimped edge. After up to 1 week holdup time in the solidification cell, the pots are transferred to the interim solids storage basin (Section 8.6).

The conceptual design of the waste container testing and load out facility is shown in Figure 8.14. At the end of the interim solids storage period, the pots are transferred underwater from the solids storage facility into the testing and load-out facility. The pots are removed from the water and undergo a series of tests in the final testing cell to ascertain that they are suitable for transportation and for handling at the final repository. The actual test requirements will ultimately be determined by a hazards analysis of the shipping and disposal schemes. The tests proposed here are believed to be indicative of what may be required.

The facility consists of a hot cell which is connected to the interim solids storage basin and to the enclosed railroad and truck loading area. Four main areas are inside the cell: a small extension of the water storage basin for storage of pots before they are tested; a station for storage in air plus monitoring of wall thickness and temperature; a hooded station for leak testing, recanning, and external contamination monitoring; and a cask load-in area. Operation within the cell is performed with the use of cranes and viewing window-manipulator stations.

Each pot is identified (by a nonremovable number or code system) and an ultrasonic wall thickness scan is performed to assure that the pot wall has not undergone severe corrosion that would weaken the pot. The wall scan is done at a predetermined number of wall locations (bottom, weld seams, solid-vapor interface). The end of the leak test tube on the pot lid is cut off and the vacuum hose of the leak testing system is attached. A large vacuum pump serves to evacuate several pots at the same time, after which each pot is isolated for final evacuation and helium mass spectrometer leak checking. Pots failing to pass the leak test (it is felt that leaks less than the range of 10^{-5} atm cm³/sec will be satisfactory) will require recanning if repairs cannot be made to the leaky pot. It is probable that leaking pots will have a small amount of water in them due to the underwater storage. Most of this water can be removed through

FIGURE 8.14. Concept for Pot Testing and Load Out Facility

the leak test tube by evaporation, or by vacuum distillation into the leak check system cold traps. A baking furnace is proposed to provide the most efficient drying of these pots. The pots would be connected to a process ventilation system during the baking.

A different type of leak check may be required for pot calcine pots because they can off-gas for several days to a few weeks during high-vacuum pumping. (A vacuum of about 100 to 150 microns can be obtained on the calcine pots during initial pumping.) One possible test would be a bubble check in water after pressurizing the pot to about 100 psi. However, this test is less sensitive and should give leak results in the order of only 10^{-3} atm cm²/sec. Pressurizing the pots plus monitoring the pressure changes would detect leak rates as low as about 10^{-1} atm cm²/sec if performed over a time period of about 12 hours with a pressure change of about 1 psi. (A 0.1 psi drop would give a factor of 10 more sensitivity.) Vacuum checking in this same manner should give at least a hundredfold better results; however, it might not be usable with pot calcine material because of the off-gassing. The 100 to 150 micron initial vacuum on the pot combined with some pressure monitoring may be the best test that can be obtained with calcine pots, unless the pots are completely outgassed with high capacity vacuum pumps.

After a pot has been leak tested and found to be leak free, the tube on the pot lid is welded shut with a technique which will permit sealing with the pot under vacuum, such as using a hydraulic shear to crimp cut the tubing prior to the seal weld.

After the pots have been out of the water for 12 to 24 hours, measurement of the pot wall temperatures provides an indirect measure of the heat generation rate in each pot. This measurement can be made with a scanning system such as a

portable thermocouple or an optical pyrometer. During this holding period, the pot is wiped at specific locations to monitor external contamination.

After the pot testing is complete, the pot is placed in the transportation cask within the loadout facility. The shipping casks are specially made for transporting the radioactive waste containers. Each cask is about 8 feet in diameter by 13 feet high with a 4-foot by 11-foot high cavity. The casks have approximately 13 inches of iron shielding the 11 inches of fins and neutron shielding.⁽¹⁾ After the cask is filled, it is closed and its temperature is monitored for up to 24 hours. It is then transferred to the railway car or truck where it is ready for shipping to the final repository.

8.8 POT SIZING AND HEAT DISSIPATION CONSIDERATIONS

Solidified wastes are collected in 10-foot tall cylindrical pots made from standard, Schedule 40 steel pipe with diameters ranging from 6 to 24 inches. The pots will normally be filled to eight feet with calcine or melt. The size of the pot and amount of waste placed in each pot depend on the bulk density and heat content of the waste, the thermal conductivity of the solidified waste, and the heat dissipation properties of the pot storage media. The recommended heat limitations for the stored waste are the same as those used in WSEP and are based on not exceeding a pot wall temperature of 427 °C or a centerline temperature of 900 °C. More restrictive temperature limitations are placed on those wastes which have remelt temperatures below 800 °C or which can segregate and/or decompose and pressurize the container at 900 °C centerline temperature. In some cases, it will be necessary to store the liquid waste for two to three years before processing to avoid exceeding these temperature limits with the minimum 6-inch-diameter pots if conventional cylindrical pots are used. This storage time can be reduced

somewhat with advanced pot designs, as discussed in Section 8.9. For the case of ultimate salt-mine storage, an additional heat-generation limit of 500 watts per foot or 4000 watts per container has been considered. For the subsequent discussion, it will be assumed that this limit is attained within ten years of out-of-reactor cooling, before shipment to the salt mine.

8.8.1 Solidified Waste Volume

Solidified waste volumes per tonne as a function of fuel burnup are presented in Figure 8.15. The solidified waste volume depends on the weight of the fission product and chemical additive oxides and the density of the calcine or melt. Representative solidified waste densities were measured in WSEP and ranged from an average 1.3 g/cm^3 for the pot calcine product to $3.0 \pm 0.3 \text{ g/cm}^3$ for the spray solidifier and phosphate glass products. The volume of the solidified PW-4m type waste, including the solidification process additives, will increase linearly with fission product content and, hence, with fuel burnup. The PW-2 type, high sulfate content waste volume is affected significantly by the quantity of previous separations process additives, which depend on the plutonium content of the fuel as discussed in Section 7.1. The nonlinear increase in plutonium content with burnup (Figure 7.10), together with the assumptions made concerning the separations process additives, result in the nonlinear increase in solidified waste volume with burnup for PW-2 type wastes, as shown in Figure 8.15.

8.8.2 Pot Wall Temperatures in Air Storage

Steady-state pot wall temperatures in air storage as a function of pot diameter and heat content are shown in Figure 8.16. The convective heat loss calculations were based on the correlations given by McAdams⁽²⁷⁾ for vertical cylinders cooled by natural air convection, using an ambient air temperature of 38°C . A pot wall emissivity of 0.7 was used for calculation of heat losses due to radiation.

FIGURE 8.15. Solidified Waste Volume as a Function of Fuel Burnup

FIGURE 8.16. Relationship Between Fission Product Heat Generation Rate and Wall Temperature for Solidified Waste Pots Cooled by Natural Air Convection

8.8.3 Allowable Heat Generation Rates in Pots

The maximum allowable heat generation rates in the pots are presented in Figures 8.17, 8.18, and 8.19 as a function of pot diameter and thermal conductivity of the solidified waste for both air and water storage. The maximum allowable heat generation rate at the time of solidification is set primarily by the restriction that the centerline temperature not exceed 900 °C for the pot calciner and the PW-4m spray calciner products and 700 °C for the potentially volatile PW-2 spray calciner products. The phosphate glass product has a remelt temperature of 700 °C; and a more restrictive, molten core limit has been specified for this product. A molten core diameter equal to one-half the pot internal diameter seems reasonable (but must be proved); under these conditions, a 900 °C centerline temperature will not be attained with a 700 °C temperature at the interface between the solidified waste and the molten core. The borosilicate PW-4m spray-solidified product has a remelt temperature of about 800 °C, but restricting the centerline temperature to 900 °C will prevent the molten core from exceeding one-half of the pot diameter.

The maximum allowable heat content for cylinders of uniform heat-generating waste is related to the effective thermal conductivity by the equation:

$$k_{\text{eff}} = \frac{Q}{4\pi L(\Delta t)} \quad (1)$$

where k_{eff} = experimental overall thermal conductivity of the solidified product (pot plus waste), $\text{W}/(\text{m}^2)(^\circ\text{C}/\text{m})$;

Q = total heat content of the pot (equal to the heat loss rate from the pot at steady-state), watts;

L = fill height of the waste in the pot = 2.44 meters;

Δt = temperature difference between the pot wall and pot centerline, °C.

Points on the curves in Figures 8.17 and 8.18 were calculated for the air-cooled storage case by using the relationship between

FIGURE 8.17. Maximum Allowable Heat Generation Rates in Waste Storage Pots to Avoid Exceeding $900^{\circ}C$ Centerline Temperature

FIGURE 8.18. Maximum Allowable Heat Generation Rates in Waste Storage Pots to Avoid Exceeding 700 °C Centerline Temperature

FIGURE 8.19. Maximum Allowable Heat Generation Rates in Pot to Avoid Exceeding the Molten Core Limit (Frozen-Wall Thickness Equal to One-Half the Pot Radius)

pot wall temperatures and heat dissipation rate from Figure 8.16 and a centerline temperature of either 700 or 900 °C to calculate the effective thermal conductivities.

The molten-core case, Figure 8.19, was calculated by the use of an equation derived by Kaser:⁽²⁸⁾

$$\left(\frac{r_m}{r_i}\right)^2 = 1 - \frac{4\pi k_w L(t_m - t_o)}{Q} + \frac{2k_w}{k_c} \ln\left(\frac{r_o}{r_i}\right) \quad (2)$$

where r_m = molten core radius;

r_i = inner wall radius of pot;

r_o = outer wall radius of pot;

k_w = thermal conductivity of waste solid, W/(m²) (°C/m);

k_c = thermal conductivity of pot wall, W/(m²) (°C/m);

t_m = temperature at molten core-solidified waste interface
= 700 °C for phosphate glass product;

t_o = outer pot wall temperature, °C;

and Q and L were previously defined.

The final term of the above equation is a relatively minor correction for the heat transport through the container wall; for all practical purposes, the experimentally determined k_{eff} (which includes the contribution of the pot wall) can be substituted for k_w in the middle term and the final term can be omitted. After rearranging and letting $r_m/r_i = 0.5$,

$$k_{eff} = \frac{Q[1 - (r_m/r_i)^2]}{4\pi L(t_m - t_o)} = \frac{0.75Q}{4\pi L(700 - t_o)} \quad (3)$$

Again, the curves in Figure 8.16 were used for the air-cooled case to obtain values of Q and t_o for use in the above equation. The relationship between k_{eff} and Q for water-cooled pot storage was calculated using equations (1) and (3) for the solid and molten core cases, respectively, using 100 °C for the pot wall temperature.

The 427 °C wall temperature constraint is shown as a plateau in the heat generation rate versus thermal conductivity curves in Figures 8.17 through 8.19. Also superimposed in these figures are the mean effective thermal conductivities determined for each of the WSEP solidified wastes. These ranged from 0.35 W/(m²)(°C/m) for the pot calcined wastes to 1.0 W/(m²)(°C/m) for the phosphate glass wastes, 1.2 for the PW-4m phosphate-based spray product and PW-2 spray products, and 1.3 for the PW-4m borosilicate spray product. From these thermal conductivities, it can be seen that the allowable heat generation rate limit for most cases is set by the maximum allowable centerline or molten-core interface temperature. The wall temperature limit provides a heat generation rate limit only for the PW-4-type spray solidified wastes stored in air-cooled, 6-inch diameter pots.

8.8.4 Maximum Waste Content of Pots as a Function of Fuel Burnup

The preceding correlations were combined to obtain the relationships between pot diameter, fuel burnup, cooling time before solidification, solidified waste storage media, and maximum allowable waste content of the pots (expressed in tonnes of fuel processed) for each type of waste processed and each solidification technique. The results are presented graphically in Figures 8.20 and 8.21.

An example calculation will be used to illustrate the method used to develop the graphs and to demonstrate how they can be used to select the optimum pot size and cooling time for a given type of waste and solidification process:

A PWR fuel with a reactor burnup of 30,000 MWd/tonne is reprocessed by the conventional Purex solvent extraction process to yield a high-sulfate, PW-2-type waste. The waste is to be solidified by the pot calcination process.

A. POT CALCINATION PRODUCT

C. PHOSPHATE GLASS PRODUCT

- POT VOLUMETRIC CAPACITY
- - - - MINIMUM AGE OF WASTE FOR POT STORAGE IN AIR AT 38 °C
- MINIMUM AGE OF WASTE FOR POT STORAGE IN WATER (100 °C)
- - - - SALT MINE HEAT LIMIT

8 FT POT FILL
POTS MADE FROM STANDARD SCH. 40 PIPE
POT WALL EMISSIVITY = 0.7
WASTE VOLUMES FROM FIGURE 8.15

FIGURE 8.20. Maximum Allowable Waste Contents of Pots as a Function of Fuel Burnup for PW-2 Type Wastes (High Iron and Sulfate Content)

A. POT CALCINATION PRODUCT

C. BOROSILICATE-BASED SPRAY SOLIDIFICATION PRODUCT (INPOT MELTING)

CODE: SOLID LINES ARE POT VOLUMETRIC LIMITS AT 8 FT POT FILL, USING WASTE VOLUMES FROM FIG. 8.15. AGES SHOWN ARE THE PRESOLIDIFICATION COOLING TIME REQUIREMENTS TO AVOID EXCEEDING POT TEMPERATURE LIMITS FOR POTS STORED IN AIR AT 38 °C (POT WALL EMISSIVITY 0.7) OR WATER AT 100 °C.

B. PHOSPHATE-BASED SPRAY SOLIDIFICATION PRODUCT

D. PHOSPHATE GLASS PRODUCT

FIGURE 8.21. Maximum Allowable Waste Content of Pots as a Function of Fuel Burnup for PW-4m Type Wastes (No Separations Process Additives)

How much waste, expressed in tonnes of fuel processed can be placed in an 8-inch diameter pot with an 8-foot fill? What is the minimum fuel cooling time allowable before the waste can be solidified and stored in air without exceeding a 900 °C centerline temperature? Will the solidified waste be cooled sufficiently to be moved to a salt-mine repository within 10 years out of the reactor?

From Figure 8.15, the waste volume for PW-2 pot calcined waste is 87.5 liters/tonne at 30,000 MWd/tonne burnup. An 8-inch diameter, Schedule 40 steel pot will hold 78.7 liters of solidified waste at an 8-foot fill, which corresponds to the waste volume from 0.9 tonnes of fuel after pot calcination. From Figure 8.17, the allowable heat content of the reference pot stored in air is 7000 watts for pot calcined product. The heat generation from fission product wastes is approximately linear with fuel burnup, so that the required cooling time can be obtained from Figure 7.9 (Section 7) by ratioing the fuel burnup and waste content of the pot to the 46,600 MWd/tonne reference fuel. Thus, the equivalent heat generation rate for the 46,600 MWd/tonne fuel would be (7000) $(46,600/30,000)(1/0.9) = 12,080$ watts per tonne; and, from Figure 7.9, a cooling time of nearly 1 year before solidification would be required to avoid exceeding the pot centerline temperature limit. At 10 years cooling, this same pot of waste will cool to 64% of 1,480 watts/tonne or to 850 watts total. This is far below the limit of 500 watts/foot or 4,000 watts per pot (8-foot fill) presently proposed for salt mine storage.

All of the above answers can be obtained directly from Figure 8.20A. This figure shows that an 8-inch-diameter pot will hold the PW-2 type waste from 0.9 tonnes of 30,000 MWd/tonne fuel and that it must be cooled nearly 1 year before solidification

for safe air-cooled storage. It also shows that 0.52 tonnes of the same waste can be solidified and stored in an air-cooled, 6-inch pot after only 0.5 year of cooling and that a 16-inch pot is the maximum air-cooled standard pot size that can be used (for solidifying 3.3 year-old waste) to avoid exceeding the salt mine heat limit for 10-year cooled waste. Figure 8.20 also shows that less cooling time prior to solidification is required for water-cooled pot storage. For the 8-inch pot example case, the waste could be solidified after only about 0.7 year cooling with subsequent water storage, compared with 1 year cooling with natural convection air storage. Cooling time requirements can be shortened further by use of internal fins or cooling channels in the waste storage pots, as discussed in Section 8.9.

The graphs for the clean, PW-4m-type wastes are considerably less complicated than those for the PW-2-type waste. The difference is due to the linearity between the PW-4m waste volume and fuel burnup. Since the heat content of the waste is also assumed to be linear with burnup, it is possible to specify a definite cooling time requirement for each pot size with PW-4m-type waste.

8.9 IMPROVED DESIGN OF RADIOACTIVE WASTE CONTAINERS (by G. Jansen, BNW)

The radioactive nuclide content that can be tolerated in a waste container can be increased by lowering the thermal resistance of the average path for heat flowing to the surroundings from the waste. Given a fixed waste thermal conductivity and a fixed maximum temperature limit, the increase in allowable total heat generation rate is a measure of the efficiency of the modification. The value of this increase in efficiency must then be weighed against the total cost of the improvement, whether in increased cost of the container or of plant operating costs. In some cases evaluation of the penalties for making

changes in design is difficult, such as in increased shipping weight or shielding costs, or the increased risk of pot failure during solidification. Because of these difficulties, no attempt has been made in this report to balance heat dissipation capacity against any other factor. Comparisons of the relative costs of heat dissipation capacities of various configurations will be presented in a separate report.⁽²²⁾

The types of modifications studied have been compared with simple cylindrical pots that contain only nonmetallic wastes such as ceramics, calcines, or glasses. These modifications include (a) annular containers, (b) internally finned containers, (c) containers with multiple internal cooling ports, (d) metal-waste composites and (e) metal-waste layered systems. The limiting temperature is assumed to be the maximum waste temperature and the volumetric heat generation rate is allowed to vary as the allowable total power varies. The calculational techniques varied widely from system to system and are described in the topical report.⁽²²⁾

The principal effects of annular containers are to shorten the path length for conduction through the solid and provide a second path for heat to flow to the surroundings. In Figure 8.22(a) the ratio of the total allowable heat generation rate in an annular container to that in a cylindrical pot is shown as a function of the ratio of the inner diameter to the outer diameter. For example, an inner to outer radius ratio of 0.25 allows 3.18 times greater heat generation rate in an annular container than in a simple cylindrical container. The increase in total heat generation rate depends only on the shape of the container and not on the relative physical dimensions of the annulus or the cylinder.

Consider two situations for which one might want to increase the total heat generation rate. In the first situation the

FIGURE 8.22. Comparison of Conditions in Annular and Cylindrical Pots at Maximum Allowable Waste Temperatures

volumetric heat generation rate has been fixed by the process design. The pot diameter must be increased by a factor of 1.84 as shown in Situation I in Figure 8.22(b) to obtain the 3.18-fold increase in the total heat generation rate. The cost of the container is approximately proportional to the sum of the inner and outer surface areas of the annulus. As shown in Figure 8.22(d) the surface heat flux increases by 1.38 times that for Situation I, or for constant unit cost of surface area the cylindrical pot is 1.38 times as expensive as the annular pot per unit of radioactive heat generating rate contained. Other costs associated with having a void section in the annular pots, such as the need for larger transportation casks and more area required for interim storage, may offset the savings in direct pot costs.

In the second situation, the maximum outer pot diameter is fixed by the storage or shipping conditions but the process can be modified to increase the volumetric heat generation rate. As shown in Figure 8.22(c) for Situation II the maximum amount that the volumetric heat generation rate can be increased is 3.39 times, which results in an increased total heat generation rate of 3.18-fold. As shown in Situation II in Figure 8.22(d) the surface heat flux is increased by 2.54 times, and for constant cost per unit of surface area the cylindrical pot is 2.54 times more expensive per unit of radioactive heat generation power contained than an annular pot of the same diameter. The savings in pot costs may be offset by the cost of the waste concentration process to achieve higher volumetric heat generation rates and the higher surface fluxes may be troublesome under interim and final storage conditions.

In the second situation another option is available. If the reprocessing step can be redesigned to result in an increase in volumetric heat generation rate (i.e., a decrease in unit solid waste volume) of 3.39 times, then one can also put the waste in a cylindrical pot that has a diameter 1.84 times smaller

than the original design and save shipping cask volume, interim storage area, and pot cost. The comparison of annular pots and cylinders in the second situation then reverts to Situation I, and the annular pot cannot be made more than 1.38 times cheaper than the cylinder per unit of radioactive heat generation power. In the limit of thin annuli, there is no way that the annulus can be made more than 1.414 times cheaper than the cylinder.

With internally finned containers, the improved heat transfer is gained by providing a high conductivity path from the more centrally located waste to the outer wall. The increased capacity is a function of the number of fins, fin thickness, fin thermal conductivity and the depth of penetration of the fins from the wall toward the container axis. The ratio of the allowable heat generation in a finned container to that in an annular container is shown in Figure 8.23 as a function of a fin conductance parameter ($K_1 Y / K R_1$ where K_1 is the fin conductivity, Y is the fin thickness, K is the waste conductivity, and R_1 is the pot radius.) Approximately a twofold increase in the total heat generation rate can be obtained with 3 to 7 fins and the volume occupied by 1/4-inch thick fins is still a small fraction (less than 2 percent) of the container volume. The effect of fin penetration is approximately proportional to the ratio of fin length to pot radius; the decision of how much penetration can be tolerated depends on whether the waste can be uniformly distributed around the fins during the filling process. The fin material itself may impose a lower temperature limit on the container because of corrosion. With the use of insertable cartridge fins that are not an integral part of the container, the cost of the fins can be balanced directly against the increased heat content. Gaps of 1/8-inch between the fins and the pot wall have only a small effect (less than 10 percent) on the heat transfer rates.

FIGURE 8.23. Effect of Fin Properties on Temperatures in Internally-Finned Pots -- Complete Fin Penetration to Center of Pot

Containers with multiple internal cooling ports are basically annuli with additional cooling tubes arranged parallel to the container axis throughout the volume of the waste. The improvement in heat transfer for this system is a function of the number, location and diameter of the internal ports, and the temperature of the coolant in the internal ports. Calculations were made with a single central port surrounded by a ring of six ports with the same diameter and the assumption that natural convection in water or air would be great enough to maintain the port temperature at ambient. The results are shown in Figure 8.24. For each port diameter an optimum location of the ring at a radius of 0.5 to 0.6 fraction of the container radius was found. The allowable total heat generation rate increased from 6 to 10 times that for a simple cylinder as the diameters of the 7 ports were increased from 8 to 25 percent of the container diameter. This was the most significant improvement found in any type of container modification tried. Comparisons on the basis of surface area per unit of radioactive heat generation power are made in the topical report.⁽²²⁾ Containers with internal ports would require more extensive verification of integrity but the dramatic improvement in heat transfer warrants further study.

Mixing of wastes with metal particles or waste cladding hulls improves the thermal conditions in simple cylindrical containers without changing the geometry or the container cost. The thermal conductivity of the ceramic-metal composite is a function of the thermal conductivities of ceramic and metal, the volume fraction of metal, whether the metal or ceramic is the dispersed phase, and the shape of the dispersed phase particles. Figure 8.25 shows the ratio of allowable heat generation as a function of metal volume fraction with the ratio of metal to glass thermal conductivities as parameters. The correlation of Cheng and Vachon⁽²³⁾ for randomly dispersed particles, which

FIGURE 8.24. Self-Heating Radioactive Waste Containers with Internal Cooling Ports -- Effect of Hole Location on Allowable Heat Generation Rate

FIGURE 8.25. Thermal Conductivity of Solidified Waste-Metal Composites

is insensitive to particle shape and orientation, was used. In the volume fraction range of 0.3 to 0.7, the thermal conductivity is double valued, depending on whether the metal or ceramic phase is continuous. The amount of allowable heat generation is directly proportional to the thermal conductivity of the composite if the metal does not impose lower temperature limits. For a typical ceramic thermal conductivity of $0.5 \text{ W/(m}^2)(^{\circ}\text{C/m)}$ [$0.29 \text{ Btu/(hr)(ft}^2)(^{\circ}\text{F/ft)}$] and a metal thermal conductivity of $10 \text{ W/(m}^2)(^{\circ}\text{C/m)}$ [$5.8 \text{ Btu/(hr)(ft}^2)(^{\circ}\text{F/ft)}$], a 2.34-fold increase in allowable heat generation is obtained at 30 volume percent metal. The value of this increase is partially offset by the increased operating costs and the price of the metal; if the metal is a waste material such as cladding hulls, a credit might be available for disposing of them.

The effective thermal conductivity of the container contents can also be improved by filling with alternating layers of metal and ceramic. The fixed parallel orientation of the layers improves the overall thermal conductivity over that for random composite orientation, but thick layers tend to reduce the effect of the metal on the central portion of the waste layer. In Figure 8.26 is shown the effect of the ratio of layer thickness to container radius on the allowable heat generation rate, with volume fraction metal and thermal conductivity ratios as parameters. If cladding wastes were compacted and alternated with ceramic in the waste pot, the mixture might even result in an overall penalty in allowable heat generation rate that could be offset by a credit for disposing of the cladding wastes. The indifference points for which greater layer thicknesses result in a decrease in allowable heat generation rate are shown in Figure 8.27 as a function of metal volume fraction. The temperature limit imposed by the metal would be less restrictive than for intimate mixtures because of the geometric separation of

FIGURE 8.26. Effect of Layer Thickness on Allowable Heat Generation in Layered Wastes

FIGURE 8.27. Conditions for Which Changing to a Layered System Has no Effect on the Maximum Waste Temperature

metal and ceramic. The advantage of greater allowable heat generation with thinner layers of waste and metal must be balanced against the higher operating costs of making thinner layers.

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SECTION 9.0 WASTE MANAGEMENT
ECONOMICS

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9.0 WASTE MANAGEMENT ECONOMICS

An economic analysis of the different waste solidification process requires more than just costing out each process. The physical characteristics of the products affect the requirements for container sizes which can dissipate the radioactive decay heat without exceeding centerline or wall temperature limits. The age of the waste at the time of solidification affects the heat generation rate which in turn affects the container size requirements. Container size will influence the solidification cost. Container size, age of the waste, and concentration of the waste in the solid influence both shipping and solid storage costs. Thus a comparative evaluation of different solidification processes requires consideration of costs for the entire waste management system including all liquid and solid storage costs and shipping costs.

A computer program developed at the Oak Ridge National Laboratories to carry out waste management optimization studies was adapted to carry out the calculations necessary for these comparative evaluations. The program is described in detail in Reference 1. Figure 9.1 shows the components of the waste management cycle provided for in the computer program. The computer program was modified to handle the solidification processes discussed in this report and to reflect bases and assumptions used for this study. The capital cost factors in the ORNL program were intended to represent early 1970 costs. To bring the capital costs to a mid-1972 basis, capital cost estimates were developed for base case facilities with assistance from the Vitro Engineering Division of Automation Industries.⁽²⁾ Appropriate factors were inserted into the program accordingly. Operating costs were also reviewed and adjusted to represent a current basis.

FIGURE 9.1. Waste Management System

In calculating waste management costs, conditions were not restricted to conform with current AEC regulations. These regulations presently require all high-level waste to be solidified within five years and for the solidified waste to be shipped to a central repository within ten years. It was felt that these results would be more informative if optimum conditions were selected without regard to current regulations. If attractive cost situations were found outside of present regulations, that in itself might have some influence on future regulations.

The analysis was carried out on a limited scale within a limited time period. Although economic comparisons of the processes are made at near optimum conditions, all parameters were not thoroughly explored and some cost reductions may yet be possible. However it is felt that the costs and trends indicated by the study are realistic, and further analyses would refine the numbers but would not affect the basic conclusions reached in the analysis.

9.1 BASIS AND ECONOMIC MODEL

Waste management costs are calculated using a discounted cash flow technique in which all costs are converted to a present-worth levelized cost representing the level amount that would have to be assessed at the time of fuel reprocessing over the entire life of the facility to cover these costs. The major components of cost were shown in Figure 9.1 and are:

1. Interim Liquid Storage.
2. Solidification.
3. Interim Solid Storage.
4. Shipment to Final Storage.
5. Final Storage in Salt Vault.

The costs are expressed in terms of mills per megawatt-hour of electricity produced from the original fuel.

An inherent characteristic of this method of assigning costs is that costs that occur some time after reprocessing are smaller relative to costs that are incurred at the time of reprocessing. This is because these later costs are discounted based on an average cost-of-money interest rate or, looking at it another way, money collected at the time of reprocessing to provide for a future expense will earn interest during the interim and this interest income will be used to help pay the expense when it occurs. As an example, using the interest rates in this study, a waste solidification operation that would cost 10 units if carried out at the time of reprocessing would cost only 8 units if deferred three years and exactly the same processing performed at that time. The 8 units set aside at the time of reprocessing would have grown to 10 units after three years. An appreciation of this discounting effect is essential to understanding the cost relationships discussed later.

The essential features of the economic model are as follows:

1. All facilities are sized to process high level waste from a 5 tonne/day fuel reprocessing plant operating at a constant rate representing a 75 percent plant factor or 1370 tonnes/year. Design concepts were those developed in Section 8.
2. Capital costs are based on 70% equity earning 15%/year and 30% bonded debt carrying 8% interest charges.
3. The economic life of the plant is 20 years and all equity investments are recovered and all bonds paid off at the end of 20 years.
4. Straight line depreciation is used for tax purposes and all investments are fully depreciated by the end of the 20-year economic life regardless of the year of investment.
5. An escrow fund is established to pay for waste management operations that occur after the 20-year economic life of the reprocessing facility. The escrow fund is invested in low-risk bonds earning 5% interest. This is a tax-exempt

fund that continues to draw interest as long as any money remains in the account. It is used to pay for later operating costs and any capital facilities required after the 20-year life of the reprocessing facility.

6. All incomes and expenses occur at year end. Capital expenditures occur at the beginning of a year. There is no provision for any costs for interest during design or construction.
7. The levelized waste management cost or charge provides for payment of all operating expenses, recovery of equity capital, return on investment, repayment of bonded debt, bond interest costs, federal income taxes, property taxes, property insurance, and accumulations of the escrow fund.

Table 9.1 identifies the economic factors used in this analysis.

TABLE 9.1. Values of Financial Parameters

Percent of Capital From Equity Funds	70%
Percent of Capital From Bonds	30%
Return on Equity	15%
Interest on Bonds	8%
Interest on Tax Exempt Escrow Fund	5%
Federal Income Tax Rate	48%
Property Tax Rate	1.5%
Property Insurance Rate	0.2%

Economic comparisons of total waste management costs were developed for five waste solidification processes and for both PW-4 and PW-2 type wastes. Three of the processes are similar except for melting equipment: the spray melter process with a non-platinum melter, the spray melter process with a platinum melter, and the spray process with in-pot melting are considered separate processes for the purposes of analysis. The cases considered in this analysis are shown in Table 9.2.

TABLE 9.2. Basic Waste Solidification Cases Evaluated

<u>Case</u>	<u>Waste Type</u>	<u>Solidification Process</u>
1	PW-4	Pot Calcination
2	PW-4	Spray Melter (Non-Platinum Liner) (Borosilicate Glass)
3	PW-4	Spray In-Pot Melting (Borosilicate Glass)
4	PW-4	Phosphate Glass
5	PW-4	Spray Melter (Platinum Liner) (Phosphate Ceramic)
6	PW-2	Pot Calcination
7	PW-2	Spray Melter (Platinum Liner) (Phosphate Ceramic)
8	PW-2	Spray In-Pot Melting (Phosphate Ceramic)
9	PW-2	Phosphate Glass

The results are all based on processing waste from fuel exposed to 33,000 MWD/tonne, and in that respect the waste is not identical to the PW-4m and PW-2 waste compositions employed in the WSEP development program. Those waste compositions were based on 46,600 and 20,400 MWD/tonne respectively. The liquid and solid waste volumes used in this analysis were adjusted for this exposure difference. There are several reasons for using the 33,000 MWD/tonne basis: (1) 33,000 MWD/tonne is more representative of exposure ranges anticipated in the foreseeable future, (2) waste management studies at ORNL have been based on this exposure and results could be more directly compared using the same exposure, and (3) decay heat calculations for 33,000 MWD/tonne using the ORIGEN program were readily available.

The conceptual designs for the solidification processes are described in Section 8.0. Brief descriptions of the facilities required for interim liquid storage, prior to solidification, and for interim solid storage prior to shipment

to final storage, are given in Sections 8.5 and 8.6. Further descriptive information on these facilities can be found in References 1, 3, and 4.

The computer program provides for final storage in salt mines. Although there is presently some question on the future of salt mine storage, consideration or evaluation of alternatives for final storage was not at all possible within the limited time for this present analysis. It is assumed that the combined waste management costs will be reasonably representative of costs for whatever method finally evolves for solid storage. The age of the waste, amount of heat in a container, volume of solid, size of containers, etc. will likely affect solid storage costs whatever the method.

A fundamental assumption in this analysis is that the lowest costs will result if the solidified waste is always canned in the largest container permitted by centerline or pot wall temperature limits and heat transfer limitations. As interim liquid storage time is increased, this results in selection of large container sizes. This in turn results in very long interim solid storage time requirements because the amount of heat in the container then exceeds the salt mine storage limit of 4,000 watts per container. Under these conditions, interim solid storage costs are increased because of the longer storage time and salt mine storage costs are reduced because of the discounting effect on deferred expenditures. Further analysis might show conditions where selection of the largest container is not the most economical decision. On the other hand, since salt mine storage is not necessarily the ultimate disposition, revision of the final storage heat limitation for some other storage method might re-enforce the

validity of this container size assumption. For example, there is not likely to be a heat limit specification for engineered storage.

9.2 COMPUTER PROGRAM

The computer program consists of a main program and eight subroutines including separate subroutines for each of the five waste management operations previously identified.⁽¹⁾ Only a summary description of the program is provided here along with a description of revisions made for this study.

In addition to the economic variables previously described in Table 9.1, other input data required by the program is described in Table 9.3 along with the values used in this study. The variables that relate to specific solidification processes are shown in Table 9.4.

Data for the decay-heat curve and a decay-heat accumulation curve are also required. The data for these curves were taken from Reference 1. The decay-heat curve represents heat produced by one metric ton of spent fuel and is shown in Table 9.5. The decay-heat accumulation curve represents the accumulation of heat from a continuous source of one metric ton per day of spent fuel and is shown in Table 9.6.

9.2.1 Main Program

The main program calculates the heat generation rate in the waste at the time of solidification and at the time of shipment, it sizes the waste containers, it calculates the heat load on the interim solid storage facility, and it calls the various subroutines as needed to compute costs for the different waste management operations.

When there is no interim liquid storage, the heat generation rate in the waste and specific ages are simply taken from

TABLE 9.3. Basic Input Data to Economic Analysis Program

Description	Value
Operating Life of Fuel Reprocessing Plant	20 years
Cooling Time Prior to Fuel Processing	150 Days
Reactor Specific Power	30 MW/tonne
Average Fuel Reprocessing Rate	1370 tonne/yr
Average Fuel Exposure	33,000 MWD/tonne
Waste Container Length	10 ft (8 ft fill)
Number of Interim Liquid Tank Fills During Operating Life	(Variable)
Round Trip Shipping Distance	2,000 Miles
Ambient Air Temperature	100 °F
Maximum Centerline Temperature of Solidified Waste	900 °C ^(a)
Radiant Emissivity of Pot Surface	0.7
Interim Liquid Storage Time	(Variable)
Interim Solid Storage Time	(Variable)

- a. 700 °C for Cases 7 and 8, and a molten core limit calculated for a 700 °C remelt temperature for Cases 4 and 9.

TABLE 9.4. Process-Specific Variables for Economic Analysis Program

Process	Pot Calcination	Spray				Phosphate Glass
		Melter		In-Pot Melting		
		Non-Pt	Pt			
- - - PW-4 TYPE WASTE - - -						
Case No.	1	2	5	3	4	
Specific Volume:						
Liquid, gal/10,000 MWD	17	17	17	17	17	
Solid, ft ³ /10,000 MWD (if undiluted)	0.32	0.27	0.44	0.27	0.65	
Thermal Conductivity of Solid, Btu/(hr) (ft) (°F)	0.20	0.75	0.69	0.75	0.58	
Specific Gravity of Solid, g/cc	1.3	3.0	3.3	3.0	2.9	
- - - PW-2 TYPE WASTE - - -						
Case No.	6	7		8	9	
Specific Volume:						
Liquid, gal/10,000 MWD	104	104		104	104	
Solid, ft ³ /10,000 MWD	0.98	1.04		1.04	0.73	
Thermal Conductivity of Solid, Btu/(hr) (ft) (°F)	0.20	0.69		0.69	0.58	
Specific Gravity of Solid, g/cc	1.3	2.9		2.9	2.9	

TABLE 9.5. Decay-Heat Curve⁽¹⁾

Time Since Reprocessing, Years (a)	Decay Heat, Btu/hr/MT	Time Since Reprocessing, Years	Decay Heat, Btu/hr/MT
0	6.7975×10^4	7.0	4.5601×10^3
0.05	6.2935×10^4	8.0	4.1722×10^3
0.25	4.8573×10^4	9.0	3.8900×10^3
0.50	3.7996×10^4	10.0	3.6738×10^3
0.75	3.1266×10^4	15.0	3.0261×10^3
1.0	2.6454×10^4	20.0	2.6291×10^3
2.0	1.5393×10^4	25.0	2.3116×10^3
3.0	1.0186×10^4	30.0	2.0392×10^3
4.0	7.4987×10^3	50.0	1.2488×10^3
5.0	6.0116×10^3	100.0	3.8838×10^2
6.0	5.1265×10^3		

a. Reprocessing at 150 days out-of-reactor.

TABLE 9.6. Decay-Heat Accumulation Curve⁽¹⁾

Time Since Reprocessing, Years (a)	Accumulation, (Btu/hr) / (MT/day)	Time Since Reprocessing, Years	Accumulation, (Btu/hr) / (MT/day)
0.0	0.0	7.0	3.6237×10^7
0.05	1.1944×10^6	8.0	3.7828×10^7
0.25	5.2209×10^6	9.0	3.9298×10^7
0.50	9.1070×10^6	10.0	4.0677×10^7
0.75	1.2280×10^7	15.0	4.6723×10^7
1.0	1.4905×10^7	20.0	5.1868×10^7
2.0	2.2271×10^7	25.0	5.6370×10^7
3.0	2.6833×10^7	30.0	6.0338×10^7
4.0	3.0012×10^7	50.0	7.2041×10^7
5.0	3.2454×10^7	100.0	8.5290×10^7
6.0	3.4476×10^7		

a. Reprocessing at 150 days out-of-reactor

the decay-heat curve by a logarithmic interpolation procedure. However, the heat generation rate per unit of waste volume is larger when waste is accumulated in a tank for one year compared to the heat generation rate per unit volume of waste simply aged one year. This important difference is taken care of by use of a heat accumulation curve. A constant production rate and perfect mixing in the waste tanks are assumed. If one assumes a filling time of Y years, the heat generation rate per unit of waste at Z years ($Z > Y$) is the difference between the heat accumulation values at Z and at $(Z-Y)$ years. The procedure is simple and exact. Intermediate values on the heat accumulation curve are obtained by logarithmic interpolation as in the case of the decay-heat curve.

The following revisions were made in the main program for purposes of this analysis:

1. A revision was included to limit solidified waste container sizes to standard schedule 40 pipe sizes for 6, 8, 10, 12, 16, 20, and 24 inch pipe. After calculation of maximum possible diameter, the next smaller standard size is selected. In the original program, container diameter was specified in the input and the program checked to see that the input value was less than the maximum allowable diameter.
2. The original program provided that in the event the input diameter was greater than the maximum allowable, the interim liquid storage time would be increased in one-year increments until the waste was cool enough to be canned in the specified size. This was revised to provide that if the waste was too hot to be canned in a standard 6-inch diameter container, interim liquid storage time was increased in one-half year increments until the waste could be canned in a 6-inch diameter container. Other revisions were made to allow for the differences in unit

volumes of solid waste and to obtain appropriate cost allocations and discounting with half-year storage increments.

3. The original program provided for maximum container diameters to be calculated by an iterative trial and error procedure based on the following equations:

$$\frac{Q \times R}{2} = HT (TS - TR) \quad (1)$$

$$HC = 0.29 [(TS - TR)/(PL - 2)]^{0.25} \quad (2)$$

$$QR = 0.173 EM \left[\left(\frac{TS}{100} \right)^4 - \left(\frac{TR}{100} \right)^4 \right] \quad (3)$$

$$HR = QR/(TS - TR) \quad (4)$$

$$TCL - TS = \frac{Q \times R^2}{4 \times TK} \quad (5)$$

Where

Q = Heat generation rate, Btu/(hr) (ft³).

R = Radius of container, ft.

HT = Total heat transfer coefficient, Btu/(hr) (ft²) (°F).

TS = Surface temperature, °R.

TR = Ambient temperature, °R.

HC = Natural convection heat transfer coefficient,
Btu/(hr) (ft²) (°F).

PL = Pot length.

QR = Radiant heat flux, Btu/(hr) (ft²).

HR = Radiation heat transfer coefficient,
Btu/(hr) (ft²) (°F).

This was modified to provide for a molten core calculation with phosphate glass (Cases 4 and 9) by substituting Equation (6) for Equation (5).

$$TCL - TS = \frac{0.75 Q \times R^2}{4 \times TK} \quad (6)$$

In this case TCL is the temperature at the molten core-solid interface and is 700 °C. A further option of water cooling was also provided where TS was set equal to 212 °F and Equation (5) was solved directly for R.

9.2.2 Interim Liquid Storage

The interim liquid storage subroutine (ILS) calculates the required tank size, number of tanks required, maximum cooling duty, etc., and then calculates the cost of all facilities associated with interim liquid storage and the levelized present-worth cost of this operation. The program was written to require specifying the number of tank fills during the life of the reprocessing facility. Thus filling time and tank size requirements are calculated based on the number of fills, life of the plant, and the reprocessing rate. The maximum liquid storage time evaluated was 15 years. No provision for replacement tank costs are included in the program. The only revisions in this subroutine relate to the cost factors which are discussed separately in Sections 9.3 and 9.4.

9.2.3 Solidification

The original calcination subroutine calculated the levelized present-worth cost for pot calcination only. It was revised to calculate costs for all five processes analyzed here.

Two of the processes, pot calcination and spray in-pot melting, are batch processes while the others are continuous processes. For the batch process, provision was made to vary cycle time with waste container sizes (according to information in Section 8), and to calculate the number of parallel processing lines required. A single solidifier is adequate for each continuous process. All of the cost calculations were replaced with relationships based on cost estimates for each specific process.

9.2.4 Interim Solid Storage

The interim solid storage (ISS) subroutine calculates the size of storage canals and other facilities required, and then calculates capital and operating costs and a levelized present-worth cost for this operation. The revisions here all relate to cost factors which are discussed separately in Sections 9.3 and 9.4.

9.2.5 Shipping

The subroutine SHIP sizes a shipping cask and calculates the number of casks required to ship the solid waste to permanent storage and then calculates a levelized present-worth cost for the shipping operation.

Based on a comparison of calculations made with this program and results published in a more recent ORNL study⁽⁵⁾ the shielding allowance appeared to be understated and was increased by 40%. This also increased cask cost since it is based on cask weight. In the cases where the solidified waste was too hot to permit shipping under the conditions built into these calculations, a provision was added to increase interim solid storage in half-year increments until shipping could take place. Other revisions relate to cost factors discussed in Sections 9.3 and 9.4.

9.2.6 Final Storage

The subroutine SALT calculates the cost of permanent storage in salt mines based on the heat generation rate of the waste container. The heat generation rate governs space requirements in the mine and is thus directly related to costs. The original program had storage limits of 7600 to 5700 watts/container for waste aged one to greater than 10 years. If these limits were exceeded, the calculation terminated. This was revised to a single 4000 watts/container limit to more nearly reflect later estimates of salt storage limits. If this limit is exceeded,

the interim solid storage time was increased in half-year increments until the waste cooled enough to pass the 4000 watt/container test. Adjustment of the cost factors is discussed in Section 9.3.

9.2.7 Other Subroutines

The several other subroutines in the program which were used without revision include:

- a) The subroutine LIFE which allows the life of a given piece of equipment to be extended; up to 25% of such extension would eliminate need for replacement.
- b) The subroutine DEPREC which calculates the depreciation schedules for the facilities required in each waste management step.
- c) The subroutine COST which handles the cash flow calculations and calculates the levelized present-worth cost for each waste management step.
- d) The function HEAT which interpolates the decay-heat and decay-heat accumulation curves.

9.3 CAPITAL COST ESTIMATES

Capital cost estimates were developed on a current-cost basis for the design concepts developed in Section 8. The estimates were made with the assistance of the Vitro Engineering Division of Automation Industries for each of the waste solidification processes and for a base-case interim-liquid-storage facility and an interim-solid-storage facility.⁽²⁾ Based on these estimates, (a) cost functions were developed for the solidification processes, and (b) cost escalation factors were developed for the other waste management functions. These results were then incorporated as revisions in the computer program.

The waste management subroutines in the computer program were originally developed as separate programs and the cost calculations do not follow a uniform pattern. As a result, the same procedure could not be used to update all of the cost routines. Overall cost escalation factors were most appropriate for the interim-liquid-storage facility, whereas revised factors for basic unit-cost components such as $\$/\text{yd}^3$ concrete, etc., were most appropriate for the interim-solid-storage facility.

All building structure estimates are based on providing tornado, flood, and earthquake protection. All capital cost estimates were revised to include an allowance of 20% for design and engineering and 30% for contingencies. In the original program the design and engineering costs were 15% in the case of liquid-storage and 18% in the case of pot calcination and interim solid storage. Contingency allowances were originally 15% for liquid storage and 20% for pot calcination and interim solid storage. These items were not separately detailed for shipping or salt mine storage and no adjustment was made.

9.3.1 Waste Solidification Facility Costs

Cost estimates for the solidification process facilities were based on the descriptions in Section 8.0. Although the final pot testing and load-out facility (Figure 8.14) is properly a part of the interim solid storage facility, it is included as a part of the solidification facility in this economic analysis as a matter of convenience in handling the computer program revisions.

It is assumed that the solidification facility will be an integrated addition to a 5 tonne/day fuel reprocessing plant and will be included in the original design. Thus only incremental costs for this additional facility are considered.

The liquid waste from the reprocessing plant will require an evaporation-concentration step whether the waste is immediately converted to a solid or whether solidification is deferred through interim liquid storage (it is advantageous to store the liquid waste at as great a concentration as practical). This primary concentration step is considered a part of the basic reprocessing plant facilities and is not included in the waste management facilities considered here. However, if interim liquid storage is included, the concentration cannot be carried as far immediately after reprocessing and a second concentration step is used just prior to the eventual solidification to reduce the heat load and sizes of the solidifiers. Thus when interim liquid storage is included in the waste management scheme, a second waste concentrator is a required part of the solidification process facilities.

The cell space requirements are somewhat different for each solidification process. The requirements used as a basis for the cost estimates were taken from Section 8, and are shown in Table 9.7. The cell space requirements for pot testing and loadout and for re-evaporation are also included in Table 9.7.

The cost estimates for solidification facilities were developed in terms of a base facility that could accommodate two pot lines for pot calcination, and the capital cost for the other processes were developed by adding incremental facilities to this base estimate. The cost estimate for the basic cell and building facilities for two pot-calcination lines is shown in Table 9.8 along with the incremental cost for each two additional lines. The cost estimate for the cell equipment, excluding calcination equipment, to serve two pot-calcination lines is shown in Table 9.9 along with the incremental cost for each additional pair of lines. The basic cell and permanent facilities (Table 9.8) were amortized

over the full 20-year life of the reprocessing plant while the cell equipment was amortized over a 10-year period.

The cost estimates for the solidification process equipment are shown in Table 9.10. It was assumed that the life of a melter for the spray melter process, either platinum-lined or Corronel-lined, or a platinum-lined melter for the phosphate glass process would be only two years. To simplify the cash flow calculations for these cases, it was assumed that these replacement costs could be represented by including the present-worth cost of two-year replacements in the original equipment costs using an average cost-of-money discount rate. This results in these melters costing 3.37 times the cost of a single melter. It may be possible to reclaim the platinum in these melters but the feasibility and cost are not known, so no credit was claimed for any platinum salvage value.

Cost estimates for the final test and loadout facility and for the evaporator facility are summarized in Table 9.11.

TABLE 9.7. Cell Space Requirements
for the Solidification Processes

Pot Calcination (2 lines)	16 ft wide x 36 ft long x 30 ft high. Add 4 ft length for every one or two additional lines.
Spray Melter	16 ft wide x 31 ft long x 48 ft high.
Spray In-Pot Melter (1 to 5 lines)	16 ft wide x 34 ft long x 36 ft high.
Phosphate Glass	16 ft wide x 34 ft long x 35 ft high.
Pot Testing and Loadout	20 ft wide x 22 ft long x 36 ft high.
Re-evaporator Cell (For cases with interim-liquid- storage)	16 ft wide x 7 ft long x 31 ft high.

TABLE 9.8. Cost Estimate for Building and Permanent Facilities
for Base Facility (for Two Pot Calcination Lines) (2)

Earth Work	\$ 20,000	
Substructure	500,000	
Super Structure	340,000	
Structural Steel	20,000	
Misc. Ironwork	24,000	
Painting - General	20,000	
Services Including Heating & Ventilating, Piping, Lighting, Fire Protection, etc.	240,000	
Misc. Items of Work	41,000	
	<hr/>	
	\$1,205,000	
General Contractors Overhead on:		
Subcontracts, 12%	145,000	
Mobilization, 5%	60,000	
	<hr/>	
Total Structural Cost for Building Including Service	\$1,410,000	\$1,410,000
Site Preparation		50,000
Piping Supports & Insulation		200,000
Electrical & Instrumentation		250,000
Service Facilities		150,000
Home Office and Field Expense		580,000
		<hr/>
Total Basic Cost Excluding Process Equipment		\$2,640,000
Engineering including Field Engineering and Startup at 20%		528,000
		<hr/>
		\$3,168,000
Contingency at 30%		950,000
		<hr/>
Total Cost (Rounded)		\$4,120,000
Incremental Cost for Space for Two More Lines Including Engineering and Contingencies		\$ 180,000

TABLE 9.9. Cost Estimate for Cell Equipment for Base Facility (for Two Pot Calcination Lines)

Crane, In-Cell	\$ 15,000
Manipulators, 4 Pairs	88,000
Shielding Windows, 4	134,000
Pot Test Station	150,000
Pot Transfer Mechanism	50,000
Pot Storage Supports	10,000
Misc. Materials	20,000
Feed Tanks, Scrubbers, etc.	200,000
Home Office and Field Expense	135,000
Total Basic Cost (Rounded)	<hr/> \$ 800,000
Design and Engineering at 20%	160,000
	<hr/> \$ 960,000
Contingency at 30%	288,000
Total Cost (Rounded)	<hr/> \$1,250,000
Incremental Cost for Each Additional Pot Line (Includes Pair of Manipu- lators and Shielding Window, Engineering and Contingencies)	\$ 110,000

TABLE 9.10. Solidification Process Equipment
Cost Estimates ^(a)

Pot Calciner Furnace Equipment, each line (for 10-year life)	\$ 60,000
Spray Melter With Non-Platinum Liner and Associated Equipment	
Equipment Other Than Melter	225,000
Present-Worth Cost of Melter and Two-Year Replacements for 10 years	165,000
Total Spray Melter Cost for 10-Year Life	<u>\$ 390,000</u>
Spray Melter With Platinum Liner	
Equipment Other Than Melter	280,000
Present-Worth Cost of Melter and Two-Year Replacements for 10 Years	2,400,000
Total For 10-Year Life	<u>\$2,680,000</u>
Spray In-Pot Melting Equipment:	
Spray Calciner and Base Equipment (for 10-year life)	475,000
Pot Furnace, Each (for 10-year life)	80,000
Phosphate Glass Equipment	
Equipment Other Than Melter	400,000
Present-Worth Cost of Platinum Lined Melter and Two-Year Replacements for 10 Years	2,950,000
Total for 10-Year Life	<u>\$3,350,000</u>

(a) All items here include a 20% engineering and 30% contingency allowance.

TABLE 9.11. Auxiliary Facilities Capital CostsTest and Loadout Facility Cost Estimates

Permanent Facilities	\$1,750,000
10-Year Life Equipment	460,000
Total	<u>\$2,210,000</u>

Evaporator Facility Cost Estimates

Permanent Facilities	\$ 750,000
10-Year Life Equipment	400,000
Total	<u>\$1,150,000</u>

It was assumed that processes other than pot calcination would require general cell service equipment equivalent to that required for four pot calcination lines. The components and total costs for the five solidification processes are shown in Table 9.12. As previously discussed, these estimates include the costs for the final test and loadout facility. In cases where interim liquid storage is required, all costs in Table 9.12 are increased for an evaporator facility by the amounts shown in Table 9.11.

For the batch processes, Cases 1, 3, 6, and 8, the cycle time per batch determines how many process lines are required. The cycle times used in these analyses are shown in Table 9.13.

9.3.2 Interim Liquid Storage Facility Costs

A cost estimate was developed for a facility consisting of five one-million gallon storage tanks described in the original liquid storage study.⁽²⁾ That study was the basis for the interim liquid storage facility used in Reference 1. Escalation factors based on a comparison of this current estimate with the original estimate were used to modify the computer program to bring costs to a current basis.

TABLE 9.12. Cost Factors for Solidification Facilities (a)

	Pot Calcination	Spray Melter (Non-Pt)	Spray In-Pot Melting	Phosphate Glass	Spray Melter (Pt)
<u>Permanent Facilities</u>					
<u>Base Costs</u>					
Process Cells (Base)	\$4,120,000	\$4,120,000	\$4,120,000	\$4,120,000	\$4,120,000
Incremental Cell Space	---	380,000	230,000	220,000	380,000
Test & Loadout	1,750,000	1,750,000	1,750,000	1,750,000	1,750,000
Total Base	\$5,870,000	\$6,250,000	\$6,100,000	\$6,090,000	\$6,250,000
<u>Additional Cell Space</u>					
Cost Per Pair of Lines After 1st Pair	180,000	---	90,000	---	---
<u>10-Year Equipment</u>					
<u>Base Costs</u>					
Cell Equipment Specific Process Equipment(b)	\$1,250,000	\$1,360,000	\$1,360,000	\$1,360,000	\$1,360,000
Test & Loadout	---	390,000	475,000	3,350,000	2,680,000
	460,000	460,000	460,000	460,000	460,000
Total Base	\$1,710,000	\$2,210,000	\$2,295,000	\$5,170,000	\$4,500,000
<u>Additional Cell Equip-</u>					
ment Cost Per Line Over Two Lines	110,000	---	110,000	---	---
<u>Additional Initial</u>					
Cost Per Line for Process Equipment	60,000	---	80,000	---	---

a. Costs for re-evaporator facility, where required, must be added to these costs.
 b. Present worth for 10-year life; see Table 9.10.

TABLE 9.13. Cycle Times for Batch Solidification Processes (Hours at 100% Plant Operating Efficiency)

Case	Process	Nominal Pot Diameter, Inches						
		6	8	10	12	16	20	24
1	Pot Calcination PW-4 Type Waste	21	29	42	55	81	126	170
3	Spray In-Pot Melting PW-4 Type Waste	31.4	31.4	31.4	31.4	31.4	31.4	31.4
6	Pot Calcination PW-2 Type Waste	35	47	64	84	123	187	264
8	Spray In-Pot Melting PW-2 Type Waste	31.4	31.4	31.4	31.4	31.4	31.4	31.4

The original estimate and current estimate are compared in Table 9.14. On the basis of this comparison, escalation factors of 1.50 (50% increase) were used in the program relative to 1965 costs for both the tanks and other facilities. These factors replaced the ORNL factors of 1.17 and 1.30 (17% and 30% increase) for tanks and other facilities respectively, that had been used to update the 1965 costs to a 1970 basis. Thus the revised factors represent increases of 28% for tank costs and 15% for other facilities relative to costs reported in Reference 1. The increases are mainly the result of the rapidly rising construction costs in the last two or three years, but may also represent some differences in interpretation of data and variations resulting from differences in the amount of detail available to the estimators. Tank replacement costs are not included.

9.3.3 Interim Solid Storage Facility Costs

In the case of the interim solid storage facility, the computer program was designed to develop costs using, for the most part, basic unit cost factors, so the cost updating was

TABLE 9.14. Comparison of Cost Estimates for Interim
Liquid Storage Facilities

	Waste-Storage Tank Cost Estimates		
	ORNL-2873 ⁽³⁾ Table A-7	Current Vitro ⁽²⁾	Escalation Factor
1 x 10 ⁶ gal. Stainless Steel Tank and Vault Liner	\$ 599,000	\$ 800,000	1.43
SS Coils	1,123,800	1,770,000	1.57
Concrete	345,300	464,000	1.34
Excavation	39,400	110,000	2.79
Appurtances	46,200	100,000	2.16
Instrumentation	10,000	16,000	1.50
Total Tank	\$2,123,700	\$3,260,000	1.53

	Complete Storage Facility		
	ORNL-2873 ⁽³⁾ Table 5	Current Vitro ⁽²⁾	Escalation Factor
Site Clearance	\$ 40,000	\$ 60,000	1.50
Operations Bldg.	819,500	1,470,000	1.79
Outside Facilities	1,071,000	1,545,000	1.44
Outside Lines	603,600	1,000,000	1.66
Equipment & Piping in Operations Bldg.	1,272,700	1,905,000	1.49
Waste Tanks, Five (1 x 10 ⁶ gal. each)	10,618,500	16,300,000	1.57
	\$14,415,300	\$22,270,000	
Construction Overhead	3,892,100	5,630,000	
Total Excluding Engineering & Contingency	\$18,307,400	\$27,400,000	1.52

primarily a matter of revising the unit cost factors. A comparison of the revised factors with those replaced is shown in Table 9.15.

One design revision results in a significant cost increase. This is the replacement of epoxy lining at $\$1.50/\text{ft}^2$ with stainless steel lining at $\$32/\text{ft}^2$ for the storage canals. Another addition of less importance was the addition of galvanized iron gratings to cover the storage canals.

9.3.4 Waste Shipping Cask Cost

Cask costs were increased from $\$1.25/\text{lb}$ to $\$3/\text{lb}$ for lead shielded casks based on information in the more recent Reference 6.

9.3.5 Salt Mine Storage Facility Cost

Capital costs for salt mine storage are not separately identified in the computer program, so no adjustments were made directly to the capital costs. However, overall costs were escalated as explained later in Section 9.4.5.

9.4 OPERATING COSTS

Operating costs were developed in terms of incremental costs assuming that overhead functions such as corporate overhead administrative costs, marketing costs, etc. would not increase as a result of these waste management activities.

9.4.1 Waste Solidification Operating Cost

Operating costs for the final test and loadout facility are included in the solidification costs. Waste solidification operating costs are based on estimates of direct labor requirements with maintenance costs taken as a proportion of equipment costs and plant overheads taken as a proportion of labor and maintenance costs. It was estimated that pot calcination and spray in-pot melting would require two men per shift for

TABLE 9.15. Comparison of Cost Bases for
Interim-Solid-Storage Facilities

	ORNL-4366 1970 Basis (1)	Current Vitro (2)
Excavation	\$5/yd ³	\$2.50/yd ³
Concrete	\$120/yd ³	\$236/yd ³
Epoxy Lining	\$1.50/ft ²	---
SSt Lining	---	\$32/ft ²
Aluminum Partitions	\$10/ft ²	\$12.50/ft ²
Galvanized Grating	---	\$10/ft ²
Cooling System		
Cooling Towers	(a)	+ 50%
Heat Exchangers	(a)	+ 20%
Pumps	(a)	+ 35%
Cranes		
Overhead, Central Canal	\$15,000	\$60,000
5-Ton Bridge	\$ 7,000	\$40/ton-ft
Double Track	\$37/ft	\$40/ft
Demineralizer	\$450/gpm	+ 10%
Radiation Monitors	(a)	+ 50%
Buildings		
Service and Office	\$35/ft ²	\$43/ft ²
Storage Canals	\$10/ft ²	\$43/ft ²
Stands for Cans		
12-in. Dia. Basis	\$39 ea.	\$45 ea.

a. In Reference 1, these costs were shown as an empirical equation, and not as a unit cost.

the first two lines plus one-half man per shift for each additional line. The spray melter and phosphate glass processes would each require two men per shift. In addition, each process would require a minimum of one man per shift for pot preparation, testing and welding and an equal number for final test and loadout. Additional men are needed for these last two functions if more than 500 pots/year are processed. The following relationships were used:

1. Operating labor for pot calcination and spray in-pot melting:
 - a) Solidification operators 4 men + 2 men/line
 - b) Pot preparation, testing, welding 3 men + larger of 1 or $\frac{\text{pots/yr}}{500}$
 - c) Final pot testing, load-out 3 men + larger of 1 or $\frac{\text{pots/yr}}{500}$
2. Operating labor for the spray melter process and phosphate glass process:
 - a) Solidification operators 8 men (2/shift)
 - b) Pot preparation, testing, welding 3 men + larger of 1 or $\frac{\text{pots/yr}}{500}$
 - c) Final pot testing, load-out 3 men + larger of 1 or $\frac{\text{pots/yr}}{500}$
3. Operating labor cost: \$11,000/yr each.
4. Supervision: 4 shift supervisors at \$13,000/yr each.
5. Maintenance: 10% of equipment cost per year.
6. Plant overhead including payroll 100% of direct labor plus
benefits: 50% of maintenance cost
7. Waste pots: $\$(1530 \times D - 200)$ for stainless steel,
 $\$(600 \times D - 80)$ for carbon steel
 where D = diameter in feet

Stainless steel pots are required for pot calcination and spray in-pot melting. Carbon steel is satisfactory for other processes.

8. Utilities, chemicals and miscellaneous material: See Table 9.16.

TABLE 9.16. Estimated Operating Costs for Utilities,
Chemicals, and Materials, Dollars Per Year

<u>Case</u>	<u>Waste Type</u>	<u>Process</u>	<u>Utilities</u>	<u>Chemicals</u>	<u>Misc. Materials</u>
1	PW-4	Pot Calcination	5,250/line	620	10,000
2	PW-4	Spray Melter (Non-Pt)	6,900	31,700	10,000
3	PW-4	Spray In-Pot Melting	3,900/line	31,700	10,000
4	PW-4	Phosphate Glass	6,900	61,400	10,000
5	PW-4	Spray Melter (Pt)	19,700	53,000	10,000
6	PW-2	Pot Calcination	7,900/line	7,900	10,000
7	PW-2	Spray Melter (Non-Pt)	29,500	64,600	10,000
8	PW-2	Spray In-Pot Melting	5,250/line	62,400	10,000
9	PW-2	Phosphate Glass	4,900	26,900	10,000

9.4.2 Interim Liquid Storage Operating Costs

Operating labor costs were increased from \$10,000 to \$11,000 per year.

9.4.3 Interim Solid Storage Operating Costs

A fixed annual operating cost of \$180,000 was replaced with a labor cost based on four men (1 per shift) for up to

500 pots per year, plus one man for each additional 500 pots per year handled, plus a maintenance cost of 4% of the capital cost. Cost of labor was taken at \$11,000/yr-man plus 100% for overheads.

9.4.4 Shipping Costs

Using the equation in the Reference (1) program, the freight cost for a 2,000 mile round trip amounts to \$99/ton. The more recent Reference (6) indicates \$100/ton, which wasn't a large enough difference to warrant a change. However, based on the more recent report, handling costs were increased from \$900/trip to \$1,000/trip + \$80/can.

9.4.5 Salt Mine Storage

Salt mine storage costs were increased by 20% to allow for general cost escalation and by another 30% to allow for the cost of opening up a new mine. It is now improbable that waste storage will be permitted in the existing mine at Lyons, Kansas.

9.5 RESULTS OF ECONOMIC ANALYSIS

The final economic comparisons of the solidification processes are based, as nearly as possible, on optimized conditions for each process within the limited time and scope of this study. It is believed unlikely that any shift in major conclusion could be developed through further optimization studies using the ground rules of this study, or that further cost reductions large enough to significantly affect the total waste management costs would occur. A change in ground rules such as defining storage time limits, or pot size limits, use of different interest rates, a different method for final storage, or something of that nature could, however, result in different conclusions regarding relative costs, and care should be taken not to extrapolate results outside of the ground rule framework of this study.

9.5.1 Liquid Volume Effects

Most of the comparisons in this analysis are based on a minimum liquid volume assumption for any interim liquid storage. (17 gal/10⁴ MWD for PW-4 type waste and 104 gal/10⁴ MWD for PW-2 type waste.) Several cases were calculated to identify the importance of this minimum volume assumption.

Figure 9.2 shows the liquid storage costs as a function of storage time with specific liquid-volume parameters. The cost of liquid storage rises steeply with increasing storage time.* Figure 9.3 shows the liquid storage costs as a function of specific liquid volume with storage time parameters. The cost increases with specific volume increases are relatively small, indicating that one should not be unduly concerned with reducing liquid volumes to an absolute minimum for storage. The advantages of scale that come with the larger tank sizes required to store the larger volumes tend to reduce the impact of the larger volumes.

Figure 9.4 shows total waste management costs versus interim liquid storage time for the pot calcination process. The cost increase with increasing storage time is not as steep as liquid storage cost when total costs are considered. The increased liquid storage cost is partly compensated by reduced costs because of discounting effects and because of lower heat generation rates at the time of solidification and solid storage.

The relationships in Figure 9.4 are not smooth functions due to the discontinuities caused by the pot size-selection procedure.

9.5.2 Liquid Storage Tank Size Effects

All of the costs in Figure 9.2, 9.3, and 9.4 are based on tank sizes required for a filling time of one-half year.

* In addition, the effects of costs of replacement tanks for long storage time, which were not in the program, would further add to these costs.

FIGURE 9.2. Effect of Liquid Storage Time on Liquid Storage Cost

FIGURE 9.3. Effect of Specific Liquid Volume on Liquid Storage Cost

FIGURE 9.4. Effect of Storage Time and Specific Liquid Volume on Total Waste Management Cost for Pot Calcination Process

This is not necessarily an optimum condition, and costs of liquid storage can be reduced by selecting a tank size related to storage time requirements.

Figure 9.5 shows the effect of tank size on liquid storage costs. When liquid storage time is increased, larger tanks are more economical. There will be an optimum tank size for each storage condition.

Figure 9.6 shows how total waste management costs can actually be reduced as liquid storage time increases if tank sizes are increased at the same time.

9.5.3 Solid Volume Effects

Another important and, to some extent, controllable variable is the specific volume of the solid waste. The volume of solid waste can be increased by diluting with additional nonradioactive solid. However, in the case of PW-2 type wastes there are potential advantages for reducing solid waste volumes because the solid waste volumes are already diluted to a great extent.

Figure 9.7 shows how specific solid volume can influence total waste management costs in the case of the spray melter process with the PW-4 type waste. The most striking effect and the most significant result of this analysis is the sharp cost reduction indicated when the solid waste is diluted enough to permit solidifying without any interim liquid storage. This is possible because of the relatively high thermal conductivity of the spray melter product. This also proved to be possible with the phosphate glass product. Although the pot calcine can be diluted to a point where solidifying without liquid storage is possible, the cost advantage of elimination of the large investment in liquid storage facilities is more than compensated for by the increased cost of the other waste management parameters.

FIGURE 9.5. Effect of Tank Size on Liquid Storage Cost

FIGURE 9.6. Effect of Tank Size on Total Waste Management Cost for Spray Melter Process (Non-Platinum) with PW-4 Type Waste

FIGURE 9.7. Effect of Specific Volume of Solidified Waste and Liquid Storage Time on Total Waste Management Costs (Non-platinum Spray Melter with PW-4 Type Waste, Case 2)

In the case of the PW-2 waste, the spray melter product was dilute enough at minimum volume to allow canning without liquid storage.

There is also an option relating to selection of interim solid storage time, at least at zero or short liquid storage times. It turns out that in nearly every instance where this option is available, the optimum solid storage time is close to five years. This is illustrated by the example in Figure 9.8.

9.5.4 Mandatory Water Cooling Effects

Heat transfer rates can be increased and larger containers used if the heat content in a pot is increased to the point that water cooling is necessary to keep the pot centerline temperature below the stated maximum. One case, the spray melter with PW-4 type waste, was examined to identify any advantages for mandatory water cooling. Results are summarized in Figure 9.9 which indicates lower costs can be achieved with mandatory water cooling. Figure 9.9 shows that the advantage for mandatory water cooling results from the ability to can the waste at zero liquid storage time with less inert dilution of the solid. The exact minimum specific volume was not identified in either situation. In the case of pots sized and their heat contents adjusted for air cooling, (although water cooling was used in the design concepts and cost estimates for all air cooling cases) zero liquid storage was achieved at a specific volume of $0.65 \text{ ft}^3/10^4 \text{ MWd}$ but could not be achieved at 0.5 ft^3 per 10^4 MWd . In the case of mandatory water cooling, zero aqueous waste storage was achieved at a specific volume of 0.5 ft^3 per 10^4 MWd but not at 0.27. The uncertainty in the exact minimum specific volume is indicated by the dashed portion of the curves in Figure 9.9. Similar benefits should be achievable by improved solids container design, but such studies were beyond the scope of this analysis.

FIGURE 9.8. Example of Interim Solid Storage Optimization
Spray Melter (Non-Pt) Process with PW-4 Type Waste

FIGURE 9.9. Effect of Specific Volume of Solidified Waste on Total Waste Storage Costs at Zero Liquid Storage Time (Non-Platinum Spray Melter with PW-4 Type Waste)

9.5.5 Comparison of Processes

In nearly all cases, when interim liquid storage times of five years or more were specified, an extended interim solid storage period was required to allow for heat generation rates to decay to the point where final storage in a salt mine was permitted. This was because of the large container sizes selected.

The optimum cases for each process are compared in Table 9.17. In addition to the levelized cost results, this table also summarizes data on physical properties of the waste, size of storage tanks, pot size, sizes of the storage canals for interim solid storage, and number of shipping casks required. The initial capital requirement for each waste management step is also shown. This initial capital is the requirement at the time the specific facility is required, but not the requirement at the time the reprocessing plant is built. For example, the initial capital investment for the solidification process in Case 1 is \$8.8 million, but this is not required until 15 years after the reprocessing plant starts up because of the 15 years of interim liquid storage.

In the case of PW-4 type waste, the lowest cost process at 28.1 mills/MWh is the spray melter process with a non-platinum liner. Pot calcination is next at 30.2 mills/MWh followed by the platinum lined spray melter process, the spray in-pot melter process, and the phosphate glass process at 30.8, 31.2, and 33.6 mills/MWh respectively. The lower capital requirement at the time waste management operations start is only \$8.5 million in the case of the spray melter (non-platinum) compared to \$24.4 million for the liquid waste storage facility in the case of pot calcination. This is probably an even greater advantage than the levelized processing cost difference. A similar advantage holds for the cases where zero liquid storage time is achieved, compared to liquid storage up to 15 years as evaluated in this study.

TABLE 9.17. Process Comparisons of Waste Management Costs for Optimum Conditions

Process	PW-4 Type Waste					PW-2 Type Waste				
	Pot Calcine	Spray Melter (Non-Pt)	Spray Melter (Non-Pt)	Spray In-Pot Melting	Phosphate Glass	Spray Melter (Pt)	Pot Calcine	Spray Melter (Non-Pt)	Spray In-pot Melting	Phosphate Glass
Case	1	2	2 (Water Cooling Required)	3	4	5	6	7	8	9
Interim Storage, Yrs.										
Liquid	15.0	0	0	10.0	0	0	15.0	0	0	0
Solid	12.0	5	5	57.5	5	5	17.5	5.0	5.0	5.0
Total	27.0	5	5	67.5	5	5	32.5	5.0	5.0	5.0
Cost Summary, Mills/MWh										
Liquid Storage	23.7	0	0	22.6	0	0	32.1	0	0	0
Solidification	2.4	9.5	9.1	3.5	13.3	12.2	3.4	10.6	18.3	13.2 (a)
Solid Storage	2.0	9.5	8.2	4.9	10.5	9.5	5.2	11.6	11.6	10.5
Shipping	0.3	2.0	1.7	0	2.5	2.0	0.5	3.1	3.1	2.5
Final Storage	1.7	7.1	7.0	0.1	7.3	7.1	1.1	7.5	7.5	7.3
Total	30.2	28.1	26.0	31.2	33.6	30.8	42.3	32.7	40.5	33.5 (a)
Specific Volume										
Liquid, gal/10 ⁴ MWD	17	17	17	17	17	17	104	104	104	104
Solid, Ft ³ /10 ⁴ MWD	0.32	0.65	0.50	0.27	0.83	0.65	0.98	1.04	1.04	0.83
Solid Thermal Cond. Btu/hr-ft-°F	0.20	0.75	0.75	0.75	0.58	0.69	0.20	0.69	0.69	0.58
Solid Density, g/cm ²	1.3	3.0	3.0	3.0	2.9	0.3	1.3	2.9	2.9	2.9
Tank Size, 10 ⁶ gal	0.41	--	--	0.41	--	--	2.1	--	--	--
Number of Tanks	6	--	--	5	--	--	6	--	--	--
Initial Capital, \$ Millions	24.4	--	--	23.9	--	--	32.1	--	--	--
Pot, Nom. Dia., Inches	12	6	6	20	6	6	24	6	6	6
Number of Process Lines	2	1	1	1	1	1	8	1	14	1
Pots Per Year	233	1830	1407	79	2336	1830	198	2928	2928	2336
Initial Capital, \$ Millions	8.8	8.5	8.5	9.5	11.3	10.7	10.4	8.5	11.4	11.3
Number of Storage Canals	4	4	4	4	4	4	4	4	4	4
Width and Length, Ft	48×57	48×49	24×75	48×81	48×62	48×49	48×256	48×78	48×78	48×62
Initial Capital, \$ Millions	3.9	11.2	9.7	11.6	12.4	11.2	23.8	13.8	13.8	12.4
Number of Casks	2	3	3	3	4	3	4	5	5	4
Pots Per Cask	9	36	36	3	36	36	3	36	36	36
Initial Capital, \$ Millions	1.0	1.8	1.8	1.2	2.3	1.8	1.8	2.7	2.7	2.3
KW/Pot at Final Storage	4.0	1.3	1.7	4.0	1.0	1.3	3.9	0.8	0.8	1.0

a. Does not include the cost of treatment and disposal of the sulfate condensate from the solidifier melter.

The non-platinum lined spray melter process is also the lowest cost process for the PW-2 type waste, and pot calcination is the highest cost process here. A large capital cost advantage also pertains to all of the processes relative to the pot calcination process.

Tables 9.18 and 9.19 show the results of calculations for each process where interim liquid storage time is varied from zero to 15 years. For cases 1 through 5 (all cases with PW-4 waste) and case 9 (phosphate glass with PW-2 waste) the first cases shown have the solidified wastes diluted to permit solidification without aqueous storage.

The levelized costs for each waste management step in each case are plotted in Figures 9.10 and 9.11. These figures show how the costs for each waste management component change with liquid storage time and also indicate the relative importance of the several waste management operations.

An example of the computer program printout is shown in the Appendix for Case 2-BA.

TABLE 9.18. Detailed Waste Management Cost Data for PW-4 Waste

Case	A. Pot Calcination						B. Spray Melter (Non-Pt)						C. Spray In-Pot Melting						D. Phosphate Glass Process						E. Spray Melter (Pt)						
	1-AC (Dil)	1-AC	1-CA	1-DA	1-EA	1-FA	2-AC (Dil)	2-AC	2-BA	2-CA	2-DA	2-EA	2-FA	3-AC (Dil)	3-BC	3-CA	3-DA	3-EA	3-FA	4-AC (Dil)	4-BC	4-CA	4-DA	4-EA	4-FA	5-AC (Dil)	5-BC	5-CA	5-DA	5-EA	5-FA
Interim Storage, Yrs.																															
Liquid	0	2.5	5.0	7.5	10.0	15.0	0	1.0	2.5	5	7.5	10	15.0	0	2.5	5.0	7.5	10.0	15.0	0	2.5	5.0	7.5	10.0	15.0	0	2.5	5.0	7.5	10.0	15.0
Solid	5.0	5.0	2.5	1.0	5.0	12.0	5	5.0	5.5	27	44	57.5	85.0+	5.0	5.5	27.0	44.0	57.5	85.0+	5.0	5.0	12.0	26.0	41.0	36.0	5.0	5.5	26.0	44.0	48.0	43.0
Total	5.0	7.0	7.5	8.5	15.0	27.0	5.0	6.0	8.0	32.0	51.5	67.5	100.0+	5.0	8.0	32.0	51.5	67.5	100.0+	5.0	7.5	17.0	33.5	51.0	51.0	5.0	8.0	31.0	51.5	58.0	58.0
Cost Summary, Mills/MWH																															
Liquid Storage	0	17.9	20.1	21.5	22.6	23.7	0	12.2	17.6	20.1	21.5	22.6	23.7	0	17.6	20.1	21.5	22.6	23.7	0	17.6	20.1	21.5	22.6	23.7	0	17.6	20.1	21.5	22.6	23.7
Solidification	20.8	8.2	5.8	4.8	3.7	2.4	9.5	8.5	7.5	5.4	4.4	3.4	2.3	14.3	8.3	5.7	4.6	3.5	2.4	13.3	10.5	7.7	6.2	5.0	3.4	12.2	9.9	7.1	5.8	4.5	3.2
Solid Storage	14.7	4.1	1.8	0.9	1.5	2.0	9.5	4.9	4.3	7.2	6.2	4.9	NA	9.5	4.3	7.2	6.2	4.9	NA	10.5	5.7	7.6	9.3	7.6	4.9	9.5	5.2	9.2	7.9	6.0	3.9
Shipping	4.1	0.8	1.3	1.2	0.7	0.3	2.0	1.0	1.1	0.2	0.1	0.0	NA	2.0	1.1	0.2	0.1	0.0	NA	2.5	1.5	1.0	0.4	0.1	0.1	2.0	1.4	0.4	0.1	0.1	0.1
Final Storage	8.0	5.2	5.8	5.7	3.2	1.7	7.1	6.2	5.0	1.2	0.3	0.1	NA	7.1	5.0	1.2	0.3	0.1	NA	7.3	5.3	2.9	1.1	0.4	0.4	7.1	5.0	1.3	0.3	0.2	0.2
Total	47.6	36.2	34.8	34.0	31.7	30.2	28.1	32.8	35.4	34.0	32.5	31.1	NA	32.9	36.2	34.3	32.7	31.2	NA	33.6	40.7	39.2	38.5	35.6	32.6	30.8	39.0	38.0	35.7	33.5	31.1
Specific Volume																															
Liquid, gal/10 ⁴ MWD	17.0	17.0	17.0	17.0	17.0	17.0	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17
Solid, Ft ³ /10 ⁴ MWD	1.6	0.32	0.32	0.32	0.32	0.32	0.65	0.27	0.27	0.27	0.27	0.27	0.27	0.65	0.27	0.27	0.27	0.27	0.27	0.83	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.44	0.44	0.44	0.44
Solid Thermal Cond. Btu/hr-ft ² -°F	0.20	0.20	0.20	0.20	0.20	0.20	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.58	0.58	0.58	0.58	0.58	0.58	0.69	0.69	0.69	0.69	0.69	0.69
Solid Density, g/cm ²	1.3	1.3	1.3	1.3	1.3	1.3	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	2.9	2.9	2.9	2.9	2.9	2.9	3.3	3.3	3.3	3.3	3.3	3.3
Tank Size, 10 ⁶ gal	--	0.07	0.28	0.41	0.41	0.41	--	0.07	0.13	0.28	0.41	0.41	0.41	--	0.13	0.28	0.41	0.41	0.41	--	0.13	0.28	0.41	0.41	0.41	--	0.13	0.28	0.41	0.41	0.41
Number of Tanks	--	7.0	4.0	4.0	5.0	6.0	--	4	5	4	4	5	6	--	5	4	4	5	6	--	5	4	4	5	6	--	5	4	4	5	6
Initial Capital, \$ Millions	--	15.9	20.9	23.7	23.9	24.4	--	14.8	15.6	20.9	23.7	23.9	24.4	--	15.6	20.9	23.7	23.9	24.4	--	15.6	20.9	23.7	23.9	24.4	--	15.6	20.9	23.7	23.9	24.4
Pot, Nom. Dia., Inches	6	6	8	8	10	12	6	6	8	12	16	20	24	6	8	12	16	20	24	6	12	16	20	24	24	6	10	16	20	24	24
Number of Process Lines	15	3	3	3	3	2	1	1	1	1	1	1	1	9	2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Pots Per Year	4504	900	520	520	330	323	1830	760	439	196	124	79	55	1830	439	196	124	79	55	2336	472	299	190	132	132	1830	454	203	129	89	89
Initial Capital, \$ Millions	11.2	9.2	9.2	9.2	9.2	8.8	8.5	9.6	9.6	9.6	9.6	9.6	9.6	10.4	9.8	9.6	9.6	9.6	9.6	11.3	12.4	12.4	12.4	12.4	12.4	10.7	11.9	11.9	11.9	11.9	11.9
Number of Storage Canals	4	4	4	2	2	4	4	4	4	4	4	4	NA	4	4	4	4	4	NA	4	4	4	4	4	4	4	4	4	4	4	4
Width and Length, Ft	48×120	24×48	24×24	24×29	24×28	24×57	48×49	24×40	24×44	48×81	48×81	48×81	NA	48×49	24×44	48×81	48×81	48×81	NA	48×62	48×49	48×117	48×194	48×194	48×194	48×49	24×72	48×131	48×131	48×131	48×131
Initial Capital, \$ Millions	17.4	5.9	3.6	2.0	4.9	8.9	11.2	6.3	5.7	12.4	11.9	11.6	NA	11.2	5.7	12.4	11.9	11.6	NA	12.4	8.5	14.2	20.5	20.0	19.5	11.2	7.1	16.3	15.7	15.3	14.9
Number of Casks	6	2	4	4	3	2	3	2	3	2	3	3	2	3	3	2	3	3	2	4	4	4	4	3	3	3	3	3	3	3	3
Pots Per Cask	36	36	9	9	9	9	36	36	16	9	4	3	3	36	16	9	4	3	3	36	9	4	3	3	3	36	9	4	3	3	3
Initial Capital, \$ Millions	3.1	1.1	1.7	1.7	1.5	1.0	1.8	1.3	1.1	1.0	1.4	1.2	1.0	1.8	1.9	1.0	1.4	1.2	1.0	2.3	2.3	1.8	1.5	1.3	1.3	1.8	1.8	1.3	1.1	1.4	1.4
kW/Pot at Final Storage	0.5	2.0	3.9	3.85	3.9	4.0	1.3	2.8	4.0	3.9	4.0	4.0	NA	1.3	4.0	3.9	4.0	4.0	NA	1.0	3.9	4.0	3.9	3.9	3.9	1.3	3.85	4.0	3.8	4.0	4.0

TABLE 9.19. Detailed Waste Management Cost Data for PW-2 Waste

Case	A. Pot Calcination						B. Spray Melter (Non-Pt)						C. Spray In-Pot Melting						D. Phosphate Glass Process					
	6-AC	6-BC	6-CB	6-DA	6-EA	6-FA	7-AC	7-BC	7-CA	7-DA	7-EA	7-FA	8-AC	8-BC	8-CA	8-DA	8-EA	8-FA	9-AC(Dil)	9-BC	9-CA	9-DA	9-EA	9-FA
Interim Storage, Yrs.																								
Liquid	1.0	2.5	5.0	7.5	10.0	15.0	0	2.5	5.0	7.5	10.0	15.0	0.0	2.5	5.0	7.5	10.0	15.0	0	2.5	5.0	7.5	10.0	15.0
Solid	5.0	5.0	2.5	2.0	9.5	17.5	5.0	5.0	11.0	23.5	21.0	16.0	5.0	5.0	11.0	23.5	21.0	16.0	5.0	5.0	25.0	39.5	32.0	32.0
Total	6.0	7.5	6.0	9.5	19.5	32.5	5.0	7.5	16.0	31.0	31.0	31.0	5.0	7.5	16.0	31.0	31.0	31.0	5.0	7.5	30.0	47.0	47.0	47.0
Cost Summary, Mills/Mwh																								
Liquid Storage	13.6	20.3	24.7	29.0	30.7	32.1	0	20.3	24.7	29.0	30.7	32.1	0.0	20.3	24.7	29.0	30.7	32.1	0	20.3	24.7	29.0	30.7	32.1
Solidification	16.7	11.9	8.5	6.6	5.1	3.4	10.6	8.1	5.8	4.7	3.7	2.5	18.3	9.8	6.7	5.2	4.1	2.9	13.2	10.5	7.6	6.2	4.9	3.4
Solid Storage	9.0	7.1	2.9	2.0	4.8	5.2	11.6	7.1	9.5	13.0	9.7	5.0	11.6	7.1	9.5	13.0	9.7	5.0	10.5	6.1	12.5	10.8	8.1	5.3
Shipping	2.4	2.7	2.1	2.3	1.0	0.5	3.1	2.8	1.1	0.5	0.5	0.5	3.1	2.8	1.1	0.5	0.5	0.5	2.5	1.6	0.2	0.2	0.2	0.2
Final Storage	6.7	5.4	5.8	5.0	2.7	1.1	7.5	5.3	3.0	1.3	1.3	1.3	7.5	5.3	3.0	1.3	1.3	1.3	7.3	5.3	1.4	0.5	0.5	0.5
Total	48.5	47.4	44.0	44.9	44.4	42.3	32	43.6	44.1	48.5	45.9	41.5	40.5	45.3	45.0	49.0	46.3	41.8	33.5	43.8	46.6	44.4	41.4	41.4
Specific Volume																								
Liquid gals/10 ⁴ MWh	104	104	104	104	104	104	104	104	104	104	104	104	104	104	104	104	104	104	104	104	104	104	104	104
Solid ft ³ /10 ⁴ MWh	0.98	0.98	0.98	0.98	0.98	0.98	1.04	1.04	1.04	1.04	1.04	1.04	1.04	1.04	1.04	1.04	1.04	1.04	0.83	0.73	0.73	0.73	0.73	0.73
Solid Thermal Cond. Btu/hr-ft ² -°F	0.20	0.20	0.20	0.20	0.20	0.20	0.69	0.69	0.69	0.69	0.69	0.69	0.69	0.69	0.69	0.69	0.69	0.69	0.58	0.58	0.58	0.58	0.58	0.58
Solid Density, g/cm ²	1.3	1.3	1.3	1.3	1.3	1.3	2.9	2.9	2.9	2.9	2.9	2.9	2.9	2.9	2.9	2.9	2.9	2.9	2.9	2.9	2.9	2.9	2.9	2.9
Tank Size, 10 ⁶ gal	0.3	0.57	1.35	2.11	2.11	2.11	--	0.57	1.35	2.11	2.11	2.11	--	0.57	1.35	2.11	2.11	2.11	--	0.57	1.35	2.11	2.11	2.11
Number of Tanks	4	5	4	4	5	6	--	5	4	4	5	6	--	5	4	4	5	6	--	5	4	4	5	6
Initial Capital, \$ Millions	16.5	17.6	25.2	31.5	31.6	32.1	--	17.6	25.2	31.5	31.6	32.1	--	17.6	25.2	31.5	31.6	32.1	--	17.6	25.2	31.5	31.6	32.1
Pot Nom. Dia, Inches	6	10	12	16	20	24	6	16	20	24	24	24	6	16	20	24	24	24	6	12	20	24	24	24
Number of Process Lines	15	10	10	9	9	8	1	1	1	1	1	1	14	3	2	1	1	1	1	1	1	1	1	1
Pots Per Year	2759	1011	712	451	287	198	2928	479	304	210	210	210	2928	479	304	210	210	210	2336	530	214	148	148	148
Initial Capital, \$ Millions	12.3	10.9	10.9	10.8	10.8	10.4	8.5	9.6	9.6	9.6	9.6	9.6	11.4	10.1	9.8	9.6	9.6	9.6	11.3	12.4	12.4	12.4	12.4	12.4
Number of Storage Canals	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4
Width and Length, Ft	48×73	48×73	24×73	24×59	48×139	48×256	48×78	48×78	48×171	48×311	48×311	48×249	48×78	48×78	48×171	48×311	48×311	48×249	48×62	48×55	48×218	48×218	48×218	48×218
Initial Capital, \$ Millions	11.8	10.6	6.0	5.0	14.9	23.8	13.8	10.8	18.2	29.1	28.6	23.1	13.8	10.8	18.2	29.1	28.6	23.1	12.4	9.0	22.8	22.2	21.8	21.2
Number of Casks	4	6	5	6	5	4	5	6	5	4	4	4	5	6	5	4	4	4	4	4	4	3	3	3
Pots Per Cask	36	9	9	4	3	3	36	4	3	3	3	3	36	4	3	3	3	3	36	9	3	3	3	3
Initial Capital, \$ Millions	2.1	3.3	2.7	3.0	1.8	1.8	2.7	3.2	1.8	1.8	1.8	1.8	2.7	3.2	1.8	1.8	1.8	1.8	2.3	2.3	1.4	1.3	1.3	1.3
KW/Pot at Final Storage	0.8	1.8	2.8	4.0	3.9	3.9	0.8	3.8	4.0	3.9	3.9	3.9	0.8	3.8	4.0	3.9	3.9	3.9	1.0	3.5	4.0	4.0	4.0	4.0

A. Pot Calcination,
Case 1

B. Spray Melter (Non-Pt)
Solidification, Case 2

C. Spray In-Pot Melting,
Case 3

D. Phosphate Glass Solidi-
fication, Case 4

E. Spray Melter (Pt) Solidi-
fication, Case 5

FIGURE 9.10.
Effect of Interim Liquid Storage
on Minimum Waste Management Costs
with PW-4 Type Waste

A. Pot Calcination, Case 6

B. Spray Melter (Non-Pt) Solidification, Case 7

C. Spray In-Pot Melting, Case 8

D. Phosphate Glass Solidification, Case 9

FIGURE 9.11. Effect of Interim Liquid Storage on Minimum Waste Management Costs with PW-2 Type Waste

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10.0 EVALUATION OF THE THREE PROCESSES
FOR COMMERCIAL USE

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10.0 EVALUATION OF THE THREE PROCESSES FOR COMMERCIAL USE

The evaluations of the three solidification processes as demonstrated in the WSEP were presented in Sections 4, 5, and 6 and design concepts were developed in Section 8. In this section, the highlights of those previous sections are used to compare on a qualitative basis the three processes as they would be applied to commercial use for each of the two study wastes and flowsheets described in Section 7.

10.1 BASES

The general design bases described in Section 8.1 also apply to the evaluations here. As much as possible, these evaluations are based on inherent characteristics of the processes and their inherent equipment requirements, rather than on any specific design. Also, the conceptual designs derived in Section 8 are used as guides where appropriate. These evaluations are primarily qualitative, with some degree of quantitateness where warranted.

The general characteristics which are believed to be those most important in the application of these processes are used for the comparisons. Those characteristics are:

- State of development and R&D requirements,
- Amenability to scale-up,
- Flexibility for handling a variety of wastes,
- Complexity, reliability, and maintainability,
- Operating and accident safety,
- Control of radionuclides in effluents,
- Characteristics of the solidified waste.

Brief comparisons for each process are made for each of these characteristics in the following sections. These comparisons represent the consensus of those who were associated with the

WSEP program and/or those knowledgeable about the technical and operational aspects of fuel reprocessing. Consequently, the overall comparisons are believed to be reasonably fair and accurate for the majority of specific cases and applications. However, it should be pointed out that these comparisons are estimates only, that they are necessarily subjective in some cases, and that they may be based upon criteria not necessarily in agreement with those of others having interest in the information.

If it is assumed that the final solidified waste and its package from any of the processes provides an acceptable degree of safety for its final disposal, then the major factor for comparison is economics. This is an important assumption which remains to be determined. Consequently, the characteristics compared here are subordinate to the cost characteristics presented in Section 9. These characteristics can be viewed for possible trade-offs with costs or with each other to satisfy specific circumstances.

10.2 STATE OF DEVELOPMENT AND RESEARCH AND DEVELOPMENT REQUIREMENTS

Because of the unusually high degree of reliability and safety required in nuclear fuel reprocessing, nearly all new processes, no matter how well developed, will normally require a small amount of research or development to optimize the process and to be assured that the process will be properly integrated into the conditions of that plant. This research and development can range from special tests made in the plant equipment during shakedown operations through laboratory to extensive pilot plant testing. In general, the processes demonstrated in WSEP are ready for application to industrial plants with PW-2 and PW-4m or similar wastes with only low to modest needs for development, as shown in Table 10.1.

TABLE 10.1. Potential Research and Development Needs for PW-2 and PW-4m Wastes

Subject Area		R&D Needs (a)		Remarks
General	Specific	Degree	Lab or P.S.	
<u>Pot Calcination</u>				
Solidification Chemistry	----	None	----	
Feed system to Solidifier	----	None	----	
Solidifier Equipment	Pot head-disconnect	Minor	P.S.	For simple, inexpensive head
	Cooling in furnace	Minor	P.S.	
	Scale-up of calcining-cooling time requirements	Modest	P.S.	
Effluent Control or Treatment	----	None	----	
Solidified Waste	----	None	----	

<u>Spray Solidification - Continuous Melting (Phosphate and Borosilicate Systems)</u>				
Solidification Chemistry	Minimize second phase solid	Minor	Lab	Optional studies for borosilicate system only
Feed System to Solidifier	Solids feeding system for some cases	Minor-Modest	P.S.	For PW-2 phosphate and PW-4m boro silicate systems
Solidifier Equipment	Scale-up, erosion of atomizing system	minor-Modest	Lab	
	Scale-up sizing of calciner and melter	Modest	P.S.	Only if desire to minimize equipment size
	Alternate melter material or design	Modest	Lab P.S.	Unlikely that alternative material exists for phosphate system
	Melt discharge design	Minor	P.S.	Confirm heat transfer design of freeze valve system
	Melter reliability	Modest	P.S.	Primarily for phosphate system
Effluent Control or Treatment	Reduce Ru volatilization	Minor-Modest	Lab	Phosphate systems only, and only if desired to reduce volatilization
Solidified Waste	Devitrification Conditions	Minor	Lab	
<u>Spray Solidification - In-Pot Melting (Phosphate and Borosilicate Systems)</u>				
Solidification Chemistry	Minimize second phase solid	Minor	Lab	Optional studies for borosilicate system only
Feed System to Solidifier	Solids feeding system	Minor-Modest	P.S.	
Solidifier Equipment	Scale-up, erosion of atomizing system	Minor-Modest	Lab	
	Scale-up sizing of calciner	Modest	P.S.	Only if desired to minimize calciner size
	Determine capacity of in-pot melting	Modest	P.S.	To minimize number of pot lines
	Multiple-pot feed system	Modest	P.S.	Not required if large pots are used
Effluent Control or Treatment	Reduce Ru volatilization	Minor-Modest	Lab	Phosphate systems only, and only if desired to reduce volatilization
Solidified Waste	----	None	---	

<u>Phosphate Glass Solidification</u>				
Solidification Chemistry	----	None	---	Some variation in glass mixtures available
	Flowsheet and additives	Minor	Lab	
Feed System to Solidifier	----	None	---	
Solidifier Equipment	Feed system to melter	Modest	P.S.	Only if desire to minimize equipment size
	Melter scale-up	Modest	P.S.	
	Melt discharge design	Minor	P.S.	
	Alternate melter material or design	Modest	Lab P.S.	
	Pt melter reliability	Modest	P.S.	
Effluent Control or Treatment	----	None	---	
Solidified Waste	Determine devitrification conditions	Minor	Lab	

<u>All Processes</u>				
Solidification Chemistry	Iodine, fluorine, bromine retention	Minor-Modest	Lab	
Feed to Solidifier	Characterize aqueous waste	Minor	Lab	
Solidified Waste	Determine overall characteristics	Minor	Lab	

a. Legend: Lab Laboratory scale
P.S. Pilot Scale

Overall, the R&D requirements for pot calcination are less than for the other solidifiers. Major studies on solidification chemistry are generally not needed, although testing of some variations in available chemistry for the phosphate glass process may be desired. Also, studies to permit retention of radioiodine, fluorine and bromine in the solid wastes are believed to be necessary for all processes. Some studies will be necessary to determine characteristics and chemical stability limits of the concentrated aqueous wastes for all systems. (Most of these studies would be required whether or not solidification is used.) Also, characterization of the specific solidified waste for all processes is believed to be necessary. The only work believed to be needed for specific feed systems to the solidifiers are those associated with significant scale-up of the atomizing feed nozzle for the spray calciner and further definition of the spray calcination systems. Remote metering of solids to the spray solidifier in an accurate, reliable system such that solids do not stick to the walls of the solidifier is a design-development problem which remains to be completed. The ball valve-airlock system used in WSEP performed satisfactorily but required considerable manual operation.

All of the schemes are in need of some R&D studies for the solidification equipment itself. For the pot calciner, some development of a pot head connect-disconnect system is required because of the good seal required and the desire to minimize the spilling of the loosely-held calcine near the pot heat joint. The remote pot head used in WSEP met these requirements but is believed to be too complex and to require excessively expensive pots for production purposes. Time requirements for the calcining-plus-cooling period with larger pots need to be confirmed, but this might be done during the initial production period if plant capacity is not critical at that time. Cooling

in the pot calciner furnace may need R&D studies if the heat rate in the pots is high enough to require water or effective air cooling. For the phosphate glass and the phosphate-based spray-melter processes, there is a considerable incentive to use a material for the melter besides platinum which is extremely expensive, has a very low thermal emissivity, and whose reliability needs to be proven. For the spray-continuous melter with the borosilicate system, material of construction studies are needed for nonplatinum melters. Similarly, in both continuous processes, there is an incentive to develop more definitive information on scale-up of the melter (which might provide for considerable reduction in the melter size), and the discharge system for the melters (which requires some experimental studies before confirming final designs).

In effluent control, it would be desirable to perform some R&D to reduce the ruthenium volatilization with phosphate systems in the spray solidifier. In all cases, some laboratory characterization of the final composition of solidified waste is believed to be necessary.

10.3 AMENABILITY TO SCALE-UP

The solidification equipment in WSEP had an instantaneous capacity for solidifying waste from up to 1 tonne/day of fuel. Near-future commercial fuel reprocessing plants in the USA will have capacities for processing about 5 tonnes/day, and plants with higher capacities may be possible in the more distant future. Consequently, the industrial need for scaling up from WSEP capacities to 5 tonnes/day already exists (concepts for 5 tonnes/day were presented in Section 8), and the need for higher capacities may exist in the future.

The spray and phosphate glass processes are continuous and therefore are inherently amenable to scale-up. However, some limits may exist. For the spray process as presently conceived,

the degree of practical scale-up appears to be limited currently by atomization efficiency of larger-capacity nozzles, by possible loss of heat transfer in the calciner in sizes greater than about three feet in diameter, by the need for extraordinarily expensive or large melter size for phosphate melts, or by the batch melting capacity of the in-pot melting pots. Cases for each solidifier were presented in the design concepts in Section 8 which appear to be acceptable but some limits to alternative solidification schemes (i.e., very short cooling times or very high-salt wastes) may be approached by existing equipment scale-up information. Further scale-up for calciners and melters of the largest dimensions in the design concepts must be confirmed and may need some development (which could result in significant modifications to the design concepts). For in-pot melting with the spray process, the maximum capacity must be confirmed to determine more precisely the need for parallel pot lines, and the multiple-pot feed system must be developed. The phosphate glass evaporator can be scaled up to almost any reasonable size, but the melter has greater potential scale-up restrictions than the smaller melter for the spray system.

The pot calciner is a batch system with batch size limited by heat generation rates within the pot and processing rates limited by heat transfer restrictions. Consequently, for a given waste and cooling time, scale-up beyond about 1 tonne/day per pot for PW-2 or about 2 tonnes/day per pot for PW-4m waste can only be done by adding parallel lines. In addition, because the pot calcine has relatively low thermal conductivity, more parallel lines of smaller-sized pots are required as wastes contain increasing amounts of heat from radioactivity decay. Other concepts for pot design which could be developed, such as those with internal fins or internal cooling provisions, should increase capacity of the pot calciner system.

10.4 FLEXIBILITY FOR HANDLING A VARIETY OF WASTES

All of the processes in WSEP can be used for processing the wastes which result from "normal" Purex reprocessing schemes. However, there are some variations in adaptability of each process to various waste constituents, as summarized in Table 10.2 for the most likely chemical constituents expected in high level wastes. Specific details of the limitations of the three processes for handling the various waste constituents have been presented in Section 3 of this report and in the preceding 10 volumes of this report series.

In general, pot calcination is the most adaptable to variations in waste compositions, because it involves a simple step of heating to evaporate water and to decompose the nitrates. The melt-making processes are somewhat more restrictive to certain constituents, with the borosilicate schemes being the most versatile in the waste composition of the final solid waste and the phosphate system the most versatile in handling the feeds to the solidifier.

Fluoride may be present in wastes if it is used in dissolution of the spent nuclear fuel or in plant flushing or decontamination operations. No work has been done on incorporating fluoride into the solidified waste in the WSEP processes. Similarly, some small percentage of the radioiodine and bromine in the fuel should report to the high level waste. In general, these constituents are expected to volatilize unless volatilization can be limited by forming stable salts (such as calcium fluoride).

10.5 COMPLEXITY, RELIABILITY, AND MAINTAINABILITY

The complexity, reliability, and maintainability of the key process equipment are very important factors in the planning and operation of any production scheme, particularly in nuclear fuel reprocessing. A qualitative estimate of these

TABLE 10.2. Relative Flexibility for Processing Varying Waste Constituents

Constituent in Waste	Process			
	Pot Calcination	Spray Phosphate	Solidification Borosilicate	Phosphate Glass
<u>Cations</u>				
Alkali metals	R/++ (d)	R/-	R/+ (c)	R/-
Iron (or Cr or Ni)	R/0	R/-	R/+	R/-
Alkaline earth metals	R/-	L/++ (d)	R/+ (c)	L/0
Aluminum	R/0	L/++ (d)	R/+	R/-
Manganese	R/0	R/+ (a)	R/+ (a)	R/++
High Fission Product	R/0	R/++	R/+	R/++
<u>Soluble Poison Materials</u>				
Boron	R/+ (a)	R/0	R/-	U
Cadmium	R/0 (a)	R/-	R/0 (a)	R/+ (a)
Gadolinium	R/0 (a)	R/++ (a)	R/+ (a)	R/++ (a)
<u>Anions</u>				
Nitrate	R/0	R/0	R/0	R/0
Sulfate	R/+ (c)	L/++	L/+ (e)	L/+ (b)
Fluoride	U	U	U	U
Iodides, etc.	U	U	U	U

Legend: R = Readily processed
 L = Limitations for processing
 U = Unknown

Chemical additives required for moderate amounts of constituents:

/0 no chemical additives required
 /+ ≤ 1 equivalent chemical additive/equivalent of constituent
 /++ > 1 equivalent chemical additive/equivalent of constituent
 /- less chemical additives are required as a result of the constituent

- a. Estimated only; experimental data not available.
 b. The sulfate is volatilized and forms another waste stream.
 c. It is also possible for additives to be reduced as a result of this constituent.
 d. For wastes containing sulfate, the chemical additive required for this constituent would likely be reduced as a result of the constituent.
 e. Sulfate will separate out as a separate solid phase.

characteristics is presented in Table 10.3 for two wastes. The key process equipment for each process is listed, with estimates shown for each equipment piece. The primary bases for the estimates are the design concepts developed in Section 8, modified with judgment factors based upon experience in WSEP as summarized in Sections 4 through 7. Other design concepts might cause revision of the estimates. Complexity estimates are based upon the amount of process equipment and the relative complexity and sensitivity of design and operation of the equipment. Reliability estimates are for the expected amount of repairs and the expected length of operation before repairs or replacement is required. Maintainability estimates are based upon the relative ease of repair or replacement of the equipment. Repair of any of the equipment listed will require shutdown of the entire solidifier (except perhaps for the pot calcination and the in-pot melting systems, the pot lines not needing repair could remain in operation).

The comparisons in Table 10.3 are complicated by significant changes in some process characteristics when processing sulfate-containing wastes (such as PW-2) and nonsulfate wastes (such as PW-4m). In addition, interim time of storage of aqueous wastes has significant effects on the batch processes, particularly pot calcination. The specific cooling time selected was 1.5 ± 0.3 years, because approximately comparable information has been developed for this case. Shorter cooling time would require more pot lines and smaller pots; longer cooling times would have the reverse effects.

The pot calcination process has the most key pieces of process equipment for the two cases selected, but it has the fewest different types of process equipment pieces. The relative disadvantages or advantages of the need for parallel but identical lines for the pot calciner (and sometimes for spray, in-pot-melting) are a matter which must be determined by the individual

ty,
nt(a)

Key Equipment	Sulfate Containing Was							
	Simplicity ^(b,c)				Reliability ^(c)			
	Spray				Spray			
	Phosphate				Phosphate			
	Pot Cal.	Pt Melter	IPM ^(d)	Phos. Glass	Pot Cal.	Pt Melter	IPM ^(d)	Phos. Glass
Feed Nozzle	--	m	m	--	--	l	l	--
Continuous Calciner	--	m	m	--	--	h	h	--
Continuous Calciner Furnace	--	m	m	--	--	h	h	--
Continuous Calciner Off-Gas System	--	l	l	--	--	m	m	--
Evaporator	--	--	--	l	--	--	--	m
Feed System to Melt Step	--	--	m	l	--	--	m	m
Continuous Melter	--	m	--	m	--	l	--	l
Continuous Melter Furnace	--	m	--	m	--	m	--	l
Cont. Melter Discharge Sys.	--	m	--	m	--	l	--	m
Melt Step Off-Gas System	--	--	--	h	--	--	--	m
Pot Calciner Off-Gas System ^(e)	1(7)	--	--	--	m(7)	--	--	--
Pot Calciner Head ^(e)	1(7)	--	--	--	m(7)	--	--	--
Pot	m	h	m	h	m	h	m	h
Pot Furnace or Receiver Sys. ^(e)	1(7)	h	m(1)	h	1(7)	h	m(1)	m
Total Pieces of Key Process Equipment	22	10	7	8				
Total Types of Key Process Equipment	4	10	7	8				

a. Comparisons are based on the cases shown in Tables 8.1, 8.2 and 8.3 which i₁

Solidifier	Melt System	PW-2 Waste			
		Pot Dia, in	Age, yrs	No. of pot lines	Pots/da
Pot Cal.	--	12	1.7	7	2.0
Spray-Melter	Phosphate	20	1.2	1	0.7
-IPM	Phosphate	20	1.2	1	0.7
-Melter	--	--	--	--	--
-IPM	--	--	--	--	--
Phos. Glass	Phosphate	16	1.7	1	0.9

tes

TABLE 10.3. Comparisons of Relative Simplicity, Reliability, and Maintainability of Solidification Equipment(a)

Key Equipment	Sulfate Containing Waste (PW-2)												Relatively Pure Fission Product Waste Without Sulfate (PW-4m)																	
	Simplicity ^(b,c)				Reliability ^(c)				Maintainability ^(c)				Simplicity ^(b,c)				Reliability ^(c)				Maintainability ^(c)									
	Spray			Phos. Glass	Spray			Phos. Glass	Spray			Phos. Glass	Spray			Phos. Glass	Spray			Phos. Glass	Spray			Phos. Glass	Spray			Phos. Glass		
	Phosphate		Borosilicate		Phosphate		Borosilicate		Phosphate		Borosilicate		Phosphate		Borosilicate															
	Pot Cal.	Pt Melter	IPM ^(d)		Pot Cal.	Pt Melter	IPM ^(d)		Pot Cal.	Pt Melter	IPM ^(d)		Pot Cal.	Pt Melter	IPM ^(d)		Pot Cal.	Pt Melter	IPM ^(d)		Pot Cal.	Pt Melter	IPM ^(d)		Pot Cal.	Pt Melter	IPM ^(d)		Pot Cal.	Pt Melter
	Pot Cal.	Pt Melter	IPM ^(d)	Phos. Glass	Pot Cal.	Pt Melter	IPM ^(d)	Phos. Glass	Pot Cal.	Pt Melter	IPM ^(d)	Phos. Glass	Pot Cal.	Pt Melter	Pt Melter	Non-Pt Melter	IPM ^(d)	Phos. Glass	Pot Cal.	Pt Melter	Pt Melter	Non-Pt Melter	IPM ^(d)	Phos. Glass	Pot Cal.	Pt Melter	Pt Melter	Non-Pt Melter	IPM ^(d)	Phos. Glass
Feed Nozzle	--	m	m	--	--	l	l	--	--	m	m	--	--	m	m	m	m	--	--	l	l	l	l	--	--	m	m	m	m	--
Continuous Calciner	--	m	m	--	--	h	h	--	--	m	m	--	--	m	m	m	m	--	--	h	h	h	h	--	--	m	m	m	m	--
Continuous Calciner Furnace	--	m	m	--	--	h	h	--	--	m	m	--	--	m	m	m	m	--	--	h	h	h	h	--	--	m	m	m	m	--
Continuous Calciner Off-Gas System	--	l	l	--	--	m	m	--	--	m	m	--	--	l	l	l	l	--	--	m	m	m	m	--	--	m	m	m	m	--
Evaporator	--	--	--	l	--	--	--	m	--	--	--	m	--	--	--	--	--	l	--	--	--	--	--	m	--	--	--	--	--	m
Feed System to Melt Step	--	--	m	l	--	--	m	l	--	--	m	m	--	--	m	m	m	l	--	--	m	m	m	l	--	--	m	m	m	m
Continuous Melter	--	m	--	m	--	l	--	l	--	l	--	l	--	m	m	m	--	m	--	l	l	m	--	l	--	l	l	m	--	l
Continuous Melter Furnace	--	m	--	m	--	m	--	m	--	l	--	l	--	m	m	m	--	m	--	m	m	m	--	m	--	l	l	l	--	l
Cont. Melter Discharge Sys.	--	m	--	m	--	l	--	l	--	m	--	m	--	m	m	m	--	m	--	l	l	m	--	l	--	m	m	m	--	m
Melt Step Off-Gas System	--	--	--	h	--	--	--	m	--	--	--	m	--	--	--	--	--	m	--	--	--	--	--	m	--	--	--	--	--	m
Pot Calciner Off-Gas System ^(e)	1(7)	--	--	--	m(7)	--	--	--	m(7)	--	--	--	1(4)	--	--	--	--	--	m(4)	--	--	--	--	--	m(4)	--	--	--	--	--
Pot Calciner Head ^(e)	1(7)	--	--	--	m(7)	--	--	--	m(7)	--	--	--	1(4)	--	--	--	--	--	m(4)	--	--	--	--	--	m(4)	--	--	--	--	--
Pot	m	h	m	h	m	h	m	h	m	h	m	h	m	h	h	h	m	h	m	h	h	h	m	h	m	h	h	h	m	h
Pot Furnace or Receiver Sys. ^(e)	1(7)	h	m(1)	h	1(7)	h	m(1)	h	1(7)	m	m(1)	m	1(4)	h	h	h	m(2)	h	m(4)	h	h	h	m(2)	h	1(4)	m	m	m	m(2)	m
Total Pieces of Key Process Equipment	22	10	7	8									13	9	10	10	8	8												
Total Types of Key Process Equipment	4	10	7	8									4	9	10	10	7	8												

- a. Comparisons are based on the cases shown in Tables 8.1, 8.2 and 8.3 which involve 1.5 ± 0.3 years interim aqueous storage. Conditions are:

Solidifier	Melt System	PW-2 Waste				Melt System	Pot Dia, in	PW-4m Waste		
		Pot Dia, in	Age, yrs	No. of pot lines	Pots/day			Age, yrs	No. of pot lines	Pots/day
Pot Cal.	--	12	1.7	7	2.0	--	6	1.6	4	4.6
Spray-Melter	Phosphate	20	1.2	1	0.7	Phosphate	12	1.3	1	1.6
-IPM	Phosphate	20	1.2	1	0.7	Phosphate	--	--	--	--
-Melter	--	--	--	--	--	Borosilicate	10	1.4	1	1.4
-IPM	--	--	--	--	--	Borosilicate	10	1.4	2	1.4
Phos. Glass	Phosphate	16	1.7	1	0.9	Phosphate	12	1.7	1	2.4
- b. Simplicity is taken as the opposite of complexity to keep three categories in parallel directions.

c. h = high quality (simple, highly reliable, little expected maintenance);
m = medium quality;
l = low quality.

d. IPM = in-pot melting.

e. The numbers in parentheses indicate the number of parallel lines required; the estimates of h, m, or l take into account the number of parallel lines required.

plant operator for his situation. The spray process (with all its variations) and the phosphate glass process have about the same numbers of key process equipment items, with the phosphate glass equipment intermediate between the somewhat lower equipment requirements of the spray in-pot melting scheme and those of the spray-continuous melting scheme.

Additional analyses of the summary in Table 10.3 require relatively detailed inspection of each category. Total evaluation will depend to a great extent on the needs, interests, and restrictions of the individual reprocessor.

10.6 OPERATING AND ACCIDENT SAFETY

Safety is obviously an important consideration in the operation of a fuel reprocessing plant. Good radioactivity safety in these plants is basically defined as good containment of radioactivity at all times.

Safety in radioactivity containment is affected by radioactivity inventory, process and process equipment design, and building and facility design. In spent fuel reprocessing, the inventory of radionuclides can be varied somewhat but it must be relatively high because of the basic function performed, which is removing, concentrating, and collecting the high quantities of radionuclides in spent fuels from many nuclear reactors. The process and processing equipment is normally designed to minimize the potential for loss of containment and to provide primary containment within the process equipment (and sometimes secondary containment within added process equipment). The hot cell generally provides secondary containment and the total facility generally provides tertiary containment.

Safety considerations for high level waste solidification are not much different than those for fuel reprocessing in

general. Processing temperatures are higher than normally encountered in aqueous fuel reprocessing, and therefore chemical reactions which are insignificant at lower temperatures could become important, and materials of construction are weaker. On the other hand, combustible materials which could lead to a serious fire are generally not present and in-process inventories are relatively low.

The in-process inventories of radionuclides are important in that they represent the amount of material available for possible loss of containment control. These inventories can vary significantly with flowsheet and operating conditions. In general, however, the continuous processes have the least in-process holdup (in the order of waste equivalent to 1 tonne of fuel) and the pot calciner and spray in-pot melting processes the highest in-process holdup (in the order of 5 to 10 tonnes equivalent).

The possible areas of concern for major accident safety considerations with the WSEP processes which may be somewhat peculiar to the processes or to high level waste handling are summarized in Table 10.4. In general, the safety concerns are related to failure of a process vessel with resultant loss of primary containment of the radioactivity. Such vessel failures could be caused by excessive pressurization and/or weakening of the vessel walls by excessive temperatures or corrosion rates. As indicated in Table 10.4, there are potential differences in accident safety with the various WSEP processes. However, it is believed that these areas of concern appear to have no greater probability, consequence, or difficulty to circumvent than other hypothetical serious incidents in some other parts of the fuel reprocessing plant.

Other areas of accident safety concerns which would exist with the solidification processes are the same as or similar to concerns for any facility handling large quantities of

TABLE 10.4. Major Safety Considerations with WSEP Processes

Possible Safety Concern	Probable Considerations		
	Pot Calcination	Spray Solidification Continuous Melter	In-Pot Melting Phosphate Glass Solidification
Explosion or pressure surge due to red-oil	Possible occurrence. Depends on prior elimination of organic from waste and on structural and ventilation safety features of process and building.	Unlikely occurrence; organic would be decomposed continuously in calciner.	Unlikely occurrence; organic would be decomposed continuously in denitrator and/or melter.
Pressurization and possible rupture of process vessel.	Remotely possible. Possible slow build-up of plug in off-gas line. Detected by instruments to permit corrective action. Possible rapid plug in off-gas line from foaming or pressure surge. Limit by design.	Remotely possible. Possible slow build-up in calciner filter Ap or melter vent hole; detected by instruments for corrective action. Possible surge in feed rate; limited by design. Melter is most likely failure point.	Remotely possible. Possible slow build-up of plug in 2 off-gas lines; detected by instruments for corrective action. Possible surge in feed rates; limited by design. Melter is most likely failure point.
Hydrogen generation and possible explosion.	Unlikely occurrence; radiolysis products grossly diluted by process vapors.	Unlikely occurrence; only minute H ₂ quantities formed in pt melter.	Unlikely occurrence; only minute H ₂ quantities formed in pt melter.
Loss of cooling in pot furnace or melter with possible resultant temperature surge.	Possible occurrence. Possible volatilization of radionuclides or failure of pot. Detected by instruments for corrective action. Design for emergency cooling.	Remotely possible. Possible volatilization of radionuclides or failure of pot or melter. Detected by instruments for corrective action. Design for emergency cooling.	Remotely possible. Possible volatilization of radionuclides or failure of pot or melter. Detected by instruments for corrective action. Design for emergency cooling.
Inadvertent addition of reactive chemical (e.g., organics) which could result in pressure surge or explosion. (a)	Possible occurrence. Design to minimize the incident. Control administratively.	Unlikely occurrence; chemical should be decomposed continuously.	Unlikely occurrence; chemical should be decomposed continuously.
Major back-flow of radioactivity into operating areas.	Unlikely for major occurrence.	Possible occurrence since aqueous waste is connected to atomizing gas through atomizing nozzle. Design to include safety features.	Unlikely for major occurrence.

a. The probability for this type of incident is expected to be higher in the aqueous waste tanks than in the solidifiers.

radionuclides. Most of these incidents of concern are related primarily to the design of the facility such as:

- flooding of the process cell
- loss of services
- leaks and spills containing radioactivity
- loss of pressure control in process building, and
- fire in process cells.

Incidents such as criticality incidents and inadvertent processing of fuel with higher exposure or shorter cooling time than expected, should not be of concern in solidification of high level radioactive wastes. In these cases, the potential for safety problems will have been detected by routine analyses and corrected before the problems are encountered in solidification of highly radioactive liquid wastes.

10.7 CONTROL OF RADIONUCLIDES IN EFFLUENTS

Conversion of high level aqueous wastes to solids results in an immediate effluent stream with radioactivity levels which are factors of 10 to 500 lower than in the original waste. With total decontamination factor requirements in the order of 1×10^{10} , considerable additional treatment of the immediate effluent is required before the waste may be discharged to the environment. However, the immediate effluent stream may generally be considered to be somewhat comparable to the aqueous raffinate from the solvent extraction system of the fuel reprocessing plant, except that its volume is factors of 10 to 50 smaller than the raffinate stream. Consequently, a reprocessing plant which must process the solvent extraction raffinate should generally be capable of processing the effluent from high level waste solidification as a small recycle stream which is combined with the raffinate stream.

Exceptions to the foregoing general statement could be the constituents in the waste whose volatilization during waste

solidification is more extensive or more important than during the normal aqueous reprocessing steps. These potentially volatile constituents are the radionuclides of ruthenium, cesium, tellurium, selenium, technetium, hydrogen, and iodine; and the nonradioactive fluorides, bromides, mercury salts, and sulfates.

A summary of the amount of materials expected in the effluents from production scale solidification equipment is shown in Table 10.5. Entrainment varies somewhat with the solidification process, but all values are acceptable. The same conclusion applies to volatilization of cesium and tellurium. The degree of volatilization of ruthenium is a most important concern. Volatilization of ruthenium during solidification varies from a low of about 2 to a high of about 80%. This range should be compared to approximately 0.1% volatilization during evaporation and concentration of the high level aqueous waste. Therefore, the amount of ruthenium in the vapor phase leaving the solidifier will be 20 to 800 times higher than that in any other process off gas in the reprocessing plant. Therefore, special steps must be taken to reduce the amount of volatilized ruthenium to that which is of the same magnitude as the rest of the waste system. Based upon WSEP experience in scrubbing of ruthenium in a waste evaporator tower, it is believed that the proposed prescrubbing of the solidifier vapors will adequately remove the volatilized ruthenium. With this accomplished, the net effect of ruthenium volatilization within the solidifier is that of the added inventory of the recycling ruthenium.

Ruthenium volatilization from the pot calcination and phosphate glass processes is in the range of 10% of the ruthenium present, as shown in Table 10.5. It is the lowest at about 2% for the spray process when converting the waste to a borosilicate glass, and the highest at up to 80% for the spray process when converting the waste to a phosphate glass.

TABLE 10.5. Materials in Immediate Effluent
from Solidification Equipment

	Percent of Material in Original Waste Which is in Solidifier Effluent ^(a)			
	Pot	Spray Solidification		Phosphate
	Calcination	Phosphate	Borosilicate	Glass
Entrainment	0.5	0.01	0.01	0.1
Radionuclide Volatilization				
Ru	10-20	2-80 ^(f)	2	10
Cs	0.1	0.1	0.1	0.1
Se	(b)	20-30	(b)	50-100
Te	(b)	0.1-0.5	(b)	1-10
Tc	5	(c)	(c)	(c)
I	(c)	(c)	(c)	(c)
H	100 ^(e)	100 ^(e)	100 ^(e)	100 ^(e)
Nonradioactive Volatilization				
SO ₄	<1	<5	<5 ^(b)	100
F	(d)	(d)	(d)	(d)
Hg	100 ^(e)	100 ^(e)	100 ^(e)	100 ^(e)
Br	(c)	(c)	(c)	(c)

- a. The material expected in the immediate effluent from well-designed production-scale solidifiers.
- b. Volatilization is expected, but it is expected to be no greater than that with the spray-phosphate system.
- c. Significant volatilization is expected to occur, and may approach 100% but suppression of volatilization may be possible.
- d. Significant volatilization is expected to occur, but suppression of volatilization may be possible by chemical means.
- e. These values were not measured experimentally.
- f. The low value is for converting to a borosilicate glass; the high range is for converting to a phosphate ceramic.

In view of the small amount of selenium present in the waste, its volatilization as shown in Table 10.5 should cause no problems except perhaps with the phosphate glass process. If the volatilization is 100%, some means for removal will be required. The extent of volatilization of radionuclides of technetium and iodine remain to be determined. Indications are less than 100% of these constituents should be volatilized. Tritium is 100% volatilized, and removal of tritium from the reprocessing plant effluent will not be accomplished with these solidification schemes.

For the nonradioactive sulfate ion, the modest volatilization for all but the phosphate glass process should not cause major problems, although the corrosiveness of the volatilized sulfuric acid or sulfur oxides requires some attention. For the phosphate glass process, the sulfate is completely volatilized and must be disposed of as a separate waste. Qualitative data on the volatilization of fluoride in WSEP systems indicate that fluoride is at least partially volatile, but quantitative data are not available. Volatilization of fluoride, if present, would cause significant corrosion problems. No data are available on the volatilization of bromine, which is present in spent fuels in small quantities as a nonradioactive fission product. Mercury, if present, would volatilize completely from all the WSEP processes. A process for prior removal of mercury from the aqueous waste has been developed in the laboratory.⁽¹⁾

10.8 CHARACTERISTICS OF THE SOLIDIFIED WASTE

Discussion of this subject was presented in Section 6, and additional details are presented in Reference 2. A brief comparison, however, is presented here in summary form.

A qualitative comparison of the more important quality and handling considerations of the solidified wastes and their

containers is presented in Table 10.6. These comparisons are made with the following bases:

- No solidified waste is suitable for interim storage or transportation without enclosure in a container.
- The main period of concern is during the first 10 years after the fuel is reprocessed, during which the waste is more likely to be converted to solids and transported to a Federal repository.
- After this 10-year time period, the solidified waste will be interred in a Federal repository.
- The total package of waste plus can plus additional containment (such as the reprocessing building or the shipping cask) can be reasonably designed to satisfy safety criteria.

As shown in Table 10.6, the overall quality of waste without sulfate (PW-4m) is higher than that with sulfate (PW-2). The borosilicate solid made by spray solidification generally has higher overall quality than the other solids, and the pot calcine has lower overall quality than the other solids. The solids from the phosphate glass and the phosphate-based spray processes are generally of intermediate quality compared to the other two solids, with the spray solid having somewhat higher quality.

Two important characteristics are listed for which a minimum amount of comparative information is presented. Comparisons of long-term stability will be developed from the WSEP program as solids undergo aging. Comparisons of effects of loss of coolant are dependent upon the other characteristics presented, and the specific normal storage conditions. For example, a sulfate-containing waste being stored at near its maximum stable temperature with water cooling must have better provisions for emergency cooling than waste with no sulfate

TABLE 10.6. Qualitative Comparison of Solidified Waste Packages

Characteristic	PW-2 Waste				PW-4m Waste			
	Pot	Spray (Phosphate)		Phosphate	Pot	Spray		Phosphate
	Calcine	Melter	IPM	Glass	Calcine	Phosphate	Borosilicate	Glass
Leachability	l	m	m	m ^(c)	l	m	h	m
Dispersibility ^(f)	l	h	m	m	l	h	m	m
Thermal conductivity	l	h	h	h	l	h	h	h
Corrosivity to container ^(a)	h	h	h	h	h	h	h	h
Long-term stability ^(b)	--	--	--	(c)	--	--	--	(c)
Total volume	h	m	m	l ^(d)	h	m	h	l
Total number of pots ^(e)	l	m	m	m	l	h	h	m
Effect of Loss-of-Coolant ^(b)	(g)	(g)	(g)	--	--	--	--	--

Legend: h = high quality, m = medium quality, l = low quality

- a. Corrosivity during normal storage conditions.
- b. Except where otherwise noted, the solids are believed to be stable based on indirect data from WSEP.
- c. Phosphate glass readily devitrifies ≥ 500 °C; it is assumed here to be devitrified.
- d. The volume of the sulfate-containing waste effluent stream is included.
- e. Number of pots is controlled by thermal conductivity and specific volume of the solidified waste.
- f. The tendency to be dispersed if the pot and its solidified waste were mechanically damaged.
- g. Loss of coolant for sulfate-containing wastes with high heat generating wastes will generally require better and quicker emergency cooling than for the other wastes.

which is relatively cool and is normally cooled with air. These effects must be determined by detailed safety analyses using the known characteristics.

REFERENCES FOR SECTION 10

1. W. E. Clark and C. L. Fitzgerald. Proposed Means for the Removal of Mercury from Radioactive Waste Solutions, USAEC Report ORNL-TM-827, Oak Ridge National Laboratory, March 1964.
2. J. E. Mendel, J. L. McElroy, and K. J. Schneider. Waste Solidification Program, Volume 10, Evaluation of Solidified Waste Products from WSEP Processes, USAEC Report, BNWL-1666 To be published.

11.0 ACKNOWLEDGMENTS

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CONTENTS

APPENDIX A:	Calculation of Pot Feeding Times and	
	Average Feed Rates.	A.1

APPENDIX ACALCULATION OF POT FEEDING TIMES AND AVERAGE FEED RATES

A mathematical model for calculating pot feeding time has previously been described for the radial deposition case.⁽¹⁾ The model assumed that the pot is initially filled with feed to the normal operating level, that the wall temperature remains constant, and that the cake deposits radially and uniformly. For no internal heat generation, this model predicts that the time required to obtain a given fill fraction is directly proportional to the square of the pot diameter. Since the total feed to the pot over that time is also proportional to the pot diameter squared, it follows that the average overall feed rate for a constant fill level and fill fraction should be a constant and independent of pot diameter. However, WSEP results, described in Section 4, showed that the average feed rates increased with pot diameter for the three pot sizes tested (6, 8, and 11-3/8 in. ID). A simplified theoretical analysis was made to resolve this apparent discrepancy and to provide a correlation useful for predicting calcination feeding times for other operating conditions. The model chosen was based on the following observations.

In WSEP, the pots were placed in the furnace and a small amount of water was added to keep the pot wall cool during furnace heat up. The feed was then introduced at a constant rate, limited to about 86 liters/hr per square foot of pot cross section, to avoid excessive entrainment during the initial high heat-flux portion of the run. This mode of operation kept the liquid level in the lower half of the pot for the first few hours of the

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1. W. E. Clark, J. C. Suddath, C. W. Hancher, R. E. Blanco, H. W. Godbee, J. M. Holmes and C. L. Fitzgerald. "Development of Processes for Solidification of High Level Radioactive Waste: Summary for Pot Calcination and Rising Level Potglass Processes," ORNL-TM-1584, August 12, 1966.

run; but with scale deposition, the boil-off rate decreased and the pot gradually filled with liquid to the normal 6-ft operating level. At this time, it was necessary to reduce the feed rate to avoid over-filling the pot. Typically, 40 to 50% of the total feed for a run was added to the pot during the 9 to 11 hour constant rate period.

Although this method of operation should result in a tapered, V-shape cake, an examination of sectioned pots from DVT runs indicated that the cavity left in a filled pot had a nearly uniform cross section and that it extended for nearly half the length of the pot. The lack of a definite taper can be attributed to cake deposition above the liquid level due to splashing and foaming of the boiling slurry. The thickness of such a cake might, in fact, be greater than that formed in the liquid zone because of the higher wall temperatures. The formation of this cake has been confirmed by pot wall temperature profiles which indicated the presence of an insulating scale in the upper half of the pot as the pot filled with liquid and, in the sectioned DVT pots, by the final cake level which extended about a foot above the normal operating liquid level. In the absence of more conclusive evidence, it was assumed that a uniform radial scale forms and extends from near the bottom to about a foot above the operating liquid level. It was further assumed in the mathematical treatment that solid deposits also fill the bottom of the pot at a rate proportional to the scale deposition rate to account for the solid cake found in the bottom of sectioned DVT pots and inferred to be present in the WSEP pots from centerline temperature profiles.

Nomenclature

- B = boil-off volume, liters
 B_C = boil-off volume during constant rate period, liters
 F = cumulative feed volume to time θ , liters
 F_C = feed volume during constant rate period, liters
 h = pot height available for conductive heat transfer, ft
 k = thermal conductivity of cake, Btu/(hr) (ft) ($^{\circ}$ F)
 L = nominal operating and fill height, ft
 ΔL = incremental cake height above liquid level, ft
 n = dimensionless exponent defined in Step 1, below
 Q = heat input, Btu
 R = pot internal radius, inches
 r = solid-liquid interface radius, inches
 s = volume occupied by solids in the feed and pot liquids, ℓ /kg solid
 ΔT = temperature difference between pot wall and boiling liquid, $^{\circ}$ F
 V_p = nominal pot operating volume = $28.3 \pi R^2 L$, liters
 V_ℓ = liquid volume in pot = $28.3 \pi r^2 (h - \Delta L)$ liters
 V_s = volume of deposited solids in pot = $28.3 \pi R^2 (L + \Delta L) - V_\ell$, liters
 w = solids content of feed, kg/ ℓ (metal oxides, sulfates, and phosphates)
 w_p = solids content of pot liquid, kg/ ℓ (assumed to be constant after concentrated sufficiently for scale to form)
 x = r/R , dimensionless inner radius of deposition
 θ = elapsed run time, hours
 θ_C = elapsed time for constant rate periods, hours
 θ_f = elapsed time for falling-rate period, hours
 λ = heat required to vaporize feed liquid, Btu/ ℓ (based on volume boiled off)
 ρ_s = density of solid cake, kg/ ℓ

Derivation of Equations

1. Let $h = (L + \Delta L)x^n$ where n is a number less than one so that the center cavity will be about half full of solids at the end of the run.
2. For heat transfer through long insulated pipes, the heat input is given by:

$$\frac{dQ}{d\theta} = \frac{2\pi h k \Delta T}{\ln(R/r)} = \frac{2\pi (L + \Delta L) x^n k \Delta T}{-\ln x}, \quad \frac{\text{Btu}}{\text{hr}}.$$

3. The boiloff rate is given by:

$$\frac{dB}{d\theta} = \frac{1}{\lambda} \frac{dQ}{d\theta} = \frac{2\pi (L + \Delta L) x^n k \Delta T}{-\lambda \ln x}, \quad \frac{\ell}{\text{hr}}.$$

4. From a solids material balance, kilograms of depositable solids in feed added = deposited solids in pot plus solids in the pot liquid:

$$wF = \rho_s V_s + w_p V_\ell$$

$$\begin{aligned} \text{where } V_s &= 28.3\pi R^2 (L + \Delta L) (1 - x^{2+n}) \\ &= (V_p/L) (L + \Delta L) (1 - x^{2+n}) \\ \text{and } V_\ell &= 28.3\pi x^2 R^2 \left[(L + \Delta L) (x^n) - \Delta L \right] \\ &= (V_p x^2/L) \left[(L + \Delta L) (x^n) - \Delta L \right]. \end{aligned}$$

For a differential addition of feed,

$$\begin{aligned} wdF &= \rho_s dV_s + w_p dV_\ell \\ \text{where } dV_s &= (-V_p/L) (L + \Delta L) (2 + n) (x^{1+n}) dx \\ \text{and } dV_\ell &= (V_p/L) \left[(L + \Delta L) (2 + n) (x^{1+n}) - 2x\Delta L \right] dx. \end{aligned}$$

5. From a volatile-liquid material balance, volatile fraction of feed volume in = volatile fraction of liquid left in pot plus the volume boiled off:

$$\begin{aligned}(1 - sw)F &= (1 - sw_p)V_\ell + B \\ \text{and } (1 - sw)dF &= (1 - sw_p)dV_\ell + dB,\end{aligned}$$

where V_ℓ and dV_ℓ were previously defined.

6. Substituting the expressions for F and dF from Step 4, the total volume of liquid boiled off at any time is given by

$$\begin{aligned}B &= (1 - sw) \frac{\rho_s V_s - w_p V_\ell}{w} - (1 - sw_p)V_\ell, \\ \text{and } dB &= (1 - sw) \frac{\rho_s dV_s - w_p dV_\ell}{w} - (1 - sw_p)dV_\ell\end{aligned}$$

After further substitution

$$\begin{aligned}dB &= (V_p/L) \left\{ \left[(1 - sw)/w \right] \left[(L + \Delta L)(2 + n) \right. \right. \\ &\quad \cdot \left. \left. (w_p - \rho_s)x^{1+n} - 2w_p x \nabla L \right] - \left[1 - sw_p \right] \right. \\ &\quad \cdot \left. \left[(L + \Delta L)(2 + n)x^{1+n} - 2x\Delta L \right] \right\} dx = f(x)dx.\end{aligned}$$

7. The value of dB from Step 6 can then be substituted into the equation derived in Step 3 to give

$$d\theta = \frac{-\lambda \ln x}{2\pi (L + \Delta L) x^n k \Delta T} \cdot f(x) dx.$$

8. The preceding equation can be integrated to solve explicitly for the elapsed time to deposit a given thickness of cake:

$$\theta_f = \theta_2 - \theta_1 = \frac{-\lambda V p}{2\pi L k \Delta T} \left((2+n) \left\{ [(1-sw)/w] (w_p - \rho_s) - (1-sw_p) \right\} \frac{\Delta E + \frac{2\Delta L}{L + \Delta L}}{w} \left[(1-sw_p) - \frac{w p}{w} (1-sw) \right] \Delta F \right)$$

$$\text{where} \quad \Delta E = (x_2/2)^2 (2 \ln x_2 - 1) - (x_1/2)^2 (2 \ln x_1 - 1)$$

$$\text{and} \quad \Delta F = \frac{x_2^2 - n}{(2-n)^2} \left[(2-n) \ln x_2 - 1 \right] - \frac{x_1^2 - n}{(2-n)^2} \left[(2-n) \ln x_1 - 1 \right].$$

9. The value of x_1 is obtained at the end of the constant rate period. At this time, the pot has just been filled with liquid so that the average boiloff rate is given by:

$$B_c/\theta_c = (1-sw) (F_c/\theta_c) - (1-sw_p) (V_\ell/\theta_c).$$

WSEP experience suggests that the initial feed rate should not exceed 86.4 l/hr-ft^2 , or

$$F_c/\theta_c = 86.4 \pi R^2 = 3.05 V_p/L.$$

F_c/θ_c also equals

$$\frac{\rho_s V_s + w V_p \ell}{w \theta_c}$$

(from Step 4), so that after appropriate substitution

$$\theta_c = \left(1/3.05w \right) \left[\rho_s (L + \Delta L) + x^{2+n} (L + \Delta L) \cdot (w_p - \rho_s) - w_p x^2 \Delta L \right]$$

$$\text{and } B_c/\theta_c = 3.05(1 - sw) V_p/L - (1 - sw_p) (V_p x^2/L\theta_c) \cdot \left[(L + \Delta L)x^n - \Delta L \right].$$

We can assume at this time that the instantaneous boiloff rate is approximately equal to the average boiloff rate for the constant rate period:

$$B_c/\theta_c \approx dB/d\theta = \frac{2\pi(L + \Delta L)x^n k \Delta T}{-\lambda \ln x} \quad (\text{from Step 3})$$

The value of x that satisfied this equation can be obtained graphically or by an appropriate iterative substitution technique.

10. The value of x_2 for the end of the feed period can be obtained by an appropriate definition of a full pot. For our purpose, we will define a full pot as one containing a volume of cake equal to the nominal operating volume of the pot, V_p . At the end of the feed period, the total solids in the pot equals that in the deposit plus that still left in the liquid cavity:

$$f\rho_s V_p = \rho_s V_s + w_p V_\ell = \rho_s (V_p/L) (L + \Delta L) (1 - x^{2+n}) + (V_p/L) (w_p x^2) \left[(L + \Delta L)x^n - \Delta L \right]$$

where f = fractional pot fill at time θ_2 .

After rearranging,

$$(L + \Delta L)(\rho_s - w_p)x^{2+n} + w_p x^2 \Delta L = \rho_s (L + \Delta L - fL)$$

which can be solved for x by trial-and-error substitution.

11. Values of the constants used in the preceding equations can be estimated from flowsheet conditions or from experimental or published data. Appropriate values of k and w_p have been calculated from WSEP results. For general application,

$$k = 0.2 \text{ Btu/(hr) (ft) (}^\circ\text{F)}$$

$$w_p = \begin{aligned} &0.35 \text{ kg/l for PW-1 waste,} \\ &0.4 \text{ kg/l for PW-2 waste, and} \\ &\leq 0.2 \text{ kg/l for PW-4m waste.} \end{aligned}$$

Results of Example Calculations

The results of example calculations for the 5 tonne/day reference plant are presented in Table A-1. The feed compositions chosen were taken from the flowsheets presented in Section 7 and the recommended pot sizes from Section 8. Separate calculations were made for the case where the central cavity extended to the bottom, Cases A and C, and for the case where the cavity was assumed to fill with settled solids [depth of central cake = $(L + \Delta L)(1 - x^{0.5})$], Cases B, D, E, and F. The different cavity-geometry assumptions had a negligible effect on the calculated times.

Separate calculations were also made for the PW-4m waste to illustrate the effects of solids content, w_p , in the "equilibrium" pot slurry on feeding time. WSEP Run PC-8 demonstrated that a wall scale formed almost immediately after introduction of a feed containing 0.126 kg metal oxides per

liter, and the short length of the constant rate period suggested that the solids content of the pot never exceed 0.2 kg/liter. This was considered to be a realistic value to use as the lower level of w_p ; the upper level was set equal to the entering feed concentration. Pot feeding times were 8 to 17% longer using the lower value of w_p , and these more conservative results were used to prepare Table 8.1.*

The final case, F, was calculated using representative WSEP operating parameters. The results, presented in Table A-1 and plotted in Figure 4.3, Section 4, appear to be in reasonably good agreement with the WSEP run results. Discrepancies can be attributed to slightly lower initial operating temperatures (PC-8), higher-than-average cake densities (PC-3 and 5), lower-than-normal fills (PC-1 and 2), and higher-than-average thermal conductivities (PC-3 and 4).

* In a subsequent laboratory test, PW-4m waste was concentrated to approximately 0.5 kg metal oxides per liter, using a heat flux comparable to that to the pot calciner wall, and scaling did not occur.

**TABLE A-1. Estimation of Feeding Time for 5 tonne/day
Reference Plant Pots**

Operating Conditions

	A	B	C	D	E	F
Type of Feed	PW-2	PW-2	PW-4m	PW-4m	PW-4m	PW-2
L, ft	8	8	8	8	8	6
ΔL , ft	1	1	1	1	1	0.75
n	0	0.5	0	0.5	0.5	0.5
h	9	9×0.5	9	9×0.5	9×0.5	6.75×0.5
s, ℓ /kg	0.2	0.2	0.2	0.2	0.2	0.2
w, kg/ ℓ	0.167	0.167	0.413	0.413	0.413	0.16
w_p , kg/ ℓ	0.4	0.4	0.2	0.2	0.413	0.4
k, BTU/hr ft $^{\circ}$ F	0.2	0.2	0.2	0.2	0.2	0.2
λ , BTU/ ℓ	2200	2200	2200	2200	2200	2200
ΔT , $^{\circ}$ F	1320	1320	1320	1320	1320	1320
ρ_s , kg/ ℓ	1.3	1.3	1.3	1.3	1.3	1.3

Calculated Results

Pot Size, in. IPS	Case	Feeding Time, hours			Feed Required, liters	Average Feed Rate, ℓ /hr
		Constant Rate	Falling Rate	Total		
6	A PW-2	15.8	8.3	24.1	354	14.7
	B PW-2	16.1	8.6	24.7	354	14.3
	C PW-4	6.2	4.6	10.8	143	13.2
	D PW-4	6.4	4.7	11.1	143	12.9
	E PW-4	6.8	3.5	10.3	143	13.9
	F PW-2	11.5	10.3	21.9	277	12.7
8	A PW-2	13.0	19.5	32.5	613	18.9
	B PW-2	13.6	19.0	32.6	613	18.8
	C PW-4	5.0	10.5	15.5	248	16.0
	D PW-4	5.3	10.2	15.5	248	16.0
	E PW-4	5.9	8.1	14.0	248	17.7
	F PW-2	9.7	21.1	36.8	480	15.6
10	A PW-2	11.1	33.3	44.4	966	21.8
	B PW-2	11.8	32.8	44.6	966	21.7
	C PW-4	4.2	18.4	22.6	391	17.3
	D PW-4	4.6	18.2	22.8	391	17.1
	E PW-4	5.2	14.3	19.5	391	20.1
12	A PW-2	9.9	49.6	59.5	1386	23.3
	B PW-2	10.5	49.4	59.9	1386	23.1
	F PW-2	7.6	52.3	59.8	1084	18.1
16	A PW-2	8.9	79.1	88.0	2166	24.6
	B PW-2	9.3	79.3	88.6	2166	24.4
	F PW-2	6.7	83.2	89.9	1694	18.9
20	A PW-2	8.1	126.0	134.1	3406	25.4
	B PW-2	8.4	126.5	134.9	3406	25.2
24	A PW-2	7.6	183.3	190.9	4927	25.8
	B PW-2	7.9	183.8	191.7	4927	25.7

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SELECTED FIGURES OF WSEP

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Neg 0692773-1

FIGURE B-1. Floor Plan of the Chemical and Materials Engineering Laboratory

FIGURE B-2. Plan View of B-Cell Equipment Arrangement

FIGURE B-4. Engineering Flow Diagram of Solidification Process
Equipment in WSEP (Sheet 2 of 2)

Neg 38340-1-CN

FIGURE B-5. The 1A Rack (Evaporator and Fractionator) Before Installation

Neg 0641684-3

FIGURE B-6. The 5A Rack (Induction Heated Pot Furnace)
Before Installation

Neg 45897-48

FIGURE B-7. The 5B-C Rack (Phosphate Glass Solidifier)
Before Installation

Neg 0662668-21-CN

FIGURE B-8. Looking West Through Air Lock
to B-Cell Doorway

Neg 0662668-7

FIGURE B-9. Looking East from the West End of B-Cell

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APPENDIX C:	Example Print-out of Waste Management Economics for One Case.	C.1
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APPENDIX C

Example Print-out of Waste Management Economics for One Case

PROGRAM VERSION.....BNW MAY.1972.....WASTE MANAGEMENT STUDY.....
CASE 2-BA PW-4 SPRAY MELTER(NON-PT) FL=17.....

THERMAL POWER (MW)	ELECTRICAL POWER (MW)		FUEL IRRADIATION	
	INSTALLED	GENERATED	POWER (MW)	BURNUP (MWD/MT)
123778.	50285.	40228.	30.00	33000.

F (CU FT SOLID/10000 MWD)	FL (GAL LIQUID/10000 MWD)	THERMAL CONDUCTIVITY (BTU/HR-FT-F)
.270	17.00	.75

FUEL REPROCESSING RATE (MT/YR)	FUEL REPROCESSING TIME (DAYS)	SOLID DENSITY (GR/CC)
1370.0	150.0	3.00

ACTIVE PERIOD (YRS)	INTERIM LIQUID STORAGE (YRS)	INTERIM SOLID STORAGE (YRS)
20.	2.50	5.50

INTEREST RATE ON BONDS	.080
RETURN ON EQUITY	.150
RETURN ON TAX-EXEMPT FUND	.050
FRACTION OF INVESTMENT IN EQUITY	.700
INCOME TAX RATE	.480
PROPERTY TAX RATE	.015
PROPERTY INSURANCE RATE	.002

R	RT	HC	HT	TS	QR	Q	TCL	TA
.33254-00	.37851-00	.88013-00	.50386+01	.12387+04	.27322+04	.17898+05	.16500+04	.10000+03

C-1

BNWL-1667

	INTERIM	LIQUID	STORAGE
STORAGE TIME (YR)			2.500
DEAD TIME (YR)			1.500
TANK-FILLS DURING ACTIVE PERIOD			20.000
NUMBER TANKS, INC SPARE			5
TANK SIZE (M ³ GAL)			.13
TANK DESIGN			
DIAMETER (FT)			40.3
HEIGHT (FT)			13.4
TANK THICKNESS (IN)			
TOP			.3125
BOTTOM			.3125
LOWER SIDE			.3125
UPPER SIDE			.3125
SAUCER			.3125
TANK WEIGHT (LB)			
TANK			54785.
SUCER			45409.
CONCRETE THICKNESS (FT)			
TOP			4.9
SIDES			2.6
BOTTOM			2.9
TOTAL CONCRETE (CU YD)			585.
COST OF ITEMS INSTALLED AT START OF PROJECT (\$)			
FILTERS			64921.
STACK			5583.
SEPTIC TANK AND FIELD			45445.
DIMINERALIZERS			28576.
ELECTRICAL SUBSTATION			400636.
DIVERSION BOX			25595.
COOLING TOWER			625896.
OPERATING BUILDING			1277146.
EMERGENCY WATER TANK			77901.
WATER SURGE TANK			194753.
CONDENSER AND CONDENSATE TANK			68952.
VENTILATING EQUIPMENT			68459.
TOTAL COST			4325794.

TANK COSTS (4.)	INTERIM LIQUID STORAGE (CONT.)
COOLING COILS	1757269.
TANK AND SAUCER	186579.
CONCRETE ENCASEMENT	144898.
EXCAVATION AND BACKFILL	19635.
INSTRUMENTATION	19050.
APPURTENANCES	80581.
TOTAL TANK COST	2208012.
DEAD PERIOD FUND	
TOTAL FUND	816328.
ANNUAL PAYMENT TO FUND	24688.
INITIAL CAPITAL COST (\$MM)	15.6
TOTAL LIQUID STORAGE COST (MILLI-MILLS/KWH)	17.6

	CONSTRUCTION SCHEDULE			
STAGE	1	2	3	4
INSTALLED AT YEAR	1	2	3	4
DESIGN YEAR	1	2	3	4
ISOTOPIC POWER (BTU/HR)				
ADDED	55906028.	27629486.	17112133.	6222526.
TOTAL	55906028.	83535514.	100647646.	106870173.
NUMBER OF TANKS INSTALLED	2	1	1	1
CAPITAL COSTS (\$)				
TANK COMPLETE (FACTOR = 1.50)	2208012.	2208012.	2208012.	2208012.
SPARE TANK	2208012.			
INITIAL CONSTRUCTION	4325794.			
HEAT EXCHANGERS	312710.	154546.	95717.	34806.
PUMPS	90853.	44901.	27809.	10112.
PIPING	974590.	487295.	487295.	487295.
ARCHITECT-ENGINEER	1847353.	291909.	276725.	261003.
CONTINGENCY	3590197.	955999.	928667.	900369.
TOTAL CAPITAL COST	15557522.	4142661.	4024225.	3901597.
ESCALATED COST (FACTOR = 1.50)	15557522.	4142661.	4024225.	3901597.
OPERATING COSTS (\$/YEAR)				
LABOR	49000.	67780.	79411.	83641.
OVERHEAD	49000.	67780.	79411.	83641.
ELECTRICITY	50137.	74915.	90261.	95841.
FRESH WATER	18087.	27025.	32562.	34575.
WATER TREATMENT	543.	811.	977.	1037.
OTHER CHEMICALS	615.	919.	1107.	1176.
MAINTENANCE (EXCL LABOR)	155575.	197002.	237244.	276260.
PROPERTY TAXES	233363.	295503.	355866.	414390.
PROPERTY INSURANCE	31115.	39400.	47449.	55252.
LIABILITY INSURANCE	7500.	7500.	7500.	7500.
TOTAL OPERATING COST	594934.	778634.	931749.	1053312.

ANNUAL OPERATING COSTS FOR DEAD PERIOD (MILLIONS OF \$)

YEAR	HEAT LOAD	LABOR	ELECTRICITY	WATER	CHEMICALS	INSURANCE			TAXES	MAINTENANCE	TOTAL
						PROPERTY	LIABILITY				
1	9.26+01	1.67-01	8.30-02	3.08-02	1.18-03	0.00	0.00		0.00	2.47-01	5.29-01
2	3.67+01	1.67-01	3.29-02	1.22-02	1.18-03	0.00	0.00		0.00	1.31-01	3.45-01

SOLIDIFICATION

POT DIAMETER (IN) 7.98 SPECIFIC HEAT GENERATION RATE (BTU/HR-CU FT) 17498. POT LENGTH (FT) 10.

POT CYCLE TIME (HR) 29.0 POT VOLUME 2.78 POT COST (\$/POT) 319.
CU FT SOLID/YR 1220.

CELL DESIGN

NUMBER OF PROCESS LINES 1
CALCIMER AREA (SQ FT) 100.
EVAPORATOR AREA (SQ FT) 225.
DECONTAMINATION AREA (SQ FT) 233.
TOTAL CELL AREA (SQ FT) 558. CELL WALL THICKNESS (FT) 5.87

COSTS (\$)

PERMANENT FACILITIES 700000.
20-YEAR ITEMS 0.
10-YEAR ITEMS 261000.
LABOR 228000.
MAINTENANCE 261000.
UTILITIES 6900.
MATERIALS 41700.
OVERHEAD 358500.
POT COST/YR 140032.
PROPERTY TAXES/YR 144150.
PROPERTY INSURANCE/YR 19220.
DEAD PERIOD FUND 2230366.
TOTAL FUND 67452.
ANNUAL PAYMENT TO FUND 9.6

INITIAL CAPITAL COST (\$MM) 9.6

TOTAL SOLIDIFICATION COST (MILLI-MILLS/KW-HR) 7.5

INTERIM SOLID STORAGE

INTERIM STORAGE TIME (YRS) 5.5 MAXIMUM HEAT LOAD (BTU/HR) 49794380.

CANAL LAYOUT

CANAL FLOOR AREA (SQ FT)	4260.	NUMBER OF SEGMENTS	4.
CENTRAL CANAL AREA (SQ FT)	1440.	SEGMENT WIDTH (FT)	24.
WATER SHIELD THICKNESS (FT)	13.29	SEGMENT LENGTH (FT)	44.

COST SUMMARY

ITEM	SIZE	COST (\$)
EXCAVATION	202549. CU FT	18755.
CONCRETE	1220. CU YD	288000.
STAINLESS STEEL LINERS	26541. SQ FT	849317.
PARTITIONS	9333. SQ FT	119933.
STANDS	2414.	81984.
COOLING TOWER	49794380. BTU/HR	194198.
HEAT EXCHANGERS	49794380. BTU/HR	248072.
PUMPS	49794380. BTU/HR	219095.
EMERGENCY POWER SYSTEM	49794380. BTU/HR	163492.
CRANES		77888.
DEMINERALIZERS	126. GPM	62544.
MONITORS		25050.
BUILDING		587686.

TOTALS (\$)

PERMANENT FACILITIES	2062968.
20-YEAR ITEMS	3065969.
10-YEAR ITEMS	598045.
OPERATING EXPENSES	348450.
PROPERTY TAXES/YR	85905.
PROPERTY INSURANCE/YR	11454.
LIABILITY INSURANCE/YR	16500.

DEAD PERIOD FUND	
TOTAL FUND	6311366.
ANNUAL PAYMENT TO FUND	190872.

INITIAL CAPITAL COST (\$MM)	5.7
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TOTAL SOLID STORAGE COST (MILLI-MILLS/KWHR)	4.3
---	-----

SHIPPING

HEAT GENERATION RATE (BTU/HR-SQ.FT.)		4887.

CASK DESCRIPTION		

DIAMETER (FT)	5.00	
SHIELDING THICKNESS (CM)	22.83	
DIAMETER OF CYLINDERS (IN)	7.98	
NUMBER OF CYLINDERS/CASK	16	
WEIGHT (TONS)	97.94	
COST (\$)	587648.15	

NUMBER OF CASKS INCLUDING SPARE	3	

ROUND TRIP DISTANCE (MILES)	ROUND TRIP TRANSIT TIME (DAYS)	TRIPS/YEAR
2000.	14.0	27.

COSTS (\$)		

SHIPPING CASKS (10-YEAR NOMINAL LIFE)	1762944.	
CRANE (20-YEAR NOMINAL LIFE)	117530.	
FREIGHT COST/YEAR	265912.	
HANDLING COST/YEAR	62543.	
PROPERTY TAXES/YR	28207.	
PROPERTY INSURANCE/YR	9402.	

DEAD PERIOD FUND		

TOTAL FUND	2365959.	
ANNUAL PAYMENT TO FUND	71553.	

INITIAL CAPITAL COST (\$MM)	1.9	

TOTAL SHIPPING COST (MILLI-MILLS/KWHR)	1.1	

SALT REPOSITORY

HEAT GENERATION RATE (WATTS/CAN)	3980.7
WASTE CYLINDERS PER YEAR	438.9
COST PER CYLINDER	7503.8

TOTAL COSTS

PERMANENT FUND	
TOTAL FUND REQUIRED (\$)	21286242.
ANNUAL DEPOSIT TO FUND (\$/YR)	643751.
ANNUAL SALT MINE CHARGES (\$/YR)	3293446.
UNIT SALT MINE CHARGES (MILLI-MILLS/KWHR)	5.0

WASTE MANAGEMENT COST SUMMARY

FACILITY	COST (MILLI-MILLS/KWHR)
INTERLY LIQUID STORAGE	17.6
POT CALCINATION	7.5
INTERLY SOLID STORAGE	4.3
SHIPPING	1.1
DISPOSAL IN SALT	5.0
TOTAL	35.4

FIXED CHARGE RATE ON CAPITAL	22.42	PERCENT
INTEREST RATE FOR DISCOUNTING	11.75	PERCENT

DISCOUNTING FACTORS BY YEAR

1 = 1.000	2 = .805	3 = .601	4 = .717	5 = .641	6 = .574	7 = .514	8 = .460
9 = .411	10 = .368	11 = .329	12 = .295	13 = .264	14 = .236	15 = .211	16 = .189
17 = .169	18 = .151	19 = .135	20 = .121	21 = .108			

PAYOUT OF INVESTMENTS DURING ACCUMULATION PERIOD (ALL FIGURES IN MILLIONS OF \$1)

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	15.558	10.890		4.667	.000	1.634	.373	.000	12.476	.998	.595	.778	2.745	9.732	4.671	4.205	2.943	1.261
2	4.143	10.847		4.609	.998	1.627	.372	.050	12.476	.998	.779	.996	3.145	9.331	4.479	4.221	2.955	1.266
3	19.361	21.445		9.161	2.047	3.217	.735	.102	12.476	.998	2.594	2.214	6.543	5.935	2.849	2.083	1.458	.625
4	3.902	22.717		9.736	3.147	3.408	.779	.157	12.476	.998	2.715	2.444	6.936	5.540	2.659	1.917	1.342	.575
5	.000	21.376		9.161	4.303	3.206	.733	.215	12.476	.998	2.715	2.444	6.890	5.586	2.681	2.142	1.499	.643
6	.000	19.876		8.518	5.516	2.981	.681	.276	12.476	.998	2.715	2.444	6.839	5.638	2.706	2.394	1.676	.718
7	.000	18.201		7.800	8.790	2.730	.624	.340	12.476	.998	2.715	2.444	6.781	5.695	2.734	2.675	1.872	.802
8	.000	16.328		6.998	8.128	2.449	.560	.406	12.476	.998	2.715	2.444	6.717	5.759	2.764	2.989	2.092	.897
9	1.880	15.552		6.865	9.533	2.333	.533	.477	12.476	.998	6.375	2.630	10.536	1.940	.931	1.306	.914	.392
10	.000	14.638		6.273	11.008	2.196	.502	.550	12.476	.998	6.375	2.630	10.505	1.972	.946	1.459	1.021	.438
11	.000	13.617		5.836	12.537	2.042	.467	.628	12.476	.998	6.375	2.630	10.470	2.007	.963	1.631	1.141	.489
12	.000	12.475		5.347	14.183	1.871	.428	.709	12.476	.998	6.375	2.630	10.430	2.046	.982	1.822	1.276	.547
13	3.208	13.445		5.762	15.890	2.017	.461	.795	12.476	.998	6.375	2.710	10.544	1.932	.927	1.698	1.189	.509
14	.000	12.257		5.243	17.683	1.839	.420	.884	12.476	.998	6.375	2.710	10.503	1.973	.947	1.897	1.328	.569
15	.000	10.929		4.854	19.566	1.639	.375	.978	12.476	.998	6.375	2.710	10.458	2.019	.969	2.120	1.484	.636
16	.000	9.444		4.048	21.542	1.417	.324	1.077	12.476	.998	6.375	2.710	10.407	2.069	.993	2.369	1.659	.711
17	.000	7.786		3.337	23.618	1.168	.267	1.181	12.476	.998	6.375	2.710	10.350	2.126	1.021	2.648	1.853	.794
18	.000	5.933		2.503	25.797	.890	.203	1.290	12.476	.998	6.375	2.710	10.286	2.190	1.051	2.959	2.071	.888
19	1.763	5.095		2.114	28.085	.764	.175	1.404	12.476	.998	6.375	3.415	10.963	1.513	.726	3.438	2.406	1.031
20	.000	2.689		1.142	30.488	.403	.092	1.524	12.476	.998	6.375	3.415	10.880	1.596	.766	3.842	2.689	1.152
21	.000	.000		.000	33.010	.000	.000	1.651	.000	.000	5.850	.000	5.850	.000	.000	.000	.000	.000
22	.000	.000		.000	38.810	.000	.000	1.441	.000	.000	5.666	.000	5.666	.000	.000	.000	.000	.000
23	3.664	.000		.000	20.921	.000	.000	1.046	.000	.000	4.122	.000	4.122	.000	.000	.000	.000	.000
24	.000	.000		.000	17.845	.000	.000	.892	.000	.000	4.122	.000	4.122	.000	.000	.000	.000	.000
25	.000	.000		.000	14.616	.000	.000	.731	.000	.000	4.122	.000	4.122	.000	.000	.000	.000	.000
26	.000	.000		.000	11.225	.000	.000	.561	.000	.000	4.122	.000	4.122	.000	.000	.000	.000	.000
27	.000	.000		.000	7.664	.000	.000	.383	.000	.000	4.122	.000	4.122	.000	.000	.000	.000	.000
28	.000	.000		.000	5.926	.000	.000	.196	.000	.000	4.122	.000	4.122	.000	.000	.000	.000	.000

MAXIMUM UNRECOVERED CAPITAL

32.5 MILLION DOLLARS

EXPLANATION OF COLUMN HEADINGS

1	YEAR
2	NEW INVESTMENT MADE AT START OF YEAR
3	EQUITY OUTSTANDING AT START OF YEAR
4	BONDS OUTSTANDING AT START OF YEAR
5	DEAD PERIOD FUND AT START OF YEAR
6	RETURN ON EQUITY AT .1500
7	INTEREST ON BONDS AT .0800
8	RETURN ON FUND AT .0500
9	INCOME FROM SALES
10	ANNUAL PAYMENT TO FUND
11	OPERATING EXPENSE INCLUDING INSURANCE
12	ANNUAL DEPRECIATION
13	TOTAL DEDUCTIBLE EXPENSE (7+10+11+12)
14	TAXABLE INCOME (9-13)
15	INCOME TAX AT .4800
16	TOWARD REDUCTION OF DEBT (9-6-7-10-11-15)
17	TOWARD REDUCTION OF EQUITY .7000 OF COLUMN 16
18	TOWARD REDUCTION OF BONDS .3000 OF COLUMN 16

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