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WASTE SOLIDIFICATION PROGRAM
VOLUME I
PROCESS TECHNOLOGY - POT SPRAY,
AND PHOSPHATE
GLASS SOLIDIFICATION PROCESSES

August 1969

AEC RESEARCH &
DEVELOPMENT REPORT

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UC-70, Waste Disposal
and Processing

WASTE SOLIDIFICATION PROGRAM
VOLUME I. PROCESS TECHNOLOGY -
POT SPRAY, AND PHOSPHATE
GLASS SOLIDIFICATION PROCESSES

By

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WASTE SOLIDIFICATION PROGRAM
VOLUME I
PROCESS TECHNOLOGY -
POT, SPRAY, AND PHOSPHATE GLASS
SOLIDIFICATION PROCESSES

ABSTRACT

This report brings together the majority of the pertinent waste solidification technology existing to date for the pot calcination, spray solidification, and phosphate glass solidification processes for converting highly radioactive liquid wastes to more refractory solids. Pertinent technology regarding characterization of high level liquid wastes, the solidified products, and the effluents from the three solidification processes is presented.

WASTE SOLIDIFICATION PROGRAM REPORTS

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

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

V. P. Kelly, Waste Solidification Program, Volume 3, Design Features of the Facilities and Equipment for the WSEP Product Evaluation Program, U.S. AEC Report BNWL-832, December 1968.

J. L. McElroy, C. R. Cooley, J. E. Mendel, W. V. DeMier, J. C. Suddath (ORNL), and J. O. Blomeke (ORNL), Waste Solidification Program, Volume 4, Pot Solidification Performance During the First Radioactive Tests in WSEP, U.S. AEC Report BNWL-814, December 1968.

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INTRODUCTION

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

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

Development of techniques for solidification of high level liquid wastes has been conducted for the past 14 years and is still in progress. Four processes for solidification of high level liquid wastes have been developed in the USA to the point of radioactive demonstrations on an engineering scale. The four processes are pot calcination, spray solidification, phosphate glass solidification, and fluidized bed calcination. Two waste solidification methods under

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

development abroad include the FINGAL process in the United Kingdom and a pot vitrification process in France.

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

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

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

As part of the waste solidification demonstration program, this report brings together the majority of the pertinent waste solidification technology existing to date for the pot, spray, and phosphate glass solidification processes and their solidified products. The report includes current information related to effluents from the solidification processes. The report is a compilation of technology prepared by technical personnel of Battelle-Northwest who are performing studies related to the demonstration program.

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(by K. J. Schneider)

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1.0 WASTE SOLIDIFICATION DEVELOPMENT

(by K. J. Schneider)

1.1 INTRODUCTION

In the generation of nuclear power, nuclear fuel elements become partly used by splitting of the atoms of fissionable materials (uranium-235 and -233, plutonium-239 and -241, etc.) into lighter chemical elements, some of which act as poisons in the nuclear fissioning process. Eventually, the amount of this fissionable material becomes sufficiently low and/or the amount of the newly-formed reactively-poison elements becomes sufficiently high to cause inefficient reactor operation. At that time, the spent fuel elements are removed from the reactor and replaced with new fuel elements. The used fuel elements still contain enough valuable fissionable and fertile materials to warrant recovery for re-use. The spent fuel elements are allowed to age for three months to one year for decay of the short-lived radioactive materials. The aged fuel elements are then sent to chemical processing plants for separation of the valuable nuclear materials from the fission product wastes. The recovered fissionable and fertile nuclear materials are then refabricated into fuel elements for re-use in the nuclear fuel cycle.

Essentially all the nonvolatile highly radioactive fission products that were separated from the valuable nuclear materials in the chemical processing plant are accumulated in a high level aqueous waste stream. These fission products and the trace quantities of some transuranic chemical elements that are present in the waste stream are highly toxic to animal life. The only known practical method that exists today

for removing from these materials the major cause of toxicity (radionuclides) is to age the material and thereby allow the radioactivity to decay. However, some of the fission products require aging for centuries, and the plutonium requires aging for hundreds of thousands of years to decay to innocuous levels. Consequently, such wastes must be kept under very careful control virtually forever.

At the present time, these highly radioactive wastes are stored as liquids in huge underground tanks. This practice has been economical and relatively safe in the young nuclear power industry. However, as the nuclear power industry expands, liquid waste volumes will increase, and controlled liquid storage will become increasingly difficult and hazardous. As a result, development of methods for conversion of the wastes for storage as solids (which are less mobile, less soluble in water, smaller in volume, and more rugged physically than the liquid wastes) has been undertaken on a world-wide basis since 1955.

A summary listing of the major development efforts on solidification of high level waste is listed in Table 1.1.⁽¹⁾ Of the processes developed in the USA, four have been developed to the point of radioactive demonstration on an engineering scale. They are the pot, spray, phosphate glass, and fluidized bed processes. The pot, spray, and phosphate glass processes have been demonstrated on a fully radioactive basis for the U. S. Atomic Energy Commission (AEC) since November 1966 at the Pacific Northwest Laboratory (PNL) operated by the Battelle Memorial Institute (Battelle-Northwest, or BNW). The fluidized bed calcination process has been demonstrated on a production scale with intermediate-level wastes since December 1963 for the AEC by the Idaho Nuclear Corporation (INC).

TABLE 1.1. *Summary of Research and Development on Solidification of High-Level Waste⁽¹⁾*

Process and Sites	Time Span	Lab Scale Radioactivity ^(b)	Pilot Plant		Product	Chemical Additives	Status of Work
			Radioactivity ^(b)	Capacity, liter/hr			
Pot Calcination							
ORNL	1958-1965	None	None	25	Calcine	Calcium, Sulfate	Done
BNW	1959-1962	None	None	10	Calcine	Sulfate	Done
	1962 to date	H	H	20	Calcine	Sulfate, Calcium	In progress
Spray							
BNW	1959 to date	H	H	20	Ceramic, Glass	Phosphate, Borophosphate	In progress
USSR	~1961 to date	?	?	20	Calcine, Glass	Borosilicate	In progress
Phosphate Glass							
BNL	1960 to date	None	None	20	Glass	Phosphate	In progress
BNW	1964 to date	H	H	20	Glass	Phosphate	In progress
Fluid Bed							
ANL	1955-1959	None	L	6	Granules	None	Done
INC	1955 to date	L	I	300	Granules	None	In progress
BNW	1959-1961	No work	None	20	Granules	None	Done
USSR	~1962 to date	?	?	30	Glass, Granules	Borosilicate	In progress
Pot Glass							
AERE	1959-1966	None	H	6	Glass	Borosilicate	Done
FAR	1962 to date	H	L	20	Glass	Boroaluminosilicate	In progress
CPP	1969 startup	No work	H	20	Glass	Phospho-silicate	In progress
ORNL	1961-1966	None	None	3	Semiglass	Boro-aluminosilicate	Done
Rotary Kiln							
BNL	1955-1963	None	None	20	Powder	None	Done
FAR	1960 to date	None	None	6	Glass	Phospho-silicate	In progress
Ceramic Sponge							
LASL	1959-1964	None	L	4	Ceramic Balls	None	Done

(a) Work is also being done in Canada, Germany, Denmark, India, Japan and Czechoslovakia.

(b) Values are based upon Reference (2)

H is > 70 Ci/kg of solid

I is 0.07 to 70 Ci/kg of solid

L is < 0.07 Ci/kg of solid

(c) Abbreviation Summary

1. ORNL Oak Ridge National Laboratory, Oak Ridge, Tennessee
2. BNW Battelle-Northwest, Richland, Washington
3. USSR Union of Soviet Socialist Republics
4. BNL Brookhaven National Laboratory, Upton, Long Island, New York
5. ANL Argonne National Laboratory, Argonne, Illinois
6. INC Idaho Nuclear Corporation, Idaho Falls, Idaho
7. AERE Atomic Energy Research Establishment, Harwell, Berks, England
8. FAR Center for Nuclear Studies, Fontenay-aux-Roses, France
9. CPP Center for Plutonium Production, Marcoule, France
10. LASL Los Alamos Scientific Laboratory, Los Alamos, New Mexico

The AEC program involving final development, design and installation, operational demonstration, and evaluation of the pot, spray, and phosphate glass solidification processes and products (the final solidified waste in its container) is being carried out by BNW in cooperation with the Oak

Ridge National Laboratory and the Brookhaven National Laboratory. This program is the Waste Solidification Engineering Prototypes (WSEP) program.

This report contains the pertinent technology from the WSEP program and from related development programs at PNL, the Oak Ridge National Laboratory (ORNL), and the Brookhaven National Laboratory (BNL) for the three processes being demonstrated in the WSEP program up to January 1969.

1.2 THE INCENTIVES FOR WASTE SOLIDIFICATION

The primary incentive for solidification of high-radioactivity-level wastes is improved safety in control of accidental release of the toxic radioactive constituents to the environment of animal life. The only known practical means for reducing the radioactivity of these wastes is aging for up to one-half million years to allow decay to nontoxic levels. Aging or storage of liquid wastes is not suitable for the long term because:

- The mobility of the liquids may permit rapid entrance of radioactivity into our environment if the container is breached.
- The relative corrosiveness of the liquid solutions causes failures of storage tanks in 15 to 40 years, ^(2,3) thereby adding to the first problem, ultimately requiring large land areas for storage and replacement of tanks, and requiring extensive continued surveillance.
- If liquid waste reached natural waters, the waste would readily mix and be dispersed with the waters. Practical recovery would be extremely limited.
- The volumes of liquids to be stored are quite large (from 30 to 1500 liters/tonne of fuel).

- The large containers required for the large liquid volumes are relatively weak structurally, and their integrity in event of occurrences such as earthquakes, floods, or enemy warfare action is questionable.
- The liquid wastes are not safely transportable across private lands, which restricts flexibility in final disposal techniques.

Conversion to solids for storage significantly reduces all of these disadvantages.

A quick comparison of the relative toxicity of some of the more toxic chemicals and radioactive elements is provided in Table 1.2.⁽⁴⁾ In general, the radioactive elements are approximately one million times more toxic than the chemical compounds, and they are present in significant quantities in the spent nuclear fuel. For example, waste from one tonne of fuel from a thermal reactor with exposure history of 45,000 MWd/tonne @ 30 MW/tonne, and aged 300 years contains approximately an equal number of permissible human body burdens of plutonium-239* and strontium-90 (two of the more toxic radioactive constituents).

The nuclear power industry in the USA is expected to grow by a factor of about 100 by 1980 and by a factor of about 400 by 1990.⁽⁵⁾ Such an enormous growth rate will greatly complicate the nuclear waste management problems, and will almost certainly cause existing practices to be outdated.

Because highly radioactive wastes must be kept out of man's environment nearly forever, the method of storing the waste is critical. Even with the significant improvement of storage as solids versus storage as liquids, man cannot completely guarantee that the radioactivity will not enter

* Assuming 0.1% waste losses during fuel reprocessing.

TABLE 1.2. *Toxicity Limits^(a) of Radionuclides Compared to Chemicals*

<u>Toxic Materials</u>	<u>Maximum Allowable Concentration in Air,^(b,c) mg/m³</u>
<u>Chemical</u>	
Ni(CO) ₄	0.007
As compounds	0.5
Be compounds	0.002
B ₅ H ₉	0.01
PH ₃	0.4
F	0.08
<u>Radionuclides</u>	
Sr-90	2 x 10 ⁻⁹
Ru-106	2 x 10 ⁻⁹
Pu-239	3 x 10 ⁻⁸
I-131	7 x 10 ⁻¹¹

a. Based on chronic exposure 40 hr/week.

b. Chemical limits from Reference (6).

c. Radioactive limits are rounded-off numbers taken from Reference (7).

our environment in potentially significant quantities. Consequently, long-term storage must be made in high-integrity man-made storage areas or in deep geological formations which will provide isolation for a half million years. The ideal storage system should not rely heavily on human surveillance for the very long time of concern. In any storage technique, ready retrievability may well be highly desirable as an added degree of protection in the event of unforeseen occurrences.

Solidification is being developed so widely because it is the only reasonably attainable technique for achieving a substantial increase in the safety associated with the storing and disposal of the high-level waste from the nuclear power industry. Other techniques, more exotic and perhaps more positive (such as transporting wastes to other planets or to stars, or "neutralizing" the radioactivity by nuclear physics), are certainly not attainable in the immediate future.

1.3 THE AEC'S WASTE SOLIDIFICATION ENGINEERING PROTOTYPES (WSEP) PROGRAM

The Waste Solidification Engineering Prototype is a pilot plant that provides for full radioactivity-level demonstration and evaluation of technical, economic, and safety aspects of three of the more promising processes for solidification of highly radioactive wastes. The three processes are: (1) the pot calcination process developed by ORNL, (2) the phosphate glass solidification process developed by BNL, and (3) the spray solidification process developed by BNW. The major objective of the program is to provide the information that is necessary to select, design, fabricate and operate a waste solidification production plant and a waste storage system.⁽⁸⁾ The program complements the fluid bed calcination demonstration by INC at Idaho Falls, Idaho, and the previous hot laboratory scale program by Battelle-Northwest in providing radioactive demonstration of developmental processes. The program is also integrated with nonradioactive development work being performed by ORNL, BNL and BNW on their respective solidification processes. The demonstration is a focal point for research and development on the program sponsored by the United States Atomic Energy Commission.

Development and design of the WSEP facility were done by the BNW staff, with frequent consultation from the staffs at BNL and ORNL. Development and design were started late in 1962 and were completed early in 1965. Construction was started early in 1963 and was completed late in 1965. The WSEP equipment was installed in B-Cell of the new Chemical and Materials Engineering Laboratory (C-MEL) near Richland, Washington during the winter of 1965-1966. Final shakedown and nonradioactive testing of the equipment was performed in Design Verification Tests (DVT's) performed through the summer of 1966. The first radioactive run was completed in November 1966. Radioactive demonstrations are planned to be continued into 1970, and evaluative measurements on the solidified wastes will be continued into 1973.

The technology to be obtained from the WSEP program includes determination and/or evaluation of:

- Effects of various fuel reprocessing conditions on the solidification schemes and the resultant solidified wastes,
- Solidification and auxiliary equipment requirements and design bases,
- Process control requirements,
- Safety and radiological control requirements,
- Effects of processing schemes on integration with the primary fuel reprocessing plant,
- Safety in long-term storage of solidified wastes,
- Cost information.

In order to obtain this technology, the following tasks must be accomplished:

- Establish the technology, operability, and safety for the spray, pot, and phosphate glass processes through demonstration with full activity level wastes on an engineering scale,
- Determine and evaluate the effects of process parameters affecting the performance of auxiliary equipment required to decontaminate effluent streams from the solidification processes,
- Define the process chemistry parameters affecting the pot, spray, and phosphate glass solidification process systems and their auxiliaries,
- Establish flowsheets and reasonable operating conditions for, improve the reliability of, and establish bases for scale up of the three solidification systems,
- Study advanced methods for high level waste solidification,
- Characterize the intermediate and low level waste effluents from solidification processes, and evaluate methods of treatment to reduce the radioactivity content to innocuous levels,
- Determine the characteristics of the products (solidified waste and container) from the WSEP processes, and determine the safety and economic aspects of these product characteristics as related to the management of high level waste,
- Perform engineering analyses of all information from the waste solidification program, and translate into a series of formal reports which will provide the information listed in the primary objective.

The WSEP program will evaluate a reasonable spectrum of waste compositions which result from Purex aqueous reprocessing of spent reactor fuels. These chemical compositions are discussed in Sections 2 and 3. The basic content of fission products

for the wastes initially in the WSEP program was that from a thermal reactor fuel which was irradiated to 20,000 MWd/tonne at 15 MWd/tonne. Later bases (starting early in 1969) include 45,000 MWd/tonne at 30 MW/tonne exposures. Solidification of wastes from fast reactor fuels are planned for 1969 and 1970. Chemical compositions for wastes are taken as one year out of the reactor, but heat levels in the solidified waste are systematically being escalated from 3.5 W/liter in the first run to the maximum tolerable for each process or product (estimated as high as 300 to 400 W/liter).

The average capacity of WSEP for processing wastes is 10 to 20 liters of liquid wastes per hour, or the equivalent of waste from about 1 tonne/day of fuel. (Nominal processing rates in WSEP to date are relatively conservative; true maximum rates have not been defined.) Maximum instantaneous processing capacity is up to 60 liters/hr in some cases. Pots made of mild steel and stainless steel are all 8 feet long and have diameters of 6, 8, and 12 inches. Nominal fill height for the pots is 6 feet. Approximately 35 pots will be filled with radioactive waste during the WSEP demonstration program.

Feed stock for the WSEP program is actual waste from the Purex reprocessing plant at Richland, Washington, operated for the AEC by the Atlantic Richfield Hanford Company. In addition, purified and concentrated fission product solutions from the same source are used to increase radioactivity levels for most demonstration runs.

1.4 THE CHEMICAL AND MATERIALS ENGINEERING LABORATORY

The WSEP program is being conducted in the AEC's Chemical and Materials Engineering Laboratory (C-MEL) at Richland, Washington.⁽⁹⁾ The C-MEL is a multipurpose

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engineering facility with separate experimental areas for extensive research and development work with highly radioactive materials, tracer-radioactivity levels, and no radioactivity. The disciplines of chemical, mechanical, and instrument engineering are emphasized in the BNW organizations working in the facility.

Equipment for the waste program is installed in three of the four working cells of the Radiochemical Engineering Cells in the C-MEL. The Floor plan for C-MEL is shown in Figure 1.1. The waste solidification equipment and its immediate process auxiliaries are installed in B-Cell, which is the largest cell. The environmental storage and testing of the pots full of solidified waste has been installed in A-Cell. Laboratory measurements made on samples of solidified wastes and process tests on decontaminating sulfate effluent from the phosphate glass process are being done in part of C-Cell.

The interior of the large A- and B-Cells can be viewed through shielding windows or by closed-circuit television. Cranes and manipulators are provided for remote access to in-cell equipment. C-Cell is a conventional manipulator-window cell for bench-scale or laboratory-scale equipment.

Most process operations for WSEP are conducted remotely from a control room on the third floor of the C-MEL facility. In-cell maintenance and sampling are conducted remotely by using master slave manipulators in conjunction with shielding windows. Brief descriptions of the major WSEP equipment are presented in Section 3.4. Detailed descriptions of the WSEP equipment and the C-MEL facility are presented in Reference 10. Description of the provisions for solidified waste evaluations are presented in Reference 11.

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FIGURE 1.1. Chemical and Materials Engineering Laboratory, First Floor Plan

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(by W. K. Winegardner)

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2.0 HIGH LEVEL WASTES

(by W. K. Winegardner)

2.1 DEFINITION OF HIGH LEVEL OR CLASS E WASTE

In the past, the term "high-level waste" has generally referred to the concentrated waste streams that result from the chemical processing of spent reactor fuel elements and that contain virtually all of the nonvolatile fission products. Currently, for all practical purposes, radioactive wastes could simply be divided into two categories: low level, those which may be discharged to the environment, and all others which must be kept out of man's environment. For operational purposes, a standard has been issued that can be used to establish a quantitative boundary between high- and lower-level wastes. This standard, sponsored by the American Institute of Chemical Engineers and accepted by the United States of America Standards Institute, is "concerned primarily with potential hazards to people."⁽¹⁾ Five radioactive waste categories, listed in Table 2.1, are proposed in the referenced standard. The previously established waste terminology (low, intermediate, and high level) is analogous to the proposed terminology for groups C, D, and E. The new categories have been defined in terms of the maximum permissible concentration (MPC) in air or water, maximum permissible exposure (MPE) from external radiation, and maximum permissible quarterly intake (MPQI) from ingested solids as recommended by the International Commission on Radiological Protection (ICRP). Reference 1 also lists (as an appendix) maximum radiation values that are for use in determining the waste classification of unidentified radionuclides (in conjunction with Table 2.1). These ICRP values, based on strontium-90, have been reprinted as Table 2.2. The values in Table 2.2 could change as new information is obtained; the definitions given in Table 2.1 should remain the same.

TABLE 2.1. *Radioactive Waste Categorization⁽¹⁾*
(not intended for regulatory use)

<u>Class A</u> (population level)	
Liquid and gas	$\leq$ maximum permissible concentration (MPC) ^(a) for members of the population at large (including persons living in the neighborhood of controlled areas)
Solid	$\leq$ maximum permissible quarterly intake (MPQI) for members of the population at large (including persons living in the neighborhood of controlled areas) per kilogram of solid
Surface radiation ^(b)	$\leq$ maximum permissible whole body exposure (MPE) ^(a) for members of the population at large ^(e) (including persons living in the neighborhood of controlled areas)
<u>Class B</u> (occupational level)	
Liquid and gas	$>$ Class A but $\leq$ (MPC) ^(a) occupational exposure (40 hr week)
Solid	$>$ Class A but $\leq$ (MPQI) ^(c) for occupational exposure/kg solid
Surface radiation ^(b)	$>$ Class A but $\leq$ (MPE) ^(d) for occupational exposure ^(e) (40 hr week)
<u>Class C</u> (low level)	
Liquid and gas	$>$ Class B but $\leq 10^4 \times$ Class B
Solid	$>$ Class B but $\leq 10^4 \times$ Class B
Surface radiation	
Class C-1	$\leq$ (MPE) ^(d) (occupational) at surface ^(e)
Class C-2	$>$ (MPE) ^(d) (occupational) at surface ^(e)
<u>Class D</u> (intermediate level)	
Liquid and gas, or Solid	$>$ Class C but $\leq 10^4 \times$ Class C
Surface radiation	
Class D-1	$\leq$ (MPE) ^(d) (occupational) at surface ^(e)
Class D-2	$>$ (MPE) ^(d) (occupational) at surface ^(e)
<u>Class E</u> (high level)	
Liquid, gas, solid	$>$ Class D
Surface radiation ^(b)	
Class E-1	$\leq$ (MPE) ^(d) (occupational) at surface ^(e)
Class E-2	$>$ (MPE) ^(d) (occupational) at surface ^(e)

(a) See References 2-4

(b) Applies to surface of container, object, or pool of liquid.

(c) $MPQI = (MPC_w \text{ for } 168 \text{ hr occupational exposure})(2200 \text{ ml/day})$
(91 days/quarter)
 $= (MPC_w)(2 \times 10^5)$; MPC_w applies to water.

(d) See Reference 6

(e) The recommended MPE to the gonads or the whole body is 5 rem/yr for occupational exposure. For the population at large, it is assumed to be 1/100 of 5, or 0.05, for whole body genetic effect (See References 4 and 5).

TABLE 2.2. *Maximum Limiting Radioactivity Values for Waste Classes.⁽¹⁾ (For unidentified radionuclides, values are based on Sr-90; if Ra-226, Ra-228, or Pb-210 could be present, values must be decreased by a factor of approximately 30.)*

Class		MPC _a , $\mu\text{Ci}/\text{cm}^3$ air	MPC _w , $\mu\text{Ci}/\text{cm}^3$ liq.	MPQI, (a) $\mu\text{Ci}/\text{kg}$	MPE, (b) rem/yr
A	Population at large (c)	1×10^{-11}	1×10^{-7}	0.02	0.05
B	Occupational (40 hr)	1×10^{-9}	1×10^{-5}	0.7	5
C	Low level	1×10^{-5}	1×10^{-1}	0.7×10^4	5
D	Intermediate level	0.1	1×10^3	0.7×10^8	5
E	High level	0.1	$>1 \times 10^3$	$>0.7 \times 10^8$	5

2.3

(a) Calculation of MPQI (MPQI values reduced to one significant place)

Population at large: air - $(1 \times 10^{-11} \mu\text{Ci}/\text{cm}^3)(2 \times 10^7 \text{ cm}^3/\text{day})(7 \text{ days/week})$

(13 weeks/quarter)=0.02 $\mu\text{Ci}/\text{quarter}$

water - $(1 \times 10^{-7} \mu\text{Ci}/\text{cm}^3)(2200 \text{ cm}^3/\text{day})(7 \text{ days/week})$

(13 weeks/quarter)=0.02 $\mu\text{Ci}/\text{quarter}$

Occupational: air - $(1 \times 10^{-9} \mu\text{Ci}/\text{cm}^3)(1 \times 10^7 \text{ cm}^3/\text{day})(5 \text{ days/week})$

(13 weeks/quarter)=0.65 $\mu\text{Ci}/\text{quarter}$

water - $(1 \times 10^{-5} \mu\text{Ci}/\text{cm}^3)(1100 \text{ cm}^3/\text{day})(5 \text{ days/week})$

(13 weeks/quarter)=0.71 $\mu\text{Ci}/\text{quarter}$

(b) The recommended MPE to the gonads or the whole body is 5 rem/yr for occupational exposure. For the population at large it is assumed to be

1/100 of 5, or 0.05, for whole body genetic effect. (See References 4 and 5).

(c) 1/30 of MPC or MPE for 168 hour occupational for somatic effect; $1/30 \times 4 \times 10^{-6} = 1.3 \times 10^{-7} \mu\text{Ci}/\text{cm}^3$; 1.3×10^{-7} is considered equal to 1.0×10^{-7} for purposes of waste categorization.

2.2 ORIGIN OF HIGH LEVEL WASTE

2.2.1 General Background

As indicated in the preceding section, high-level wastes usually result from the chemical processing of spent nuclear reactor fuels. The extraction of fissionable material from spent fuel results in high-level waste streams containing essentially all (>99.9%) of the intensely radioactive nonvolatile fission products. As will be revealed later, these aqueous wastes are usually acidic inorganic salt solutions with nitrate as the predominant anion.

High-level or Class E wastes have been generated over the past 24 years in the United States. Originally, large volumes of waste were accumulated as the result of the processing of spent fuel from plutonium-producing reactors. Only plutonium was retained, and uranium along with the fission products were stored in the aqueous phase in underground tanks. The practice of storing the fission products in the aqueous phase in large underground tanks has continued. The original separations process (the bismuth phosphate process based on separation by precipitation), however, has now been replaced by more efficient processes based on separation by solvent extraction. Since their inception, solvent extraction processes have gained wide acceptance. Processes have been developed not only for the separation of plutonium, uranium, and gross fission products (e.g., at USAEC plants at Richland, Washington and at Savannah River, North Carolina), but also for the separation of uranium, thorium, and specific fission products.⁽⁷⁾ With the more efficient fuel processing methods supplanting the older process, stored high-level waste has seen an increase in the

concentration of fission products per unit volume of stored waste. Typical volumes of stored waste per unit of spent fuel processed range from 4000 liters/tonne from the first wastes generated to as low as 40 liters/tonne as can be currently produced.

2.2.2 Solvent Extraction Processes

Most reactor fuels are currently being processed by solvent extraction techniques. Extensive experience has now been obtained, and current concepts for commercial processing plants are either based entirely on processing by solvent extraction or utilize solvent extraction as the first key processing step.

The first solvent extraction process used on a large scale was the Redox process.⁽⁸⁾ In this process, feed solution is contacted in packed columns with hexone solvent and an aqueous solution of aluminum nitrate (salting agent) to remove the fission products. The Redox process has now been replaced by a second solvent extraction process (the Purex process) primarily because (1) the organic solvent of the Purex process, tributyl phosphate diluted with a kerosene type of hydrocarbon, is less toxic and less inflammable than hexone and (2) nitric acid alone is the salting agent, thus significantly reducing the bulk of the high-level waste.⁽⁷⁾ In addition, in the Purex process, fission product decontamination is obtained with fewer contactors, which are either pulse columns or mixer-settlers. Currently, most of the reactor fuels in the United States are processed using the Purex process, and the process is the outstanding contender for fast reactor fuels.

An excellent description of the solvent extraction processes and the appropriate flowsheets are contained in Chapter 8 of Reference 7. A simplified or schematic fuel reprocessing flow-sheet, based on solvent extraction, is shown in Figure 2.1. As shown in this figure, fission products are removed from uranium and plutonium in what is termed the first cycle. The uranium and the plutonium are then separated from each other in the second cycle.

2.3 CHARACTERISTICS OF HIGH LEVEL WASTES

2.3.1 Fission Product Content

The most striking characteristic of high level wastes is the fact that such wastes contain essentially all of the intensely radioactive, nonvolatile, fission products. The primary fission products consist of a mixture of more than 30 elements with atomic numbers ranging from 30 to 64. Most of the primary fission products are radioactive, and more than 300 different isotopes have been observed.⁽⁷⁾ Fortunately, the situation is somewhat simplified for solidification of high-level wastes, since only the long-lived radioisotopes make significant contributions. As shown in Table 2.3, the number of important radioactive species reduces to less than a dozen nuclides.

The fission product distributions shown in Table 2.3 were calculated for a fuel exposure of 45,000 MWd/tonne (at 30 MW/tonne).⁽⁹⁾ The preceding values were selected since an exposure of 45,000 MWd/tonne is believed to be a probable maximum for future thermal reactors.⁽¹⁰⁾ For comparison, the last column in Table 2.3 gives values for a fuel exposure of 20,000 MWd/tonne (at 15 MW/tonne), a value selected as typical of current power reactors. (The Yankee Pressurized Water Power Reactor was used as a basis.)

(a) Organic Wastes Are Treated and Re-used.

(b) This Waste Can Be Combined with First Cycle Waste or Treated Separately

FIGURE 2.1. Basic Fuel Reprocessing Steps (Aqueous, Solvent - Extraction Process)

TABLE 2.3. Distribution of Fission Products from a Power Reactor Fuel (9) (45,000 MWd/tonne at 30 MW/tonne)

Element	Avg. Atomic Weight	After 1 year (a)		After 5 years		After 1 year	
		Curies/tonne	Grams/tonne	Curies/tonne	Grams/tonne	45,000 MWd/tonne	Moles/liter (378 liters/tonne) 20,000 MWd/tonne (b)
Rb	86	-----	463	-----	470	0.014	0.007
Cs	135	3.68×10^5	3952	19.09×10^4	3677	0.077	0.037
Sr	89	1.05×10^5	1191	9.16×10^4	1124	0.035	0.016
Ba	138	-----	2184	-----	2459	0.042	0.017
Y	89	1.12×10^5	622	9.16×10^4	621	0.018	0.009
La	139	-----	1729	-----	1729	0.033	0.015
Ce	141	4.41×10^5	3440	1.26×10^4	3305	0.064	0.028
Pr	141	4.41×10^5	1611	1.26×10^4	1611	0.030	0.013
Nd	145	-----	5531	-----	5665	0.101	0.043
Pm	147	1.03×10^5	111	3.58×10^4	39	0.003	0.002
Sm	150	-----	1039	-----	1111	0.018	0.008
Eu	153	0.16×10^5	270	-----	256	0.004	0.001
Gd	156	-----	127	-----	144	0.002	-----
Zr	93	0.26×10^5	5050	-----	5116	0.143	0.064
Nb	95	0.55×10^5	-----	-----	-----	-----	-----
Mo	98	-----	4856	-----	4859	0.131	0.058
Tc	99	-----	1153	-----	1153	0.031	0.014
Ru	102	2.84×10^5	3118	1.80×10^4	3040	0.081	0.033
Rh	103	-----	520	-----	520	0.013	0.007
Pd	106	-----	1736	-----	1814	0.043	0.016
Ag	109	-----	68	-----	68	0.002	0.001
Cd	111	-----	103	-----	103	0.003	0.001
Sn	123	-----	78	-----	78	0.002	0.001
Sb	123	-----	22	-----	16	-----	-----
Te	130	-----	705	-----	711	0.014	0.006
Total		19.5×10^5	39,679	45.3×10^4	39,689	0.904	0.397

(a) Additional information, calculated for only 6 months of out-of-reactor cooling is presented in Table 2.6.
 (b) Exposure at a specific power of 15 MW/tonne

2.3.2 Content of Chemicals Other Than Fission Products⁽¹¹⁾

High-level wastes contain several chemical species other than the fission products. Solvent extraction using nitric acid or nitrate salts is essentially the only production scale means currently used for the first stage removal of fission products from the fissionable material in spent nuclear fuel. Consequently, all high-level wastes are primarily aqueous solutions of inorganic nitrate salts. Differences in wastes occur mainly in the amount and type of salts added to the solutions during reprocessing of the spent reactor fuel.

Table 2.4 lists five waste compositions which bracket the range of chemical compositions of wastes expected from fuel reprocessing by solvent extraction. All compositions are shown at a volume of 378 liters/tonne of uranium fuel, although concentrations greater than about 4N in total metallic ions will generally cause precipitation which is unmanageable for extended storage.^(12,13,14) The compositions shown in Table 2.4 assume the fuel cladding is not dissolved with the fuel; consequently, the fuel cladding constituents are not present in the high-level waste. In addition, soluble neutron poisons (e.g., boron and cadmium) that may be used during fuel dissolution to prevent an accidental nuclear excursion are not included in compositions listed.

Waste composition number 1 is typified by a very high content of iron and low content of other constituents. This waste has been generated by one reprocessor⁽¹⁵⁾ by dissolving an iron fuel processing container with the fuel. Composition number 2 is a moderately "dirty" waste from first cycle

**TABLE 2.4. Concentration of Chemicals
(other than fission products)
in High Level Wastes^(a)**

Constituent	Concentration, molarity at 378 liters/tonne ^(b)				
	No. 1 ^(c)	No. 2 ^(c)	No. 3 ^(c)	No. 4 ^(c)	No. 5 ^(c)
<u>General Chemical Composition of Inert Materials</u>					
Na	low	high	high	low	low
Fe	high	med	med	low	low
Al	0	0	0	0	high
SO ₄	0	high	high	0	0
<u>Actual Chemical Composition of Inert Materials</u>					
H	3.7	3.93	(-)0.01	6.29	4.25
Fe	0.93	0.445	0.445	0.05	0.05
Cr	0.012	0.024	0.024	0.012	0.012
Ni	0.005	0.010	0.010	0.008	0.008
Al	0.001	0.001	0.001	0.001	0.65
Na	0.138	0.93	3.67	0.10	0.10
U	0.010	0.010	0.010	0.010	0.010
Hg	<0.001	<0.001	<0.001	<0.001	<0.001
NO ₃	7.5	5.37	2.0	6.66	6.5
SO ₄	-----	0.87	0.87	-----	-----
PO ₄	0.003	0.006	0.006	0.003	0.003
SiO ₃	0.010	0.010	0.010	0.010	0.010
F	<0.001	<0.001	<0.001	<0.001	<0.001
EM ⁺ _{chem} ^(d)	3.03	2.48	5.22	0.365	2.31
kg oxide/ tonne	31.7	28.1 ^(e)	60 ^(e)	4.6	17.2

(a) Soluble neutron poisons which may be used during fuel dissolution are not included. Concentration of these materials (e.g., boron and cadmium) could be as high as 100 to 200 g/liter in the high level waste.

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

(c) In WSEP, wastes 1, 2, 3, etc., are designated PW-1, PW-2, PW-3, etc., when they contain fission products from fuels irradiated to 20,000 MWd/tonne at 15 MW/tonne; when wastes contain fission products from fuels irradiated to 45,000 MWd/tonne at 30 MW/tonne, the wastes are designated PW-1m, PW-2m, PW-3m, etc.

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

(e) Does not include the sulfate. If sulfate is not volatilized, approximately 27 kg/tonne of additional oxides are formed.

waste combined with second cycle waste that contains sulfate and iron that comes from a reductant in the uranium-plutonium partitioning step (see Figure 2.1). Waste number 3 is the same as waste number 2 except that it has been neutralized before storage. Waste number 4 is a "clean" waste which would come from the first solvent extraction cycle with reasonable care in maintaining a flowsheet relatively free of nonradioactive chemicals. This is expected to be a fairly typical waste in the near future. Waste number 5 is one generated in a process where aluminum nitrate is used for the salting agent in the solvent extraction process.

Chemical adjustment to supply stoichiometric amounts of a stable anion to waste number 3 is required before solidification, since direct calcination will form chemically unstable, hygroscopic Na_2O . If chemically adjusted by acidification with sulfuric acid, this waste then is similar to waste number 2. Waste number 5 is believed to have only minor importance in the future. Consequently, wastes 1, 2 and 4 bracket the range of the most likely high-level liquid waste compositions (without the soluble neutron poisons). In the WSEP program, wastes 1 and 2, which contain fission products from fuel irradiated to 20,000 MWd/tonne at 15 MW/tonne, are designated PW-1 and PW-2, respectively; waste 4, which contains fission products from fuel irradiated to 45,000 MWd/tonne at 30 MW/tonne, is designated PW-4m.

Comparison of the concentrations of fission products given in the last two columns of Table 2.3 and the appropriate values of Table 2.4 show that the chemical content of fission products is significant in all possible combinations of power reactors and fuel reprocessing schemes. In fact, with only moderate attempts to minimize the inert contaminants

in the waste, the chemical equivalents of fission products would exceed those of the nonradioactive contaminants, and the chemistry of the fission products would be a major controlling factor in waste treatment steps.

2.3.3. Heat Generation in High-Level Wastes

Since high-level wastes contain essentially all of the fission products, the rate of heat generation in the mixture (arising from beta and gamma emission) is significant. In fact, Purex processes result in waste with sufficient fission product heat generation rates that the stored waste boils for many years. In addition, waste programs involving solidification could be designed to concentrate fission products to the point where decay heat is sufficient to result in a partially molten product.

The decay heat associated with the fission products from a fuel exposure of 45,000 MWd/tonne at a specific power of 30 MW/tonne, an exposure of 20,000 MWd/tonne at 15 MW/tonne, and an exposure of 100,000 MWd/tonne at 200 MW/tonne (for core fuels from fast reactors) are shown in Figure 2.2 as a function of time out-of-reactor. The two lower exposures, associated with thermal reactor fuel, are the same as those used in Table 2.3. Review of Figure 2.2 will reveal a substantial decrease in the rate of decay of heat generation after about five years of cooling. Obviously, interim storage of liquid waste from power reactor fuels beyond approximately eight years offers little benefit when solidification processes are considered.

FIGURE 2.2. Approximate Fission Product Heat Generation Rates^(9,16)

2.3.4 Future Wastes

Continued development of the production of electrical power from nuclear fission will result in spent fuels which were irradiated to higher exposures and at higher specific powers. A preliminary study was undertaken to provide a limited assessment of the possible aqueous waste resulting from processing of fast reactor fuels.⁽¹⁶⁾ The study is summarized in this section to illustrate some of the problems that could be associated with fuels irradiated to higher exposures.

Obviously, higher fuel exposures and specific powers will result in wastes with significantly higher specific fission product content and therefore heat generation. The approximate fission product content of fast reactor core fuel (with anticipated exposure to 100,000 MWd/tonne at 200 MW/tonne) is compared to that previously described as a probable maximum for thermal power reactor fuel (45,000 MWd/tonne at 30 MW/tonne) in Tables 2.5 and 2.6, while total heat generation was compared previously in Figure 2.2 (see Section 2.3.3).

In addition to causing changes in the total specific fission product content, fast neutron fissioning also changes the relative amount of many fission products. Of particular significance is the fact that the relative amounts of ruthenium, along with cadmium, tin, antimony, and tellurium will increase (although the total amount of the latter four will still be relatively small). Some of these latter fission products, notably antimony and tellurium, tend to be volatile like ruthenium at high temperatures and could complicate waste solidification processes.

TABLE 2.5. *Approximate Chemical Content of Fission Products in Irradiated Fuel^(9,16)*

Element	Quantity, grams/tonne	
	Fast Reactor Core Fuel ^(a,b)	Thermal Reactor Fuel ^(c)
Se	166	68
Rb	609	462
Sr	1310	1201
Y	677	624
Zr	7584	5045
Nb	60	9
Mo	8800	4841
Tc	2384	1153
Ru	8535	3154
Rh	2490	519
Pd	6660	1701
Ag	756	68
Cd	440	103
In	42	2
Sn	436	78
Sb	160	23
Te	1666	704
Cs	10830	4003
Ba	3540	2134
La	3058	1729
Ce	7110	3518
Pr	3125	1610
Nd	10168	5453
Pm	1015	127
Sm	2470	1023
Eu	407	273
Gd	323	127
Tb	30	2
Dy	20	----

(a) Does not include gases or elements present in quantities less than 10 grams/tonne in core fuel.

(b) 100,000 MWd/tonne at 200 MW/tonne, 6 month cooling.

(c) 45,000 MW/tonne at 30 MW/tonne, 6 month cooling.

TABLE 2.6. *Approximate Amounts of Radionuclides and Heat Rates in Irradiated Fuel^(9,16)*

Nuclide	Fast Reactor Core Fuel ^(a)		Thermal Reactor Fuel ^(b)	
	Ci/tonne	W/tonne	Ci/tonne	W/tonne
Sr-89	2.37×10^5	815	0.52×10^5	178
Sr-90 ^(c)	1.11×10^5	749	1.02×10^5	692
Y-91	4.90×10^5	1,800	$.98 \times 10^5$	360
Zr-95	12.10×10^5	6,046	1.80×10^5	898
Nb-95	23.46×10^5	11,280	3.50×10^5	1684
Ru-103	4.04×10^5	1,434	0.46×10^5	152
Ru-106 ^(c)	32.00×10^5	30,400	4.00×10^5	3796
Cd-115m	0.07×10^5	27	----	----
Sn-123m	0.61×10^5	203	----	----
Sb-125	0.69×10^5	223	0.10×10^5	32.69
Te-125m	0.15×10^5	13	0.02×10^5	----
Te-127m ^(c)	0.32×10^5	60	0.04×10^5	2
Te-129m ^(c)	0.11×10^5	53	0.02×10^5	3
Cs-134	2.00×10^5	2,027	2.64×10^5	2674
Cs-137 ^(c)	3.35×10^5	1,620	1.46×10^5	704
Ce-141	1.80×10^5	266	0.26×10^5	39
Ce-144 ^(c)	30.50×10^5	24,888	6.87×10^5	5609
Pm-147	9.50×10^5	342	1.18×10^5	42
Sm-151	0.15×10^5	2	----	----
Eu-154 ^(c)	0.03×10^5	27	0.09×10^5	85
Eu-155	1.31×10^5	118	0.08×10^5	8

(a) 100,000 MWd/tonne, 200 MW/tonne, 6 month cooling.

(b) 45,000 MWd/tonne, 30 MW/tonne, 6 month cooling.

(c) Watts include short-lived daughter

Although development is needed, solvent-extraction is currently the outstanding contender for processing fast reactor fuels. The range of concentrations of chemicals other than fission products would then not be grossly different from those previously described. Obvious exceptions to the preceding statement could arise from the processing of advanced fuels (e.g., carbide fuels) or from advanced processing schemes. Wastes from processing of carbide fuels could even contain soluble organic compounds that could still further complicate waste solidification.

Finally, it should be noted that because of the significantly lower exposure of fast reactor blanket fuel, the severity of some of the above increases can be lessened simply by mixing core and blanket fuel for processing.

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3.0 WASTE SOLIDIFICATION PROCESS CONSIDERATIONS

(by K. J. Schneider)

3.1 THE FOUR SOLIDIFICATION PROCESSES IN USA

In the USA, as in other parts of the world of nuclear power, research and development has been performed on many processes for solidification of high-level liquid wastes. In 1963, development in this country was narrowed to the four most promising processes: pot calcination, spray solidification, phosphate glass solidification, and fluidized bed calcination. The four processes are shown schematically in Figure 3.1. The pot, spray, and phosphate glass processes are being demonstrated in WSEP with full-activity-level wastes in engineering-scale equipment; the fluidized bed process has been demonstrated with intermediate-activity level wastes in large-scale equipment at the National Reactor Testing Station by the Idaho Nuclear Corporation for nearly five years.

In all four processes, heat is applied to raise the temperature of the waste to 400 to 1200 °C. At these temperatures, essentially all the volatile constituents (primarily water and nitrates) are driven off, leaving a solid or a melt that will cool to a solid. The final solid has, therefore, been exposed to a high temperature environment, which is, in effect, an environment that accelerates the aging process. Because of this pre-aging process, and because chemical reactions are generally quite slow after the treatment, the resulting solids are relatively stable at temperatures lower than those during processing.

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a. Pot Solidification

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b. Spray Solidification

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c. Phosphate Glass Solidification

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d. Fluidized Bed Solidification

FIGURE 3.1. Primary Solidification Techniques in the United States

3.1.1 Pot Calcination

Pot calcination is a batch process in which the principal processing vessel, the pot, is also the final container for the solidified waste.^(1,2) In pot calcination, shown in Figure 3.1a, liquid waste is added to a pot that is heated in a multiple-zone heating and cooling furnace. The waste is concentrated at a constant volume to the point that scale (salt cake) forms on the walls of the pot. As calcination continues, the scale grows in thickness and reduces the capacity for heat transfer from the pot wall to the boiling sludge, and therefore, the feed rate must be reduced proportionately. When the feed rate is reduced to an "unprofitable" rate (about 3 to 5 liters/hr), the feed is shut off. At this point, the scale has grown inward from the pot wall and upward from the bottom of the pot to fill the pot, except for a thin cone-shaped liquid-containing void in the upper 2 to 3 feet of the salt cake. Heating is then continued until the liquid is boiled to dryness and all of the waste in the pot has been calcined and has reached the temperature of 850 to 900 °C. The pot is then cooled in the furnace, removed, sealed, and taken to storage.

The product from pot calcination (i.e., the solidified waste) is a mixture of oxides (and sulfates, if sulfate is present in the waste) of the metallic constituents in the original liquid waste. The product is a porous, friable calcine with a low thermal conductivity and a relatively high solubility in aqueous solutions.

3.1.2 Spray Solidification

In spray solidification, liquid waste is continuously converted to a dried powder in a spray calciner. The powder

is then melted in a continuous melter, and the molten waste is discharged into the receiver-storage pot. In the spray calciner (see Figure 3.1b), liquid waste (which contains some or all of the melt-making additives) is fed through a pneumatic atomizing nozzle into the top of a cylindrical tower which is heated to 500 to 800 °C. The atomized waste is sequentially evaporated, dried, and calcined to a powder as it falls into a continuous melter below the calciner where it is melted at temperatures of 800 to 1200 °C. Process gases from calcination flow into the adjacent filter chamber, carrying much of the calcined powder. The powder collects on the porous metal filters as the gas passes through. The powder deposits are periodically blown off the filters by sudden pulses of high-pressure steam or air directed backward through the filters by small nozzles. The dislodged dust falls into the melter with the remaining powder stream. The molten calcine flows through an overflow weir or a freeze valve into the receiver-storage pot below. After the pot is filled, it is cooled in the furnace, sealed, and taken to storage.

The product from spray solidification is a monolithic solid formed after cooling the melt. The solid is a tough, microcrystalline, rock-like material with a good thermal conductivity and a moderately low solubility in aqueous solutions. (Glassy solids have also been made in the spray solidifier, but primary emphasis has been on microcrystalline materials.)

3.1.3 Phosphate Glass Solidification

In phosphate glass solidification (see Figure 3.1c) liquid waste is continuously concentrated to a thick slurry in an evaporator. The slurry is drawn from the evaporator to a continuous melter for conversion to a glass. Liquid waste which

contains all of the melt-making additives is first fed to the evaporator where it is concentrated and denitrated by factors of 2 to 10 to a thick, syrupy, aqueous phosphate slurry. The slurry is fed to the continuous melter where final volatilization of the water, nitrates, and other volatile constituents is accomplished, and the material is heated to 1000 to 1200 °C to form a molten glass. The molten glass flows through an overflow weir or a freeze valve into the receiver-storage pot below. After the pot is filled, it is cooled in the furnace, sealed, and taken to storage.

The product from the phosphate glass process is a monolithic, moderately brittle glass formed after cooling the melt. The glass has a good thermal conductivity and a low solubility in aqueous solutions.

3.1.4 Fluidized Bed Calcination

In fluidized bed solidification, liquid waste is continuously converted to granular solids. The liquid waste is heated in a fluidized bed of the solids, and the solids are continuously withdrawn from the calciner to storage bins. (The solids may be further converted to monolithic forms; see Figure 3.1d.) The liquid waste is injected through pneumatic atomizing nozzles into the side of a heated (400 to 600 °C) bed of granular solids which is continuously agitated (fluidized) by gas sparging upward through the fluidized bed reactor. Contact of the waste with the hot, granular bed evaporates and calcines the feed into coatings of the bed particles. The calcine that is entrained with the process gases from the calciner is removed from the gas stream by cyclone separators or filters, then returned to the main stream of particles. The main stream of particles is continuously removed from the reactor and transported to storage bins.

The product from fluidized bed solidification is granular with a mean particle diameter of about 500 micrometers. The granules may be composed of crystals or amorphous solids. The granules are generally spherical and are moderately soft and friable. The thermal conductivity of the bulk calcine is relatively low, and the solubility is relatively high.

3.2 GENERAL CHEMICAL CONSIDERATIONS FOR WASTE SOLIDIFICATION

As discussed in Section 2, all high-level wastes are primarily aqueous solutions of inorganic nitrate salts (which will decompose at temperatures below 500 °C). The spectrum of expected compositions of chemicals in wastes were presented in Tables 2.3 and 2.4.

All processes for solidification of high-level waste generate additional waste streams that contain intermediate levels of radioactivity. These are the vapor or condensate streams from the solidifier that have been decontaminated by factors of 10 to 1000. From this point, decontamination requirements of the effluents are generally comparable to those from the high-level liquid waste handling system of the reprocessing plant. (This subject is discussed briefly in Section 3.3 and in detail in Section 9.)

The amount of major chemical materials resulting from fissioning in thermal reactors with moderate and high exposure histories was shown in Tables 2.3 and 2.5 to be significant. With only moderate attempts to minimize the inert contaminants in the waste, the chemical equivalents of fission products will exceed those of the inert contaminants, and the chemistry of the fission products will be the controlling factor in the waste treatment steps.

The absolute minimum weight of solidified waste (that of fission product oxides alone) is about 1.1 kg/1000 MWd thermal exposure. Contributions from inert chemicals in the compositions shown in Table 2.4 can increase that amount by a factor up to 4. Additional chemical additives are often needed to perform chemical functions during solidification. These additives are based on the total composition of chemicals present, and can increase the weight of the final solidified waste by as much as an additional factor of 3.

Solidification processes that form melts require significant chemical modification of almost any waste composition. Compositions for waste solidification by melting generally require at least 70 mole % of inert chemicals to incorporate the fission products into materials that are meltable at reasonably low temperatures, or less than about 1000 °C. (A more typical value for the inert chemical content in melts is 85 mole %.)

Melts in which the major melt-making fluxes are phosphates, (3,4,5,6) borophosphates, (7,8,9) silicates, (10,11) borosilicates, (7,10,11) and borates. (12) have been developed. In most cases, potentially workable chemical composition ranges have been defined. However, because of the complex interaction of all the constituents in the wastes, in no case has a general correlation for chemical composition been defined. Thus, paper study development of a workable melt composition cannot be done unless the composition is modified to one that has been developed. Therefore, a laboratory investigation of each new melt-forming composition is required before melt solidification can proceed. Similar studies are usually necessary to predict occurrence of special problems (such as ruthenium or sulfate volatilization, foaming, stickiness, etc.) for all solidification processes.

Three of the inert chemical constituents listed in Table 2.4 are sufficiently troublesome in solidification to merit effort to keep them out of high-level liquid wastes. These constituents are sulfate, fluoride, and mercury ions. The sulfate ion is generally unstable chemically at the higher range of temperatures reached in solidification (700 °C and higher) and tends to volatilize. Retention of sulfate in the solidified waste at temperatures above 700 °C is difficult and requires chemical additives (usually calcium).⁽¹⁾ Retention of sulfates in melts is nearly impossible above 850 to 900 °C.⁽³⁾ Such volatilization would result in added corrosion problems in the off-gas system, recycle and increased sulfate concentrations in the liquid waste for cases of partial volatilization, or another medium-to-high-level waste stream that requires special treatment and disposal for cases of complete volatilization. Sulfate also causes severe precipitation and resultant solution handling problems from sodium-rare earth sulfates when present at concentrations of approximately 0.5M or greater.⁽¹⁸⁾

Fluoride is difficult to retain (by using calcium) in solidified waste processing up to temperatures of about 600 °C,⁽¹⁴⁾ and is probably impossible to retain significantly at higher temperatures.⁽¹⁵⁾ If it cannot be retained, it must be disposed of by another means such as in the gaseous stream out of the plant stack or in a separate lower-level waste stream. A fluoride content of much more than about 0.001M will significantly increase corrosion of stainless steel and titanium (used generally in waste processing systems), although this corrosion can be partly overcome by use of complexing agents (aluminum, zirconium, etc.).

Mercury cannot be retained in solidified waste processed at temperatures above 400 to 500 °C. When volatilized, the mercury and its oxides condense at temperatures of about 350 °C and provide relatively serious potential plugging problems. A means for pre-treating the waste for removal of mercury has been developed in the laboratory.⁽¹⁶⁾

Ruthenium, one of the ever present fission products, is just as cantankerous in waste solidification as it is in fuel reprocessing. One to eighty percent of the ruthenium will usually oxidize and volatilize during solidification, depending on the specific chemical flowsheet and the waste. Ruthenium is usually more difficult to remove from the off-gas stream than are the nonvolatile materials. Chemical additives that reduce the oxidizing potential during solidification are sometimes required to minimize oxidation to the volatile RuO_4 form. Even then, volatilization of at least 1% is usually encountered.

3.3 EQUIPMENT AND FACILITY REQUIREMENTS FOR WASTE SOLIDIFICATION

The overall equipment process requirement for waste solidification may be divided into two major categories. The first category is the solidification equipment itself. The second category is the auxiliary processing equipment which is required to process the effluents from the waste solidification equipment.

3.3.1 Solidification Requirements

Major equipment and facility requirements directly related to the solidification equipment are:

- A shielded facility for solidification processing,
- The solidification vessels,
- Furnaces for heating the solidifiers to the necessary high temperatures,

- Cooling (and frequently heating) furnaces for the solidified wastes as they are being formed and before they are transferred to storage,
- The containers for the solidified waste,
- Feed treatment and preparation facilities,
- Facilities for transporting the aqueous waste to the solidification plant and for transporting the solidified waste to the storage site,
- An ultimate storage facility,
- The associated service equipment for these.

Additional solidification-related items that may be required include the following:

- Interim aqueous storage facilities if the wastes are aged before solidification,
- Pre-treatment provisions before solidification (e.g., for removal of trace organic materials, for removal of mercury or other materials, pre-concentration etc.),
- Initial clean-up of the vapors from the solidifier (e.g., filtration for spray or fluid bed processes),
- Initial condensation of vapors if similar capability is not provided elsewhere.

3.3.2 Auxiliary Requirements

The auxiliary equipment is required to reduce the amount of radioactivity in the effluents from the solidification equipment to levels that are nontoxic. Total cleanup of some of the radioactive constituents that are present in the feed to the waste solidification system is required to the point of final human consumption, or cleanup by factors up to 1×10^{12} . Cleanup the radioactive waste to the effluents directly from the solidification equipment is normally in the range of

10 to 1000. Consequently, cleanup of these effluents to the extent of 10^8 to 10^{11} is required in the auxiliaries from the solidification equipment and in the final disposal system. Ultimately, effluents from wastes from the Purex process (which is the only commercially competitive process today) can be converted into a partly-cleaned nitric acid-water stream which is reusable for fuel dissolution or other process steps during fuel reprocessing, a water stream which must be nontoxic, and a nontoxic gaseous discharge (which arises from air purges and leaks into process equipment). Most if not all of this extensive cleanup can be and usually is accomplished in relatively standard processing equipment such as redistillation followed by condensation, acid-water fractionation, gas filtration, and gas scrubbing.

In general, the amount of radioactivity present in the immediate effluent stream from the solidification processes themselves is less than that in the high-level liquid waste handling system of a fuel reprocessing plant. In addition, the volume of this effluent stream from solidification is no more than 10% of that fed to the high-level waste concentration system in the fuel reprocessing plant. Consequently, in most cases, these immediate effluents from waste solidification could be combined with those from the reprocessing plant itself with only a minor increase in the capacity or other requirements for this equipment. Such integration would result in essentially no change in the fuel reprocessing plant due to solidification except for the solidification equipment itself. This subject is described schematically in Figure 3.2 and discussed in more detail in Section 9.

If a solidification plant were located far from the fuel reprocessing plant, the solidification plant would need a

FIGURE 3.2. Role of Waste Solidification in Nuclear Fuel Reprocessing Plants

complete smaller capacity version of similar intermediate-level waste treatment facilities. In addition, shipment of the high-level liquid waste to the solidification plant and shipment of recovered nitric acid with low-to-intermediate-level radioactivity content back to the separations plant would be required. Therefore, considerable economic and safety incentives exist for integration of solidification plants with the primary reprocessing plant.

3.4 PROCESS AND EQUIPMENT CONSIDERATIONS IN WSEP

3.4.1 Overall WSEP Considerations

The major objective of the WSEP program is to provide the currently-unavailable information that is necessary to select, design, fabricate, and operate a waste solidification production plant. The prototype program complements all other American developmental processes and programs.

Using the major program objective as a basis, the primary design criteria and objectives were established. Six of the most important of the design bases are:

1. The prototypes must provide for evaluation on comparable bases of the three processes selected.
2. The prototypes must provide for process evaluation on a meaningful size scale. To do this, the average capacity was established at 10 to 20 liters/hr of liquid waste, or the waste equivalent of approximately 1 tonne/day of power reactor fuel.
3. Demonstration must be performed with radioactivity levels equivalent to those of power reactors with moderate-to-high fuel burnup. The basic design activity level is that of waste from the Yankee Atomic

Power Reactor. This waste is from uranium fuel irradiated to 20,000 MWd/tonne (th) at a power level of 15 MW/tonne aged one year and concentrated to a liquid volume of about 380 liters/tonne. Later demonstrations will be made on wastes from thermal reactor fuels with considerably higher exposure history, and possibly, on fast reactor wastes.

4. The prototypes must have the flexibility and the instrumentation to allow study of a wide variety of feeds, flowsheets, equipment, and equipment arrangements, with a reasonable amount of turnaround time.
5. The long-range cost of the equipment must be reasonable.
6. The prototype equipment must be operationally safe.

Detailed descriptions of WSEP designs are presented in Reference 17 and are discussed briefly here. The main process features of the prototypes are shown in Figure 3.3. Liquid waste is brought into the plant in a cask, and is chemically adjusted in a feed tank to reproduce a variety of waste solutions. Concentrated fission product solutions are similarly brought into the plant and added to the feed tank to reproduce wastes with varying heat generation characteristics. Digestion may be done in the feed tank, or preconcentration may be done in the evaporator for feed preparation, if necessary. From the feed tank or the evaporator, the wastes are fed directly to one of the three solidification processes. The vapors from these solidifiers are routed through a single off-gas (or auxiliary treatment) system common to all processes. These vapors are first routed through a condenser, then are recycled to the evaporator where they are reconcentrated. The vapors from the evaporator are decontaminated from entrained aerosols, first in the evaporator tower and again by condensing and feeding to an acid fractionator. The vapors from the fractionator are condensed and collected for disposal. The remaining gases are

FIGURE 3.3. WSEP Schematic Flow Diagram

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passed through additional treatment before discharge to the atmosphere. The recovered acid and condensate are recycled to the production separations plant.

The solidified waste is collected in "pots" that are sealed, then stored in the cells (in air or water as required) for prolonged observations.

Although all three processes are being demonstrated, only one may be demonstrated at one time in one of two positions in the cell. Consequently, process equipment for one solidification process must be in standby condition while the other two are installed.

Two waste compositions which bracket a broad range of Purex-type wastes were selected for design guides. These feed compositions are designated PW-1 and PW-2, and are shown as wastes 1 and 2, respectively in Table 2.4.

Since the prototype is a developmental facility, many features for process flexibility, monitoring, and control are included but may not be required in a production plant. The following is a summary of the more important basic features of the WSEP:

- The entire process system is always maintained under a slight vacuum relative to the cell atmosphere. The primary process vent system is maintained at a negative pressure of 5 to 30 inches of water. The secondary process vent system which vents service tankage is maintained at a vacuum of 2 to 10 inches of water.
- All solidification equipment has emergency vents to a second enclosed routing system through water-filled seal pots in case of inadvertent undesirable reduction of vacuum.

- The equipment is highly instrumented to provide ample data for process evaluations. The facility is operated by electronic instrumentation in the remote control room. Only a few operations such as sampling and pot positioning are done manually, using manipulators and hoists.
- Double containment is provided for equipment exposed to potentially severe environments. Specifically, this feature is included for the solidification pots, the continuous melters, and the pot storage system.
- Design and operation are aimed at producing gaseous and liquid effluents with low activity levels. Moderately extensive off-gas cleanup is included to accomplish this.
- Pot sizes and heat content of the solidified waste will be selected to limit the maximum internal pot temperatures at 900 °C and the maximum pot wall temperatures at 427 °C.
- A maximum amount of interchangeability has been provided.
- A digital computer is used for continuous data logging and on-line calculations of material balances, heat transfer, and equipment performance.
- Major equipment with similar functions is grouped together into semi-portable racks (which may be moved independently from each other) and "plugged" into shielding walls to permit connections on the backside by direct contact maintenance. A major process rack is shown in Figure 3.4.
- Process equipment was designed so that it could be usable in future in-cell programs.

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FIGURE 3.4. A Major Process Equipment Rack in WSEP

These items comprise the major overall process design features of the prototype. In the following sections the overall features of some of the more important WSEP equipment are summarized.

3.4.2 Solidification Equipment in WSEP

In the phosphate glass process, the denitrator-evaporator is a short-tube calandria type which is constructed of commercially pure titanium. The removable tube bundle has large 2-inch diameter tubes for good recirculation flow, good heat transfer, and minimum scaling tendencies during operation with viscous slurries. Heat transfer is further improved by a removable variable speed agitator. Denitrated waste is air-lifted from the bottom of the evaporator to a small pot which overflows into the melter feeder. Here the feed flows through a small jacketed platinum tube into the heated zone of the melter. The all-platinum melter hangs by an integral lip from the upper flange of the single-zone furnace. Melt is discharged through an internal overflow weir or a freeze valve through separate small heated chambers with provisions for cooling. The discharging melt drops into the melt receiver pot. The melt receiver pot is inside a 6-zone heating-cooling furnace. The vapors from the melter are routed to the melter condenser where all parts that contact the process solution are made of Nionel and all Nionel surfaces are water-cooled for additional corrosion protection.

In the spray solidification process, feed is pumped through a removable pneumatic atomizing nozzle at the top of the removable stainless steel, cylindrical drier section of the spray calciner. This drier section is heated externally by a 3-zone electric furnace. The dried powder from the spray

calciner falls into the all-platinum melter which is essentially identical and interchangeable with the melter used for the phosphate glass process. Similarly, the melted waste is discharged batchwise through a freeze valve or continuously through an overflow weir into the receiver pot below. The gases from the spray calciner flow through sintered stainless steel filters which are periodically cleaned on-line by pulses of reverse-direction jets of steam or air.

In the pot calcination process, feed is pumped into the top of the pot through an integral tube which extends slightly into the pot. The stainless steel pot is heated by the same type of 6-zone heating-cooling furnace used for the other processes. The vapors from the pot flow through an off-gas line with partial reflux to keep the line clean.

Two basic sizes of pots are used in the prototypes: 8 inches and 12 inches in diameter and 8 feet long. In addition, some pots with 6 inch diameters will be used for wastes with high heat rate density. All pots will be filled to the 6 foot level.

Two types of pots are used: the calcine pots for pot solidification, and the melt pots for spray or phosphate glass solidification. Calcine pots have small diameter heads for the four fluid process connections required. Melt pots contain no internal fluid piping, and have a wide mouth to provide a better target for molten waste flowing from the melters. Both types of pots have internal thermocouples in thermocouple wells and external wall thermocouples. The pots are made of either stainless steel or carbon steel. Stainless steel pots are used for pot calcination; either may be used for spray solidification and for phosphate glass solidification.

3.4.3 Auxiliary Equipment in WSEP

The waste evaporator is a medium-length thermosyphon type constructed of titanium, and designed to operate with liquid volumes from 70 to 1300 liters. The evaporator tower consists of four stages of de-entrainment to provide a good decontamination of process vapors.

The all-titanium acid fractionator has a remotable tube bundle similar to the one in the waste evaporator. The two-section packed tower includes a de-entraining sieve plate and an integral reflux condenser, and will separate liquid feed with 0.8M nitric acid into 0.01M overheads and 10M bottoms.

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CONTENTS4.0 MELT FORMATION FROM HIGHLY RADIOACTIVE WASTE

(by J. E. Mendel)

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4.0 MELT FORMATION FROM HIGHLY RADIOACTIVE WASTE

(by J. E. Mendel)

4.1 HISTORY

The handling and control of highly radioactive waste has been the subject of an enormous amount of study in the short 25 year history of the atomic energy industry. As the studies became more sophisticated, safety considerations dictated a turning away from the initial liquid storage to calcine powder and finally to monolithic ceramic and glass forms. Glass and pottery form the most lasting man-made artifacts. Known examples have survived thousands of years relatively untouched. Most efforts are now aimed at incorporating radioactive waste into solids with similar or, hopefully, better survival characteristics.

The study of incorporating radioactive waste into glassy, or rocklike, substances has been going on world-wide for some 13 years. Results of these studies are well documented in a series of symposia sponsored by the U.S. Atomic Energy Commission and the International Atomic Energy Authority, an organization affiliated with the United Nations.⁽¹⁻⁷⁾ A recent (1968) assessment of waste solidification in the United States has also been made.⁽⁸⁾

Because of the large scale of the waste solidification efforts, many approaches were tested. Earliest approaches involved absorption on natural clays and zeolites which were subsequently dried, but not melted, because of the very high melting points. Capacity was quite low, necessitating a preliminary separation of long-lived fission products.^(9,10) The first studies of incorporating waste into melts used natural glass forming materials, such as nepheline

syenite [(Na,K) AlSi_3O_8] in Canada,⁽¹¹⁾ basalt in Czechoslovakia,⁽¹²⁾ and silica, soda and limestone at the Massachusetts Institute of Technology in the United States.⁽¹³⁾

The high temperatures needed to form satisfactory melts, approximately 1400 °C, caused excessive amounts of fission product cesium and ruthenium to volatilize. In tests at Hanford, another naturally occurring mineral, colemanite (nominally $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$) formed satisfactory melts with radioactive wastes at about 950 °C.⁽¹⁴⁾ In recent years, emphasis has shifted to specially designed melts having properties optimized for use in waste solidification processes. The important melt properties needed are described in Table 4.1.

Although the melts being studied for the incorporation of radioactive waste do not always form true glasses, the potentially glass forming silicate, borate, or phosphate systems are being used to obtain the desirable ceramic characteristics of low leachability, high temperature stability, physical integrity, and good thermal conductivity (when compared to calcines). Sulfate systems have satisfactory radiation stability and have been considered as a waste storage media.⁽¹³⁾

Traditional ceramic technology has had limited applicability in waste solidification for several reasons. A major reason is that the maximum temperatures currently used in waste solidification, approximately 1100 °C, are lower than commonly used in most ceramic technology. The continuous melters used in the United States waste solidification processes require relatively low melt viscosities (less than 200 poise) even at these low temperatures. A second major difference is that portions of the melts from radioactive waste may be held molten or semimolten for months or even years: a circumstance not duplicated in any standard ceramic technology. In addition, significant segregation of the melt during the few hours

TABLE 4.1. *Melt Characteristics Required by Waste Solidification Processes*^(a)

Characteristic	Desirable Range	Reasons for Requirements
Melting Point (Viscosity <200 poise)	750-950 °C	Fission product volatilization from melt, Ru and Cs in particular, may become significant above 950 °C. Processing rate is reduced when melting point is high because of limitation on the transfer of heat into the melt. Transfer by convection currents decreases as melting point increases. Platinum reflectivity lowers the effective heat transfer as melting points increase. Processing temperature must be at least 800 °C to assure decomposition of all nitrate.
Slump Point (Viscosity <10,000 poise)	550-900 °C	Corrosion during filling of storage containers is excessive at temperatures above 900 °C (700 °C in mild steel containers). Maximum centerline temperature in storage containers may be controlled by fission product segregation. The highest possible slump temperature is desirable to reduce ion mobility and possible resulting segregation.
Viscosity	Less than 200 poise at melter operating temperature	Relatively low viscosity required for proper exit flow from melter. Low viscosity permits rapid fining and shorter processing time. Low viscosity facilitates voidless filling of storage containers.
Homogeneity	Nonhomogeneities up to 1 cm diam. are allowable	Uniform distribution of fission products avoids hot spots. Melts aren't stirred, homogeneity must be a natural characteristic of the system. Heavy or more viscous phases can preferentially accumulate in continuous melters and ultimately stop operation.
Fission Product Content	20-30 wt% (16-24 mole %) as oxides	Melts with high capacity for fission product incorporation offer many processing economies. Heat removal becomes limiting at higher fission product concentrations.
Corrosivity in Continuous Melter	Less than 0.002 in./yr at 1100 °C	For efficient processing, melter must operate approximately 100 °C above nominal melting point of melt. Expense of platinum melter makes long life essential.
Corrosivity in Storage Containers	Less than 0.02 in./day at 900 °C Nil at 450 °C	Container temperature must equal melt slump point during filling which may require 2 to 3 days. Fission product decay heat may maintain melt:container wall interface at temperatures up to approximately 450 °C for months to years.

a. *Melt characteristics listed are for processes using a continuous melter, as do both of the melt-forming WSEP processes.*

holdup in the continuous melter cannot be tolerated. Another distinction is the extremely complex composition of radioactive waste. Over 15 elements appear in significant concentrations, whereas most technical ceramics contain perhaps 4 to 5. It is understandable then that, for the present at least, design of melt compositions for the incorporation of radioactive wastes is relatively empirical.

The melt systems being used in the United States generally are of the phosphate type; the melt systems in Europe are generally borosilicate, supplemented with phosphate in some cases.

4.2 THE PHOSPHATE SYSTEM

Of the three major glass formers (phosphate, borate, and silicate), phosphate is least used in commercial ceramic materials. However, for waste solidification the phosphate system has several highly desirable characteristics:

- Phosphate is easily added remotely as H_3PO_4 to highly radioactive aqueous waste solutions.
- Phosphate precipitates formed in feed solution are hydrous, noncaking and "friendly," unless highly concentrated.
- Phosphate systems form melts at lower temperatures than silicate or borosilicate systems.
- The phosphate system is very versatile. Most cations are readily incorporated into homogeneous phosphate melts.
- Phosphate systems can be devised to accommodate over 10 wt% sulfate in a fairly stable homogeneous product. Nonhomogeneous melts with a sulfate-rich layer floating on the parent melt are formed in the borate and borosilicate systems.

4.2.1 Relation of Total Metal Equivalents and Phosphorus Content

The study of the structure of phosphate glasses is complicated. However, abundant evidence is available to indicate that phosphate melts contain anionic groups consisting primarily of chains with the general formula $(P_nO_{3n+1})^{(-n+2)}$, which are analogous to the silicate ions $(Si_nO_{3n+1})^{(-2n+2)}$. The chains are not permanent entities, but are constantly breaking and reforming at a rate that depends on the temperature.⁽¹⁷⁾ As temperature decreases, the structure freezes in place to form glasses or rearranges to more stable crystalline configurations. Time-averaged structures (see Table 4.2) form a convenient basis for understanding the effect that the ratio of metal ion equivalents to phosphorus moles (M/P ratio) has on melt and solid characteristics.

The M/P ratio, as shown in the third column of Table 4.2, is the method adopted in the WSEP program by Battelle-Northwest for expressing the relationship of metal ion equivalents to phosphorus in a given solution or product. In this relationship, M is the total metal ion equivalents present, and is obtained by multiplying the total moles of each metallic element by its assumed valence in the system. It is arbitrarily assumed that molybdenum and silicon exist as the anions MoO_4^{-2} and SiO_3^{-2} . Their equivalent value is therefore subtracted from the total metal ion equivalents. The value for P is the total molarity of phosphorus present. The M/P ratio is analogous to the M_2O/P_2O_5 ratio commonly used in mineralogy literature.

Melts with M/P ratios ranging from 0.95 to about 3 can be used for waste solidification. Because of differing process requirements of the two WSEP processes which utilize phosphate melts, (discussed in Section 4.2.3) the phosphate

TABLE 4.2. Relation of Total Metal Equivalents and Phosphorus Content

Chain Length(a)	Representative Structure	M/P Ratio	Melt Characteristics	Characteristics of Frozen Product
n = 1	$\begin{array}{c} \text{M} \\ \\ \text{O} \\ \\ \text{M}-\text{O}-\text{P}-\text{O}-\text{M} \\ \\ \text{O} \\ \text{Orthophosphate} \end{array}$	3	Low viscosity; sharp freezing point; relatively high freezing point.	Microcrystalline; sharp melting point; relatively high melting point; Relatively rugged, nonbrittle
n = 2	$\begin{array}{c} \text{M} \quad \text{M} \\ \quad \\ \text{O} \quad \text{O} \\ \quad \\ \text{M}-\text{O}-\text{P}-\text{O}-\text{P}-\text{O}-\text{M} \\ \quad \\ \text{O} \quad \text{O} \\ \text{Pyrophosphate} \end{array}$	2	Intermediate viscosity; relatively high freezing point.	Microcrystalline; glassy if quenched rapidly from melt.
n = ∞	$\begin{array}{c} \text{M} \quad \text{M} \quad \text{M} \quad \text{M} \\ \quad \quad \quad \\ \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \\ \quad \quad \quad \\ \text{-P-O-P-O-P-O-P-} \\ \quad \quad \quad \\ \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \end{array} \quad \text{Metaphosphate}$	1	Higher viscosity; viscosity changes slowly with temperature; no sharp freezing point; relatively low freezing point.	True glass; relatively low melting point; brittle.
n = ∞ plus excess P ₂ O ₅	$\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{M}-\text{O}-\text{P}-\text{O}-\text{P}-\text{O}- \\ \quad \\ \text{O} \quad \text{O} \\ \quad \\ \text{-O-P-O-P-O-M} \\ \quad \\ \text{O} \quad \text{O} \end{array} \quad \text{Ultraphosphate}$	<1	Slowly evolves P ₂ O ₅ from melt and tends to approach metaphosphate composition	Hygroscopic

a. Where n is the number of phosphorus atoms in the average molecule $(\text{P}_n\text{O}_{3n+1})^{-(n+2)}$. As n becomes large, many types of cross linking and ring formation can occur which are not indicated in the simple diagrams.

glass process operates at an M/P ratio of 1.0 and the spray solidifier at an M/P ratio between 2.0 and 3.0. If the M/P ratio is much less than 1.0, the melt is unstable because of the presence of free P_2O_5 . The excess P_2O_5 could pose potential corrosion problems in the storage container and makes the product hygroscopic if exposed to air. When the M/P ratio is over 3, free metal oxides are present and the melts become more nonhomogeneous.

4.2.2 Effects of Common Waste Constituents

Although the ratio of metal ions to phosphorus is a most important factor, the properties of the individual metal ions also greatly influence melt and product characteristics. Radioactive wastes may vary considerably in concentration of specific elements, depending upon reprocessing techniques, and, to a smaller extent, upon irradiation history (see Section 2). But in most cases, the same very diverse mixtures of metal ions will be present. The potentially significant elements in radioactive waste are listed in Table 4.3.

Melt chemistry is obviously very complicated in a mixture with as many components as appear in Table 4.3. Nevertheless, it is desirable to understand as much as is possible the effects of individual components upon overall melt behavior. Although some data on these effects have been accumulated during the relatively short time that phosphate waste melts have been studied, a much larger body of data has been accumulated for the silicate system over many years. A resume of these data follows.

Cationic parameters that have been used to classify effects upon melt characteristics include ionic radius, electronegativity, field strength, valence, and coordination number.

TABLE 4.3. *Elements^(a) Present in Radioactive Waste*

	Element	Probable Concentration Range, mole %	Source	Effect upon Phosphate Melt and Product Characteristics
Group A	Si	0.5 - 1.0	Processing	Glass formers; increase viscosity.
	P	0.1 - 0.4	Processing	
	B	0 - 26	Processing ^(b)	
	Te	0.3 - 1.4	Fission Product	
Group B	Al	0 - 0.1	Processing	Network dwellers; increase viscosity and durability.
	Zr	3.5 - 14.0	Fission Product	
Group C	Fe	4.0 - 60	Processing	Network dwellers with relatively easy change in coordination number; tend to decrease viscosity.
	Cr	0.7 - 1.5	Processing	
	Ni	0.3 - 0.7	Processing	
	U	0.6 - 1.0	Processing	
	Mo	3.0 - 12	Fission Product	
	Tc	0.7 - 3.0	Processing	
Group D	Cd	0.04 - 0.25	Processing ^(b)	Network modifiers; in- crease durability and melting point; tend to decrease viscosity.
	Sr	1.8 - 7.2	Fission Product	
	Ba	0.8 - 3.3	Fission Product	
Group E	Na	9.0 - 55	Processing	Loosely bound in net- work; reduce viscosity, melting point, and durability.
	Cs	1.8 - 7.5	Fission Product	
	Rb	0.3 - 1.5	Fission Product	
	Ag	0.04 - 0.15	Fission Product	
Group F	Y	0.4 - 1.8	Fission Product	Enter into network struc- ture with difficulty, tend to form separate phase.
	La	0.7 - 3.1	Fission Product	
	Ce	1.4 - 5.5	Fission Product	
	Pr	0.7 - 2.8	Fission Product	
	Nd	2.4 - 9.4	Fission Product	
	Pm	0.002- 0.008	Fission Product	
	Sm	0.5 - 2.1	Fission Product	
	Eu	0.008- 0.03	Fission Product	
Group G	Gd	0.002- 0.008	Fission Product	Enter into network struc- ture with difficulty; tend to form separate phase.
	Ru	1.7 - 7.6	Fission Product	
	Rh	0.4 - 1.3	Fission Product	
	Pd	0.9 - 4.0	Fission Product	
Group H	S	0 - 30	Processing	Volatile, require special handling when present.
	F	0 - 0.07	Processing	
	Hg	0 - 0.07	Processing	

a. Actinide fission products are not included.

b. Could become major waste component if used as a neutron poison during reprocessing.

Glass forming in oxide systems is enhanced by small ionic radius, high valence, and low coordination number. In general terms, nonglassforming cations can be either network-dwellers (may participate in the glass lattice construction, but their oxides cannot form single-system glasses by themselves), network-modifiers (tend to compete with glass formers for oxygen), or be not tightly bound in the lattice (their ions migrate through the interstices of the lattice).⁽¹⁸⁾

For ease of discussion the cations which, either by theory or actual observation, exhibit similar melt behavior are arranged by groups in Table 4.3. The groups, arbitrarily numbered A through H, will be discussed in the following sections.

Group A: Si, P, B, and Te. These elements are normally present in very low concentrations in radioactive wastes. The silicon in the waste is from bonding alloys used in fabrication of the fuel elements; any phosphate present results from the degradation of the organic extractant, tri-n-butyl phosphate, used in reprocessing. Tellurium is a fission product. Although not present in current radioactive wastes, boron may appear in future wastes if it is used as a neutron poison during reprocessing. Since all four elements are glass formers, their presence is generally welcome in the melt. Any adverse process implications are in behavior of the feed solutions. At the high acid concentrations (4 to 8M) usually present, silicon is present as solid silicic acid, which contributes to the overall solids content of the waste and can act as a foaming agent in some circumstances. Phosphate can be present in several forms, residual tri-n-butyl phosphate, plus degradation products di- and mono-n-butyl phosphate and ortho phosphoric acid. Di-n-butyl phosphate is an active foaming agent and can cause severe foaming problems during concentration of the aqueous waste.⁽¹⁹⁾

The effect of tellurium in radioactive waste solutions has not been studied. Tellurium dioxide by itself does not form glass. However, in binary compounds glasses are formed with a large number of elements. Ternary systems in which tellurium is the glass former have been used for optical glasses.^(20,21) In the WSEP program, sulfate has been used as a stand-in for tellurium in order to obtain somewhat similar aqueous behavior, recognizing that there would be no parallel in melt behavior.

If boron is used as a neutron poison during reprocessing, it may appear in the wastes at concentrations of about 0.1 to 0.4M in 378 liters/tonne waste, or 0.05 to 0.2 that of the phosphate normally required as fluxing agent. Boron is more compatible with phosphate melts than is silicon.⁽²²⁾ Experience in this laboratory has shown that in formulations with an M/P ratio above 2.0, boron can be substituted on a mole for mole basis for up to 20% of the phosphate without causing a marked change in melt properties.

Group B: Al and Zr. Aluminum and zirconium are network dwellers that tend to increase both the viscosity of melts and the chemical durability of solidified products.

Aluminum phosphate has been of interest to glass theoreticians because AlPO_4 is electronically similar to SiSiO_4 and might be expected to exhibit the same desirable technological properties. Such is not the case. Aluminum phosphate melts at about 2000 °C to form a very fluid melt in contrast to the high viscosity of silica melts. Fused AlPO_4 is evidently a true salt without any glassy character. Although not contributing as a glass former, aluminum in concentrations of up to 10 mole% can be easily accommodated in phosphate melts of

radioactive waste. These concentrations are well above the nominal concentrations for power reactor wastes given in Table 4.3. In WSEP demonstrations, aluminum concentrations above 10 mole% have been encountered on several occasions because of the high concentrations of aluminum in Hanford Purex feedstock. Feed adjustments, which are described in Section 4.2.3, are sometimes required to counteract the tendency for the higher concentrations of aluminum to raise the melting point and viscosity, particularly at M/P ratios above 2.0. At an M/P ratio of 1.0, aluminum behaves much like iron, and laboratory tests indicated that waste solutions containing 60 mole% aluminum could be processed without changing the standard chemical flowsheet used in the phosphate glass process.

Zirconium is one of the fission products with the highest yield. Consequently, zirconium is an important constituent of radioactive waste phosphate melts. Studies of the specific effect of zirconium in waste melts have not been made, but melts from wastes containing up to 14 mole% zirconium have been prepared satisfactorily. Zirconium phosphate is quite insoluble and forms a hydrous precipitate in the feed solutions. The precipitate does not cake and is not known to cause any processing problems.

Group C: Fe, Cr, Ni, U, Mo, Tc, and Cd. This is a large and diverse grouping of cations which generally appear quite amenable in phosphate melts. In most cases, variable valences and coordination numbers are possible and not much is known about the states of these individual cations in radioactive waste melts.

The most prevalent cation of the group, iron, is probably almost totally Fe^{+3} in the melts. Recent studies on the spectra

of iron in alkaline earth phosphate glasses indicate the dominant coordination number is six.⁽²³⁾ Iron phosphate glasses containing at least 38 mole% Fe_2O_3 can be prepared.⁽²⁴⁾ Iron has a homogenizing effect for the rare earths in phosphate melts. If not initially present in large enough quantities, iron will be added to wastes from high exposure fuel to take advantage of this effect (see Section 4.2.3).

Chromium and nickel are present in radioactive waste only from corrosion of the stainless steel processing vessels. The concentrations should always be quite low. No melt effects attributable to either chromium or nickel have been observed.

Uranium is present in radioactive waste as a waste loss from reprocessing of spent uranium fuels. The concentration of uranium in radioactive waste is normally quite low because of the very efficient solvent extraction procedures currently used in reprocessing. Off-standard operation could produce concentrations well above the 1.0 mole% indicated in Table 4.3. However, Wirkus and Wilder have prepared uranium phosphate glasses containing 40 wt% U.⁽²⁵⁾

Molybdenum is compatible with phosphate in almost all ratios.⁽²⁶⁾ Molybdenum phosphate melts generally have low melting points, in the range of 900 to 950 °C. It may be concluded that high concentrations of molybdenum can be tolerated in phosphate melts containing radioactive waste. Molybdenum is a major constituent of the solids found in radioactive waste solutions. The precipitate contains molybdenum, zirconium and phosphate in an undetermined stoichiometry. Upon prolonged boiling of the waste solutions, the precipitate becomes less hydrous and more dense. The precipitate has not been observed to cause process problems. It does not

cake, but it does tend to form thin gummy deposits on surfaces. The solubility of the precipitate varies inversely with acidity.

No experience with technetium in phosphate melts has been recorded. The possibility exists that significant quantities of technetium may volatilize since it is known that Tc_2O_7 begins subliming at about 1000 °C. Molybdenum has been used as a chemical stand-in for technetium in the WSEP runs. (The trace amounts of technetium in the Purex feedstock produce such low concentrations in the WSEP feed solutions that analyses of the process condensate for technetium have been attempted in only one instance. In a pot calcination run the fraction of technetium found in the pot condensate was 3.4 times greater than the fraction of nonvolatiles entrained from the pot.) Since both molybdenum and manganese (another element having chemical similarities to technetium) have been shown to be compatible with phosphate melts, it can be assumed that technetium has no adverse effect upon melt properties. Manganese has been found to produce an undesirable precipitate in the highly concentrated aqueous solution in the phosphate glass denitrator-evaporator. By analogy, technetium may also.

No information is available on the effect of cadmium in phosphate melts. Zinc, the next lighter element in the same periodic group, is very compatible in phosphate melts. Zinc tends to lower softening temperatures and increase devitrifying tendencies, and cadmium probably behaves similarly. At present, only fission product cadmium is present in radioactive wastes, and the concentration is inconsequential. Cadmium may become a more important constituent of wastes if it is used as a neutron poison during reprocessing. In that event, the effect of cadmium in phosphate melts will have to be determined experimentally.

Group D: Sr and Ba. Alkaline earth elements, in particular calcium, are constituents of almost all technical glasses. They are used to lower melt viscosity without having the adverse effect on product durability of alkali metals. Barium is often substituted for calcium in compositions where a lower softening point is desired, such as enamels.

The presence of strontium and barium in waste phosphate melts is expected to enhance durability, but no specific data are available.

Because the solubility of strontium and barium nitrate is very dependent upon total nitrate concentration, it is possible for these fission products, particularly barium, to precipitate in highly acid, highly concentrated aqueous solutions. The heavy crystalline precipitate is not easily suspended or moved, but is easily dissolved in more dilute solutions.

Group E: Na, Cs, Rb, and Ag. Even though most radioactive waste solutions contain considerable amounts of nonradioactive sodium, additional amounts are usually added in the preparation of phosphate melts. Sodium (and lithium) is added to obtain less viscous melts and to reduce the pour points to 950 °C or less. (An equimolar mixture of sodium and lithium has been found more effective in some instances.) These melt qualities are so necessary that they outweigh an undesirable effect from sodium or lithium: reduced durability in the product. The other major effect of sodium or lithium is to cause an increase in the coefficient of thermal expansion.

All of the alkali metals tend to volatilize at elevated temperatures. The volatilization of cesium from phosphate melts becomes significant at temperatures above 1000 °C.⁽²⁷⁾

Rubidium, the other fission product alkali metal, probably behaves similarly, but data are not available. Since the concentration of rubidium is lower than that of cesium by a factor of six, and, since the radioactive isotope, Rb-96, has a short half-life, the behavior of rubidium is of much less concern than that of cesium.

The concentration of silver in radioactive wastes is very low. Consequently, fission product silver is not expected to have an effect on the properties of waste phosphate melts. W. A. Weyl et al. have prepared phosphate glasses containing up to 15 wt% Ag_2O to study their use as radiation dosimeters.⁽²⁸⁾

Group F: Y, La, and the Rare Earths. In recent years, many silicate glasses containing as much as 50 wt% (13 mole%) rare earth oxide have been made which are chemically durable and have other desirable properties.⁽²⁹⁾ Nevertheless, the rare earths have proven particularly difficult to incorporate into radioactive waste melts of the phosphate type.

The rare earths tend to settle to the bottom of waste melts. This tendency has been described by English workers⁽³⁰⁾ and was observed during development of phosphate-based flow-sheets for PW-4m waste, which contains about 20 mole% rare earths, in the WSEP program. The rare earths were miscible in melts with an M/P ratio of 1 but not in melts with M/P ratios above about 2. In the latter case, the behavior of equivalent molar amounts of the trivalent cations (aluminum, iron, and rare earths) were compared in phosphate melts. In comparison with melt compositions that were homogeneous when containing aluminum or iron as the only trivalent cations, considerable amounts of the rare earths separated as a crystalline deposit in the bottom of the melts. It is probable that both the relatively high atomic weight and large ionic radius of the rare

earths contribute to tendencies toward immiscibility. Addition of iron so that there is about four times as much iron as rare earths on a mole basis homogenizes the rare earths in phosphate melts at higher M/P ratios (see Section 4.2.3).

Group G: Ru, Rh, and Pd. The noble metals are well known in ceramic technology as mineralizers which act as nucleating agents for devitrification. Their presence favors crystallinity rather than glassiness.⁽³¹⁾ However, simulated solidified waste product from the phosphate glass process containing full flowsheet concentration of ruthenium (1.3 wt%) has been prepared in the glassy state in the laboratory.

Of the three fission product noble metals, ruthenium is by far of the most interest due to its volatility. At the present state of waste solidification technology, all effort has been devoted to methods of suppressing volatilization in order to incorporate ruthenium into the melt. Very little information is available on the behavior of ruthenium in the melt although volatilization from the melt does not appear to be a problem. All evidence indicates that low temperature ruthenium volatilization (below 500 °C) is dependent upon the presence of an aqueous phase where the volatile oxide, RuO_4 , can be formed by oxidation. Ruthenium volatilization from an oxide melt does not become appreciable until the temperature is at least 1000 °C. Barton has reported ruthenium segregation at the bottom of phosphate melts.⁽³²⁾

No information is available on the behavior of rhodium and palladium in phosphate waste melts. Because of cost considerations, chemical substitutes have been used for the noble metals in studies in the WSEP program. Either manganese or iron has been used in substitution for up to

90% of the ruthenium (10% of the nominal ruthenium concentration has been added as inert $\text{Ru}(\text{NO}_3)_3$; cobalt has been substituted for 100% of the rhodium; and nickel for 100% of the palladium.

The noble metal fission products have been found to migrate very gradually into the walls of platinum vessels that are used to contain molten phosphate melts. No weakening of the vessels results.⁽³³⁾

Group H: SO_4 , F, and Hg. These potentially volatile waste components are all introduced during the fuel processing operation. Therefore, their concentration, and even presence, is subject to control.

Sulfate is a major constituent of the waste from all three fuel processing plants (1 private, 2 government) presently operating in the United States. The sulfate in the waste is derived from a ferrous sulfamate and sulfamic acid mixture used as reducing agents in the process. Other reducing agents which do not add salts to the waste can be used, such as uranium (IV), which is used extensively in Europe.

It is expected that sulfate will ultimately be eliminated from all radioactive wastes, but since present wastes do contain sulfate, considerable effort has been spent on the problem of handling sulfate containing wastes. One of the three "standard" WSEP waste compositions, PW-2, contains 0.87M sulfate in aqueous waste at 378 liters/tonne of fuel.

Stability of sulfate compounds is enhanced if the cation has a large radius and a low charge. Kellogg⁽³⁴⁾ and Stern and Weise⁽³⁵⁾ have prepared recent summaries of the high temperature properties of sulfates. Most alkali metal and

alkaline earth sulfates exhibit good thermal stability up to about 950 °C (see Figure 4.1). Sulfate is retained in the product from the pot calcination process by assuring, by addition if necessary, that the feed contains sufficient alkali metal and/or alkaline earth ions to accommodate all of the sulfate present.

When phosphate melts are prepared from sulfate-containing wastes, the situation becomes more complicated. Phosphate forms stronger bonds and tends to displace sulfate from melts, and this tendency increases with a decrease in M/P ratio. At an M/P ratio of 1.0, sulfate is completely volatilized from a phosphate melt, even a melt with high alkali. This volatilization results in another waste stream of intermediate radioactivity which must undergo further treatment before complete fixation is achieved. At higher M/P ratios, the rate of sulfate volatilization from phosphate melts decreases. With: (1) an M/P ratio greater than 2.25; (2) the addition of considerable alkali metal and alkaline earth ions; and (3) maximum melt temperatures of 875 °C, a flowsheet which retains over 95% of the sulfate per pass has been demonstrated for the spray solidifier process (for details, see Section 4.2.3). By recycling the small amount of volatilized sulfate back to the feed solution, 100% sulfate retention can be achieved.

Phosphate melts containing sulfate are about 10 times as leachable as those which do not. Their stability for long term storage above about 550 °C is problematical at this time.

As would be expected, sulfate precipitates in the feed solutions can cause solution handling problems, and indeed

FIGURE 4.1 Decomposition Pressure of Sulfates

have caused problems in the WSEP. Because they are heavy and crystalline, the sulfate precipitates settle rapidly and tend to cake. Aside from barium and strontium sulfate, large amounts of mixed sodium rare earth sulfates may precipitate. Precipitation of the latter sulfate can be decreased by dilution of the feed to sulfate concentrations less than about 0.5M, but this is usually undesirable. The caking tendencies of the sulfate precipitates are greatly diminished after phosphoric acid is added to the feed solution.

An alternative technique for handling wastes containing large amounts of sulfate is preparation of melts in which sulfate is the only anion. This technique is discussed in Section 4.3.1.

Minor amounts of fluoride can appear in waste solutions. Fluoride is used in chemical decladding of Zircalloy-clad fuel elements and as a complexant in some ion exchange processes. Corrosive hydrogen fluoride will tend to volatilize from the acidic waste solution during evaporation and calcination unless special precautions are taken. Workers at NRTS have processed wastes containing up to 3.2M fluoride in a fluidized bed calciner. When calcium was added to maintain a Ca/F mole ratio of at least 0.5, fluoride volatility was restricted to less than 2% at the 400 °C processing temperature.⁽³⁵⁾

The use of calcium to stabilize fluoride at calcination temperatures of 400 °C appears promising. No studies of fluoride retention in waste melts at fusion temperatures (950 to 1000 °C) have been made. Phosphate melts containing at least 35 mole% fluoride are described in the literature.⁽³⁷⁾ In the standard silicate glass technology, substantial amounts of fluoride (6 mole%) are often added to enamel formulations.⁽³⁸⁾

The effect of fluoride is similar to that of an alkali metal: i.e., product durability and melting point are generally reduced.

Small amounts of mercury will be present in the waste if mercury is added to reduce radioiodine evolution during processing. Mercury is by far the most volatile of the potential waste constituents. No method is available to stabilize mercury at temperatures greater than 400 °C. To prevent buildup of troublesome deposits of mercury, or its oxides, and potential plugging problems in the solidification process off-gas lines, mercury should be removed prior to waste solidification. A chemical displacement on metal turnings removal procedure has been developed at ORNL.⁽³⁹⁾

4.2.3 Techniques and Requirements for Preparing Phosphate Melts from Wastes

The two WSEP melt processes, the spray solidification process (discussed in Section 6) and the phosphate glass process (discussed in Section 7), are quite dissimilar. Entirely different considerations are used in selecting the chemical additives, which when added to a waste solution in the proper amounts will make a feed solution that will process properly via the given process. Of course, the additives for each process will also vary depending upon composition of the waste. Therefore, each process uses a different chemical flowsheet for processing each of the three major waste compositions which are currently being studied in the WSEP. (The three waste compositions are defined in Section 2, and the chemical flowsheets for the spray and phosphate glass solidification processes are shown in Table 4.4.)

The flowsheets for the three specific waste compositions were developed empirically based on the results obtained in the laboratory with a large number of melts prepared from several

TABLE 4.4. Phosphate Melt Compositions Used in the WSEP Demonstrations

Initial Waste Solution(a)	Spray Solidification		Phosphate Glass Solidification	
	Additives(b)	Product Characteristics	Additives	Product Characteristics
PW-1	0.5M NaOH 0.5M LiOH 1.74M H ₃ PO ₄ (M/P = 2.75)	18 wt% (14 mole %) F.P.'s 48 wt% (39 mole %) waste 52 wt% (61 mole %) additives Density = 2.8 g/cm ³ Microcrystalline M.P. = 925 °C	2.45 M NaOH 6.23 M H ₃ PO ₄ (M/P = 1.0)	8 wt% (6 mole %) F.P.'s 21 wt% (17 mole %) waste 79 wt% (83 mole %) additives Density = 2.7 g/cm ³ Glass, devitrifies at 550 °C M.P. approx 825 °C
PW-2	1.17M LiOH 0.6M Ca(OH) ₂ 0.25M Al(NO ₃) ₃ 1.61M H ₃ PO ₄ plus 1.27M NaPO ₃ to melter (M/P = 2.7)	10 wt% (6 mole %) F.P.'s 38 wt% (34 mole %) waste 62 wt% (66 mole %) additives Density = 2.8 g/cm ³ Microcrystalline M.P. = 750 °C	3.36 M H ₃ PO ₄ (M/P = 1.0)	14 wt% (13 mole %) F.P.'s 35 wt% (34 mole %) waste(c) 65 wt% (66 mole %) additives Density = 2.7 g/cm ³ Glass, devitrifies at 550 °C M.P. approx 825 °C
PW-4m	0.9M Fe(NO ₃) ₃ 0.75M LiOH 0.75M NaOH 2.85M H ₃ PO ₄ (M/P = 2.25)	25 wt% (20 mole %) F.P.'s 30 wt% (28 mole %) waste 70 wt% (72 mole %) additives Density = 2.8 g/cm ³ Microcrystalline M.P. = 950 °C	0.5M Fe(NO ₃) ₃ 1.5M NaOH 5.7M H ₃ PO ₄ (M/P = 1.0)	18 wt% (13 mole %) F.P.'s 21 wt% (19 mole %) waste 79 wt% (81 mole %) additives Density = 2.7 g/cm ³ Glass, devitrifies at 550 °C M.P. approx 850 °C

a. Compositions are given in Tables 2.3 and 2.4.

b. Expressed as moles per liter of waste at 378 liters/tonne of fuel.

c. Excluding sulfate, which is driven off during processing.

different waste compositions.⁽⁴⁰⁾ Examples of the types of data that were used are given in Figures 4.2, 4.3, and 4.4. The data in Figures 4.2 and 4.3, taken from Reference 41, were obtained with a simulated Hanford Purex waste composition similar to WSEP PW-2. The drip temperatures shown in Figure 4.2 are the temperatures at which the melts begin to flow from a platinum funnel. The drip temperature measurement is a laboratory technique for determining the melt temperature required for discharge of the process melter. For this specific waste, the drip point is lowest at M/P ratios of 1.0 and about 2.2. For most wastes, a melting point minimum occurs at an M/P ratio of 1.0. Other melting point minimums, if any, do not necessarily occur at M/P = 2.2, however.

The leachability of the series of products with the highest fission product content is shown in Figure 4.3. The results illustrate two effects which are found in most phosphate melt systems: (1) a high melt temperature increases resistance to leaching; and (2) the microcrystalline products formed at M/P ratios above about 2.2 are more leachable than the more glassy products formed at lower M/P ratios. The isotherms presented in Figure 4.4, taken from Reference 42, were developed from the results obtained with 49 melts in the $\text{PW-1:Na}_2\text{O:P}_2\text{O}_5$ system. Comparison with the results in Figure 4.2 illustrates how melting behavior varies with waste composition. It has been found that any substantial change in waste composition (about $\pm 10\%$ in a major component) requires revision of additive concentrations. At the current stage in the development of melt technology, the effect of any such revision must be checked by laboratory testing. However, progress is being made toward defining flowsheet criteria that are generally applicable to wastes of varying compositions and which may reduce the amount of such checking that is required.

FIGURE 4.2. Drip Temperatures of Phosphate Melts

FIGURE 4.3. Leachability of Phosphate Melt Products

FIGURE 4.4. PW-1:Na₂O:P₂O₅ Calcine
Melting Point Isotherms

Phosphate Glass Solidification Process

Feed preparation for the phosphate glass process consists primarily of adding sufficient phosphoric acid, as 70 to 85% H_3PO_4 , to the waste solution to make a feed solution in which the M/P ratio is 1.0. As will be discussed shortly, addition of some cations may also be required. Sufficient phosphate ion is added to convert all cations present to metaphosphates, and as shown in Table 4.2, this produces a glassy product after dehydration and denitration.

In the phosphate glass process, the feed solution is concentrated by a factor of about 4 in a denitrator-evaporator and then transferred as a liquid directly to a platinum melter where final evaporation and melt formation is accomplished. The melt is discharged into a receiving vessel where the product is collected as a dark-green, almost black, glass.

Since the phosphate glass process is nearly an all-liquid phase process, viscosity considerations become of paramount importance. The viscosity in the denitrator-evaporator must be below 5 poise (at a boiling point of approximately 135 °C) to have good flow control in the transfer of concentrated solution to the melter. The viscosity of the melt must be below about 200 poise (at operating temperature of 950 to 1100 °C) to assure proper drainage of a continuous melter.

Viscosity control in the phosphate glass process is achieved by adjusting the ratio of nonbridging sodium ions to multivalent cations in the feed solution. Increasing the ratio decreases viscosity in both the denitrator-evaporator and the melter. Adding sodium to increase the ratio has adverse effects upon product properties, however. Leachability

is increased and the product is further adulterated since a phosphate anion must be added for each additional sodium cation. A reasonable compromise results when the ratio of sodium to multivalent cations is about 0.5, where the multivalent cations term is expressed in metal ion equivalents.

In summary, waste which is fed to the phosphate glass solidification process is prepared as follows:

- (1) Add sodium (as NaNO_3), if required, until the $\text{Na}^+/\text{multivalent } \text{M}^+ = 0.5$. (If the ratio in the initial waste is over 0.5, it does not have to be reduced.)
- (2) Add phosphate (as H_3PO_4) until $\text{M/P} = 1.0$.

This is a very generalized procedure. The optimum flowsheet for a specific waste can be determined experimentally using these guidelines. In some instances, further additives are desirable. For example, addition of iron was found to promote homogeneity in the flowsheet for "clean" waste (WSEP waste designation PW-4m).^{*} The additives used for preparing phosphate glass feed from PW-4m waste and the other two "standard" waste compositions used in WSEP are shown in Table 4.4.

The phosphate glass process readily accommodates all of the cations commonly found in radioactive wastes. (Manganese, which is not normally a constituent of radioactive wastes, has caused precipitation problems in the denitrator-evaporator.) Glasses are formed which contain less than 1 volume% crystallites. Phosphate glass products devitrify rapidly when held at 550 °C or higher.

^{*} PW-4m is comprised of waste number 4 in Table 2.4 with fission products from fuel irradiated to 45,000 MWd/tonne at 30 MW/tonne in Table 2.3.

Sulfate, if present, is completely volatilized from the melter during phosphate glass processing.

Spray Solidification Process

In the spray solidification process, the waste solution is dried and almost completely denitrated (up to 99.8%) in a spray calciner. The fine calcine powder falls from the calciner into a directly coupled platinum melter where denitration is completed and melting occurs. The melt is discharged into a receiving vessel where the product is collected as a microcrystalline solid.

The walls of the spray calciner are heated to about 700 °C. Therefore, the "stickpoint" of the calcine must be above this temperature to prevent excessive deposition on the walls of the calciner. The "stickpoint" is defined as the temperature at which globs of calcine first begin to adhere to a stainless steel rod imbedded in calcine powder.

The calcine must have a "stickpoint" above approximately 700 °C to prevent fouling the calciner walls, yet it must fuse to a pourable melt at about 950 °C or lower for proper discharging of the continuous melter to take place. These requirements make microcrystalline products with their relatively sharp melting points favored for the spray solidification process. Glassy products with indistinct melting points and gradual changes in viscosity are somewhat plastic and tend to agglomerate at calcination temperatures. The relationship is illustrated by the typical viscosity curves in Figure 4.5. Experience has shown that the M/P ratio in feed solutions to a spray solidifier must be maintained above 2.0, or out of the normal glass-forming region as shown in Table 4.2.

FIGURE 4.5. Comparison of Viscosities

The above criteria and the criteria listed in Table 4.1 were used to devise additive formulations for processing PW-1, PW-2, and PW-4m wastes for the WSEP program. The formulations are shown in Table 4.4.

As a result of chemical melt-making flowsheet development for the three "standard" waste compositions used in WSEP, a formula for converting a waste which does not contain sulfate to a phosphate melt with the spray solidification process has been derived. The formula consists of a set of three empirical expressions. When each expression is satisfied a spray solidifier feed solution may be prepared from any waste composition with additions of only iron, sodium, and phosphate ions. The expressions are:

$$\text{Fe} > 2.0 \text{ (F.P. + Al)}$$

$$\begin{aligned} \text{Na}^* &> 0.33 < 0.67 \text{ (F.P. + Al + Fe)} \\ &(\text{if Na} > 0.67 \text{ [F.P. + Al + Fe] add Fe}) \end{aligned}$$

$$\text{P} > 0.36 < 0.45 \text{ (F.P. + Al + Fe + Na)}$$

where F.P. is Fission Products.

The metal concentrations are expressed in gram equivalents/liter of waste (gram equivalents are defined as gram moles multiplied by metal ion valence). In order to avoid complications due to dilution from the additives, all concentrations are calculated for the volume of waste initially present. Note that it is

* A mixture of equal concentrations of sodium and lithium yields melts of slightly lower melting point (approximately 25 °C) than either sodium or lithium alone. Therefore, an approximately 50:50 mixture of sodium and lithium is used as the alkali metal additive in WSEP.

necessary to know the concentration of only four elements in the waste: sodium, iron, aluminum, and fission products. (In a commercial plant which is processing waste with the complete fission product spectrum, the fission product concentration can be related to the analysis of a single isotope, for instance Cs-137.)

As described in Section 4.2.2, large amounts of aluminum in the waste tend to raise the fusion temperature of spray solidifier-type melts produced from that waste. Aluminum concentrations as low as 10 mole% produce an increase in melting point of approximately 25 °C. Large amounts of rare earths (20 mole%) tend to create nonhomogeneities in the melt. The presence of sufficient iron in the melt, as provided for by the formula above, will erase these tendencies. Other multivalent cations, for instance zinc and lead, are even more efficient for this purpose but are potentially unsafe for use with platinum melters.

The flowsheet used to process sulfate-containing PW-2 waste is specially modified to retain sulfate. Two principal modifications are used: (1) alkali metal and alkaline earth cations are added to stabilize sulfate in the melt; and (2) alkali metal cations are added to reduce the melting point to permit reducing the operating temperature of the melter by about 200 °C, to 875 °C. (This is approaching the practical minimum melter operating temperature. A temperature of at least 800 °C is considered necessary to assure complete denitration.) A small amount of aluminum (0.25M) is added to help raise the calcine "stickpoint". Aluminum also contributes to sulfate retention in the melt.

A low melting point (and melter operating temperature) is made possible by adding a solid flux, NaPO_3 , directly to the melter. Sulfate evolves from the melt even at 850 °C. (See Figure 4.6) However, the rate is sufficiently low to make a recycle flowsheet feasible. In the WSEP runs, less than 5% of the sulfate was volatilized per pass.

Spray Solidifier Process, In-Pot Melting Modification

In the phosphate glass and spray solidification processes, platinum melters are required because the melts corrode other metals at the operating temperatures of 950 to 1200 °C. In-pot melting is an alternative technique which might simplify and reduce the cost of the process, since the costly platinum melter is eliminated.

In-pot melting is practical since many materials, including types 310 and 304L stainless steels, can be used up to about 900 °C. In the in-pot melting modification of the spray solidifier process, the melter is removed from the system, and the calcine is dropped directly into the ultimate storage container, a stainless steel canister. A solid, low melting fluxing agent is metered into the canister along with the calcine. The canister must be held above 800 °C to assure complete denitration, and below about 875 °C to avoid excessive corrosion.

The spray solidifier flowsheet for sulfate-containing waste (PW-2) may be operated by the in-pot melting modification without any change in chemical additives, since the melting temperature is designed to be 850 °C. This operation has been demonstrated in an engineering-scale pilot plant.^(43,44) Operation was very satisfactory as long as good control of

FIGURE 4.6. Sulfate Loss from PW-2 Spray Solidified Melt (Standard Melt Composition in mole% = 16.4 SO_3 , 27.2 P_2O_5 , 2.3 Al_2O_3 , 11.3 CaO , 11.0 Li_2O , 20.8 Na_2O , 4.2 Fe_2O_3 , 6.1 fission product oxides, and 0.7 other waste oxides. Flowsheet details are shown in Table 4.4.)

the flow of NaPO_3 flux was maintained. Foaming, due to sulfate evolution, can occur if the NaPO_3 content is allowed to become excessive. The effect of NaPO_3 concentration on sulfate evolution is shown in Figure 4.7. A threefold increase in NaPO_3 concentration (above the nominal 1.27M) increases the SO_3 evolution rate by only about 50%, yet excursions in NaPO_3 concentration of less than a factor of two caused foaming in the pilot plant, thereby demonstrating that the combination of melt viscosity and container configuration in the system is quite susceptible to foaming problems.

In-pot melting flowsheets, utilizing NaPO_3 as the melt-making flux, have also been devised for sulfate-free (PW-1 and PW-4m) wastes. (See Figure 4.7.) The products are less homogeneous and durable than those produced by the standard spray solidifier flowsheets at higher temperatures. At the temperatures being used for in-pot melting, phosphate melts are no more corrosive to stainless steel than borosilicate melts. At temperatures above about 900 °C, however, stainless steel becomes very unreliable in contact with phosphate melts. Corrosion tests give anomalous results, evidently because of a passivation-depassivation phenomenon.

4.3 OTHER SYSTEMS

The choice of melt systems considered for solidification of radioactive waste is influenced by many factors, such as: (1) the composition of the waste to be solidified; (2) the equipment to be used for solidification; (3) available raw materials; and (4) desired characteristics of the final solid. Hence, sulfate melts have been studied at Hanford where there is a large quantity of sulfate-containing waste; borosilicate melts, which have relatively low corrosivity

FIGURE 4.7. In-pot Melting with Sodium Metaphosphate

at high temperatures, have been studied in Europe where continuous platinum melters are not being used; and basalt melts have been studied in Czechoslovakia where basalt abounds.

Another promising approach is that of incorporating calcined waste in a matrix of glass or metal. The matrix serves both as a stable fixation medium and as a heat conduction medium for removal of the heat from radioactive decay.

4.3.1 Alkali Metal Sulfate Systems

Many of the important advantages of converting radioactive waste to a monolithic solid form are gained by incorporating wastes in alkali metal sulfate melts. The melts are nonhomogeneous mixtures containing insoluble oxides, and thus are not suitable for processing in continuous equipment but can be reasonably formed directly in the ultimate storage container. Formation of sulfate melts after batch calcination has been described by Shefcik⁽⁴⁵⁾ and after spray calcination by Allemann et al.⁽⁴⁴⁾

4.3.2 Silicate and Borate Systems

Through the intensive efforts of workers principally in England and France, melt development for waste solidification in borosilicate matrices is at about the same stage as phosphate melt development has reached in the U.S.^(47,48) Certain general comparisons can be made between the borosilicate and phosphate systems, as shown on Table 4.5. The two systems contrast mostly in the ease of feed solution handling and in the corrosivity of the melts. Solution handling is much simpler in the phosphate system while borosilicate melts can be held in stainless steel at somewhat higher temperatures. The

TABLE 4.5. *Comparison of Borosilicate and Phosphate Systems*

	Type of Melt	
	Borosilicate	Phosphate
<u>Solution Characteristics</u>		
Chemical Adjustment	Limited. Silica and frits are abrasive, require special pumps, suspending agents.	Flexible. All feed adjustments via liquid additions (solid additions can also be made).
Handling	Difficult to handle. Viscous precipitates with acidic borates. Feed adjustment with solid silica or frit cannot be done beforehand, must be done in situ.	Easy to handle. Precipitates are hydrous, flocculant and noncaking. Feed adjustment can be done beforehand, allows readjustment to be made, if required.
<u>Melt Characteristics</u>		
Pour Point	Easy to obtain melts which flow at 1000-1050 °C.	Easy to obtain melts which flow at 900-950 °C.
Homogeneity	Sulfates separate as second phase.	Up to 20 mole % sulfate can be retained homogeneously long enough to complete processing.
Corrosivity	FINGAL process operates at 950 °C in stainless steel.	Must operate below 900 °C in stainless steel.
<u>Product Characteristics</u>		
Leachability, ^(a) g/cm ² -day	10 ⁻⁷ -10 ⁻⁵	10 ⁻⁶ -10 ⁻⁴
Density, g/cm ³	2.6-3.0	2.7-3.1
Thermal Conductivity, W/cm-sec	0.5-0.8	0.4-1.0

a. In water at 25 °C.

solidified products formed from either borosilicate or phosphate melts appear to be very suitable media for the long term storage of highly radioactive waste.

Other combinations of fluxing agents such as borophosphates, silicophosphates, and borosilicophosphates are possible, and have received some attention.^(32,49) However, such additives generally diminish important advantages of the phosphate system in that solution handling is complicated and the melt viscosity and melting point are increased.

4.3.3 Glass or Metal Matrix Systems

Most of the matrix process investigations made so far have used borosilicate glass frit⁽⁵⁰⁾ or the metals, aluminum or tin-lead, as matrices.⁽⁵¹⁾ The glass frit matrix systems are potentially capable of great versatility. Calcines produced by different calcination processes and from widely different waste compositions can be utilized. Some problems in obtaining relatively void-free solidified products have been encountered.

The use of metal matrices is very attractive because increases in the thermal conductivity of the stored waste by factors of 10 to 100 over the current processes are attainable. The major technological problem lies in developing a method for dispersing the calcine homogeneously in the matrix and obtaining satisfactory bonding between calcine and metal.

Demonstration of a matrix process, the details, of which are not completely established at this time, are presently planned to be included in the WSEP program.

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5.0 THE POT SOLIDIFICATION PROCESS

(by J. L. McElroy)

5.1 PROCESS DESCRIPTION

5.1.1 Background

Engineering development work on the pot calcination process was carried out at Oak Ridge National Laboratory.^(1,2,9) This process is a batch operation which involves concentrating waste to a salt cake and then denitrating the cake at high temperatures to produce a porous friable calcine. Extensive nonradioactive studies at ORNL were made with Darex, Purex High Sulfate, and TBP-25 Wastes.⁽²⁾ Additional nonradioactive tests were made by BNW at PNL⁽³⁾ with waste types simulating those from power reactor fuels with moderate burnups. Radioactive bench-scale tests were also carried out by BNW,⁽⁴⁾ and more recently a series of engineering-scale high-level radioactive runs was completed in the WSEP.⁽⁵⁾ All tests have shown favorable results for the process.

Another version of pot solidification with phosphate melts is the Rising Level Glass (RLG) process.⁽⁹⁾ This process is similar to the FINGAL process (which uses a borosilicate melt system)⁽⁶⁾ developed at Harwell, England. ORNL later adapted the process by using an alkali phosphate melt system with the pot calcination equipment.^(9,14,23) The RLG process did not receive as much development effort as the pot calcination process, and is not fully developed. Development of low melting glasses could make this process attractive from both a chemical and processing standpoint. However, severe corrosion observed in some tests indicates a serious lack of knowledge regarding the mechanisms and control of phosphate melts containing sulfate and multivalent metals such as iron and chromium.⁽²³⁾

At modest temperatures (less than about 850 °C), sulfate, with proper feed formulation, can be held in the waste, and processing is possible in stainless steel containers. (To minimize corrosion during RLG processing, the temperature of the stainless steel pot must be limited to 850 °C with existing phosphate feed formulations.) Two nonradioactive RLG runs were made by BNW in WSEP.^(3,17) A run with a special "FTW-65" waste was successful, but a later run with PW-1 waste was not successful due to corrosive failure of the pot.

An attractive feature of both versions of the pot process is that the processing vessel is also the final storage vessel. The process in concept is the simplest of all solidification processes. An additional advantage of the pot calcination process is that it is adaptable to a wide variety of feed compositions with a minimum amount of laboratory flowsheet development. Its disadvantages are that a stainless steel pot is required, the amount of heat which can be incorporated into a pot is limited by the poor thermal conductivity of the calcine, the capacity of a system must be increased by multiple-pot lines, and the solidified waste is quite water soluble and friable.

5.1.2 Pot Solidification Processes

The basic equipment flow diagram for the pot solidification process is shown in Figure 5.1. Feed is continuously fed to the pot at a gradually diminishing rate where it undergoes concentration and calcination, and for the RLG modification is converted into a glass with a low melting point. Additive chemicals may be added either in the feed or proportionally to the pot as a separate feed stream. Vapors from the process

FIGURE 5.1. Pot Solidification Processes

are partially refluxed to keep the off-gas line clean. The refluxed condensate may be collected with the primary condensate stream.

5.1.3 Pot Calcination

In pot calcination, liquid waste is added to a pot that is heated in a multiple-zone heating and cooling furnace (Figure 5.2). The waste is concentrated at a constant volume to the point that scale (salt cake) forms on the walls of the pot. As calcination continues, the scale grows in thickness and reduces the capacity for heat transfer from the pot wall to the boiling sludge, and therefore the feed rate must be reduced proportionately. When the feed rate is reduced to an "unprofitable" rate (about 5 liters/hr), the feed is shut off. At this point, the scale has grown inward from the pot wall and upward from the bottom of the pot to fill the pot, except for a thin cone-shaped liquid-containing void in the upper 2 to 3 feet of the salt cake. Heating is then continued until the liquid is boiled to dryness and all of the waste in the pot has been calcined and has reached the temperature of 850 to 900 °C. The pot, which serves as the final storage vessel, is then cooled in the furnace, removed, sealed, and taken to storage. At ORNL, the pot process was also operated close-coupled to a waste evaporator, condensed vapors from the pot calcine were combined with incoming waste in the waste evaporator and reduced in volume as much as possible before the mixture was pumped to the calciner.

The product from pot calcination (i.e., the solidified waste) is a mixture of oxides (and sulfates, if sulfate is present in the waste) of the metallic constituents in

FIGURE 5.2. Eight Inch Pot Calciner for WSEP

the original liquid waste. The product is a porous, friable calcine with a low thermal conductivity and a relatively high solubility in aqueous solutions.

The basic elements of equipment required for pot calcination⁽⁵⁾ are (1) a multiple-zone furnace for heating and cooling the calcine, (2) a pot for calcining the waste, and (3) an off-gas line from the pot to the first process condenser which can be washed down continually.

A multiple-zoned furnace is required because the heating and cooling needs are different for each vertical portion of the pot at any given time. Solids from the feed and some of the 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. 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 and may be superfluous. Maximum furnace heating requirements are based on pot diameter. For 8- and 12-inch diameter pots, approximately 35 and 70 kilowatts of net heating capacity are needed, respectively, during the period of maximum boilup rates. Cooling is also required in the furnace to remove the heat of radioactive decay from the calcine after all material has been calcined. Zone cooling is required for the same reasons zone heating is needed.

Because the pots serve as the processing vessels, they are exposed to severe corrosion conditions during calcination and must be made of corrosion-resistant material. Corrosion, however, has been negligible in stainless steel pots at 900 °C when the proper balance of chemical equivalents has been

used.^(1,2,9) Pots must have liquid level and temperature measurement devices. Liquid level may be measured with either a standard gas-purged dip tube or with an internal temperature sensor near the top of the pot.

The off-gas line from the calciner must be washed down continuously, if possible, or at least at frequent intervals. If not done, the line would plug with entrained calcine or sludge after the filling of as few as two or three pots. Continuous washing by condensing about 10% of the vapors has been performed successfully in WSEP.⁽⁵⁾ Routing this condensate to the same place as the majority of the condensate has also been demonstrated in WSEP. Washing the neck of the pot near the end of each batch has also been demonstrated in WSEP to keep the neck of the pot clean. Prior to each batch, the addition of 15 to 30 liters of water to the pot via a vent line spray provides additional vent line cleaning while establishing a starting liquid volume in the pot.

5.1.4 Rising Level Glass

The RLG Process involves adding liquid feed containing glass-forming materials to a stainless steel pot held at a maximum temperature of about 850 °C. Three phases are always present in the pot during filling: fluid glass at the bottom, a layer of calcine (sinter), and a concentrated pool of aqueous waste liquor on top of the calcine. Operation involves slowly adding feed at a mass rate (of nonvolatile components) equal to the mass rate of melt formation. This control keeps the liquid and calcine holdup at a minimum and improves process stability. Heat transfer is primarily by radiation from the hot walls of the pot, and thus the area of the surface of the liquid pool is directly

proportional to the processing rate. Additional processing capacity was demonstrated during a demonstration run by BNW by directing the feed to flow as a film down the centerline thermocouple well.⁽³⁾ Equipment requirements are identical to those for pot calcination with the exception that minor modifications of the pot are required for film feeding, and pot thermocouple locations must be staggered vertically to give maximum information on pot operating levels.

Criteria for determining the stable capacity of this process has been established for the FINGAL process⁽⁸⁾ and is dependent on operating temperature and pot cross sectional area. With film feeding, additional area for evaporation of feed prior to forming a melt is made available and consequently permits higher feed rates to be used. Figure 5.3 is an extension of FINGAL data⁽⁸⁾ and presents the estimated capacity parameters of the RLG process as a function of temperature and total heat transfer available.

5.2 PROCESS TECHNOLOGY

5.2.1 Chemistry

For the many waste types which have been demonstrated in pot solidification processes, the major problem has been the retention of volatile components such as sulfate. In addition, other volatile components in radioactive waste (e.g., ruthenium and mercury) present similar problems. How volatilization may be eliminated or reduced significantly in most cases is indicated in the rest of this section.

FIGURE 5.3. Rising Level Glass Capacity Parameters

Sulfate, Sodium and Cesium Volatility and Retention in the Solid

Retention of sulfate is desirable to prevent process equipment corrosion and to yield a nitric acid condensate relatively free of sulfate. Sulfate can be retained almost quantitatively ($>98\%$) in the solid calcine⁽⁹⁾ by adjusting the ratio:

$$\frac{\text{Chem. equiv. (alkali + alkaline earth metals)}}{\text{Chem. equiv. (nonvolatile anions)}} \geq 1.1$$

Nonvolatile anions include SO_4^{-2} , PO_3^{-3} and BO_2^{-} . Chemical additives to meet this ratio are usually calcium or sodium nitrates. The above ratio also holds for phosphate melts if the processing temperature is not excessively greater than the fluid point of the melt.

Since the ratio above includes potentially volatile alkali metal oxides, the following ratio should also be met:

$$\frac{\text{Chem. equiv. alkali metals}}{\text{Chem. equiv. (nonvolatile anions)}} \leq 1$$

The sulfate preferably combines with all of the alkalies and any excess of metals will be alkaline earths which form rather nonvolatile and stable oxides. However, if alkalies do form oxides, only a small amount (less than 1%) should volatilize at 900 °C due to their moderately low vapor pressures at this temperature, unless the solid is subjected to prolonged heating. In the WSEP radioactive pot calcination runs, no distinguishable difference was observed between nonvolatile and cesium entrainment from the pot calciner.⁽⁵⁾

Ruthenium Volatility.

Volatilization of ruthenium during pot solidification of nitrate waste depends upon the initial oxidation state of the ruthenium, and the initial ruthenium chemical compound. Ruthenium is discussed in detail in Section 9. Discussion in this section is restricted to ruthenium behavior immediately after its volatilization from a phosphate melt or calcine.

A study⁽⁶⁾ on the effects of ruthenium behavior after volatilization from a phosphate melt indicates the temperature of the vapor environment affects the distribution of the volatile RuO_4 and nonvolatile RuO_2 species immediately above the vaporizing interface. Thus, at vapor temperatures in excess of approximately 400 °C, $\text{RuO}_4(\text{g})$ rapidly decomposes to $\text{RuO}_2(\text{s})$. At temperatures greater than approximately 800 °C $\text{RuO}_2(\text{s})$ vaporizes to $\text{RuO}_4(\text{g})$ in an oxidizing atmosphere. Similar observations at NRTS⁽¹⁰⁾ with fluid bed waste calcination have been noted. In pot calcination, if the vapor temperature exceeds 400 °C prior to the condenser, the greater portion of the volatilized ruthenium can be expected to deposit as RuO_2 on available surfaces. In the WSEP pot design, deposition within the pot and in the vent line prior to the refluxing portion could cause choking of the line. This is particularly true since RuO_2 deposition also encourages other deposits to form⁽⁶⁾ and also accelerates the further decomposition of RuO_4 .⁽¹¹⁾ Design and process preventative measures to restrict RuO_2 deposition have been provided in WSEP.⁽⁷⁾ In the first series of six WSEP pot calciner demonstrations, deposition between the calciner pot and the condenser inlet was prevented by the reflux provided.⁽⁵⁾

In laboratory scale calcination experiments,⁽¹²⁾ the volatilization of ruthenium was decreased markedly by the

addition of phosphite or hypophosphite ions as phosphorous acid to waste solutions (shown in Figure 5.4). Figure 5.5 is a plot of the evolution of ruthenium from the pot calciner during the WSEP runs. For sulfate-containing wastes (WSEP "standard" PW-2 Composition), 15 to 30% of the ruthenium in the feed to the pot was volatilized, while only 5% was volatilized from waste lower in sulfate (WSEP "Standard" PW-1 composition). However, these differences in volatilization may not be attributable to waste type only, since the PW-1 waste batches were continually boiled prior to feeding the pot while the PW-2 wastes were not.

Multiple startups and shutdowns during a pot calcination run apparently do not adversely affect ruthenium volatilization.⁽⁵⁾

Mercury Volatility and Removal from the Waste

The presence of mercury in waste solutions is likely to create a problem in the high temperature fixation of any waste, because mercury forms no compounds that are stable at temperatures greater than 600 °C. As discussed in Section 2, mercury may originate in the waste during spent fuel element processing where it is sometimes added as a catalyst for dissolution of aluminum bearing fuels and is added to other reprocessing streams for the purpose of complexing fission product iodine. A promising method for handling mercury requires that it be removed from the waste solution before calcination. In laboratory tests, greater than 99% of the mercury has been removed by passing simulated waste solution through beds packed with copper.⁽¹³⁾ However, this method is not feasible with waste in which the acid concentration

FIGURE 5.4. *The Effect of H_3PO_3 on Ruthenium Volatilization from Purex 1WW Waste Solution During Evaporation and Calcination in Pyrex Equipment.*

FIGURE 5.5. Cumulative Ruthenium in the Pot Condensate During WSEP Pot Calcination Demonstrations

is greater than about 0.5M. A column filled with aluminum was successful in removing 98% of the mercury from a concentrated FTW-65 waste (defined in Table 5.1) containing 1.5M free acid.⁽⁹⁾

Entrainment

Entrainment from the pot calciner, when operated on a reasonable basis, is approximately 0.4% of the total feed.⁽⁵⁾

5.2.2 Product Characteristics

Calcine and RLG Products

Three types of waste (Darex, Purex High-Sulfate, and TBP-25) were extensively studied in nonradioactive pot calcination tests at ORNL. These same wastes along with several other Purex waste variations were also tested during design verification tests of WSEP equipment. The solids appear cellular, are generally quite porous, and have bulk densities ranging from 0.5 kg/liter for TBP-25 waste to 1.4 for Purex and Darex wastes. The calcine has a relatively low thermal conductivity of 0.15 to 0.3 Btu/(hr)(ft²)(°F/ft). The products from RLG processing are generally quite similar to products from spray solidification (see Sections 6 and 8 for discussions of the spray solidification process and product characteristics).

Pot Solidification Feed Formulations

For a calcine feed formulation, the only major requirement is that additives are required to prevent sulfate and alkali metal volatilization as described in Section 5.2.1.

TABLE 5.1. Pot Calciner and Rising Level Glass Compositions

Component	WSEP Waste Designation					
	FTW-65	PW-1	PW- 2	PW-4m		
H ⁺	3.0M	3.7	3.93	4.5		
Fe ⁺³	0.11	0.93M	0.445M	0.05		
Cr ⁺³	0.02	0.012	0.024	0.012		
Ni ⁺²	0.01	0.005	0.010	0.008		
Al ⁺³	0.05	0.001	0.001	0.001		
Na ⁺	0.33	0.138	0.930	0.10		
Hg ⁺²	--	<0.001	<0.001	<0.001		
SiO ₃ ⁻²	0.02	0.01	0.01	0.01		
NO ₃ ⁻	3.10	7.5	5.37	6.5		
SO ₄ ⁻²	0.16	--	0.870	--		
PO ₄ ⁻³	--	0.003	0.006	0.003		
U ⁺⁶	--	0.01	0.01	0.01		
F ⁻	--	<0.001	<0.001	<0.001		
Fission Products						
(Cs+Rb) ⁺	0.02	0.043	0.043	0.092		
Sr ⁺²	0.01	0.0155	0.0155	0.0356		
Ba ⁺²	0.01	0.0195	0.0195	0.0410		
(Y+RE) ⁺³	0.05	0.1195	0.1195	0.274		
ZrO ⁺²	0.02	0.065	0.065	0.143		
MoO ₄ ⁻²	0.03	0.065	0.065	0.130		
TcO ₄ ⁻²	--	0.014	0.014	0.031		
Ru	0.03	0.032	0.032	0.0816		
Rh+Pd	--	0.0246	0.0246	0.0558		
Additives For:	Glass	Calcine	Glass	Calcine	Glass	Calcine
PO ₄ ⁻³	1.33	--	2.0	--	2.2	--
SO ₄ ⁻²	--	0.11	--	--	--	0.20
Li ⁺	0.89	--	1.0	--	1.37	--
Na ⁺	1.0	--	0.84	--	1.37	--
Ca ⁺²	--	--	--	0.5	0.2	--
Al ⁺³	0.28	--	--	--	--	--
NaH ₂ PO ₂ ·H ₂ O	--	--	--	--	0.1	--
Melting Point, °C	675	--	850	--	750	--

Typical additives which will assure successful calcination of PW-1, PW-2, and PW-4m wastes are listed in Table 5.1. The sulfate additive listed for PW-4m waste is estimated and has not yet been confirmed experimentally. Other adjustments (such as using phosphate in place of sulfate) may result from laboratory testing.

Personnel at ORNL^(9,14) have studied various glasses (or ceramics) which vary in composition from those in which sodium and iron sulfates are the principal constituents to those containing predominantly sodium or aluminum. Most of these compositions have been computer coded and documented.⁽¹⁵⁾

The main requirements for a good product from melts are:

1. Relatively low melting point (700 to 900 °C).
2. Negligible corrosion to stainless steel at the operating temperatures.
3. Retention of volatile components such as Cs^+ , RuO_4 , and SO_4^{-2} .
4. Good physical characteristics such as low porosity, low solubility and good thermal conductivity.

Table 5.1 lists the pertinent formulations for the WSEP tests. The FTW-65 waste composition shown in Table 5.1 was operated successfully in the WSEP during design verification testing.^(3,16) The PW-1 and PW-2 glass formulations are those once planned for demonstration of the RLG process in WSEP. (Radioactive demonstrations of the RLG process with PW-1 and PW-2 are currently not planned to be run in WSEP.) Additional development of both formulations is required as evidenced by the gross corrosive failure of the processing pot during one of the RLG runs with PW-1 waste in WSEP.⁽¹⁷⁾ Corrosion data pertinent to this run is included in Section 5.2.3. Engineering scale demonstrations have been made on several glass compositions from FTW-65 wastes at ORNL.⁽⁹⁾

Nitrate Retention

Retention of nitrate and water in calcines and glasses is dependent upon the processing temperature and the time at temperature. With suitable conditions, residual nitrate contents of less than 0.1% are attained in pot solidification processes. Figure 5.6 shows residual nitrate content as a function of temperature for some calcines. In tests at ORNL, the residual nitrate content of calcine held at 900 °C was less than 0.1% for holding periods ranging from 2 to 36 hours.⁽⁹⁾

5.2.3 Corrosion and Materials of Construction

Containment pots for pot calcine also serve as processing vessels and are thus exposed to rather severe corrosion conditions during the few days required for calcination. Three hundred series stainless steels, generally 304 L or 310, were selected as the material of construction for the pots. Corrosion of these materials is slightly less than 0.1 in./yr during processing⁽²²⁾ and negligible after processing. Table 5.2 gives corrosion results that are typical of many tests that were made at ORNL. When a proper ratio of sulfate to alkali and alkaline earth metals was maintained, corrosion (as detected by ultrasonics and from test sections) was negligible in all large-scale tests in stainless steel pots at 900 °C conducted by ORNL and PNL.

The Rising Level Glass (RLG) process is based upon the use of glass forming additives which combine with the waste constituents at temperatures of 700 to 900 °C to produce fluid melts. These melts are more corrosive than pot calcines, partly because the increased fluidity permits higher diffusion

FIGURE 5.6. Nitrate Content of Calcined Waste

TABLE 5.2. Summary of Pot Calcine and RLG Corrosion: Small-Scale Tests⁽⁹⁾

Environment	Alloy Tested	Temp, °C	Hours at Temp ^(a)	Corrosion Rate ^(b) in./yr
Air	304L	900	24	0.017
<u>Calcine from Wastes Designated</u>				
TBP-25	304L	900	24	0.06
		900	168	0.02
TBP-25	347	900	24	0.13
		900	168	0.02
1WW + Ca ⁺² and Na ⁺	304L	900	24	0.08; 0.09 ^(c)
1WW + Ca ⁺² and Na ⁺ (after calcination at 1000 °C)	304L	900	123	0.04
FTW-65	Ti	1050	168	Disintegrated
	Ti-0.2% Pd	1050	168	Disintegrated
FTW-65 + Ca ⁺²	304L	1050	168	~0.5 ^(h)
<u>RLG from Wastes Designated^(j)</u>				
TBP-25 (Melt 263)	304L	920	19	0.51
		910	345	0.06
1WW ^(d)	304L	900	24	1.4; 1.7 ^(c,e)
	304L	850	1	Negligible
	Step 1	950	2	16 ^(e)
	Step 2	950	75	0.23 ^(e)
	Step 3	950	78	0.68
	Overall			
FTW-65 (Melt 48; HPO ₃ ⁻²) ^(f)	304L	1050	24	Very severe
FTW-65 (Melt 48; PO ₃ ⁻³) ^(f)	304L	1050	29	3.4
FTW-65 (Melt 2 HPO ₃ ⁻²) ^(f)	304L	1050	24	Disintegrated
FTW-65 (Melt 2 PO ₄ ⁻³) ^(f)	304L	1050	24	Very severe
Darex ^(g)	304L	950	24	4.4
	304L	950	168	2.0
Darex Melt 334	304L	900	24	3.0
	304L	900	168	1.1
Darex Melt 302	304L	1000	24	3.0
	304L	1000	168	Disintegrated
Purex 1 (Melt 478) ⁽ⁱ⁾	304L	≥950	68	Very severe
Air Atmosphere	310	≥950	68	Disintegrated
Air Purge	304L	~850	24	Moderate
	310	~850	24	Moderate
Argon Atmosphere	304L	825-850	72	Moderate
	310	825-850	72	Severe
Argon Atmosphere	304L	825	24	Slight
	310	825	24	Slight

a. Plus approximately 3 hr to evaporate and bring to temperature shown.

b. Overall rates; no allowance made for intergranular or pitting attack.

c. Duplicate exposures.

d. Additives were: Na₂B₄O₇, 0.13M; H₃PO₄, 1.52M; NaOH, 0.98M; Ca(OH)₂, 1.1M
(contained excess anions; not currently recommended).

e. Intergranular attack.

f. Melts 2 and 48 are identical except that in 2, Li⁺ is the additive instead of Na⁺ as in 48. Operating temperatures are ~1000 °C for 48 and ~900 °C for 2; therefore the corrosivity of 2 can be decreased by lowering the temperature 150 °C vs 50 °C for 48. As indicated both melts were tested with all P added as HPO₃⁻² and as PO₄⁻³, respectively.

g. Additives were NaH₂PO₄, 2.0M; H₃PO₄, 0.4M; Al(NO₃)₃, 1.4M; B₂O₃, 1.1M.

h. Outer layers of specimen converted to magnetite; exact extent of attack not determined with accuracy.

i. In these tests specimens were exposed in remelted material from UNOP's Runs 91 and 92. Evaporation and calcination steps were not included. Temperature variation under the air atmosphere may have been ±50 °C.

j. Melt compositions are given in Reference 15.

rates of reactants and reaction products. As shown in Tables 5.2 and 5.3 erratic results were obtained from tests in which 304 L and 310 stainless steel specimens were exposed to RLG type melts. Attack ranged from slight to catastrophic in similar exposures. The corrosion observed in these tests and in large scale engineering tests indicates a serious lack of knowledge regarding the mechanisms and control of corrosion with these phosphate melts containing sulfates and multivalent metals such as iron and chromium. It is believed that stainless steel exhibits a border-line passive-active condition in this system, and occasional activation results in excessive corrosion. A suitable material for containing RLG type melts above approximately 850 °C has not been found.

5.2.4 TBP Decomposition

The presence of significant amounts of organic such as tributyl phosphate (TBP) in the waste can lead to an explosive chemical reaction during the waste fixation step.⁽²¹⁾ Normally, the many steps taken during processing to assure that all organic is removed from the waste should assure an organic-free waste. Any organic that is present, however, can be decomposed prior to waste fixation by digesting the waste. Figure 5.7 shows the decomposition of TBP, and its degradation products dibutyl phosphate and monobutyl phosphate, versus time in a boiling nitric acid solution. Tributyl phosphate is sufficiently removed after 20 hr of digestion. (See Section 9 for the effects of organic in waste on ruthenium volatilization from boiling acid waste.)

5.2.5 Pot Calcination Time Cycles and Capacities

Pot calcination is a batch process that may be divided into three major portions: (1) the period of feeding and concentrating at constant feed rate, (2) the period of pot wall

TABLE 5.3. Corrosivity of Rising Level Glass PW-1 Type Melts

Conditions: Sixteen-hour exposures of coupons 50 to 75% immersed
in melts contained in alumina crucibles.

Molarity of Additives at 378 Liters Waste/Tonne				Corrosion Rate, in./yr					
			M ⁺ /P Ratio	304 L			310		
<u>PO₄</u>	<u>Na</u>	<u>Li</u>		<u>850 °C</u>	<u>900 °C</u>	<u>950 °C</u>	<u>900 °C</u>	<u>950 °C</u>	<u>1000 °C</u>
2.00	0.62	1.24	2.86	--	>22	--	0.07	0.07	--
2.00	0.93	0.93	2.86	--	>22	--	0.07	0.11	--
2.00	1.12	0.74	2.86	--	>22	--	>22	0.11	--
1.88	0.62	1.24	3.04	--	--	>22	--	0.15	2.5
1.88	0.93	0.93	3.04	--	--	>22	--	0.07	1.5
1.88	1.12	0.74	3.04	--	--	>22	--	0.11	0.73
2.50	1.38	1.38	2.66	0.37	33	--	>22	16	--
2.34	1.21	1.21	2.70	0.37	33	--	1.3	3.6	--
2.37	1.51	1.51	2.92	0.37	33	--	>22	0.73	--
2.96	1.50	1.50	2.33	--	33	--	>22	9.1	--

FIGURE 5.7. Decomposition of Tributyl Phosphate in Boiling 6M HNO_3

scaling and calcining, causing gradual reduction of feed rates, and (3) the calcining and cooling period when feed is turned off and the calcine is heated to 850 to 900 °C, then is cooled in preparation for removing the pot from the furnace. Typical time requirements for each of the steps are summarized in Table 5.4. Since diameter of the pot has a relatively small effect on the overall processing capacity, an increase in capacity must be obtained by changes in pot geometry (e.g., annular pots) or by multiple pot lines. Longer pots provide a slight increase in capacity because there is no marked increase in calcining and cooling times. Figure 5.8 shows the feed rates and feed consumption for typical 8- and 12-inch diameter pot demonstrations containing radioactivity in WSEP. Maximum boilup rate is limited by entrainment in the upper part of the pot or by the cross-sectional area of the pot. Some feeds may contain significant amounts of foam-making constituents (e.g., dibutyl phosphate from the reprocessing plant) or they may be inherently prone to foaming. If foaming is present, feed rates during the initial boiling period must be reduced from those shown in Table 5.4 or suitable antifoam agents must be added.

5.2.6 Temperature Control

Furnace temperatures are used for temperature control in the pot solidification process. Pot wall temperatures, especially in the calcination process, are unsuitable for control because of the varying conditions that the wall encounters (i.e., low temperatures during concentration and high temperatures following calcine deposition). Also during concentration, the wall temperatures are in error (i.e., they read higher than the true temperature by 50 to 100 °C)

FIGURE 5.8. Typical Pot Calcination Processing Rates in WSEP

TABLE 5.4. *Time Cycles and Capacities for Pot Calcination*^{(5)(a)}

Pot diameter, in.	8	12
Pot Height of fill, ft	6	6
Volume of Calcine, liters	60	120
Feed Volume, liters ^(b)	500	1000
Initial Feed Rate, liters/hr ^(c)	30	60
Time of Initial Feed Rate, hr ^(c)	10	10
Time of Reducing Feed Rate, hr	20	30
Calcining and Cooling Time After Feed Off, hr	<u>10</u>	<u>30^(d)</u>
Total Time Cycle, hr	40	70
Overall Cycle Capacity, liters/hr	12	14
Equivalent Waste Processing Capacity, tonnes/day with Feed Concentration = 378 liters/tonne	0.75	0.9

(a) For pots containing 5 kW internal heat generation rate

(b) Average volume will be approximately 20% lower for PW-2 and 20% higher for PW-1, and PW-4m.

(c) For feeds relatively free of foaming tendencies.

(d) Estimated. Exact data not available.

due to radiant heat pickup from the furnace. Thus, while the furnace can be set to operate at one temperature, the pot wall temperature varies depending on conditions in the pot.

Sufficiently high temperatures are required in the pot calcination process to insure complete denitration of the calcine. Excessive temperatures, however, can cause volatile constituents to escape from the waste and may lead to unwanted melting of the calcine. The volatility of fission products at excessive temperatures is unknown but is not expected to be significant at temperatures up to 1100 to 1200 °C.

Operation at higher pot centerline temperatures would allow increases in the number of curies (or the amount of heat) that can be handled in a given pot of calcine. However a pot centerline limit of 900 °C has been established by BNW for the waste solidification program based on the strength of the stainless steel and the unknown variables of melting and fission product volatilization. In studies with simulated internal heat generation in the calciner, Jury proposed programmed cooling of the pot wall to prevent excessive calcine temperatures during processing of heat generating waste.⁽¹⁸⁾ Figure 5.9 shows the proposed temperature profiles in the pot during the entire calcining cycle assuming no sloughing off at the pot walls. (Figure 5.9 may also be used to designate the real case of sloughing from the pot walls for any one horizontal section through the pot.) Following concentration of the waste, calcine deposition occurs on the pot wall. The wall temperature then increases to that of the furnace control setting and levels off there. As the calcine cake grows radially inward from the pot wall, internal self-heating from the radioactive waste increases until the heat flux from the furnace to the pot wall decreases to zero. That is, no further outside heat is required to keep the pot wall at the operating temperature. Furthermore, if cooling of the pot wall is not started, internal self-heating will increase the calcine temperature upward above the wall temperature, and internal temperatures will become excessive. It is at this point that Jury recommended that programmed cooling of the pot wall be started. As seen in Figure 5.9, the wall should be cooled at a rate such that the maximum desired temperature proceeds inward toward the inner face of the cake as a "heat wave." After the feed is turned off, wall cooling is continued until the maximum temperature is

FIGURE 5.9. Calcine Cake Temperature During Idealized Pot Calcination Run

at the pot centerline when the pot is filled radially or at the inside surface of the calcine where a void exists. The pot is then ready for storage. The pattern described is based on uniform radial deposition of calcine in an 8 foot long cylindrical pot. Since these conditions do not actually occur, and because longitudinal differences in the calcine deposition do occur, multizone heating and cooling of the pot is required.

Temperature control has been successfully demonstrated in highly radioactive calcination runs in WSEP using a simple 3-step reduction of furnace temperatures as described in the next section.

5.2.7 Temperature Profiles

Knowledge and interpretation of temperature profiles are essential to operating and understanding both pot solidification processes. In the calcination process, temperatures reveal the various stages of operation, such as concentration, denitration and cooling. During radioactive operation, understanding temperatures is essential if temperature excursions are to be prevented. Figure 5.10 shows typical temperature patterns for a WSEP calcination test with a relatively high internal heat generation rate (4.3 kilowatts total in an 8 inch pot). During this test, temperature overshoot was controlled successfully by a simple manual three-step reduction in furnace temperatures as follows:

1. Partial reduction of furnace temperatures in individual zones when the pot wall and furnace temperatures are approximately equal.

FIGURE 5.10. Pot Calciner and Furnace Temperatures in WSEP Run PC-5

2. Maximum reduction of furnace zone temperatures when the pot centerline is dry (temperature equal to or greater than 600 °C).*
3. Start of furnace zone cooling when the pot centerline reaches 800 °C.

To simplify the description of the control used for the pot in Figure 5.10, temperatures of zone number 4 only are shown in Figure 5.11. Because of heat losses at the ends of the pot, zone 4 (i.e., the fourth zone from the top, and the third zone from the bottom) is usually the hottest zone in WSEP. During the first 16 hours the furnace was on, 4 kilowatts of heating were used in zone 4, and the furnace temperature controller was set at 900 °C. After 4 hours, calcine deposition started 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. Feed to the pot was shut off at 28 hours. About 3 hours later the first indication of a "heat wave" was seen. The pot wall temperature was definitely greater than the furnace temperature and the intermediate calcine temperature started to rise. The furnace heat was turned off and the cooling air to all zones was turned on at 36 hours. The "heat wave" continued as expected and peaked 2 1/2 hours later at 910 °C. When all of the temperatures were below 900 °C (at 39 hours), the cooling air was turned off and the pot temperatures were allowed to come to steady state with the pot in the furnace. (The maximum temperature inside the pot was 940 °C briefly in zone 2.)

* For pots having diameters greater than 8 inches, an additional partial reduction of furnace temperatures may be required when the calcine midway between the pot wall and pot centerline is dry.

FIGURE 5.11. Zone 4 Temperatures During WSEP Run PC-5

In actual practice, if no thermocouples are present in the pot, the entire operation will require programming on the basis of the heat generation rate of the feed delivered to the pot and the general power requirements and characteristics of each furnace zone. If programmed properly, the calcining and cooling period may be shortened to where the pot will be ready for removal from the furnace very shortly after the feed is shut off.

Temperature patterns in the RLG process are at present the only method of determining the operating level. They also provide critical information about the process (depth of melt, calcine, or aqueous liquid). During radioactive operation, the temperature patterns in zones filled or partially filled with melt may be changed due to radiolytic heat generation. Figure 5.12 shows a typical temperature profile for the RLG process. (The three thermocouples in each zone were staggered at approximately 4-inch vertical intervals.) The section of the temperature profiles outlined by the dashed line is typical for the RLG run made during design verification tests in WSEP.^(3,16) At the beginning of the outlined section of Figure 5.12 all furnace zones were operating at 800 °C and zones 1, 2, and 3 centerlines were recording liquid temperatures which were indicative of wet feed flowing down the centerline well. Zone 4 intermediate temperature was starting to indicate calcine formation, and zone 3 intermediate temperature was indicating vapor space temperature above the liquid. In general, a 100 °C temperature indicated dilute fresh feed. This temperature increased to 150 °C as the feed was concentrated.

A decreasing internal temperature was indicative of a vapor space. Nonchanging temperatures between 175 and 300 °C

FIGURE 5.12. Typical Rising Level Glass Process Temperature Patterns

followed by an increase in temperature were calcine temperatures. The increasing calcine temperatures became melt temperatures at about 675 °C.

5.2.8 Process Control

Three methods of liquid level detection can be used in the pot calciner. These are a thermal type probe developed at ORNL,⁽⁹⁾ a steam purged pneumatic dip tube, and pot thermocouples.

The thermal probe consists of a thermocouple imbedded in a solid bar of copper which is jacketed with a 3/8 inch diameter stainless steel tube and sealed. The rod below the thermocouple acts as a variable heat path and allows the thermocouple temperature to change as a function of the liquid or foam height on the rod and the pot wall temperature. The pot wall must be at 700 °C or greater to provide response of the probe, and under these conditions gas temperatures at the pot head may be greater than 400 °C. This condition promotes RuO_4 decomposition and RuO_2 deposition, but with a self washing off-gas line such as that used in WSEP no line plugging should occur.

The pneumatic dip tube probe is a standard bubbler detector^(5,7) which is continuously purged with steam to prevent plugging by calcine. Solution foaming can cause erroneous readings.

Both level detectors can be used to control feed addition to the pot by cascading the liquid level instrument signal to the controller for the feed flowmeter and control valve.

In WSEP, reliance has been placed on both devices to assure proper liquid level in the pot. In addition, pot internal temperatures can be interpreted to give substantial liquid level information.⁽⁵⁾ Although the pneumatic dip tube was originally intended to serve only as a secondary indication of liquid level, it has been particularly useful during the last 5 to 10 hours of operation when the thermal probe tends to become insensitive. Some additional development is needed before the thermal probe is fully satisfactory; furthermore, successful functioning of the pneumatic dip tube has not been completely established, since it has not been operated submerged in the solution during most of the run.

Level detection in the RLG process is done by mass and volume balances and by interpretation of temperatures as discussed in Section 5.2.7.

5.2.9 Process Flowsheets

Data from WSEP have been used to project typical flowsheets for processing both PW-1 and PW-2 wastes. Although exact PW-1 and PW-2 flowsheets have not yet been demonstrated in WSEP, sufficient confidence in radioactive operation has been achieved to specify most of the necessary details. Flowsheets based upon WSEP experience for the two wastes are presented in Figures 5.13 and 5.14. Precautions that must be observed include a possibility of excessive sodium-rare-earth sulfate solids in the sulfate-containing PW-2 waste at the concentrations shown. These solids are fast settling and readily form very hard cakes. When they exist, it will be necessary to dilute the waste to a sulfate concentration of 0.45M, or to add complexants such as phosphate to gelatinize the solids. Sulfate-free PW-1 waste, on the other hand, even with a small amount of additive sulfate can be handled at a much greater concentration (approximately 325 liters/tonne of fuel).

BASIS: WSEP size equipment plant to solidify waste at 378.5 liter/tonne of fuel from processing power reactor fuel with an exposure of 20,000 MWd/tonne at 15 MW/tonne

NOTES: (a) Stream descriptions are in text
 (b) ΣM_t^+ = total salt content as metal ion equivalents
 (c) Fission product heat rate
 (d) If a second pot is being filled during final baking, cooling and changeout of the first pot, then 0.80 pots/day can be filled, and the average processing rate is 1.26 tonne/day. (If the two pot lines are run concurrently, 1.88 tonne/day can be processed.)
 (e) Entrainment of nonvolatile species is $\leq 0.5\%$ of concentration in feed.
 L = Liquid, S = Solid, G = Gas or Vapor
 B'CH = Batch

	Stream Number (a)								
	1	2	3	4	5	6	7 ^(e)	8	9
Phase	L	L	L	L	S	L	L	G	L
Na, $\underline{M}$	0.138	----	0.136	---	-----	---	-----	---	-----
Fe + Cr, $\underline{M}$	0.94	----	0.924	---	-----	---	-----	---	-----
Al, $\underline{M}$	-----	----	-----	---	-----	---	-----	---	-----
Li, $\underline{M}$	-----	----	-----	---	-----	---	-----	---	-----
Ca, $\underline{M}$	-----	----	-----	---	-----	---	-----	---	-----
NO ₃ , $\underline{M}$	6.5	----	6.4	---	<0.1 wt%	---	6.2	---	6.2
SO ₄ , $\underline{M}$	-----	6.5	-----	---	-----	---	-----	---	-----
PO ₄ , $\underline{M}$	-----	-----	-----	---	-----	---	-----	---	-----
Fp's as M^{+} (b)	0.91	----	0.895	---	9.0	---	-----	---	-----
Others	-----	----	-----	---	-----	H ₂ O	-----	---	-----
ΣM_t^{+} (b)	3.95	----	3.84	---	39	---	-----	---	-----
% Ru	100	----	100	---	95	---	4.5	---	0.5
% Cs	100	----	100	---	99.5	---	0.45	---	0.05
% Ce and other Fp's	100	----	100	---	99.5	---	0.45	---	0.05
ℓ/tonne	378	----	384	---	38	---	408	---	0.05
Volume per pot, ℓ	595	10	605	---	60	20	563	---	62
Flow, ℓ/hr avg	B'CH	B'CH	20	---	-----	B	19	---	2
Density, g/cm ³	1.37	----	1.37	---	1.4	1.0	-----	---	-----
B+γ, Ci/ℓ	2650	----	2600	---	-----	---	-----	---	-----
Heat rate per 8-in. pot kW(c)	5.5	----	5.5	---	5.5	---	-----	---	-----
Flow time/pot, hr	-----	----	30	---	-----	---	-----	---	-----
Baking and cooling time, hr	-----	----	-----	---	10	---	-----	---	-----
Pot changeout time, hr	-----	----	-----	---	5	---	-----	---	-----
Total time, hr	-----	----	-----	---	45	---	-----	---	-----
Processing rate, tonne/day(d)	-----	----	-----	---	0.94	---	-----	---	-----

FIGURE 5.13. Pot Calcination Flowsheet for Sulfate-Free PW-1 Waste (8-inch pot)

BASIS: WSEP size equipment plant to solidify waste at 378.5 liters/tonne of fuel from processing power reactor fuel with an exposure of 20,000 MWd/tonne at 15 MW/tonne

- NOTES: (a) Stream descriptions are in text
 (b) EM_t^+ = total salt content as metal ion equivalents
 (c) Fission product heat rate
 (d) If a second pot is being filled during final baking, cooling, and changeout of the first pot, then 0.96, 8-inch pots per day can be filled, and the average processing rate is 1.0 tonne/day. (If the two pot lines are run concurrently, 1.26 tonne/day can be processed.)
 (e) Entrainment of nonvolatile species is $\leq 0.5\%$ of concentration in feed.
 (f) During final stages of calcining
 L = Liquid, S = Solid, G = Gas or Vapor
 Tr = Trace, B'CH = Batch

	Stream Number (a)								
	1	2	3	4	5	6	7 ^(e)	8	9
Phase	L	L	L	L	S	L	L	G	L
Na, $\underline{M}$	0.93	---	0.93	---	6.2	---	---	---	---
Fe + Cr, $\underline{M}$	0.47	---	0.47	---	3.1	---	---	---	---
Al, $\underline{M}$	-----	---	-----	---	-----	---	---	---	---
Ca, $\underline{M}$	-----	---	-----	5	3.3	---	---	---	---
NO ₃ , $\underline{M}$	5.37	---	5.37	10.0	<0.1wt%	---	6.05	---	6.05
SO ₄ , $\underline{M}$	0.87	---	0.87	---	5.8	---	Tr	---	Tr
PO ₄ , $\underline{M}$	-----	---	-----	---	-----	---	---	---	---
FP's as M ⁺ (b)	0.91	---	0.91	---	6.1	---	---	---	---
Others	-----	---	-----	---	-----	water	-----	steam	-----
EM_t^+ (b)	3.33	---	3.33	---	29	---	---	---	---
% Ru	100	---	100	---	80	---	18	---	2
% Cs	100	---	100	---	99.5	---	0.45	---	0.05
% Ce and other FP's	100	---	100	---	99.5	---	0.45	---	0.05
ℓ /tonne	378	---	378	---	57	---	397	---	397
Volume per pot, ℓ	400	---	400	40	60	20	378	50	42
Flow, ℓ /hr avg	B'CH	---	18	1.8	-----	B	15	5	2
Density, g/cm ³	1.37	---	1.37	1.54	1.4	1.0	-----	---	-----
$\beta + \gamma$, Ci/ ℓ	2750	---	2750	---	-----	---	-----	---	-----
Heat rate per 8-in. pot, kW ^(c)	5	---	5	---	5	---	-----	---	-----
Flow time/pot, hr	-----	---	25	---	-----	---	-----	10 ^(f)	-----
Baking and cooling time, hr	-----	---	-----	---	10	---	-----	---	-----
Pot changeout time, hr	-----	---	-----	---	5	---	-----	---	-----
Total time, hr	-----	---	-----	---	40	---	-----	---	-----
Processing rate, tonne/day ^(d)	-----	---	-----	---	0.63	---	-----	---	-----

FIGURE 5.14. Pot Calcination Flowsheets for Sulfate-Containing PW-2 Waste (8-inch pot)

<u>Stream</u>	<u>Description</u>
1	Incoming waste from reprocessing 20,000 MWd/tonne at 15 MW/tonne power reactor fuel.
2	Nonradioactive chemical additives to feed tank.
3	Feed to pot: See Section 5.2.5 regarding pot feeding rates.
4	Chemical additive to pot. For proper proportional control of the separate additive stream, this stream should be equal to 10 vol% of the feed.
5	Calcine product.
6	The vent line is sprayed with approximately 15 liters of water at the start of a run and 2 to 5 liters at the end of a run. This spray provides additional cleaning of the vent line and pot throat, and the addition prior to the run also serves as a water charge for startup. If a steam-purged pneumatic dip tube is employed for pot level control, an additional 1 liter/hr of water as steam condensate will be used for purging the dip tube.
7	Condensed vapors from the solidifier.
8	A steam spray is desirable to be added to the condenser during the final stages of calcination when sulfate wastes are being processed. This steam serves to dilute any sulfate that may be volatilized since concentrated sulfate is very corrosive.
9	Reflux from the calciner vapor line. The reflux is drawn off as a separate stream, but is usually routed to the same location as the rest of the condensed calciner vapors.

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(by J. D. Kaser, W. R. Bond, and J. D. Moore)

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6.0 THE SPRAY SOLIDIFICATION PROCESS

(by J. D. Kaser, W. R. Bond, and J. D. Moore)

6.1 INTRODUCTION

6.1.1 Background

Spray solidification initiated at the Pacific Northwest Laboratory is a continuous process that has been extensively developed and is about ready for commercial use. It has been demonstrated on both a laboratory scale and a pilot plant scale, with no radioactivity and with full level radioactivity. Its advantages are that it is a continuous process with very little hold-up, it is adaptable to a moderately wide variety of feed compositions, and it produces a good quality product. Its disadvantages are that it is somewhat complicated; it requires good flow control of feed solutions, high quality atomization, and, at present, it must use a relatively expensive platinum melter. Development requirements for specific applications are nonradioactive laboratory and pilot plants tests on the particular feed compositions. Current pilot plant testing of melting the calcined powder in the receiver pot may eliminate the need for a platinum melter.

6.1.2 Process Description

In spray solidification, liquid waste is continuously converted to a powder in a spray calciner. The powder is then continuously melted in a platinum crucible, and the molten waste is discharged into the receiver and storage pot. In the spray calciner (see Figure 6.1) liquid waste, which contains some or all of the melt-making additives, is fed through a pneumatic atomizing nozzle into the top of a heated

FIGURE 6.1. The Spray Solidification Process

cylindrical tower. The atomized waste is dried, partially calcined, and falls as a powder into a continuous melter below the calciner where it is melted at temperatures of 800 to 1200 °C. Process gases from calcination flow into the adjacent filter chamber, entraining much of the calcined powder. The powder collects on the porous metal filters while the gas passes through. The powder deposits are periodically blown off the filters by sudden pulses of high-pressure steam or air directed backward through the filters by small nozzles. The dislodged powder falls into the melter with the main powder stream. The molten waste flows through an overflow weir or a freeze valve into the storage pot below. After the pot is filled, it is cooled in the furnace, sealed, and taken to storage.

6.2 PROCESS TECHNOLOGY

6.2.1 Chemistry and Volatilization

Allemann, Roberts, and Upson⁽¹⁾ found that ruthenium was the fission product most easily volatilized during solidification of radioactive waste solutions. These observations were verified in both radioactive and nonradioactive runs in the WSEP spray solidifier.^(2,3) In the nonradioactive runs, ruthenium volatilization varied from 50 to 80% when processing acidic PW-1 and PW-2 wastes. Allemann et al. found normal release of ruthenium from other acidic wastes was 20% and could be reduced to 3% by using reducing agents such as sugar or phosphites. Ruthenium did not volatilize significantly more than other fission products from neutral or basic wastes when reducing agents were used.

These results indicate that the initial form of ruthenium in the waste solution may determine ruthenium volatilization

during calcination. For example, in an alkaline nitrate solution it is known that the hydroxyl forms of ruthenium persist over nitrate forms. Calcination of hydroxyl forms does not result in appreciable ruthenium volatilization even in the presence of decomposing nitrates. Furthermore the results indicate that chemical reductants play a dual role in the initial acidic and basic waste. In the acid waste, chemical reductants shift the distribution of nitrato-nitro complexes to the more stable nitro form (see Section 9.2.3) and, in both waste types, they provide an atmosphere of NO in the calciner which may reduce significant amounts of volatilized RuO_4 to solid RuO_2 which is caught on the filters, thereby decreasing ruthenium release from the calciner. This effect was noted by Rhode, et al.⁽⁵⁾

In the spray solidification process, it is desirable to retain sulfate in the product to prevent condensed sulfuric acid from forming damp powder deposition on the calciner walls and filters. In addition, relatively concentrated sulfuric acid can excessively corrode the off-gas condenser and its piping.

Sulfate retention is relatively poor (50 to 80%) when either colemanite ($\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$) or phosphoric acid is used as a flux with acidic Purex wastes (see Table 6.1). If alkali metals are added with phosphoric acid, sulfate retention increases to greater than 97%. In addition to melt composition, sulfate retention is dependent upon melt temperature and residence time at that temperature. Figure 6.2 shows that sulfate evolution increases rapidly with time above 750 °C. These data were obtained in a small crucible using a melt with equal alkaline and sulfate equivalents and an M^+/P of 2.3. Engineering scale spray solidification

FIGURE 6.2. Effect on Time and Melt Temperature on Sulfate Retention

tests with this type of waste at a melt temperature of 750 to 800 °C verified the laboratory data. Less than 4% of the sulfate was volatilized from the melter with a melt residence time between 3 and 4 hours.

6.2.2 Product Characteristics

The product of spray solidification is a monolithic solid formed from cooling the melt. The solid is a tough,

microcrystalline material with high thermal conductivity and low solubility in water. (See Section 8 for details on characteristics of the product from spray solidification.)

6.2.3 Waste Processing Performance

In general, feed composition has a strong effect on the performance of the spray solidification equipment. Excessive amounts of low melting components such as sodium nitrate or phosphoric acid may seriously reduce process capacity by lowering the permissible calciner operating temperature. Also, some components such as sulfuric or phosphoric acid may plug the filters by vaporizing and recondensing on the filters. However, with the proper choice of operating temperature and the correct amount of melt-forming flux, it is possible to obtain good process performance. (See Section 4 for details of melt formation.)

The operating temperature for a calciner is determined by knowing the "stick" temperature of the calcine product. This is the temperature at which a calcine will adhere to a heated surface. Figure 6.3 shows the "stick" temperatures of a PW-1 calcine with varying amounts of PO_4 (M^+/P ratio) and Na. Operating the calciner below the "stick" temperature results in little accumulation of powder on the walls.

Figure 6.4 shows the "stick" and melting temperatures of a PW-2 calcine with varying M^+/P ratios. Since this waste composition contains sulfate, retention of sulfate in the melt will require a melter operating temperature below the calcine melt point. Thus, additional melt-forming fluxes need to be added directly into the melter to blend with the calcine to produce the lower-melting product. The two isolated

FIGURE 6.3. *Effect of Sodium on Fusion and Stick Points of PW-1 Phosphate Melts*

FIGURE 6.4. *Fusion and Stick Points of PW-2 Phosphate Melts*

points on Figure 6.4 indicate the effect on calcine "stick" and melting temperature after the calcine composition was adjusted in the melter. With the use of this technique, melting points of products may be adjusted as desired, regardless of the initial calcine melting or "stick" temperature.

Table 6.1 summarizes process performance with other simulated waste compositions. Wastes of the Purex type are the most widely generated during fuel reprocessing. These wastes are characterized by their moderately high iron, sodium, and fission product content.

In addition to phosphate, the boron-containing fluxes (colemanite, boric acid, and borax) have been tested as glass-forming additives. The main advantages of colemanite are that it is processed smoothly at high calciner temperatures (since it has the relatively high melting point at 800 °C), and is a naturally occurring low-cost mineral. When borax or boric acid is used, the filters often become plugged, presumably by the volatile boric acid. When any of the three borate fluxes is used with Purex waste, Na_2CrO_4 forms a light yellow crystalline phase which separates from the melt.

The most extensive testing has been done with Purex wastes containing phosphate and alkali metal fluxes. The best processing characteristics with this type of feed are achieved with phosphate concentrations in the M^+/P range between 2.0 to 3.0. In this range, the phosphate volatilized from calcined feed does not blind the calciner filters, and the powder has a desirable melting point range from about 850 to 1000 °C. Below an M^+/P of 2.0, excess phosphoric acid can be volatilized to form an impermeable

TABLE 6.1. Process Performance of Spray Solidifier with Various Water Solutions

Inert Constituents	PW-1 (a) M _(b)	PW-2 (a) M _(b)	PW-4 (a) M _(b)	Purex 1WW M _(b)	Redox M _(b)
Fe	0.93	0.445	0.05	0.095	0.85 0.200
Cr	0.012	0.024	0.012	0.014	0.017 0.068
Ni	0.005	0.010	0.008	0.007	--
Al	0.001	0.001	0.001	0.36	27.2 37.4
Na	0.138	0.93	0.10	0.32	31.4 21.8
SiO ₃	0.01	0.01	0.01	0.005	-- --
PO ₄	0.003	0.006	0.003	0.0036	-- --
NO ₃	7.5	5.37	6.66	4.61	118.4 139.6
H	3.7	3.93	6.29	3.95	3.4 8.8
Hg	-- (c)	--	--	0.002	-- --
Ca	--	--	--	0.009	-- --
CO ₃	--	--	--	0.006	-- --
F	--	--	--	--	-- --
SO ₄	--	0.87	--	0.11	0.34 0.68
Cr ₂ O ₇	--	--	--	--	0.17 2.38
NH ₄ Mn	--	--	--	--	0.46 0.68
Fission Products					
ZrO	0.065	0.065	0.065	0.017	-- --
MoO ₄	0.065	0.065	0.065	0.02	-- --
Sr	0.0155	0.0155	0.0155	--	-- --
Ba	0.0195	0.0195	0.0195	--	-- --
Rb + Cs (used K)	0.042	0.042	0.042	0.011	-- --
Y + Re	0.12	0.12	0.12	0.036	-- --
Ru (used Fe)	0.032	0.032	0.032	--	-- --
Rh (used Co)	0.0074	0.0074	0.0074	--	-- --
Ag + Cd (used Cu)	0.0016	0.0016	0.0016	--	-- --
Te (used SO ₄)	0.0064	0.0064	0.0064	--	-- --
Pd (used Ni)	0.017	0.017	0.017	--	-- --
Tc (used MoO ₄)	0.014	0.014	0.014	--	-- --

TABLE 6.1. (contd)

Additives	PW-1 ^(a) <u>M</u> ^(b)		PW-2 ^(a) <u>M</u> ^(b)		PW-4 ^(a) <u>M</u> ^(b)		Purex 1WW <u>M</u> ^(b)		Redox <u>M</u> ^(b)	
Na	0.9	0.5	1.27	--	1.5	--	--	--	--	63.8
Li	--	0.5	1.17	--	--	--	--	--	--	--
PO ₄	1.81	1.74	1.61	1.61	1.1	0.42	--	--	--	43.5
PO ₃	--	--	1.27	--	--	--	--	--	--	--
Ca ₂ B ₆ O ₁₁ ·5H ₂ O	--	--	--	--	--	--	0.292	--	--	--
Na ₂ B ₄ O ₇ ·10H ₂ O	--	--	--	--	--	--	--	0.178	22.5	4.71
SiO ₂	--	--	--	--	--	--	--	--	44.9	--
OH	--	0.5	1.17	--	--	--	--	--	--	63.8
NO ₃	0.9	0.5	1.95	--	1.5	--	--	--	--	--
H	5.43	5.22	4.83	4.83	3.3	1.26	--	--	--	130.5
Al	--	--	0.25	--	--	--	--	--	--	--
Ca	--	--	0.6	--	--	--	--	--	--	--
C ₁₂ H ₂₂ O ₁₁	--	--	--	--	--	--	--	--	--	5.34
Calciner Performance	Good	Good	Good	Good to Poor	Good to Poor	Good to Poor	Good	Good to Poor	Good to Poor	Fair
Filter Performance	Good to Fair	Good to Poor	Good	Poor	Good to Poor	Good to Poor	Good	Poor	Good	Fair
Melter Operation	Good	Good	Good	Good	Good	Good	Good	Good	Good	Poor
Sulfate Loss (Percent)	----	----	<2.0	>50	----	>30	~20	~20	----	----
Product Crystallinity	Non-Glassy	Non-Glassy	Non-Glassy	Non-Glassy	Non-Glassy	Non-Glassy	Non-Glassy (Two-Phase)	Non-Glassy (Two-Phase)	Glassy	Semi-Glassy
Product Volume (ℓ/tonne U)	39	33	69	40	27	9	21	13	291	----

(a) See Tables 2.3 and 2.4 for more information on WSEP designated wastes.

(b) Concentrations are at 378 liters/tonne U

(c) Blank spaces designate 0 concentration.

glaze on the filters. Above M^+/P of 3.0, the calcine melting point becomes excessively high (greater than 1000 °C).

Waste with high concentrations of aluminum (such as that from the Redox process) produces homogeneous, glassy products when fluxed with either borax and silica or borax and phosphoric acid. The borophosphate calcine, however, foams excessively during melting, thereby decreasing the melter capacity and making it difficult to discharge the melt. Both feeds formed calcine deposits on the inner walls of the calciner during processing. Tests with these feeds, however, were made with external-mixing spray nozzles which did not atomize the feed as finely as the internal-mixing nozzles used later with other waste types. Calciner deposits with these feeds would undoubtedly decrease significantly if an internal-mixing nozzle were used.

6.2.4 Melt Viscosity

Viscosities of several melts were measured at various temperatures (see Figure 6.5) in order to define the workable viscosity range for melter operation. Using an apparatus developed by Lodge⁽⁷⁾ viscosities were determined by measuring the time required for a platinum-iridium ball to drop a given distance through the molten sample. The samples were held in beakers which were contained in a furnace heated to the desired temperature.

The upper limit of viscosity at which melt would drain from the weir of the WSEP platinum melter was encountered with a melt formed by fusion of the calcine with borosilicate glass balls (see Curve 7 at the extreme right in Figure 6.5). This melt viscosity was estimated at 200 poises. At this viscosity, the melt discharged from the

FIGURE 6.5. Viscosity of Spray Solidifier Melts

weir in strings rather than drops. The melting process was slowed by the low rate of mixing of powder and liquid in the melter.

A more practical operating viscosity range exists between approximately 5 and 50 poises. In this range, melt discharges readily from the melter tubes, and powder and liquid mix freely in the melter.

6.2.5 Corrosion and Materials of Construction

Materials of construction considered for the spray calciner equipment included Hastelloy X, Inconel, 310 stainless steel, and 50Cr-50Ni alloy. Laboratory tests indicated 50Cr-50Ni alloy possessed excellent corrosion resistance.⁽¹⁸⁾ However, the alloy was not commercially available at that time. Spray chambers constructed of Hastelloy X and of 310 stainless steel performed satisfactorily during pilot plant operation, whereas a spray chamber constructed of Inconel developed cracks in the weld area after 150 hours of operation. AISI type 310 stainless steel was specified for the prototype unit. No appreciable corrosion of the unit has been noted after 400 hours of intermittent service. The off-gas piping associated with the calciner is made of 304-L stainless steel. Little apparent attack has occurred after 400 hours of exposure. The off-gas filters were constructed of sintered 316-L stainless steel. Replacement of the filters was required after about 400 exposure hours. However, failure appeared to be a result of fatigue or fatigue corrosion⁽⁸⁾ and an improved filter design involving increased structural support of the filter is expected to significantly reduce the fatigue problem.

Laboratory tests indicated chromium and a $77\text{Cr}-23\text{Al}_2\text{O}_3$ cermet are suitable materials of construction for the spray solidifier melter when operating temperatures are limited to 1000 °C maximum.⁽⁹⁾ However, many melt compositions with WSEP process require a melter temperature in excess of 1000 °C. Platinum or platinum-0.5 wt% rhodium are suitable as materials of construction for the spray solidifier melter at temperatures up to 1300 °C. Corrosion rates for platinum in this system are low (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 leads to rapid failure. This fact was demonstrated in a laboratory test⁽¹⁰⁾ in which a platinum crucible containing spray solidified melt from PW-2 wastes and a one gram cube of 304-L stainless steel was heated to 1200 °C with the results shown in Figure 6.6. The crucible evidenced cracking as well as severe localized attacks after 300 hours exposure. This same reaction caused failure of a WSEP melter during nonradioactive testing when stainless steel was inadvertently dropped into the melt.⁽¹³⁾ The corrosive agent in this reaction was elemental phosphorus formed by the reduction of phosphate by the stainless steel which dissolved rapidly. Jedelev⁽¹¹⁾ and Fisher⁽¹²⁾ have found that trace amounts of phosphorus in platinum leads to embrittlement due to formation of a fusible eutectic.

Laboratory tests, made with waste solutions containing 1 wt% of powdered stainless steel, sugar, or powdered carbon, showed that these substances did not promote cracking of the platinum. The waste solutions were fed semicontinuously to an aluminum oxide crucible held at 1000 °C for 50 to 120 hours and equipped with an overflow weir. Platinum specimens exposed to the melt and to the vapor phase were unattacked.

Neg 466-2064A

5X

Bottom of Crucible

Neg 466-2065A

100X

Local and Intergranular Attack of a Section through Platinum Crucible

FIGURE 6.6. *Platinum Crucible After Exposure to a Phosphate Melt Containing Stainless Steel*

The undesirability of burners operating on a propane-air mixture was demonstrated in the laboratory.⁽¹⁵⁾ Propane-air burner heating of platinum in contact with melt from PW-2 waste at about 1000 °C indicated prolonged exposure would lead to embrittlement and cracking of the platinum. For more details on platinum and platinum alloy materials see Chapter 7, Section 7.2.3.

Stainless steels of the 300 series appear suitable as materials of construction for melt receiver pots when temperatures are limited to less than 900 °C. Mild steels are adequate when the wall temperature does not exceed 600 °C. The use of mild steel is not only limited by the corrosiveness of the melt product at higher temperatures, but also by air oxidation. Data⁽¹⁶⁾ showing the oxidation of mild steel in air are presented in Figure 6.7. Air oxidation of a mild steel receiver during filling with melt product at 600 to 700 °C can be reduced about 5 times by purging the surroundings with nitrogen.⁽¹⁷⁾ A receiver can be filled uniformly with spray solidifier melt product without applying external heating if the melt is discharged batchwise into the receiver. Consequently, either stainless or mild steel can be used during filling with only minimal corrosion occurring for this case. The results of laboratory tests of potential container materials are presented in Table 6.2.

6.2.6 Feed Atomization

For any spray process it is necessary to have a reliable and efficient means for atomizing the liquid feed. Only nozzles using some kind of pneumatic atomization were considered for the WSEP spray solidification equipment. These nozzles have the desirable features of low feed pressure, narrow spray angles, and lack of moving parts.

FIGURE 6.7. Air Oxidation of Mild Steel

TABLE 6.2. Corrosion of Potential Spray Solidifier Melt Container Materials

Melt (a)	Additives	EM ⁺ /P (b)	Temp, °C	Exposure Time, hr	Corrosion Rate, in./yr				References
					Mild Steel	304L	310	50Cr-50Ni	
PW-1	PO ₄ ⁺³	1.8	600	1000	0.004	0.0004	0.0001	----	7
PW-1	Li ⁺ , Na ⁺ , PO ₄ ⁺³	2.75	800	145	-----	0.001	-----	0.007	7
PW-1	Li ⁺ , Na ⁺ , PO ₄ ⁺³	2.75	900	80	-----	-----	-----	0.1	2
PW-1	NaPO ₃	1.8	750	48	-----	0.09	-----	-----	7
PW-1	NaPO ₃	2.0	800	48	-----	0.3	0.02	-----	7
PW-1	NaPO ₃	2.3	900	48	-----	0.2	0.04	-----	7
PW-1	Colemanite	(c)	700	1000	0.07	0.004	0.001	-----	7
PW-2	PO ₄ ⁺³	1.8	600	1000	0.005	0.0007	0.0004	-----	7
PW-2	PO ₄ ⁺³	2.5	600	1000	0.005	0.0007	0.0004	-----	7
PW-2	Ca ⁺² , Li ⁺ , Al ⁺³ , NaPO ₃ , PO ₄ ⁻³	2.7	800	145	-----	-----	-----	0.06	2
PW-2	Ca ⁺² , Li ⁺ , Al ⁺³ , NaPO ₃ , PO ₄ ⁻³	2.7	900	165	-----	-----	>6.0	0.1	2
PW-4	Na ⁺ , Fe ⁺³ , PO ₄ ⁺³	2.3	925	115	-----	0.05	0.01	-----	7
PW-4	Na ⁺ , Fe ⁺³ , PO ₄ ⁺³	2.3	100	38	-----	dissolved	dissolved	0.05	7

(a) See Tables 2.3 and 2.4 for definition of waste compositions.

(b) The ratio of metal equivalents to phosphorus atoms.

(c) 610 g Colemanite (Ca₂B₆O₁₁·6H₂O) per liter of PW-1 waste at 378 liters/tonne

A small external mix pneumatic atomizing nozzle, Spraying Systems Company Setup 5 was initially tested in WSEP equipment. However partially dried feed formed excessive deposits in the bottom of the tower. This external mix nozzle was tested in the laboratory and was found to produce a narrow stream of poorly atomized liquid in the center of the spray. Several nozzles were tested for flow distribution, and Spraying Systems Company Setup 42, an internal mix nozzle, was chosen to replace Setup 5. Setup 42 produced a more uniform spray without large drops, while the liquid orifice was as large as the liquid orifice of Setup 5 (0.1 inch inside diameter), thereby permitting solid particles to pass through.⁽¹⁹⁾

Further testing of Setup 42 showed that partial obstruction of the air orifice or moderate deposition on the outside surface of the nozzle had no significant effect on drop size. The effect of changing nozzle size was measured for three internal mix nozzles of similar design with the results given in Table 6.3.

Results of duplicate tests indicate the experimental uncertainty. The smaller nozzle, 22B, gave significantly better atomization than either Setup 42 or 72. However, it was felt that the liquid orifice of Nozzle 22B is too small to freely pass the solid particles suspended in the waste solutions.

The ratio of liquid to atomizing air flow rate largely determines the size of droplets produced. This relationship is shown in Figure 6.8 for Spraying Systems Company Setup 42 nozzle using both water and simulated PW-2 waste solution with air as the atomizing gas. The simulated PW-2

TABLE 6.3. Effect of Nozzle Size on Drop Diameter

Spraying Systems Co. Nozzle No.	Air Orifice diam, in.	Liquid Orifice diam, in.	Mass Median Drop Size, micrometers	
			Water Rate 15 liters/hr	Water Rate 20 liters/hr
22B	0.110	0.040	37	39
			36	64
42	0.125	0.100	48	117
			34	84
72	0.250	0.250	121	137
			127	123

waste had a density of 1.25 g/ml and contained 19 vol% solids. The solid particles were small rods about 5 micrometers in diameter and 60 micrometers long. Because the difference between atomization of water and the atomization of this simulated waste is not significant, a single line was fitted to all the data. The data plotted in Figure 6.6 covers liquid flows ranging from 5 to 30 liters/hr and air flows ranging from 71 to 425 liters/min at 14.7 psia and 21 °C.

It should be noted that some waste slurries may atomize quite differently from water. Preliminary data obtained from another batch of simulated PW-2 waste solution shows appreciably smaller drops for the waste slurry than when solids were removed by centrifuging.⁽²⁴⁾ In the latter case, the drop sizes approached water drop sizes as shown in Table 6.4. This waste slurry contained more solids (30 volume %), was more dense (1.4 g/ml), and the particles were smaller (20 micrometers long by 3 micrometers in diameter) when compared to the slurry used to obtain data for Figure 6.8.

FIGURE 6.8. *The Effect of Liquid to Atomizing Air Ratio on Drop Size*

TABLE 6.4. *Atomization of Simulated Waste. Nozzle: Spraying Systems Co. Setup 42 (Atomizing Air Rate 190 liters/min @14.7 psia and 21 °C)*

	Mass Median Drop Size in Micrometers	
	For Liquid Rate of 15 liters/hr	For Liquid Rate of 20 liters/hr
Feed with Solids	19	30
	16	31
Feed without Solids	62	82
	71	72
Water	48	120
	34	84

6.2.7 Drying Capacity

The spray calciner evaporative capacity is arbitrarily defined as the feed rate at which droplets are just dry when they hit the calciner wall. Any increases in feed rate beyond this would cause excessive deposition on the wall and would not permit continuous operation. In practice complete drying is insured by keeping the spray temperature above 250 °C at a distance of 3 feet below the nozzle. Figure 6.9 shows how the more important operating parameters affect capacity. Increasing atomizing gas pressure increases capacity by forming smaller droplets and by increasing convective heat transfer.

The use of a draft tube inside the calciner increases the capacity of the calciner as much as 15% due to the increased gas circulation which increases convective heat transfer from the walls. The drawbacks of the draft tube are that it is sometimes difficult to remove deposits from it, and the draft tube itself can cause deposition where the vapors reverse direction for return up to the top of the drying chamber.

Capacity increases as the calciner wall temperature increases. The maximum wall temperature is limited by the stick point of the powder. The capacity curves shown in Figure 6.9 are for water. Capacities for nonmelting simulated waste are about 30% less than the water capacities, probably because the hot walls are partially insulated with powder.

An analysis of the radiative heat transfer from the walls to the spray has been reported.^(20,21,22) This analysis provides

FIGURE 6.9. Spray Calciner Drying Capacity Parameters

valuable insight into the drying process, but its application to accurate scale-up is questionable. For rough estimates, limited experimental data indicate that the evaporative capacity without a draft tube is proportional to the square of the calciner diameter, while the capacity with a draft tube is proportional to the first power of the calciner diameter and the square root of the draft tube length.

6.2.8 Off-Gas Filtration

The spray solidifier off-gas dust removal system consists of sintered stainless steel powder metal filters cleaned by a pulsed steam or air blowback system. Venturis are mounted on the top of each filter to increase the reverse pumping of clean gas by the primary blowback gas pulse in order to augment the internal pressurization of the filter. For the permeability range anticipated in the spray solidifier, tests indicated that the blowback pulse is best augmented by a narrow-throated venturi. Thus a ratio of the blowback nozzle to venturi throat diameter was specified as 0.22 for the WSEP unit. Pilot plant testing of sintered powder metal, sintered fiber metal, sintered wire mesh, and wire-wound filters indicate that a sintered powder metal filter with a mean pore opening of 65 micrometers is the best compromise between filtration efficiency (>99%) and ease of cleaning by the pulsed blowback system.

The filter permeability must be kept high enough to allow the off-gas to be drawn through the filters without pressurizing the solidifier. Feed composition and spray solidifier operating conditions have an important effect on permeability. Changes that can be made in spray solidifier operating conditions to increase the filter permeability are increasing the blowback gas pressure and decreasing the blowback cycle time. The blowback gas should be superheated to greater than 300 °C, and the filter temperature should be above 200 °C to ensure that the filter cake stays dry. To avoid pressurization of the solidifier as the result of pressure surges caused by the pulses of blowback gas, it is necessary to limit the blowback gas pressure,

the number of filters blown back at one time, and the off-gas line flow resistance. On the WSEP spray solidifier, it was highly desirable to limit the number of filters blown back at a time to two and also to minimize the off-gas line flow resistance in order to provide latitude in the pressure of the blowback gas that could be used. Typical operational data for the filter blowback of the prototype solidifier is as follows:

Solidifier vacuum	8-10 in. of water
Solidifier vacuum during blowback	2-4 in. of water
Filter face velocity	3-5 ft/min
Filter pressure drop	3-6 in. of water
Filter chamber temperature	300-350 °C
Blowback gas pressure	40-50 psig
Blowback gas temperature	300 °C
Blowback cycle time	2 min
Blowback pulse duration	2 sec

6.2.9 Process Flowsheets

Figures 6.10 and 6.11 show the spray solidification standard process flowsheets for PW-1 and PW-2 wastes which have been successfully demonstrated in the WSEP.* The chemical flowsheets for solidifying PW-1 waste and PW-2 waste differ in that solid NaPO_3 flux is metered directly into the melter when PW-2 waste is processed. With this technique, the waste will not stick to the calciner walls. If all the flux were added to the aqueous waste for this chemical flowsheet, the calciner temperature would have to be limited to about 500 °C to prevent sticking with the calcine.

* See Tables 2.3 and 2.4 for definition of these waste compositions.

- NOTES: (a) ΣM_t^+ = Σ total salt content as metal equivalents
 (b) Batch operation - numbers are equivalent continuous flow
 (c) Fission product heat rate
 (d) Time from start of processing
 (e) Steady-state processing rate
 V = Vapor, L = Liquid, S = Solid

BASIS: Plants to solidify equivalent waste at 378.5 liters/tonne from reprocessing power reactor fuel at an exposure of 20,000 MWd/tonne at 15 MW/tonne.

	Stream Number						
	1	2	3	4	5	6	7
Phase	L	L	L	-----	S	V	L
Na, $\underline{M}$	0.14	2.1	0.50	-----	7.0	-----	-----
Fe + Cr	0.94	-----	0.74	-----	10.4	-----	-----
Al	-----	-----	-----	-----	-----	-----	-----
Li	-----	2.1	0.39	-----	5.5	-----	-----
NO ₃	7.5	-----	5.9	-----	-----	-----	6.3
SO ₄	-----	-----	-----	-----	-----	-----	-----
PO ₄	-----	6.4	1.4	-----	19.2	-----	-----
Others	-----	-----	-----	-----	-----	air	-----
ΣM_t^+ chem	2.96	4.2	3.11	-----	46.5	-----	-----
ΣM_t^+ fp	0.95	-----	0.75	-----	10.5	-----	-----
ΣM_t^+ (a)	3.91	4.2	4.1	-----	57	-----	-----
% Ru-106	100	-----	100	-----	30	-----	70
% Ce-Pr-144	100	-----	100	-----	99.8	-----	0.2
% Sr-90	100	-----	100	-----	99.8	-----	0.2
l/tonne	378	-----	480	-----	34	-----	450
Volume/pot, l	660	180	840	-----	60	-----	780
Flow, l/hr avg	11.8 ^(b)	3.2 ^(b)	15	-----	1.1 ^(b)	10 ⁴	14
Density, kg/l	1.33	1.35	1.34	-----	3.2	-----	1.16
$\beta + \gamma$, kW/l	2.8	-----	2.2	-----	27	-----	0.3
Heat rate, kW/8-in. pot ^(c)	12.8	-----	12.8	-----	10.5	-----	2.3
Time, hr ^(d)	-----	-----	56	-----	56	56	56
Processing rate, tonne/day ^(e)	-----	-----	0.75	-----	0.75	-----	-----

FIGURE 6.10. Spray Solidification Flowsheet for PW-1 Feed

- NOTES: (a) ΣM_t^+ = Σ total salt content as metal equivalents
 (b) Batch operation - numbers are equivalent continuous flow
 (c) Fission product heat rate
 (d) Time from start of processing
 (e) Steady-state processing rate
 V = Vapor, L = Liquid, S = Solid

BASIS: Plants to solidify equivalent waste at 378.5 liters/tonne from reprocessing power reactor fuel at an exposure of 20,000 MWd/tonne at 15 MW/tonne.

	Stream Number						
	1	2	3	4	5	6	7
Phase	L	L	L	S	S	V	L
Na, <u>M</u>	0.93	-----	0.68	NaPO ₃	11.2	-----	-----
Fe + Cr	0.47	-----	0.34	-----	2.4	-----	-----
Al	-----	0.70	0.18	-----	1.3	-----	-----
Li	-----	3.3	0.85	-----	6.0	-----	-----
NO ₃	5.4	-----	3.9	-----	-----	-----	4.7
SO ₄	0.87	-----	0.64	-----	4.4	-----	-----
PO ₄	-----	4.5	1.18	NaPO ₃	14.7	-----	-----
Others	-----	Ca 1.7	Ca 0.44	-----	Ca 3.1	air	-----
ΣM_{chem}^+	2.34	8.8	4.0	25	34.5	-----	-----
ΣM_{fp}^+	0.95	-----	0.69	-----	4.8	-----	-----
$\Sigma M_t^{+(a)}$	3.29	8.8	4.7	25	39.3	-----	-----
% Ru-106	100	-----	100	-----	20	-----	80
% Ce-Pr-144	100	-----	100	-----	99.8	-----	0.2
% Sr-90	100	-----	100	-----	99.8	-----	0.2
ℓ/tonne	378	-----	520	20	72	-----	434
Volume/pot, ℓ	310	110	420	16	60	-----	376
Flow, ℓ/hr avg	8.9 ^(b)	3.1 ^(b)	12	0.45	1.7 ^(b)	10 ⁴	10
Density, kg/ℓ	1.4	1.25	1.36	2.5	2.8	-----	1.16
β+γ, kW/ℓ	6.1	-----	4.4	-----	27	-----	0.8
Heat rate, kW/8-in. pot ^(c)	12.8	-----	12.8	-----	10.1	-----	2.7
Time, hr ^(d)	-----	-----	35	35	35	35	35
Processing rate, tonne/day ^(e)	-----	-----	0.55	-----	0.55	-----	-----

FIGURE 6.11. Spray Solidification Flowsheet for PW-2 Feed

A detailed chemical flowsheet for a PW-4m waste* is currently being developed. Work to date has shown that operable flowsheets can be made from PW-4m wastes by adding 0.2 to 1.0M iron, 1.5M sodium or lithium, and sufficient phosphate to give a M+/P of 2.2 to 2.8 to the aqueous waste.

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(by J. N. Hartley and M. R. Schwab)

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7.0 PHOSPHATE GLASS SOLIDIFICATION PROCESS

(by J. N. Hartley and M. R. Schwab)

7.1 PROCESS DESCRIPTION

7.1.1 Background

The phosphate glass process for converting highly radioactive aqueous wastes to stable solids has been under development at the Brookhaven National Laboratories (BNL) for the last eight years.⁽¹⁾ Phosphate glass solidification has been demonstrated on both a laboratory and pilot plant scale, without radioactivity and with full-level radioactivity.^(2,3) The process is continuous and forms a good quality glass product, but requires a moderately complicated system. The system requires operation with slurries that are sometimes difficult to handle. Also, it requires the use of a relatively expensive platinum melter, and it cannot retain sulfate in the final product.

7.1.2 Phosphate Glass Solidification Process

The major components of the phosphate glass solidification process are shown in Figure 7.1. The continuous process is carried out in three steps: feed preparation, low temperature denitration-evaporation, and high temperature glass-forming. Feed preparation involves addition of glass-forming chemicals (primarily orthophosphoric acid) to the aqueous wastes. For forming a good quality glass, one mole of H_3PO_4 is required for each equivalent of total metal cations. The presence of the phosphate anion also permits considerable denitration and concentration of the solution with relatively little precipitation of granular solids after digestion of the feed. The phosphate waste mixture is fed to a denitrator-evaporator where it is partially

FIGURE 7.1. Phosphate Glass Solidification Process

denitrated and concentrated to a thick, syrupy, aqueous phosphate slurry. Most of the nitric acid and water is volatilized from the solution at temperatures of 120 to 160 °C, giving a volume reduction of 2 to 7 and a nitrate removal of 60 to 90%. Concentration of the solution is continued until the viscosity becomes the limiting factor. This concentration-denitration reduces the heat requirement for the glass forming step. The concentrated slurry is fed to the continuous melter where final volatilization of water, nitrates, sulfuric acid when present, and other volatile constituents is accomplished, and the concentrate is heated to the range of 1000 to 1200 °C to form molten glass. The molten glass is drained continuously through an overflow weir or may be batchwise dumped through a drain freeze-valve into a final storage pot which is cooled, sealed, and removed for storage.

The basic elements of equipment required for phosphate glass solidification are: (1) a continuous denitrator-evaporator to remove nitric acid and to concentrate the feed to a syrupy concentrate, (2) a means for controlled feeding of the syrupy concentrate to the melter, (3) a continuous melter for the final evaporation and melting of the waste, (4) a furnace for heating the melter, (5) a pot for receiving the molten waste, and (6) a multiple-zoned furnace for heating and cooling the receiver pot.

The evaporator must have the capability to handle corrosive liquids with viscosities up to about 10 poise and boiling points up to about 160 °C, with a net heat transfer capability of about 0.8 kW/liter/hr of feed rate.^(3,4) Designs which provide low hold-up volume, maximize control of foaming, and maximize suspension of solids are desirable. Titanium is an acceptable construction material.

The system of feeding the melter must reliably pump and meter small flow rates (about 3 liters/hr in a plant that processes wastes from 1 tonne of fuel/day) of the thick slurry from the denitrator-evaporator. The feeding system must keep the slurry near its boiling point to maintain a free flow and to prevent excessive precipitation in the feedline, and must keep the temperature below calcination temperature (about 160 °C) as the material enters the melter. Special designs using recirculation of large flow rates have been developed for this purpose,⁽⁵⁾ but the use of a wiped film evaporator would likely be another solution to this problem.

The continuous melter, like the spray solidifier melter, is constructed of platinum, which is the only metal known to withstand the environment of corrosion and high temperature. Because platinum has a low radiant emissivity, it requires special design, increased melter size, or increased furnace temperature to obtain a given melting capacity. In addition, platinum is very expensive, but the initial high cost of the platinum melter is probably tolerable for a vessel which will last for years.

The net heat transfer requirements for the phosphate glass melter are 2 to 4 kilowatts for each liter/hr of the melt formed. This heat load is 50 to 100% higher than for the spray solidifier melter, primarily because of the added evaporation load. The desired freeboard requirements above the melt level are somewhat higher because of a modest foaming tendency in the melter.⁽⁶⁾ The capacity of the WSEP platinum melter, which is 10 inches in diameter and has a 14-inch high heated section, is about 2.5 liters/hr of slurry feed. (The melter produces glass at about 1.0 liter/hr at a melt temperature of 1050 to 1100 °C).⁽⁷⁾ The melter used in the nonradioactive pilot plant at BNL has a similar heat

transfer area, but the melt capacity is about double this value.⁽⁸⁾ This can be partially attributed to the increased furnace and melt temperatures which are about 50 to 100 °C higher. The vapors from the WSEP melter are routed through a 2-inch diameter platinum tube into the bottom of the melter condenser. This line is heated to 350 to 500 °C to prevent condensation which in turn minimizes corrosion and scale buildup on the line.

The pot for receiving the molten glass is similar to that for the spray solidification process, except that mild steel pots are satisfactory for dropwise or batch filling all flowsheets (see Section 8). This added degree of freedom is because the lower slump point (600 to 700 °C) and the continuous viscosity-temperature relationship for glasses, as opposed to microcrystalline solids, permit filling of pots by slow continuous dripping of melt while the pot is heated only to 400 to 600 °C.^(7,9) Mild steel can tolerate these conditions during the filling of one pot.

A multiple zoned furnace-cooler is required if the melt is discharged through the overflow weir at a constant rate to the melt receiver. Furnace heating capability must be provided to maintain the glass product at about 700 °C to insure that stalagmites do not form. The actual number of zones required is not definitely known, but six zones for a pot to be filled to six feet is definitely adequate. If the melter is batch discharged through the drain freeze-valve, heating of the melt receiver is not necessary. However, as with the weir overflow method of melt discharge, cooling of the melt receiver is necessary. Air cooling capability up to 15 kilowatts must be provided

to maintain the receiver at safe temperatures after processing. Water quenching would be necessary if greater heat removal is required. Another possible method of preventing stalagmite formation during filling could be to insulate the product receiver. (10)

The phosphate glass process can readily solidify high level waste solutions which contain sulfate, but the sulfate is completely volatilized from the melter. In this case, a separate condenser is required for the vapor stream from the melter, and a separate stream of intermediate level waste is formed. This stream contains all the sulfate and normally about 30% of the nitrate, 5 to 10% of the radioruthenium, and less than 0.5% of all other radioactivity that was original in the liquid waste stream. (7,11,12) Because the sulfate cannot be reused, it requires special treatment for final disposal. When sulfate is not present, the condensate from the melter contains only nitrates and can be combined with the condensate from the denitrator-evaporator, or condensed separately and recycled to the denitrator-evaporator to reduce the overall off-gas activity from the solidifier to less than 1% for radioruthenium and 0.1% or less for all other activity using data from WSEP. (7,12,13)

7.2 PROCESS TECHNOLOGY

7.2.1 Chemistry

Waste solutions to be interfused into phosphate glass require the addition of phosphate, as discussed in Section 4. In the case of Purex waste containing fission products,

iron and sodium nitrates, and sulfate, the addition of one mole of phosphate per mole equivalent of nonvolatile cation in the waste is required to form a "good" metaphosphate glass. If the M/P is less than or greater than 1.0 a poor grade phosphate glass will be formed. When the M/P is less than 1.0 the excess phosphate will be evolved until the M/P is about 1.0 or a ceramic will be formed. A short digestion period after the addition of phosphate as orthophosphoric acid permits the solution to equilibrate as evidenced by color changes in the solution in some instances. The addition of phosphoric acid causes the fission product zirconium to precipitate, if it is not already precipitated, along with complexes of phosphomolybdate of which cesium phosphomolybdate is the most common in acid waste. The net result is a waste solution with 30 volume percent settled solids that should be agitated at all times. When the mole percent of the oxides of the alkali metals is less than about half of that of the total metal oxides in the melt, additional alkali metals are added to the waste solution (usually as sodium nitrate) to obtain a glass that forms at a reasonable temperature (850 to 1000 °C), remelts at a lower temperature (650 to 700 °C), and has good handling properties. The chemically adjusted feed is usually moderately friendly--the solids are gelatinous and are to some extent reasonably suspended.

The addition of sodium for a sulfate-free PW-1* flow-sheet decreases the viscosity of the denitrator-evaporator concentrate, but causes the solution to become more non-homogeneous with solids settling out at a higher rate. Also, volume reduction decreases somewhat as the sodium concentration is increased.

* See Tables 2.3 and 2.4 for definitions of PW-1 and PW-2 wastes in WSEP.

In phosphate glass flowsheets where there is excess aluminum in the waste, it is possible to substitute the excess aluminum for all or part of the iron present on a mole per mole basis without significantly changing the melting characteristics of the glass product or the properties of the denitrator-evaporator concentrate. (9,15)

Concentration in the denitrator-evaporator sometimes progresses through stages of foaming and formation of heavy crystalline deposits at lower and higher than normal concentration factors. Manganese is the only known chemical which forms heavy solids in the denitrator-evaporator at normal operating conditions, and its presence should be eliminated.

Figure 7.2 summarizes the characteristics of the denitrator-evaporator concentrate for typical sulfate-containing PW-2 waste.* Good agreement was obtained in WSEP for the PW-2 curves. However, since a number of different compositions were used for PW-1 wastes, the data were not summarized on a plot. The data were obtained at BNL using the WSEP denitrator-evaporator design. (3,14) On the basis of viscosity, density, percent denitration, etc., a boiling point range of 130 to 133 °C for PW-1 waste and 135 to 137 °C for PW-2 waste are the most suitable operating temperature ranges in the denitrator-evaporator. (7,9) If the temperature exceeds 135 °C for PW-1 waste, plugging of pipes and dip tubes with solids may occur. Since substantial volume reduction is achieved at these temperatures, the heat requirements in the subsequent glass forming step are reduced significantly. Further volume reduction is not appreciably beneficial for the WSEP type denitrator-evaporator because the increased viscosity causes solution handling problems.

* See Tables 2.3 and 2.4 for definitions of PW-1 and PW-2 Wastes in WSEP.

FIGURE 7.2. Denitrator-Evaporator Concentrate Properties for Sulfate-Containing PW-2 Waste

Significant denitration and dehydration of the waste solution occurs in the denitrator-evaporator at boiling temperatures of 120 to 160 °C. Nitric acid is distilled as well as displaced from the solution by the presence of excess phosphoric acid and sulfuric acid. If sulfuric acid is present, complete denitration is difficult (see Figure 11.13) even at higher evaporation temperatures because of the formation of $\text{HNO}_3\text{-H}_2\text{SO}_4$ complexes.

During denitration, mercury and possibly silicon fluoride (if present), will volatilize from the solution. Ruthenium behaves as with most nitric acid systems (see Section 9); about 0.5 to 1% will volatilize, which indicates that the nitrate complexes of ruthenium in the feed are not affected by the presence of phosphate. Consequently, the initial feed digestion period may be reduced substantially without increasing the ruthenium volatilization. No appreciable sulfate or phosphate volatilization has been experienced from the denitrator-evaporator in the work at PNL and BNL. Ruthenium volatilization from the denitrator-evaporator during the first six WSEP radioactive demonstrations with the phosphate glass process was less than 1%. Entrainment of nonvolatile materials from the denitrator-evaporator was less than 0.1% in these same six WSEP radioactive runs. (7,11,12,13)

During denitration and concentration, additional solids appear in the concentrate solution. At boiling points of 135 to 140 °C, the concentrate contains 85 to 95 vol% solids. These solids are metallic phosphates whose solubility has been exceeded^(16,17,18) and have precipitated

out as gelatinous solids or fine crystals. However, they are generally kept in suspension by boiling, agitation, and the high viscosity effects. During dilution of the concentrate, the addition of either nitric acid or water at a reasonable addition rate (about 50 liters/hr) will not cause serious gelling. Pouring boiling concentrate into cold water results in a relatively stable gel. The use of sulfuric acid will reduce the viscosity and freezing point of the concentrate,⁽¹⁴⁾ which explains the greater fluidity of the concentrates from the PW-2 wastes compared with those from the PW-1 wastes at equal cation concentration.

During some of the first six WSEP radioactive runs, foaming of concentrates in the denitrator-evaporator caused serious operating problems. From 10 to 38% of the waste fed to the denitrator-evaporator was lost due to foam-over into the emergency vent system. The source of foaming was dibutyl phosphate (DBP) present in the Purex waste solution in concentrations as low as 30 ppm.^(7,12,19) Dow Corning Antifoam B was found to be an effective counteractant against the DBP-induced foaming and successfully controlled the foaming in concentrations of about 100 ppm in the denitrator-evaporator. For one WSEP demonstration wherein the feed was made using radiocerium solution as the only source of radioactivity (without Purex waste), foaming did not occur and no antifoam was added to the denitrator-evaporator.

After denitration and concentration, the hot concentrate (at greater than 100 °C) is transferred into the melter where the concentrate is further reduced in volume by factors of 2 to 3 to a glassy melt.⁽⁷⁾ Temperatures of the melt are 1000 to 1200 °C after the remaining nitrate,

water, sulfate (if present), and a small amount of phosphate are volatilized. Some gassing from the melt promotes better heat transfer and mixing with incoming feed. Prolonged heating of the melt at high temperatures will cause a slow continuing loss of phosphate from the melt, probably as P_2O_5 . (See Figure 11.7 for phosphoric acid vapor pressures.) One to ten percent of the ruthenium fed to melter volatilized from the melter in WSEP tests, with higher values for PW-1 wastes and lower values for PW-2 wastes. Physical entrainment was less than 0.3% for the nonvolatile fission products. (7,11,12,13)

It has been demonstrated at BNL that very short residence times (viz. less than one minute) are sufficient for the conversion of denitrator-evaporator concentrate to a good quality glass at 1100 °C. (14)

7.2.2 Product Characteristics

The product from the phosphate glass process is a monolithic, moderately brittle glass formed after cooling the melt. The glass has a good thermal conductivity and low solubility in aqueous solutions. More detailed discussion of the characteristics of phosphate glass are presented in Section 8.

Viscosities of PW-1 and PW-2 phosphate glass melts have been determined over the range of 800 to 1200 °C. (14) The results are given in Figure 7.3. The hysteresis exhibited by viscosity difference in the heating-cooling cycle

FIGURE 7.3. *Temperature Effects on Melt Viscosity for PW-1 and PW-2 Phosphate Glass*

may be caused by crystals present in the glass during the heating cycle, but the crystals disappear once the glass has completely melted. Above 900 °C the viscosity is essentially the same for both legs of the cycle.

7.2.3 Corrosion and Materials of Construction

Corrosion studies pertinent to the phosphate glass solidification process have been investigated at BNL and PNL using corrosion specimens under laboratory and pilot plant conditions. Corrosion rates have been obtained for the candidate materials of construction for the denitrator-evaporator, the melter, the melter off-gas train, and the solidified waste containers.

The results of corrosion tests for the thirteen most suitable candidate materials of construction for the denitrator-evaporator are given in Table 7.1. Zircaloy-2 has the best corrosion resistance to these solutions followed by titanium, uranium SD and Haynes-25. Corrosion in the vapor phase was generally a factor of 2 to 5 less than in the liquid phase. Those materials which have been evaluated more fully for the denitrator-evaporator are listed in Table 7.2 which compares the laboratory corrosion data with the corrosion data available from coupons installed in the pilot plant denitrator-evaporator at BNL. On the basis of the data in Tables 7.1 and 7.2, titanium and Zircaloy-2 are the two best materials for use in the denitrator-evaporator. Titanium was selected for the WSEP denitrator-evaporator.

The primary corrosion variables in the denitrator-evaporator are the phosphate concentration and temperature. The phosphate concentration was found to be the more important of the two corrosion variables, as seen in Figure 7.4. The

TABLE 7.1. *Effect of Temperature on Corrosivity of Phosphate Glass Feed Solutions in the Denitrator-Evaporator (20-23)*

(Conditions: Twenty-four hour exposures to solutions at given boiling temperatures.)

Material (c)	Corrosion Rate, in./year					
	PW-1 Solution(a)			PW-2 Solution(b)		
	120 °C	130 °C	140 °C	120 °C	130 °C	140 °C
Zircaloy-2 ^(d)	0.00012	0.00060	0.030	0.00084	0.0049	0.017
Titanium	0.018	0.031	0.056	0.028	0.029	0.055
Uranus SD	0.028	0.071	0.058	---	---	---
Haynes 25	0.036	0.077	0.086	---	---	---
Hastelloy G	---	0.18	---	---	---	---
Corronel 230	0.22	0.19	0.11	---	---	---
50Cr-50Ni	0.35	0.24	0.14	---	---	---
Nionel	0.22	0.31	0.42	0.0084	0.077	0.084
HAPO-20	0.37	0.37	0.23	---	---	---
310L SS	---	---	0.23	---	---	---
Tophet M	---	---	0.29	---	---	---
Carpenter 20	0.41	0.66	0.61	0.010	0.12	0.080
304L SS	0.43	0.78	0.82	0.10	0.20	0.30

(a) 1 l of PW-1 waste solution plus 406 ml of 14.6M H_3PO_4 and 168 g of $NaNO_3$ (1.98M Na, $\Sigma M_T/P=1.0$).

(b) 14.6 M H_3PO_4 ($\Sigma M_T/P = 1.0$).

(c) Carpenter 20 is a registered trademark of The Carpenter Steel Co. Haynes 25 and Hastelloy G are registered trademarks of Union Carbide Corp. Corronel 230 is a registered trademark of Henry Wiggins Co. Uranus SD was developed by Compagnie des Ateliers et Forges de la Loire. Tophet M alloy was developed by Wilbur B. Driver Research Laboratory. HAPO-20 alloy was developed by the Hanford Atomic Products Operation. Nionel is a registered trademark of the International Nickel Co. and is now available as Incoloy-825.

(d) Zircaloy-2 tests were made after construction of the WSEP denitrator-evaporator.

TABLE 7.2. *Corrosion Data for Denitrator-Evaporator Materials of Construction in PW-1 Phosphate Glass Concentrates(a)*

Material	Solution Temperature, °C	Exposure Time, hr	Corrosion Rate, in./yr		Type of Corrosion ^(b)	Source	
			Liquid	Vapor		Reference	Type
Titanium	133 ^(e)	19	0.060	0.016	u	20	Lab ^(c)
Titanium	140	24	0.056	---	u	21	Lab
Titanium	130	69	0.034	---	u	22	pp ^(d)
Titanium	138	88	0.013	---	u	23	pp
Titanium	136	280	0.10	0.008	u	23	Lab
304 SS	138	88	0.65	---	u	23	pp
304L SS	140	24	0.82	---	i	21	Lab
304L SS	130	69	0.084	---	---	22	pp
310L SS	140	24	0.23	0.15	i	21	Lab
347 SS	130	69	0.11	---	---	22	pp
Carpenter 20	140	24	0.61	---	i	21	Lab
Carpenter 20	138	88	0.62	---	i	23	pp
Nionel	140	24	0.42	---	i	21	Lab
Nionel	138	88	0.79	---	i	23	pp
Haynes 25	140	24	0.09	---	---	21	Lab
Haynes 25	136	185	0.10	0.056	---	23	Lab
Haynes 25	138	88	0.16	---	u	23	pp
Tantalum	137	280	0.0005	0.0002	u ^(f)	23	Lab
Tantalum	130	69	<0.001	---	---	22	pp

(a) 1 l of PW-1 waste solution plus 406 ml of 14.6M H_3PO_4 and 168 g of $NaNO_3$ (1.98M Na, $\Sigma M_T/P=1.0$).

(b) Corrosion by u=uniform attack; i = intergranular attack

(c) Laboratory corrosion tests.

(d) Pilot plant corrosion tests wherein corrosion coupons were installed in the BNL pilot plant denitrator-evaporator and exposed to normal processing conditions.

(e) PW-1 with fluoride: 1 l of PW-1 waste solution plus 420 ml of 14.6M H_3PO_4 and 208 g of $NaNO_3$ (2.45M Na) at a $\Sigma M_T/P=1.0$ including additives of 0.43M Fe, 0.50M Al and 0.10M HF.

(f) Tantalum has a low, uniform corrosion rate but it embrittles badly. (20)

FIGURE 7.4. Titanium Corrosion Rates in PW-1
Phosphate Glass Concentrates (20,21)

corrosion rates increase as the ratio of M/P decreases. At M/P ratios less than 1.0, corrosion rates increase very rapidly. The corrosion rates at temperatures above 130 °C may be somewhat low because of the protective action of the additional solids in the concentrated solutions at higher temperatures. The substitution of aluminum for the normal sodium additive in the PW-1 phosphate glass feed was found to reduce the titanium corrosion rate in the PW-1 phosphate glass concentrates, probably due to the formation of aluminum phosphate complexes.

Of all the metals tested to date, only platinum or high platinum alloys have shown the necessary corrosion resistance to molten phosphate glasses.⁽²⁵⁾ (See Table 7.3.) Platinum-5% gold alloy was the only platinum alloy tested that was as corrosion-resistant as pure platinum as shown in Figure 7.5. Platinum and its alloys are relatively weak at the temperatures for the melter, and potential creep failure must be considered in design. A platinum creep rate of about 1% in 1000 hours of operation at 1200 °C at 100 psi stress is predicted.^(26,31)

Platinum-0.5% rhodium alloy has lower creep rates than pure platinum by a factor of about 2,^(26,27) with an interpolated minimum sacrifice in corrosion resistance. These creep rate data are shown in Figure 7.6.

Many alternative materials have been studied for use in the phosphate glass melt formation step. Several of the best candidates including tantalum, Inconel 825, Carpenter 20, Hastelloys B and D, and stainless steel types 304 and 316 were tested in molten phosphate glass at temperatures up to 1100 °C.⁽²⁵⁾ These metals showed good corrosion resistance below 900 °C, but all the test coupons were totally destroyed

TABLE 7.3. Corrosion Data for the Melter Materials of Construction in Phosphate Glass Melts

Material	Melt	Temperature, °C	Exposure Time, hr	Corrosion Rate, in./yr		Source	
				Liquid	Vapor	Reference	Type
Platinum	PW-1 (a)	1100	48	0.003	---	20	Lab (b)
Platinum	PW-1	1000	24	<0.001	0.0036	29	Lab
Platinum	PW-1	1000	24	0.0014	<0.001	29	Lab
Platinum	PW-1	1100	24	<0.001	<0.001	29	Lab
Platinum	PW-2	1200	3000	<0.001	---	30	Lab
Platinum	PW-2	300	528	---	0.0024	32	Lab
Platinum	PW-2	1200	1000	<0.001	---	31	pp (c)
Platinum-5% Au	PW-2	1200	3000	<0.001	---	31	Lab
Platinum-5% Ir	PW-2	1200	3000	0.002	---	31	Lab
Platinum-5% Rh	PW-2	1200	3000	0.0075	---	31	Lab

(a) 1 l of PW-1 waste solution plus 420 ml of 14.6M H_3PO_4 and 208 g of $NaNO_3$ (2.45M Na) with 0.43M Fe, 0.50M Al, 0.10M HF additives with $\Sigma M_T/P=1.0$

(b) Laboratory corrosion tests

(c) Pilot plant corrosion tests

50X

Exposure Conditions: ~3000 Hours at 1200 °C (Reference 25)
FIGURE 7.5. Micrographs of Platinum Alloys in Phosphate Glass

FIGURE 7.6. Creep and Rupture Strength of Platinum and Platinum Alloys

within an hour above 1050 °C. A platinum coupon tested over the full temperature range and beyond with a total of 3000 hours at 1200 °C showed no sign of corrosion. Platinum can be corroded by the reaction of platinum, phosphorus and free metal. Platinum to stainless steel contact in the presence of phosphate glass melts can result in severe, localized intergranular attack of the platinum and embrittlement from the free phosphorus formed by reaction with the metals. The presence of as little as 30 ppm phosphorus in platinum reduces the high temperature strength by a factor of two.^(25,36) To date, stainless steels, molybdenum and Inconel as metal coupons or as powdered metal, have been shown to cause rapid intergranular corrosion of platinum and platinum alloys when added to the phosphate glass melts.⁽³⁸⁾ Consequently, it becomes quite important to keep metallic iron and iron alloys clear of those platinum parts which are exposed to phosphate glass melts. Specifically, these parts are the melter, the melter off-gas line, the melter feed line (reflux condenser and heat shield parts), and the melter weir and drain freeze-valve (and their heat shields). Figure 6.6 shows photographs of corrosion of platinum caused by free metal in phosphate glass.

While many ceramic materials have been scouted as possible substitutes for the expensive platinum melter, only alumina has shown good corrosion resistance to phosphate glass melts.⁽²⁸⁾ However, while several laboratory scale tests with alumina crucibles were satisfactory, the single pilot plant scale tests with an alumina melter confirmed that the poor resistance to thermal shock severely restricts their use as a phosphate glass melter. An alumina melter (5 inch diameter, 1/4 inch thick walls, and 6 feet long) cracked due to excessive thermal stresses after only 18 hours at normal phosphate glass processing conditions.^(2,25)

Platinum and to a lesser extent platinum alloys are attacked by a refluxing phosphoric acid solution which can occur in the melter off-gas line when there is an excess of phosphate (i.e. an M/P less than 1.0) in the phosphate glass feed. A maximum penetration rate of 0.02 inches/year was observed for the platinum-5% iridium melter off-gas line after 80 hours of WSEP operation.⁽⁹⁾ This corrosion rate is reduced to less than 0.0002 inches/year by heating the off-gas line (to about 300 °C) to prevent condensation of phosphoric acid.⁽³²⁾

Processing the melter off-gases and their condensates from sulfate-containing phosphate glass wastes requires special considerations for materials of construction. At present, essentially all of the sulfate, when present in the phosphate glass feed, is evolved with the melter off-gases. The acidic melter off-gases flow through the vapor piping and enter the melter condenser at about 400 °C. Platinum-5% iridium alloy and Nionel have shown the greatest resistance to corrosion by these sulfuric-nitric acid solutions as shown in Table 7.4. Consequently, the melter off-gas line in WSEP was made of platinum-5% iridium while the melter off-gas condenser was made of Nionel. Figure 7.7 is a micrograph of corrosion of platinum alloys by melter off-gas condensates.

Once in the melter condenser, the melter off-gases should be rapidly quenched (such as with a steam spray) to cool and dilute the vapors. A two-fold dilution of the sulfate-containing melter condensates reduced the corrosion rate for Nionel by a factor of 10. Data in Table 7.4 indicates that most stainless steels are adequate for storage of sulfuric acid solutions as long as the temperature of the solution is below about 40 °C.

TABLE 7.4. *Laboratory Corrosion Data for Materials Exposed to the Phosphate Glass Melter Vapors and Condensates*

Material	Solution	Solution Temperature, °C	Exposure Time, hr	Corrosion Rate, in./yr		Source	
				Liquid	Vapor	Reference	Type
Pt	PW-1 Melt Vapors (M/P=0.56)	~400 ^(a)	24	----	0.0036	29	Lab
Pt	PW-1 Melt Vapors (M/P=1.0)	~400 ^(a)	24	----	<0.002	29	Lab
Pt	0.8M HNO ₃ -2M H ₂ SO ₄ -0.25M H ₃ PO ₄	300	528	0.0035	0.0024	32	Lab
Pt-5% Ir	0.8M HNO ₃ -2M H ₂ SO ₄ -0.25M H ₃ PO ₄	240	216	0.0002	0.0001	32	Lab
Pt-3 1/2% Rh	0.8M HNO ₃ -2M H ₂ SO ₄ -0.25M H ₃ PO ₄	300	528	0.0004	.0004	32	Lab
Pt-5% Rh	0.8M HNO ₃ -2M H ₂ SO ₄ -0.25M H ₃ PO ₄	300	528	0.0004	0.0012	32	Lab
Pt-10% Rh	0.8M HNO ₃ -2M H ₂ SO ₄ -0.25M H ₃ PO ₄	300	528	0.0046	0.0024	32	Lab
Nionel	PW-2 Melter Vapors	~400 ^(a)	14	----	0.03	29	Lab
Nionel	10M HNO ₃ -5M H ₂ SO ₄ -0.1M H ₃ PO ₄	~110 ^(b)	24	0.03	----	29, 20	Lab
Nionel	5M HNO ₃ -2.5M H ₂ SO ₄ -0.05M H ₃ PO ₄	~110	24	0.002	----	29, 20	Lab
Nionel	10M HNO ₃ -2.5M H ₂ SO ₄ -0.1M H ₃ PO ₄	~110	24	0.013	----	29, 20	Lab
Nionel	5M HNO ₃ -5M H ₂ SO ₄ -0.1M H ₃ PO ₄	~110	24	0.013	----	29, 20	Lab
Nionel	PW-2 Melter Condensate ^(c)	~110	100	0.002	----	21	Lab
Nionel	PW-2 Melter Condensate ^(d)	~110	100	0.001	----	21	Lab
Nionel	2.5M HNO ₃ -5M H ₂ SO ₄ -0.2M H ₃ PO ₄	~110	240	0.002	0.006	29, 20	Lab
Nionel	0.5M HNO ₃ -1M H ₂ SO ₄ -0.04M H ₃ PO ₄	~110	240	<0.001	<0.001	29, 20	Lab
304L SS	PW-2 Melter Condensate ^(c)	~110	100	0.008	----	21	Lab
304L SS	PW-2 Melter Condensate ^(d)	~110	100	0.001	----	21	Lab
304L SS	PW-2 Melter Condensate ^(c,d)	60	100	0.0002	----	21	Lab
Titanium	2M HNO ₃ -4M H ₂ SO ₄ -0.2M H ₃ PO ₄	~110	240	0.066	0.0005	20	Lab
Zircaloy-2	2M HNO ₃ -4M H ₂ SO ₄ -0.2M H ₃ PO ₄	~110	240	0.0001	0.0001	20	Lab
Carpenter 20Cb3	10M HNO ₃ -5M H ₂ SO ₄ -0.1M H ₃ PO ₄	~110	24	0.053	----	29, 20	Lab

(a) The temperature of the melter vapors ranged from 300 to 450 °C.

(b) The corrosion coupons were submerged in boiling melter condensate with the composition shown above.

(c) Melter condensate from the WSEP Design Verification Test, Run CPG-6 (nonradioactive) was collected during the period with a steam spray addition to the melter off-gas condenser (E-117). The diluted melter-condensate was used to perform laboratory corrosion tests with Nionel and 304L stainless steel coupons.

(d) Melter condensate from the WSEP Run CPG-6 (Cold Phosphate Glass No.6) was collected without the steam spray addition for laboratory corrosion tests.

FIGURE 7.7. Micrographs of Platinum Alloys in Melter Off-Gas Condensate

Candidate construction materials for the melter condensate vacuum distillation equipment for treating sulfate-containing phosphate glass melter condensate were evaluated. (33,34,35) (See Section 7.2.6.) Even though the evaporator and its immediate vapor and condensate handling system are operated at a vacuum to significantly reduce the operating temperature, the corrosion rate on many acid-resistant materials is severe. Based on the corrosion data given in Table 7.5, tantalum was recommended for the vacuum distillation unit and is used for the demonstration vacuum distillation unit in WSEP.

Candidate construction materials for receiving and storing phosphate glasses are discussed in Section 8. In general, the corrosivity of phosphate glass is significantly less than the corrosivity of air (oxidation).

7.2.4 Process Capacity

The denitrator-evaporator capacity is primarily dependent on the turbulence and viscosity of the solution. The short tube calandria used in WSEP is not notably an evaporator with high heat transfer rates, but it is moderately suited for viscous materials with relatively high undissolved solids content provided the solids are not too dense. The WSEP denitrator-evaporator is capable of boil-off rates greater than 50 liters/hr.

Performance of the phosphate glass denitrator-evaporator in WSEP with radioactive feed was best when the boiling point range for PW-1 waste solution was 130 to 133 °C and for PW-2 was 135 to 137 °C. These preferred solution temperatures are conservatively based on viscosity, density, and

TABLE 7.5. *Corrosion Data for Materials Exposed to PW-2 Phosphate Glass Melter Condensate during Distillation*

Material	Solution	Solution Temperature, °C	Exposure Time, hr	Corrosion Rate, in./yr		Reference	Source Type
				Liquid	Vapor		
Tantalum	1M HNO ₃ -5M H ₂ SO ₄ -0.2M H ₃ PO ₄	110 to 240	8	0.005	-----	33, 35	pp (a)
Tantalum	0.3M HNO ₃ -0.4M H ₂ SO ₄ -0.1M H ₃ PO ₄	27 to 356	6	0.002	-----	34	pp
Tantalum	15.4M H ₂ SO ₄	150	4	0.0002	-----	35	Lab (b)
Tantalum	15.4M H ₂ SO ₄	220	4	0.002	-----	35	Lab
Gold	15.4M H ₂ SO ₄	220	4	0.00004	-----	35	Lab
Platinum	15.4M H ₂ SO ₄	220	4	0.00005	-----	35	Lab
Platinum	17.4M H ₂ SO ₄	250	200	0.0036	<0.001	38	Lab
Platinum	14.6M H ₃ PO ₄	500	200	0.0012	0.0012	38	Lab
Illium G	15.4M H ₂ SO ₄	150	4	0.37	-----	35	Lab
Illium 98	15.4M H ₂ SO ₄	150	4	0.72	-----	35	Lab
Lead	15.4M H ₂ SO ₄	220	4	2.68	-----	35	Lab

(a) *Pilot plant data for coupons installed in the BNL vacuum distillation evaporator.*

(b) *Laboratory data for coupons installed in the bench scale vacuum distillation evaporator at BNL.*

percent denitration as discussed in Section 7.2.1. If the solution temperature exceeds 135 °C for a PW-1 flowsheet, plugging of pipes and dip tubes with granular solids may occur. No difficulties should occur with PW-2 solutions at temperatures up to 145 °C.

The capacity of the melter is dependent on variables affecting the heat-transfer rate from the furnace to melt. This heat-transfer rate depends on available temperature gradient and the emissivity of platinum at 1200 °C which is approximately 0.15. This low emissivity requires a relatively high temperature gradient from a radiant heat supply to the platinum melter. Surface treatment of platinum can theoretically increase its emissivity to about 0.5. The melt viscosity and melt circulation rates are dependent on the specific glass composition and outgassing properties of melting materials at operating temperature. The sulfate evolution from sulfate-containing PW-2 wastes causes improved circulation in the melter compared to PW-1 wastes, thereby increasing the melter feed processing capacity. The capacity of the WSEP melter is about 2.5 liters/hr of concentrated feed (about 1.0 liter/hr glass production). The melter used in the nonradioactive pilot plant at BNL has a similar heat transfer area, but the melt capacity is about double this value.⁽⁸⁾ Addition of gas purging through the melt helps increase the circulation in the melter somewhat, but it does not appear to increase capacity. This feed rate is equivalent to steady-state processing rates of 0.2 to 0.3 tonnes/day for PW-1 waste and 0.4 to 0.6 tonnes/day for PW-2 waste (as shown during the first six WSEP radioactive runs).⁽⁷⁾ The higher value for PW-2 is more representative of PW-2 waste.

7.2.5 Process Flowsheets

Data from WSEP have been used to project typical flowsheets for processing both PW-1 and PW-2 wastes. Flowsheets for these wastes based upon WSEP experience are shown in Figures 7.8 and 7.9. Disposition of melter condensates which contain sulfate during processing of sulfate-containing PW-2 waste is discussed in Section 7.3.

Foaming in the denitrator-evaporator adversely affects the operation of the denitrator and in feeding the melter. Therefore, since foaming agents are expected to be present in the waste, antifoam is required (see Section 7.2.1).

The PW-1 waste solution had undesirable properties which can cause plugging of pipes and dip tubes and make it difficult to feed the melter. More development is presently being done at BNL to improve the characteristics of PW-1 waste concentrates.

7.2.6 Sulfate-Containing Melter Condensate

The melter condensate from the phosphate glass solidification process is an intermediate-level waste stream and requires further treatment for disposal (or reuse). Melter condensates from processing of sulfate-free waste from the phosphate glass process can be simply treated by recycling back to the denitrator-evaporator or back to the acid recovery system of the fuel reprocessing plant. The melter condensate from sulfate-containing waste, however, contains greater than 98% of the sulfate in the original waste.⁽⁷⁾ This sulfate cannot be reused in fuel reprocessing without very extensive decontamination, and therefore would probably be disposed of by some other means.

BASIS: Plant to solidify equivalent waste at 378.5 liters/tonne from reprocessing power reactor fuel at an exposure of 20,000 MWd/tonne at 15 MW/tonne

NOTES: (a) Stream descriptions are in text
 (b) ΣEM_t^+ = Total salt content as metal equivalents
 (c) Fission product heat rate
 (d) Time from start of processing
 (e) Steady state processing rate equivalent to tonne of fuel
 (f) Fuel out of reactor 0.2 years
 V = Vapor, L = Liquid, S = Solid

B'CH = Batch

	Stream Number (a)									
	1	2	3	4	5	6	7	8	9	10
Phase	L	L	L	L	S	L	L	L	L	V
Na, M	0.138	3.95	1.6	-----	10.4	5.6	-----	-----	-----	-----
Fe + Cr	0.942	-----	0.58	-----	3.76	2.03	-----	-----	-----	-----
Al	0.001	-----	-----	-----	-----	-----	-----	-----	-----	-----
Li	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
NO ₃	7.5	3.95	6.15	6.0	-----	4.33	5.2	-----	1.7	-----
SO ₄	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
PO ₄	-----	10.3	3.94	-----	25.5	11.1	-----	-----	-----	-----
Others	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
ΣM_t^{chem}	3.03	-----	3.38	-----	21.9	9.52	-----	-----	-----	-----
ΣM_t^{fp}	0.91	-----	0.56	-----	3.63	1.58	-----	-----	-----	-----
$\Sigma EM_t^{\text{total}} (b)$	3.94	-----	3.94	-----	25.5	11.1	-----	-----	-----	-----
% Ru-106	100	-----	100	-----	95	99	<1	-----	4.0	-----
% Ce-Pr-144	100	-----	100	-----	99.7	99.9	<0.1	-----	0.2	-----
% Sr-90	100	-----	100	-----	99.7	99.9	<0.1	-----	0.2	-----
ℓ/tonne	378	-----	612	-----	95	216	658	-----	554	-----
Volume per pot, ℓ	240	148	388	84	60	137.5	418	84	352	275
Flow, ℓ/hr avg	B'CH	B'CH	7.1	1.5	1.1	2.5	7.6	1.5	6.4	5.0
Density, kg/ℓ	1.37	-----	1.37	1.19	2.8	1.8	1.2	-----	1.06	1.0
$\beta + \gamma$, kCi/ℓ (f)	7.9	-----	4.9	-----	31.4	13.8	-----	-----	-----	-----
Heat rate per 8-in. diam pot, kW (c)	11.8	-----	11.8	-----	11.7	11.7	-----	-----	-----	-----
Time, hr (d)	-----	-----	55	55	55	55	55	55	55	55
Processing rate, tonne/day (e)	-----	-----	-----	-----	0.28	-----	-----	-----	-----	-----

FIGURE 7.8. Phosphate Glass Solidification Flowsheet for Sulfate-Free PW-1 Waste

BASIS: Plant to solidify equivalent waste at 378.5 liters/tonne from reprocessing power reactor fuel at an exposure of 20,000 MWd/tonne at 15 MW/tonne

NOTES: (a) Stream descriptions are in text
 (b) ΣEM_t^+ = Total salt content as metal equivalents
 (c) Fission product heat rate
 (d) Time from start of processing
 (e) Steady state processing rate equivalent to tonne of fuel
 (f) Fuel out of reactor 0.5 years
 V = Vapor, L = Liquid, S = Solid
 B'CH = Batch

	Stream Number (a)									
	1	2	3	4	5	6	7	8	9	10
Phase	L	L	L	L	S	L	L	L	L	V
Na, M	0.93	----	0.78	-----	6.98	2.12	-----	-----	-----	-----
Fe + Cr	0.46	----	0.39	-----	3.45	1.06	-----	-----	-----	-----
Al	0.001	----	-----	-----	-----	-----	-----	-----	-----	-----
Li	-----	----	-----	-----	-----	-----	-----	-----	-----	-----
NO ₃	5.37	----	4.51	6.0	-----	1.49	3.52	-----	0.56	-----
SO ₄	0.87	----	0.73	-----	-----	1.70	0.08	-----	0.65	-----
PO ₄	-----	13.3	2.80	-----	25.0	7.63	-----	-----	-----	-----
Others	-----	----	-----	-----	-----	-----	-----	-----	-----	-----
$\Sigma EM_t^{\text{chem}}$	2.42	----	2.03	-----	-----	-----	-----	-----	-----	-----
ΣEM_t^{fp}	0.91	----	0.76	-----	-----	-----	-----	-----	-----	-----
$\Sigma EM_t^{\text{total (b)}}$	3.33	----	2.80	-----	-----	-----	-----	-----	-----	-----
% Ru-106	100	----	100	-----	97	99	<1	-----	2.0	-----
% Ce-Pr-144	100	----	100	-----	99.7	99.9	<0.1	-----	0.2	-----
% Sr-90	100	----	100	-----	99.7	99.9	<0.1	-----	0.2	-----
ℓ/tonne	378	----	450	-----	45	165	478	-----	435	-----
Volume per pot, ℓ	504	96	600	101	60	168	637	101	442	335
Flow, ℓ/hr avg	B'CH	B'CH	9.0	1.5	0.9	2.5	9.5	1.5	66	5.0
Density, kg/ℓ	1.36	----	1.45	1.03	2.7	1.80	1.18	-----	1.0	1.0
$\beta + \gamma$, kCi/ℓ (b)	4.49	----	3.59	-----	37.8	10.3	-----	-----	-----	-----
Heat rate per 8-in. diam pot, kW (c)	10.8	----	10.8	-----	10.7	10.7	-----	-----	-----	-----
Time, hr (d)	-----	----	67	67	67	67	67	67	67	67
Processing rate, tonne/day (e)	-----	----	-----	-----	0.48	-----	-----	-----	-----	-----

FIGURE 7.9. Phosphate Glass Solidification Flowsheet for Sulfate-Containing PW-2 Waste

Description of pertinent flowsheet streams for Figures 7.8 and 7.9 are as follows:

<u>Stream</u>	<u>Description</u>
1	Incoming waste from processing power reactor fuel irradiated at 20,000 MWd/tonne at a power level of 15 MW/tonne
2	Nonradioactive chemical additives
3	Feed to process: See Section 7.2.4 for process capacities
4	Nitric acid sprayed onto tube bundle to prevent scaling
5	Final product
6	Denitrator-Evaporator concentrate
7	Off-gases and aqueous effluents to acid recovery system for processing
8	Antifoam is added when foaming agents are present in waste
9	Melter condensate recycled back to process or to acid recovery system if sulfate is not present. If sulfate is present it must be reprocessed as discussed in Section 7.2.6.
10	Steam is sprayed into melter condenser to dilute incoming vapors when sulfate is present in the waste since concentrated sulfate condensate is very corrosive.

Several potentially applicable methods for cleanup and/or disposal of sulfate-containing melter condensate were evaluated.^(14,24) Among these were scavenging, precipitation, distillation, sulfate precipitation, crystallization, incorporation into asphalt or cement, reduction to gaseous sulfur oxides, ion exchange, and sulfate melts. Vacuum distillation^(14,24) of the condensate to provide sufficient decontamination to permit incorporation of the decontaminated sulfate into asphalt^(36,37) for final disposal is believed to have the most promise.

Although the reduction of SO_3 to SO_2 offered a direct means of decontaminating and disposing of the sulfate component, the reduction step had the disadvantage of requiring temperatures above 1000 °C. In addition, because sulfur dioxide is an important air pollutant, and because a possible explosive condition might develop, other methods were investigated.

During vacuum batch distillation, water, nitric acid, and sulfuric acid are sequentially distilled, leaving a residue of phosphoric acid and fission products and other salts. The vapors evolved are condensed and collected as a water and nitric acid fraction and a sulfuric acid fraction. Since the boiling point of the sulfuric acid is very high, even under vacuum, substantially all water and nitric acid are removed first and collected before the sulfuric acid is distilled to its receiving tank.

A reduction in the absolute pressure to about 30 Torr, (which reduces the boiling point of the melter condensate) resulted in ruthenium decontamination factors of about 10^3 for composition A in Table 7.6.⁽¹⁴⁾ Higher vacuums (i.e. lower

TABLE 7.6. *PW-2 Melter Condensate Composition for Vacuum Distillation Runs at BNL*

	Composition A,	Composition B, (a)
	<u>M</u>	<u>M</u>
NO ₃	1.04	1.0
SO ₄	5.45	1.1
PO ₄	0.19	0.2
Ru	0.0067	0.0032

(a) *BNW estimated PW-2 melter condensate composition.*

boiling points) were generally required to obtain similar decontamination factors with a melter condensate of composition B in Table 7.6. A decontamination factor of about 200 (to a final radionuclide concentration of 1 Ci/liter) is required to permit incorporation of the sulfate fraction into asphalt. The variation in ruthenium decontamination with respect to distillation pressure is shown in Figure 7.10.⁽¹⁴⁾ Redistillation of the sulfate component yields a further ruthenium decontamination factor of 10^4 . Thus, with two successive distillations, the overall ruthenium decontamination factor could be as high as 10^7 . Volume reductions from 20 to 50 can be achieved with the separation efficiency increasing with lower boiling temperatures and lower distillation rates.^(14,41,42) However, some evidence shows that higher distillation rates result in increased ruthenium decontamination factors.⁽¹⁴⁾

Demonstration of vacuum distillation of actual sulfate-containing condensates from phosphate glass processing in WSEP is currently planned in engineering scale equipment.⁽⁴¹⁾ No work is currently planned for the demonstration of incorporation into asphalt.

FIGURE 7.10

Distillation Pressure Effects on Decontamination of Sulfate-Containing Melter Condensates

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CONTENTS8.0 CHARACTERISTICS AND STORAGE OF SOLIDIFIED WASTE

(by R. J. Thompson, J. E. Mendel, and K. J. Schneider)

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8.0 CHARACTERISTICS AND STORAGE OF SOLIDIFIED WASTE

(by R. J. Thompson, J. E. Mendel, and K. J. Schneider)

8.1 GENERAL INFORMATION

The desired characteristics for solidified waste are obvious: high thermal conductivity, low leachability, low dispersibility, low friability, low porosity, high resistance to thermal shock, coefficient of expansion to match that of the container, minimum volume, minimum cost, good chemical stability, good radiation resistance, and low corrosivity. The ideal characteristics of the storage environment are: good capability for heat dissipation or absorption, good shielding for nuclear radiation, and high integrity for preventing escape of radionuclides into man's environment for very long time periods. However, no one solid waste product or disposal scheme will be ideal, and combinations of more or less desirable characteristics will be exhibited by all solidified wastes and disposal schemes. One of the basic purposes of the AEC's waste solidification development programs is to provide fundamental information that will lead to sound solidification and storage principles.

Prime consideration must be given to the safety and health of the general populace by effectively minimizing release of radionuclides to man's environment. Potential release and release mechanisms bear directly on the form of the solidified waste, storage environment, container integrity, and retrievability, of the waste. Solidified waste characteristics such as dispersibility, chemical and radiation stability, and corrosiveness bear directly on safety considerations during transport and storage. It is significant that the high-level waste must be held for 500 to 1000 years to permit the fission products to decay to nontoxic levels and must be held for about 500,000 years to permit the plutonium present to decay to

nontoxic levels. These extremely long time requirements for controlled storage are almost incomprehensible when compared to modern, sophisticated materials technology which is concerned with about a few decades. The changes that will occur in civilization, technology, and even geology during these storage times are most unpredictable, but yet must be considered in ultimate disposal schemes.

Closely associated to safety considerations are the economics and the technology of solidification and storage. It is imperative that the cost of storage and solidification be optimized within the framework of safety considerations. Obviously, the technology is closely related to economics and safety. Factors such as thermal conductivity, corrosivity, chemical and radiation stability, solubility, dispersibility, and mechanical integrity will determine the economics and technology of solidification and storage of high level wastes.

One unresolved concern in the ultimate disposal of radioactive wastes is that of desired waste characteristics and storage system versus retrievability of the waste. Since wastes must truly be kept under control "forever", allowance should be made for the uncertainty of nature and man and his technology over the long time period of concern. Therefore, provisions for retrieving the waste may be desirable for potential reprocessing for various reasons, or because the storage vault is "worn out". When ready retrievability is provided, the solidified waste package may be permitted to have somewhat less desirable characteristics compared to those of a solidified waste package with better integrity in a poorly retrievable storage system. Comparable safety may likely be provided in either case.

Several potential storage techniques are under study to determine their applicability for high-level wastes. These

techniques involve the use of mausoleums or man-made storage vaults, salt mines (studied by ORNL),⁽¹⁾ and the deep rock disposal (studied by SRL).⁽²⁾ The salt mine and deep rock concepts are based on permanent disposal in stable geological formations. The economics, technology, and safety of each concept will ultimately determine the concept's suitability for waste disposal.

Table 8.1 gives a summary of approximate physical properties for the products from the four solidification processes developed in the United States: the pot calciner, spray solidifier, phosphate glass solidifier, and fluidized bed calciner. Values presented in Table 8.1 point out the order of magnitude of physical properties of the solidified products from Purex wastes. More specific values can be quoted for specific cases.

The heat generated by the decay of fission products in high-level wastes necessitates special design of the solidification processes and the storage conditions. In the BNW waste solidification program, the following limitations were imposed for interim storage conditions. These restrictions are expected to be similar to those required initially in commercial applications.

- Maximum temperature of the solidified waste (in the center of a pot) when cooled by natural air convection is 900 °C.
- Maximum temperature of the wall of the pot containing solidified waste when cooled by natural air convection is 427 °C.
- Minimum thickness of the frozen wall of a solidified waste melt is one half of the radius of the pot when cooled by natural air convection.

These limitations have been imposed to assure safe operating conditions in WSEP. The integrity of the waste container from internal and external corrosion was the main consideration in

TABLE 8.1. Approximate Characteristics of Solidified High Level Waste

Form Description	Pot Calcine		Spray Melt		Phosphate Glass		Fluidized Bed	
	Calcine Cake	Scale	Monolithic	Microcrystalline (a)	Monolithic	Glass	Granular	Amorphous (b)
Chemical Composition, mole %								
Fission product oxides	15 to ~80		5 to 30		5 to 25		5 to 50 (c)	
Inert metal oxides	10 to 50		40 to 50		10 to 30		10 to >90	
Sulfur oxides (if in waste)	0 to 40		0 to 40		0		0 to 40	
Phosphorous oxides	~0		25 to 40		~60		~0	
Bulk Density, g/ml	1.0 to 1.5		2.6 to 3.3		2.6 to 3.0		1.0 to 1.7	
Thermal Conductivity, W/(m) (°C)	0.30 to 0.44		1.3 to 1.7		0.84 to 1.3		0.17 to 0.43	
Maximum Heat, W/liter solid (d)	85		205		190		70	
Leachability in Cold Water, g/(cm ²) (day)	1.0 to 10 ⁻¹		10 ⁻³ to 10 ⁻⁵		10 ⁻⁴ to 10 ⁻⁶		1.0 to 10 ⁻¹	
Hardness	Soft		Hard		Very Hard		<Hard	
Friability	Crumbly		Tough		Brittle		Moderate	
Residual Nitrate, wt% of Product	<0.05		<0.005		<0.005		<4.0	
Volume, liters/1000 MWd _t	1 to 2.5		1.2 to 3		1.5 to 5		--	
Maximum Stable Temperature, °C	~900		Phase separation at ~900 (e)		Devitrifies at ~500			
Container Material	SS		MS or SS		MS or SS		--	

a. Glassy products can also be made with some difficulty.

b. Microcrystalline products can also be made.

c. Composition ranges for fluid bed are also for Purex waste and are estimated.

d. Approximate values for storage in air in 8 in. diameter cylindrical pots maintain pot centerline temperatures less than 900 °C and pot wall temperatures less than 425 °C. Average k values were used.

e. With sulfate present, phase separation occurs at approximately 700 °C.

establishing these limits. Sections 8.2.2 and 8.2.5 discuss in detail the factors that influence the limits. Higher heat inputs are possible if water cooling is substituted for natural air convection cooling. The limits imposed in the waste solidification demonstration program will be studied in the program to determine if they are more or less restrictive than those required for ultimate industrial practice.

8.2 CHARACTERISTICS OF SOLIDIFIED WASTE

8.2.1 Leachability

The ideal solidified waste would release less than Maximum Permissible Concentration (MPC) levels of fission products when the solid is brought into contact with water. Such a waste would provide the ultimate in safe control of contamination of man's water supplies. The least soluble of the solidified wastes have leachability rates about one million times lower than those of liquid wastes. Even so, the actual attainable solids are far from ideal.

Figure 8.1 shows typical leachability in recirculating and replenished cold water for the phosphate glass solidifier and spray solidifier products. In general, a steady-state leachability is attained after 6 to 8 weeks of leaching. The phosphate glass product from PW-1 waste is approximately 20 times less leachable than the comparable spray solidifier product. However, upon devitrification of the phosphate glass, leach rates of the two products were comparable. Figure 8.1 shows that there is reasonable agreement between spray solidifier product leachability for nonradioactive engineering laboratory and radioactive engineering scale tests. The difference between sodium and cesium leach rates appears to be small for spray solidifier

FIGURE 8.1. *Leachability Comparison for Spray and Phosphate Glass Solidified Waste*

PW-1 product. For comparison purposes, the approximate leachability of Pyrex glass is 5×10^{-8} g/(cm²)(day) for boiling water in 6 to 8 hour tests.⁽³⁾

Leachability of (undevitrified) phosphate glass solidified waste from sulfate-free (PW-1) and sulfate-bearing (PW-2) wastes are quite similar. The steady-state leach rate for cesium-137 was found experimentally to be 9×10^{-7} g/(cm²)(day) and 1×10^{-6} g/(cm²)(day) for PW-1 and PW-2 wastes, respectively. These data are typical of "grab" samples from radioactive engineering-scale tests.⁽⁴⁾ Leachability measurements for isotopes other than sodium and cesium are underway in waste solidification demonstration program. Experiments on phosphate glass PW-2 solid has shown, for example, that the cerium leachability is approximately one order of magnitude lower than cesium.

Nonradioactive studies of leachability of the products from all three solidification processes is being carried out at this time. A series of nonradioactive laboratory studies designed to determine the effects of time of processing, product cooling rate, storage temperature, and processing temperature on phosphate glass product, spray solidifier product, and pot calciner product are underway in the waste solidification program. Three wastes are being studied: sulfate-free (PW-1), sulfate-bearing (PW-2), and "clean" wastes (PW-4). (See Tables 2.3 and 2.4 for waste compositions.)

Table 8.2 shows the first results of leachability studies from the nonradioactive laboratory work. The leachability measurements are based on accelerated tests on crushed solid particles between 250 and 350 micrometers proposed by Barton.⁽³⁾ The results are reported in weight percent of product loss after 24 hours in boiling water. No replicates are available for

TABLE 8.2. *Accelerated Laboratory Measurements of Leach Rates of Nonradioactive PW-2 Phosphate Glass (Conditions: Boiling water for 24 hours)*

Glass Forming Process Temperature, °C	Time at Process Temperature, hr	Cooling Rate, °C/hr	Storage Temperature for 8 Weeks, °C	Form of Product	Solubility in Boiling Water, wt%
1000	1	30	100	Glassy	5.6
1000	1	100	100	Glassy	4.5
1000	25	30	100	Glassy	5.1
1000	25	100	100	Glassy	1.5
1000	1	30	600	Devitrified	41.4
1000	1	100	600	Devitrified	33.8
1000	25	30	600	Devitrified	39.3
1000	25	100	600	Devitrified	35.9
1200	1	30	600	Glassy	1.9
1200	1	100	600	Devitrified	41.4
1200	25	30	600	Glassy	7.4
1200	25	100	600	Devitrified	35.3
1200	1	30	100	Glassy	1.2
1200	1	100	100	Glassy	1.4
1200	25	30	100	Glassy	1.6
1200	25	100	100	Glassy	2.2

a complete analysis. However, samples stored at 600 °C where devitrification occurs are approximately 10 times more soluble than those stored at 100 °C. No relationship between the accelerated solubility test of Barton and the slow (6 to 8 week) cold water leachability tests from the waste solidification program are available at this time.

No leachability data are available on pot calciner product from the WSEP product evaluation work. However, previous tests have shown pot calciner product to be much more soluble than either phosphate glass or spray solidifier product.

8.2.2 Thermal Conductivity

Thermal conductivity of the solidified high level waste will be a major factor in determining the heat that can be put into a waste container. Therefore, detailed information has been and is being gathered on the effective thermal conductivity of engineering-scale radioactive products and on the thermal conductivity of laboratory nonradioactive samples.

Table 8.3 lists the effective thermal conductivities of the solidified wastes produced by the radioactive engineering-scale tests. These effective conductivities are calculated from pot heat content determined calorimetrically, and from centerline and wall thermocouple readings for the pots.

Figure 8.2 shows thermal conductivities of various calcines and glasses produced in the solidification processes. Thermal conductivities of at least 0.2 W/(m)(°C) are desirable for heat dissipation from stored calcine waste. Ceramics and glasses have thermal conductivities considerably higher than those of calcine and are in the order of 1 to 2 W/(m)(°C) as noted.

TABLE 8.3. *Effective Thermal Conductivity
of WSEP Radioactive Solidified Wastes*

<u>Solidified Waste</u>	<u>WSEP Run Number</u>	<u>Pot Temperature, °C</u>		<u>k_{eff}, W/(m) (°C)</u>
		<u>Centerline</u>	<u>Wall</u>	
Pot Calcine	1	140	70	0.41
	2	485	250	0.35
	3	410	190	0.35
	4	477	165	0.44
	5	725	230	0.41
	6	940	240	0.30
Phosphate Glass	1	315	225	1.0
	2	355	220	0.94
	3	655	400	0.98
	4	510	335	0.94
	5	710	350	1.1
	6	780	400	1.1
Spray Solid	1	170	140	1.5
	2	315	250	1.7
	3	318	227	1.3
	4	505	285	1.1
	5	633	355	1.2
	6	767	459	1.4
	7	930	480	1.2

a. To convert $W/(m)(^{\circ}C)$ to $Btu/(hr)(ft^2)(^{\circ}F/ft)$
multiply by 0.57833.

The thermal conductivity of nonradioactive laboratory samples is being studied based on the same process variables as the leachability tests, process feed type, process temperature, time of processing, cooling rate, and storage temperatures. Table 8.4 shows the thermal conductivity of three phosphate glass PW-2 products as a function of temperature for various processing parameters. In general, storage temperature appears to be the most important variable. The devitrified material appears to have about 25% higher thermal conductivity. Devitrification was observed for samples stored at 600 °C.

a. $1.73 W/(m)(^{\circ}C) = 1 Btu/(m)(ft^2)(^{\circ}F/ft)$

FIGURE 8.2. Thermal Conductivity of Various Materials

Good thermal conductivity is obviously desired to remove the heat of radioactive decay from the outer wall of the solidified waste with a minimum temperature rise to the center of the waste.

TABLE 8.4. Thermal Conductivity of Phosphate Glass PW-2 Laboratory Solidified Waste

Glass Forming Process Temperature, °C	Time at Process Temperature, hr	Cooling Rate, °C/hr	Storage Temp for 8 Weeks, °C	Form of Product	Sample Temp, °C	k, W/(m)(°C)
1000	1	30	100	Devitrified	75	0.82
					125	0.84
					175	0.78
					225	0.84
					275	0.86
					325	1.02
					375	1.09
1200	1	30	100	Glassy	75	0.64
					125	0.72
					175	0.69
					225	0.73
					275	0.69
					325	0.82
					375	0.81
1200	1	30	600	Devitrified	75	0.82
					125	0.80
					175	0.80
					225	0.86
					275	0.89
					325	0.90
					375	1.09

The temperature difference from the center to the wall of a solid cylinder of self-generating heat varies as:

$$\Delta T \propto \frac{1}{k} \cdot Q \cdot r^2 \text{ where } \Delta T = \text{temperature difference}$$

k = thermal conductivity
Q = heat rate/unit volume
r = radius of cylinder.

A lower thermal conductivity will linearly increase the temperature at the center of a given pot, or will reduce the amount of self-generating heat that can be included in a pot, or will reduce the allowable size of a pot. The net effect of lower thermal conductivity is to reduce the amount of allowable heat stored in a pot. In addition, this limitation can result in undesirable increases in the amount of time that liquid waste must be stored before solidification, or it increases the minimum volumes for solidified wastes. These effects are summarized in Figure 8.3 for values that are typical for wastes from thermal reactors. The heat content of wastes from future fast reactors can be 5 times those in Figure 8.3 for the first few years.

In the WSEP processing cell, the heat input to a given container is largely limited by the product thermal conductivity. A temperature limit of 900 °C centerline and a molten core radius of one-half the pot radius have been established as operating limits for B-cell. These limits and the pot wall temperature limits (discussed in Section 8.2.5) establish cell operating conditions for the WSEP program.

8.2.3 Dispersibility

A special test has been devised by BNW to determine solidified waste dispersibility.⁽⁵⁾ A standard blunt-end weight (2.9 pounds)

FIGURE 8.3. Effects on Heat Removal from Solidified Waste Pots

is used to crush a 1.0 inch diameter by 0.5 inch long cylindrical sample. The drop height of the weight is 5 feet onto the sample. The resulting particles are sieved and classified as to weight and size. Table 8.5 gives typical results from tests on non-radioactive laboratory samples of phosphate glass PW-2 solids. The data will be used to estimate the fraction of the product that could be released under accident conditions. Data on spray solidifier and pot calciner are not available. In the case of phosphate glass melt, the fraction of particles less than 0.02 inches is significantly less for crystalline material than for

glassy material. The crystalline phosphate glass material appears to be the more desirable form with respect to dispersibility.

TABLE 8.5. *Typical Particle Size Distribution from Dispersibility Tests on PW-2 Phosphate Glass Product*

Sample No.	%wt < 0.02, in.	0.02 < %wt < 0.1, in.	%wt > 0.1, in.	Product Form
7	1	2	97	Devitrified
9	2	1	97	Devitrified
14	18	31	51	Glassy
17	18	30	52	Glassy

NOTE: 0.02 inches is 510 micrometers

8.2.4 Linear Coefficient of Thermal Expansion

The linear coefficient of thermal expansion (LCTE) has been measured for several laboratory samples of phosphate glass PW-2 product. The LCTE values ranged from approximately 2 to 14×10^{-6} cm/(cm)(°C).⁽⁵⁾ No particular difficulties in differential expansion of product and pot material (mild steel and stainless steel) are foreseen for this product. Additional data on pot calciner and spray solidifier are being collected.

Previous studies by DeMier^(6,7) showed that no particular problems should result from differential thermal expansion of the container and melt products. However, continued exposure to thermal cycles (50 to 100) could cause fractures due to low cycle fatigue.

Since the pot calcine is relatively porous, soft, and crumbly no differential expansion problems are expected.

8.2.5 Other Properties

Table 8.6 gives a summary of bulk density measurements on radioactive solidified wastes that are available from WSEP Program and its product evaluation program.

Phosphate glass and spray solidified solids are considerably more dense than pot calciner product. Spray solidified solids are slightly more dense than the phosphate glass.

The spray solidifier product has the lowest specific volume of the three processes for the PW-1 wastes. For sulfate-containing PW-2 waste, the specific volumes for the phosphate glass and pot calcine are similarly low, but an extra effluent stream is evolved from the phosphate glass process which requires special treatment and disposal. In general, the pot calcine will have the smallest volume for cleaner wastes.

Crystallinity measurements of WSEP solidified waste will not be available until core drill samples have been taken. Laboratory studies of sixteen phosphate glass samples of PW-2 type products have shown that all samples exhibited some crystallinity. The unetched microstructures of these 16 samples are shown in Figure 8.4. Storage temperature has the most significant effects upon the microstructure. Rate of cooling melt temperature, and time in the melt have less significant effects.

In samples stored at 600 °C, the crystals are larger and more abundant than those stored at 100 °C. Porosity is greater in samples melted at 1000 °C and stored at 100 °C than in samples melted at 1200 °C and stored at 600 °C. The samples heat-treated at 600 °C were softer to abrasion than the samples which were heat-treated at 100 °C.

TABLE 8.6. *Bulk Density and Specific Volume
of Solidified Wastes from WSEP*

<u>Process/Run Number</u>	<u>Waste Type</u>	<u>Specific Volume, l/tonne fuel</u>	<u>Density, g/cm³</u>
PC-1	PW-2	50	1.44
PC-2	PW-2	45	1.34
PC-3	PW-2	47	1.44
PC-4	PW-1	41	1.51
PC-5	PW-1	43	1.56
PC-6	PW-2	50	1.33
PG-1	PW-2	42	2.80
PG-2	PW-2	46	2.88
PG-3	PW-2	51	2.80
PG-4	PW-2	61	2.92
PG-5	PW-1	108	2.71
PG-6	PW-1	94	2.81
SS-1	PW-1	32	3.09
SS-2	PW-1	32	3.17
SS-3	PW-2	65	2.55
SS-4	PW-2	63	2.86
SS-5	PW-1	33	3.24
SS-6	PW-1	35	3.25
SS-7	PW-1	36	3.07
Nonradioactive laboratory, avg of 16 samples	PW-2		2.92

Neg 0683910

20X

FIGURE 8.4. Microstructure of Nonradioactive Phosphate Glasses

Microstructure analysis and visual observation of samples 2, 4, and 6 in Figure 8.4 also revealed porosity in samples which were considered nonporous by mercury porosimeter measurements. Thin sections of the samples have been prepared and further microstructure analysis is continuing. Samples 2, 5, 8, and 14 will be examined for phase composition by electron-beam microprobe spectroscopy and X-ray diffractometry. Samples of spray solidified and pot calcine product will be compared with phosphate glass product when similar data are available.

Some phosphate glass solids exude a black "ooze" of unknown composition. This has been observed in laboratory work and engineering-scale nonradioactive work. The "ooze" has been observed primarily coming from laboratory samples that have been exposed to air.

The chemical stability of melt products has come under considerable scrutiny because of the possibility of pressurization and potential for rupture of the primary solid waste container. When sulfate-retaining spray solidifier melts are heated to 600 °C in open laboratory containers, sulfur oxides are evolved (essentially 100% of that present in a period of a few weeks). However, when a closed container simulating a large pot was held with a temperature gradient of 800 °C centerline and 375 °C surface for sixteen weeks, no sulfur oxide evolution and no container pressurization occurred. It is believed that the sulfur oxides were released from the hot zones (centerline) and reabsorbed or recombined in the colder zones.

Knowledge of the corrosion of the primary waste container is important to insure that the primary container is not

breached. Standard coupon samples of 304L and 310 stainless steel were exposed to solids from all three processes and standard coupon samples of mild steel exposed to the spray and phosphate glass melts. The corrosion rates were a few tenths of a mil to a few mils per year at 600 to 700 °C. Pot calciner pots are not fabricated from mild steel due to the presence of acidic aqueous solutions and high temperatures.

It is worthwhile to note that air oxidation of mild steel at temperatures greater than 500 °C and air oxidation of stainless steel at temperatures greater than 800 °C may be orders of magnitude greater than the product corrosion rates on the containers. Specific examples for calcine and melt are cited below and in Table 8.7.

Mild steel is suitable for storage containers for phosphate glasses as long as the container wall temperature is less than about 500 °C to prevent excessive air oxidation. In general, the corrosion rates for mild steel in phosphate glass at 500 to 700 °C (see Table 8.7) are about 100 times less than the air oxidation rates at the same temperatures.^(8,9) Types 304L and 310 stainless steels are suitable for phosphate glass containers as long as the container wall temperature is less than about 800 °C to prevent excessive air oxidation.^(9,10)

TABLE 8.7. Corrosion Rates of Storage Vessels

Process	Melt	Temp, °C	Exposure Time, hr	Corrosion Rate, in./yr			
				Mild Steel	304L SS	310 SS	50 Cr-50 Ni
Phosphate Glass ↓	PW-1	600	1000	0.0019	0.0004	0.0004	--
	PW-1	700	1000	0.007	0.0023	0.002	--
	PW-1	800	145	--	--	--	0.017
	PW-1	800	49	--	0.011	--	--
	PW-1 ^(a)	800	49	--	0.012	--	--
	PW-1	825	93	--	0.012	--	--
	PW-1	850	170	--	--	--	0.010
	PW-1	875	47	--	0.143	--	--
	PW-1	900	80	--	--	--	0.24
	PW-1	950	114	--	--	--	0.047
	PW-1	1000	120	--	--	--	>5
	PW-4m	850	170	--	--	--	0.011
	PW-4m	950	114	--	--	--	0.018
	PW-4m	1000	114	--	--	--	0.069
Spray Melt ↓	PW-1	600	1000	0.005	0.0007	0.0004	--
	PW-1	600	1000	0.002	0.0004	0.0004	--
	PW-1	700	1000	0.007	0.002	0.002	--
Pot Calcine	PW-2	600	1000	0.002	0.0002	0.0002	--

a. 0.03M fluoride in PW-1 waste solution.

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9.0 AUXILIARY PROCESSING

(by P. C. Owzarski, M. R. Schwab, and J. L. McElroy)

9.1 SOLIDIFICATION EFFLUENT TREATMENT

Solidification of radioactive wastes generates effluents with reduced but still toxic levels of radioactivity. These effluent streams must be treated to remove radioactivity to permit discharge to the environs. Intermediate and low level streams must be recycled to points within the reprocessing plant for further treatment. This section describes the present technology for cleanup of solidification effluents using a condensing system (as opposed to a noncondensing system operated at temperatures above component dew points). Details of WSEP auxiliary processing equipment and their design criteria are found in Reference 44.

9.1.1 Effluent Characteristics

Effluents from solidification processes consist of volatilized material from the waste and additives, entrained liquid or solid aerosols, and air from in-leakage through equipment joints (and atomizing air from the spray solidification process). Volatilized material from nitrate wastes consists primarily of water, nitric acid, and various oxides of nitrogen. Each liter of waste processed will give about 1400 liters of steam (at 100 °C and 1 atmosphere) plus additional gases in amounts depending on nitrate and additive concentrations.

Nearly all the effluents are condensible. Those that are not can be chemically absorbed or consist of in-leakage air (or process air as for the spray solidification process). Both condensible and noncondensable streams from solidifiers need

treatment for removal of radionuclides. The noncondensable streams must be discharged continuously to the atmosphere after treatment.

Condensation itself is an important decontamination step. It is desirable to condense and scrub out as much of the volatile fission products and entrained aerosols as possible in the first operation, so that recombining noncondensable and vapor streams downstream will not lead to contamination of the latter. A condenser designed with efficient scrubbing capabilities would certainly be beneficial. Other considerations that should go into condenser design are adequate heat exchange capabilities and down-draft flow direction for reduced aerosol entrainment.

If initial waste solutions are 10,000 Ci/liter, and if the solidifier decontamination factor is 100, the liquid effluent usually must be decontaminated by a factor of 10^{12} before discharge. This is virtually impossible in a single step after condensation. Thus, several recycle streams are likely to be generated by necessary additional decontamination steps.

9.1.2 Integration with a Fuel Reprocessing Plant

Economic and safety reasons dictate the desirability of combining solidification processes with a fuel reprocessing plant. The interface between the two reprocessing steps creates the need for considerations that will be discussed here. The schematic flow diagram (shown in Figure 9.1) illustrates how the processes might fit together.

The WSEP auxiliary process system employs a waste evaporator, acid fractionator, and caustic scrubber in series downstream from the process condenser (see Figure 9.3). Each step generates

liquid effluents that may require added treatment (usually evaporation followed by condensation). The evaporator bottoms can be either a high level waste concentrate to be solidified or an intermediate level nitric acid stream containing mostly ruthenium and some entrained solids (see Section 9.1.3 for explanation of evaporator operations). If the solidification process failed to incorporate more than about 50% of the ruthenium in the solidified waste, the recycle amount of ruthenium may become prohibitively high. The fractionator overhead stream is desirably less than MPC* in both fission products and nitric acid (about 0.001M), but may need further treatment. The spent caustic scrub solution may be a low level waste solution that could satisfy the needs for sodium in waste concentrates for certain melt-making solidification flowsheets. Hopefully, water may replace caustic as a scrub solution. In general, the criteria for placement of recycle streams are: (1) the streams should be chemically similar; (2) they should be of the same radioactivity level (e.g. Reference 29); and (3) the recycled stream should be small with respect to the mainstream unless design foresight allows otherwise.

9.1.3 Modes of Operation

In a condensing auxiliary system the evaporator can be operated in one of the three ways described in Figure 9.2 and still remain an effective decontaminator device. Mode A designates the use of the evaporator as a boiling collection tank for process condensate, while the high level waste is fed directly to the solidification process from another vessel. Mode B designates the use of the evaporator as a waste concentrator and simultaneously as the collection tank for the process condensate, while the process waste is fed as in Mode A. Mode C designates the use of the evaporator as a

* MPC = maximum permissible concentration, or 10^{-4} $\mu\text{Ci/liter}$ based on Reference 29.

FIGURE 9.2. WSEP Process Options

simultaneous concentrator of high level waste and process condensate and as a feed tank to the solidifier. Mode C is essentially the same as Mode B without the added feed tank.

Mode A provides the most decontamination of the process effluents since the radioactivity level in the evaporator is normally one or more orders of magnitude lower than the original waste and is a controllable independent variable. Mode A requires a separate feed tank and an additional evaporator. Mode B is useful for integration with the waste evaporation system of the reprocessing plant by the addition of a feed tank only for the solidifier. Mode C eliminates the need for a special feed tank but creates the problem of inflexibility during continuous operation due to direct coupling without surge capacity. Mode A is the most flexible but requires the most equipment.

9.1.4 Process Vent Systems

Requirements for process vent systems are based on the need to provide flow direction of gases and vapors, including in-leakage air from imperfect equipment joints, and to clean up gas streams and cell air before discharge to the environment. Some considerations involved in vent systems design will be illustrated by brief description of the WSEP vent system, below.

The primary methods for removal of aerosols from the WSEP process off-gas are three separate cycles of evaporation plus condensation followed by a stage of highly efficient filtration. These systems, in turn, are backed up by a scrubber and another stage of high-efficiency filters* before the gas

* High efficiency filters are rated to remove at least 99.95% of particles 0.3 micrometers in diameter at air face velocities less than 5 ft/sec. They are more efficient on larger and smaller particles.

is vented to the building ventilation exhaust for additional cleaning (where the air is filtered again). Each stage of high-efficiency filtration is protected from excessive moisture by an upstream condensing-heating cycle.

The auxiliary processing vessels (e.g., feed, storage, collection tanks), which are not part of the primary processing vent system, do not generate as large a quantity of aerosols as those in the primary solidification-evaporation system. In WSEP, these auxiliary vessels are sealed from the primary vent system and are connected to a secondary vent system which contains one stage of high-efficiency filtration before joining the primary off-gas stream at the beginning of the backup treatment train. The two vent systems, including the estimated cleanup factors, are shown schematically in Figure 9.3. Decontamination factors greater than 10^{12} are required to reduce effluents from high level wastes to levels safe for discharge. (29) In the WSEP system, decontamination factors of 10^9 were obtained on liquid effluents.

Individual equipment decontamination factors in the WSEP system depended slightly on the type of solidification process used. Fractions of total feed activity (not including ruthenium) found in the various tanks have averaged approximately: (54) 10^{-2} for phosphate glass and 10^{-3} for spray solidification and pot calcination in the evaporator, 10^{-6} in the fractionator bottoms for all three processes, and 10^{-8} in the caustic scrubber for all three processes. Ruthenium fractions were 100 to 1000 times larger in the fractionator streams and scrubber. The evaporator usually held about 99% of the ruthenium volatilized.

The entire process system is maintained under a slight vacuum relative to the cell pressure to minimize release of radioactive contamination to the cell and to other nonprocess areas. The

FIGURE 9.3. Process and Vessel Vent Systems, WSEP

primary process vent system is maintained at a negative pressure of 5 to 30 inches of water. This vacuum is automatically controlled by recycle of discharge gases from the ejector which generates the primary process vacuum at the end of the off-gas processing train. This system discharges into the secondary process vessel vent system which is maintained at a vacuum of 2 to 10 inches of water by a single-stage turbine-type centrifugal blower located outside the cell.

Piping connectors between tanks at different operating vacuums are sealed to minimum vacuum differences of 36 inches of water by appropriate dip legs in the tanks. Therefore, a small heel of liquid is required in all tanks during processing. The routinely disconnected pot-to-off-gas system is in a hood to further minimize contamination.

All solidification equipment is equipped with emergency vent piping through water-filled seal pots in event of inadvertent undesirable reduction of vacuum. The designs of the seal pots provide variable pressure differential seal (up to 29 inches of water) to other tanks for added vapor capacitance and/or alternate vents. Other topics related to off-gas decontamination are discussed in Section 9.2.2 and Reference 52.

9.1.5 Other Basic Requirements and Vessels

Nitric acid recovery is normally integrated with the auxiliary system. Conventional fractionators are adequate to produce a bottoms concentration of 8 to 10M nitric acid and an overheads concentration of 0.001M.* This fractionator would produce a beneficial decontamination factor on the order of

* 0.001M is close to the maximum permissible concentration of 45 ppm NO_3^- for drinking water (see Reference 38).

1000 and would recover acid worth about \$10/tonne based on waste volumes of 378 liters/tonne with 4M nitrate ion.

A number of in-cell process service vessels are needed as liquid containers, mixing vessels, preheaters, and coolers. These should be stainless steel and should generally be equipped with cooling and heating coils, agitators, flushing systems, and sparges and measuring devices for pressure, specific gravity, and temperature, and sometimes towers for scrubbing and deentrainment.

Combined process off-gases may require scrubbing before discharge to the atmosphere. A packed tower with a recirculatory pump and a cooled caustic reservoir tank is a simple and effective scrubbing system, but other types can be used. The tower must remove radioruthenium, radioiodine, and possibly acid vapors and nitrogen oxides. The last item will probably set design limits since nitrogen oxides are difficult to remove to suitable levels for discharge to the atmosphere. Caustic will have the largest capacity for scrubbing but should not be much more efficient than water if the off-gas components are very dilute. Other methods for nitrogen oxide removal are available, such as catalytic reduction of the oxides in the presence of natural gas.

9.2 WASTE EVAPORATION

9.2.1 Primary Function

Waste from the most current aqueous separations plants is normally relatively dilute with respect to salt constituents when it emerges from the solvent extraction columns. Consequently, it is concentrated by evaporation to a point just below

where most of the salt constituents would precipitate during liquid storage. The feed to future waste solidification plants will likely be the concentrate from the evaporator in the fuel reprocessing plant, although some additional aging of the waste may be desirable in some cases. Consideration must be given to the aging time of wastes to be solidified. For example high power levels in the waste may demand some aging to reduce heat-generating levels in the solidified waste.

Feed Preparation. Some additional degree of concentration of the waste may be desirable due to chemical additions, dilution due to process transfers by steam jets, or to reduced volume to improve efficiency of the solidifiers. Other needs may be boiling digestion for decomposition of organics or mixing of chemical additions. (Figures 11.15 and 11.16 show relationships of boiling temperatures and densities for most waste solutions.)

Acid Stripping. The primary condensate from waste solidification normally contains 0.1 to 1% of the nonvolatile radioactivity and 1 to 50% of the volatile radoruthenium present in the feed. Since these quantities are higher than those desired in the recovered acid from the solidification plant, stripping of the acid from this stream to one with less radioactivity is done by re-evaporation. This evaporation-stripping can be done by adding (recycling) water to the evaporator during nitric acid evaporation, while maintaining the desired concentrations of stable chemical constituents and minimizing corrosive conditions.

Effluent Treatment. Re-evaporation of solidification effluents can provide additional decontamination from entrained aerosols in the solidification off-gases, if they are vented through the evaporator. In addition, volatilization (and decontamination

of ruthenium) is significantly affected by oxidizing conditions and acid concentration in the evaporator. Ruthenium control is discussed more fully in Section 9.2.3.

9.2.2 Particulate Entrainment

Entrainment in liquid-vapor systems such as evaporators, fractionators, condensers, etc. is affected by many variables such as unit area boilup rates, vapor velocities, depth of submergence, geometry, and liquid and vapor physical properties. In general, more entrainment results from the expenditure of more energy. Entrainment is generated by rupture of thin liquid films that form as vapor bubbles break from the liquid surface, and by break-up of liquid jets that form when liquid rushes in to fill the cavity left by the escaping vapor bubble. Distribution of the smaller size range of water droplet entrainment in a thermosyphon evaporator⁽¹⁴⁾ is shown typically in Figure 9.4. In the case shown, a deentrainment factor of one million is obtainable if all particles having diameters greater than about 2 micrometers are removed. Such particle removal efficiency is about one order of magnitude better than in most nuclear evaporation systems, and achieving that performance requires careful design and operation.

Efficiency of removal of particles by inertial impaction (the most common method used in most evaporators) is also shown in Figure 9.4. Impaction removal of particles smaller than about 3 micrometers is extremely difficult in practical installations. A factor that is very important to particle removal by impaction is reentrainment. This effect can be minimized in two ways: (1) by limiting the vapor velocity past a wet surface to the range of 20 to 40 ft/sec; and (2) by removing large droplets before they enter the higher velocity separation stages so that breakup of the larger particles does not occur as a result of high-velocity impaction.

FIGURE 9.4. Evaporator Entrainment Distribution and Impact Velocity

Removal of small particles (about one micrometer and smaller) is generally much more efficient by Brownian movement effects through relatively deep beds with large surface/volume ratios. In this case, random motion is imparted to the particles by collision with the gas molecules. As a result of this random motion, the probability for impaction on the many small surfaces is increased considerably. Increased removal by this means is generally accomplished by lower "filtration" velocities, thicker beds, more dense packing, and bed fiber diameter close to that of the particle. Practical limits are mechanical strength (wet and dry, corrosion resistance, and manufacturing limits of the small fibers. In addition, loading or plugging capacity and drainability of the collected moisture limit overall performance.

9.2.3 The Chemistry of Volatile Ruthenium

Ruthenium Volatilization from Solution. Ruthenium in acidic wastes can be easily volatilized during both evaporation and solidification. To minimize this undesirable effect, adequate measures of precautions can be taken. Present understanding of ruthenium behavior is described in this section. Ruthenium chemistry in waste processing is extremely complex and is further complicated by being directly related to nitrogen-oxygen chemistry (which is also complex) in all solid, liquid, and vapor phases encountered. The most important aspects of controlling ruthenium chemistry relate to preventing ruthenium volatilization and controlling ruthenium behavior if it exists in the vapor phase.

Ruthenium tetroxide (RuO_4) has been established^(9,10) as the principal volatile form from boiling nitric acid solutions. Pure RuO_4 forms yellow crystals (with a melting point of 25.4 °C) and dissolves in water to 2 g/100 g water at 20 to 40 °C.⁽¹⁶⁾

It is very soluble in nonpolar solvents. Ruthenium tetroxide is the product in the following series of reactions. (10)

Both the nitrato and nitro forms exist in aqueous nitrate solutions, and their distribution depends on the oxidizing conditions of the solution. (19) If ruthenium is to be retained in boiling nitric acid solution, reducing conditions must exist where the nitro complex (the slower reacting species) prevails over the nitrato complex. Table 9.1 shows oxidation rates of the species to RuO_4 using ammonium ceric nitrate as an oxidizing agent. Nitric acid retards ceric oxidation in this case.

TABLE 9.1. *Oxidation of Ruthenium Species in Nitric Acid Solution with Ammonium Ceric Nitrate at 20 °C* (10)

Ru Species (a)	Ru Conc, M	% Ru to RuO_4					
		Oxidation in 0.1M HNO_3			Oxidation in 2.4M HNO_3		
		1 min	10 min	1 hr	1 min	10 min	1 hr
(RuO_4)VI Nitrate	10^{-3}	100	100	100	100	100	100
RuNO Nitrato complexes	10^{-3}	51	74	96	50	70	93
	10^{-8}	61	82	100	10	31	62
RuNO nitro complexes	10^{-3}	3.6	13	32	0	0	0
	10^{-8}	3.9	14	30	0	0	0

(a) Ruthenium species originally in equilibrium in 3M HNO_3 . Oxidation started immediately after dilution. Ceric ion was 0.073M.

Measurements of RuO_4 vapor pressures under various conditions made by Barton⁽³⁾ are shown in Figure 9.5. From these data it is evident that complete stripping of RuO_4 from boiling solutions can occur if boiling under stripping conditions persist for days. It is also interesting to note that the vapor pressure of RuO_4 is appreciably greater in salt solutions than in acid solutions of equal normality. This is attributed by Barton to a salting-out effect of salt solutions due to a possible RuO_4 acid complex formed in the acid solutions.

Measurements by Maness⁽⁷⁾ on the oxidation potential of nitric acid solutions are shown in Table 9.2. It is not surprising that chromium in waste solutions results in increasing ruthenium volatilization under boiling conditions. Other constituents in waste solutions could behave in a similar manner.

The conditions which affect the distribution of the various ruthenium species have been partly discussed. However, it should be emphasized that these distribution are dependent on the kinetics and equilibria of various simultaneous parallel and series reactions. Information on the rate of formation of ruthenium species under various conditions may be obtained from Reference 5. It is further concluded on the basis of that work that reducing conditions must prevail in boiling acidic nitrate solutions as much as practical to retain the bulk of ruthenium as the aqueous nitro species.

The data from extensive observations on ruthenium volatility and its suppression under various conditions^(1,2,6,11,12) are shown in Figure 9.6. Although the data on volatility are plotted against distillate nitric acid content, and some correlations exist for very specific solutions, the range in volatilization for a constant distillate acidity is as much as five orders

FIGURE 9.5. RuO_4 Vapor Pressure from Solutions

TABLE 9.2. Oxidation Potential of Nitric Acid Solutions

Solution	Temp, °C	Oxidation Potentials at Smooth Pt Electrode, ^(a) mV
4M HNO ₃	100	910
	106(bp)	950
6M HNO ₃	100	960
	109(bp)	980
8M HNO ₃	100	1000
	112(bp)	1010
10M HNO ₃	100	1025
	116(bp)	1050
13M HNO ₃	100	1050
	119(bp)	1050
Purex Waste ⁽⁶⁾ No Cr	100	970
	112(bp)	1010
Purex Waste + 0.1M Cr ³	100	990
	112(bp)	1000
Purex Waste + 0.1M Cr ⁶	100	1040
	112(bp)	1050
Purex Waste ± 0.1M Cr ³ + 0.1M Cr ⁶	100	---
	112(bp)	1060

(a) Versus saturated calomel electrode at 25 °C

(b) For a typical Purex waste composition,
see Tables 2.4 and 2.5.

of magnitude. Apparently, this range of volatilization represents extremes in the oxidizing potential of the tested solutions. In light of the function of a nitric acid stripping waste evaporator (to distill nitric acid) and corrosion restrictions imposed on materials of construction, free acid concentrations are optimum. For these conditions, it can be

FIGURE 9.6. RuO₄ Volatilization from Boiling Nitrate Solutions

seen from Figure 9.6 that the most significant effect on Ru volatility in the range of expected distillate acidity operation (1.0 to 0.6N) is not the acidity of the distillate, but rather the oxidation potential of the concentrator bottoms. Ruthenium tetroxide is unstable in aqueous solutions and readily decomposes to lower oxidation states particularly if no oxidizing agent is present⁽⁸⁾ or if reductants are present. It is important to note the increasing potential with acidity and the influence of chromium on the potential under boiling conditions. The effect of chromium content on ruthenium volatility is shown in Table 9.3. These data were compiled from selected data from Reference 12. Chromate ion has been used in the Redox process to volatilize ruthenium from feed solutions.⁽⁹⁾

TABLE 9.3. *Chromium Effect on Ruthenium Volatility*

Solution	Boiling Point, °C	HNO ₃ in Distillate, M	Molarity					DF ^(+c)
			[H ⁺]	[NO ₃ ⁻]	[SO ₄ ⁼]	[M _T ⁺] ^(b)	[Cr]	
HNO ₃	109	0.8	6	6.4	---	---	---	200
TBP Waste	111	0.5	1.3	6.6	---	5.2	---	35
Purex Waste ^(a)	112	1.2	5.6	6.0	1.0	2.4	0.01	15
Purex Waste ^(a)	112	0.83	2.0	7.2	---	5.2	0.38	4

(a) As defined in Section 2

(b) Metal ion equivalents

(c) DF = Concentration of Ru in bottoms ÷ concentration of Ru in distillate

Estimates of the reductant requirements added to or existing in the solutions of the above data were made,⁽¹³⁾ and the data tabulated in Table 9.4. The Reductant Oxygen Demand (ROD) is the estimated half-molar oxygen required per liter of solution to completely oxidize the reductants to their highest oxidation state. These data point out that most waste evaporation is conducted with large amounts of favorable reductants which suppress ruthenium volatilization. Waste evaporation prior to waste solidification processing may not

TABLE 9.4. Reductant Requirements for Suppression of RuO_4 Formation

Solution	Ru DF	ROD (a)	Source	Reductant in Solution
HNO_3	1,100	0	Reference 2	-----
	5,000	0.08	Reference 2	0.2 g/l $NaNO_2$
	20,000	0.10	Reference 2	2.4 g/l $NaNO_2$
	100,000	~1.0	Reference 2	30% Tri Butyl Phosphate in Kerosene
TBP Waste	30	0	Reference 12	-----
	550	0.1	Reference 12	0.1M PO_3
Purex Waste ^(b)	10	0	Reference 12	-----
	550	0.1	Reference 12	0.1M PO_3
	1,300	1.0	Reference 6	-----
	100,000	~1.65	Reference 6	0.013M $NaNO_2$
	100,000	~2.20	Reference 6	0.001M
Darex Waste ^(c)	4	0	Reference 12	-----
	140	0.1	Reference 12	0.1M PO_3

(a) Reductant oxygen demand

(b) See Tables 2.4 and 2.5 for definition.

(c) A sulfate-free Purex waste containing about 300 ppm HCl and 1 to 2M stainless steel.

be so highly endowed with organic reductants from extraction preprocessing, since many of these organics will have been decomposed by heat and radiolysis during the storage interval before solidification. Consequently, to achieve suppression of ruthenium volatilization comparable to that in reprocessing plant auxiliaries, calculated amounts of reductants may need to be added continuously to the evaporator while the waste is being evaporated.

Knowledge of the effectiveness of various reductants to this date is not complete. Sugar has been used to "kill" nitric acid and to suppress ruthenium volatilization for a number of years.⁽⁶⁾ A long cooking time and high concentration of nitric acid are general requirements in the successful use of sugar, so that residual sugar (or carbon) has been reduced to the point that it is not a problem for further processing. References 17 and 28 examine the kinetics of the sugar-nitric acid reaction. More research is needed with other organic reductants for use in evaporators and solidification processing.

Decomposition of RuO₄

The previous discussion dealt with the chemistry of minimizing the formation of volatile RuO₄. No known solidification process or waste evaporation containing ruthenium in any state other than RuO₂ will fail to volatilize ruthenium in some degree. Tolerable levels of volatilization will depend on decontamination capabilities downstream. The following discussion will examine RuO₄ once it is volatilized.

Pure RuO₄ exerts the following vapor pressures in dry nitrogen:⁽²⁰⁾

Solid phase: $\log_{10} P = -3190/T + 11.813$ torr at 0 to 20 °C

Liquid: $\log_{10} P = -1975/T + 7.7189$ torr at 24 to 70 °C

The boiling point is 135 °C (at one atmosphere) by extrapolation. Ruthenium tetroxide is stable to 55 °C, but some decomposition occurs above 60 °C in the gas phase. Ruthenium tetroxide decomposition has been detected at even lower temperatures with water present.⁽²⁴⁾ Gas phase decomposition often leads to RuO₂ fines less than 0.25 micrometers.⁽⁴⁰⁾ Ruthenium tetroxide has been known to decompose on stainless steel, glass, nonfluorinated plastics, and on other reducing surfaces such as formaldehyde saturated silica gel (or on the gel itself). The black decomposition product has been assumed to be RuO₂, but only that solid forming over 400 °C has X-ray crystallographic patterns of RuO₂. At temperatures greater than 400 °C, the equilibrium for the reaction

has been carefully studied.⁽²⁶⁾ Ruthenium tetroxide is thermodynamically unstable over 100 °C, and its gas phase equilibrium concentration in an oxygen system is very small as shown by

$$\log \left(\frac{p(\text{RuO}_4)}{p(\text{O}_2)} \right) = \frac{4764}{T} - 0.236$$

However, the decomposition of RuO₄ is retarded by the presence of nitrogen oxides found in nitrate calcination off-gases.⁽²³⁾ A study of Barton⁽²¹⁾ and WSEP spray solidifier run data⁽²⁷⁾ indicate that RuO₄ is kinetically stable, enough to require removal by gas treatment or conversion to particulate RuO₂ for removal as an aerosol. Barton showed that RuO₄ readily deposited on stainless steel and glass, but the RuO₄ that formed was autocatalytic for reducing additional RuO₄. The decomposition rate increased rapidly over 160 °C. For plug flow reactor velocities on the order of 1 ft/sec or more, the decomposition rate of RuO₄ on walls was limited by the mass transfer rate of RuO₄ from the gas stream to the walls.

In summary, data on volatilized ruthenium indicate that RuO_4 can be expected to deposit as a lower valence oxide on vessel walls at temperatures of 100 °C, to react with water or nitric acid in saturated vapor-liquid systems, and/or to decompose in the gas phase and produce solid oxide fines that may be difficult to scrub. To remove ruthenium from the gas phase, a combination of some of the following may be required:

- Use of ruthenium traps to collect RuO_4 . These may be a silica gel bed or iron oxide pellet bed. (41,42,43)
 - Use of high-efficiency filters to trap RuO_2 fines.
 - Use of condensers and scrubbers to remove RuO_4 by dissolution in films on wetted walls or packing.
- Other scrubbing techniques should also suffice.

9.2.4 Waste Evaporation Considerations

Waste evaporation will be a routine operation in a fuel reprocessing plant, since concentrations will often be orders of magnitude lower than required. Any special evaporator to aid in the solidification process should match the process. Size and maximum boiling rate will be major considerations. Operating mode (see Section 9.2.1) will also have to be considered.

A thermosyphon type evaporator with a steam heated tube bundle (as in WSEP) is a possible choice. A large range in operating volume is desired if it must feed a batch process. For acid stripping needs, the distillate must be maintained at less than 1M (and perhaps as low as 0.5M) for ruthenium control, while process strip water and nitric acid from the solidification condenser are added. Control of the evaporator boilup rate should be based on distillate concentration which can be measured by electrical conductivity.

Design considerations must include steps to minimize aerosol generation.⁽²⁶⁾ This is normally accomplished by having low boilup rates per unit area of solution and by avoiding extremely concentrated heat sources. Since special evaporators will probably have to handle viscous slurries, evaporator design should try to minimize possible sludge formation and settling.

Aerosol de-entrainment requirements are stringent: a de-entrainment factor of 10^6 or better. Good de-entrainment can be accomplished by using multiple stages to minimize formation of additional smaller particles in the removal of larger particles. Each succeeding stage removes smaller particles, some of which could be generated at the process stage.⁽¹⁴⁾ These stages might be a series of impingement devices (such as baffles and dry impingement caps) followed by a high efficiency aerosol remover.

9.3 NITRIC ACID AND CONDENSATE RECOVERY

9.3.1 Functions

The condensable off-gases from the solidification processes (after prior decontamination in the evaporator) will still contain toxic concentrations of radioactivity as well as nearly all the nitric acid originally present in the liquid waste. Most of the nitrogen can readily be recovered as 8 to 12M nitric acid. This slightly contaminated acid can be profitably returned to the separations plant for reuse under most chemical processing schemes. If the excess water in the solidification off-gas has little reuse value, it must be further decontaminated to the point where it is

not toxic for disposal to the environs (Section 9.1.5). An acid fractionator and its associated condensers perform part of these functions.

9.3.2 Fractionation

Overheads and Bottoms Product. The overhead product from fractionation should ideally contain nontoxic concentrations of nitric acid (less than 0.001M) and radioactivity (less than 10^{-3} $\mu\text{Ci}/\text{cm}^3$). Based upon fractionation difficulty, the design basis for the WSEP overheads was established at 0.01M nitric acid (about $10 \times \text{MPC}$). The bottoms product should contain all the radioactivity in the fractionator feed. This radionuclide level (up to about 1 $\mu\text{Ci}/\text{cm}^3$) is very acceptable for reasonable handling requirements during recycle to the "front end" of the separations plant.

Transfer Units Required and Efficiency. Calculations for the number of stages required to fractionate nitric acid are straightforward. However, measurements of stage or transfer unit height were not found in the literature for packed columns. Therefore, the efficiency of 1-inch diameter titanium Raschig Ring packing was determined at Battelle-Northwest.⁽¹⁵⁾ A summary of the data pertinent to the packed sections of the WSEP tower on the basis of liquid feed with 0.8M HNO_3 is:

	<u>Number of Transfer Units</u>	<u>Height of Transfer Unit</u>
Exhausting Section		
(0.1M HNO_3 , $L/V = 0.3$)	9.4	0.65
Rectifying Section		
(10M HNO_3 , $L/V = 1.1$)	2.4	2.3

From these data, the WSEP fractionator was designed, using an $L/V = 0.4$ in the exhausting section. Poorer separation

will occur if nitrogen dioxide exists in the gas phase in the fractionator. Considerably more transfer units are required to reduce fractionator overhead concentrations to 0.001M HNO_3 .

Conditions of Feed. Although the WSEP design was based on liquid feed, saturated vapor feed may be accomplished by not condensing the vapors from the evaporator. Liquid feed provides essentially one more separation stage in the exhausting (upper) section of the column, at the expense of a slight reduction of separation in the rectifying section. Also, additional heat load is imposed upon the reboiler due to liquid feed. Complete condensation of the feed removes the vaporized (and some particulate) ruthenium. This benefits the overall decontamination of the tower.

9.3.3 Aerosol Attenuation

Some considerations should be made for removing aerosols in the fractionator. The existence of wet packing can remove only the very fine (less than 0.01 micrometer) aerosols. An impingement sieve plate and scrubber at the top might be included. Design for low vapor and liquid rates per unit area would help de-entrainment and minimize entrainment.

9.4 CORROSION CONSIDERATIONS IN AUXILIARY EQUIPMENT

Four types of solutions are encountered which require special alloys or techniques to prevent corrosion in auxiliary equipment. The solutions are:

- Acidic nitrate wastes containing various cations.
- Nitric acid condensates.

- Fluoride bearing wastes
- Condensates containing high concentrations of sulfuric acid.

Simple nitric acid condensates present the least problems, and 304L stainless steel or titanium are adequate materials for condensers, piping and tanks encountering these.

Nitric acid wastes containing large amounts of ferric iron (such as in PW-1 waste) produce high corrosion rates on stainless steel. For this reason, waste evaporators should be constructed of titanium or zircalloy. Sulfate ions decrease this corrosion rate significantly. For high acid PW-1 wastes (containing 6M HNO_3 and 0.45M Fe^{+3}) the corrosion rate on 304L stainless steel was about 0.2 in./year at boiling, whereas the addition of 0.4M sulfate halved that rate. In an identical waste except lower in nitric acid (1M), boiling corrosion rates on 304L varied from 0.09 in./year with no sulfate to 0.012 in./year with 0.75M sulfate ion.

Tests at Oak Ridge National Laboratory⁽³⁷⁾ revealed that all iron and nickel alloys tested with simulated refluxing Purex high level waste solutions or similar environments developed intergranular corrosion in the vapor phase (with penetration rates of up to 0.05 in./year) after periods varying from 24 to 500 hours. The presence of ruthenium accelerated the onset of corrosion. Titanium corrosion, however, was less than 0.01 in./year in boiling 15M HNO_3 - 1M H_2SO_4 . This rate decreased with time and was not adversely affected by ruthenium.

Table 9.5 compares the corrosion rates of titanium and 304L stainless steel in boiling Darex waste, which is corrosive to stainless steel due to ferric ions, chloride, and ruthenium. Consequently, titanium appears to be a good choice of material under most conditions, and was the

choice for WSEP. Excessive corrosion of titanium (or stainless steel) condensers can occur if sulfuric acid vapors are present with little accompanying nitric acid, or if relatively modest quantities of fluoride are present in incoming vapors.

TABLE 9.5. *Comparison of Corrosion of 304L Stainless Steel and Titanium in Boiling Simulated Darex Wastes⁽³⁷⁾ a,b*

Alloy	Position	Corrosion Rate, in./year			
		Initial		Final	
		168 hr	336 hr	168 hr	336 hr
304L	Vapor	0.008	0.008	0.016	0.016
	Interface	0.046	0.062	0.12	0.14
	Solution	0.068	0.094	0.15	0.18
Ti 45A	Vapor	0.0004	<0.0001	0.0	<0.0001
	Interface	<0.0001	<0.0001	c	c
	Solution	<0.0001	<0.0001	c	c

a. Low acid waste, $H^+ = 0.75M$. Final solution was $1.0M H^+$ and other components were concentrated by 1.3. Initial ruthenium concentration was $0.01M$.

b. See Table 9.4 for Darex waste composition.

c. Weight gain.

Actual titanium corrosion rates in boiling nitric acid with various fluoride ion concentrations are shown in Table 9.6.

TABLE 9.6. *Titanium Corrosion in 6M Boiling HNO_3*

<u>F^-, M</u>	<u>Corrosion Rate, in./year</u>
0	<0.001
0.001	0.025
0.005	0.10
0.025	4.16
0.1	15.9

Stainless steel suffers from corrosion in fluoride solutions, but this corrosion can also be attenuated by the addition of cations. Aluminum complexes the fluoride to reduce corrosion, and zirconium is ten-fold more effective than aluminum for reducing fluoride corrosion on stainless steel. This complexing is evidently due to a hundred-fold reduction in HF volatility in nitric acid obtained by adding 2 moles $\text{Al}(\text{NO}_3)_3$ per mole of fluoride ion.

Tests on titanium revealed corrosion in a sulfate bearing waste, PW-2. (See Table 2.3 and 2.4 for definition of PW-2 waste.) Table 9.7 shows how the corrosion rates varied with sulfate concentration.

Zircaloy-2, Nionel^(R) and 304L stainless steel show good corrosion resistance to sulfate-containing wastes. Tables 9.8 and 9.9 show results of some tests in acid mixtures. Use of 304L stainless steel in WSEP auxiliary piping, connectors, and storage tanks has revealed no significant corrosion. Therefore, 304L appears to be an adequate choice for some auxiliary equipment. However, Zircaloy or Nionel are preferred materials for a high sulfate concentration condensate such as found in the melter condensate from the phosphate glass process.

9.5 MECHANICAL EQUIPMENT

9.5.1 Pumping Requirements

Pumps are required to supply feed to the process, to supply feedline flush water, and to circulate caustic or other scrub solutions through scrubber towers.

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TABLE 9.7. *Titanium Corrosion in Melter Condensates from Phosphate Glass Solidification Plus PW-2 Waste Solution*

Conditions: Five 48-hour exposures to boiling solutions.

Solution	Average Corrosion Rate, in./year	
	Liquid	Vapor
Composition a	0.024	0.00024
Composition b	0.167	0.0006

	Molarities							
	H ₂ SO ₄	HNO ₃	H ₃ PO ₄	NaNO ₃	Fe(NO ₃) ₃	Ba(NO ₃) ₂	Ce(NO ₃) ₃	Ni(NO ₃) ₂
Composition a	2.0	4.1	1.9	0.51	0.26	0.25	0.23	0.025
Composition b	4.0	4.9	2.2	0.58	0.30	0.29	0.29	0.03

TABLE 9.8. *Corrosion of Titanium and Zircaloy-2 in Phosphate Glass Melter Condensate from PW-2 Waste*

Conditions: Nionel specimens exposed for five 48-hour periods, 304L specimens exposed for three 100-hour periods.

Solution Molarity			Temp, °C	Material	Average Corrosion Rate, in./year	
H ₂ SO ₄	HNO ₃	H ₃ PO ₄			Liquid	Vapor
5	2.4	0.2	Boiling	Nionel	0.0024	
1	0.5	0.04	Boiling	Nionel	<0.001	<0.001
5	2.5	0.2	45	304L ^(a)	<0.001	
1	0.5	0.04	45	304L ^(a)	<0.001	

(a) Weldment was fabricated from 1/2 in. plate and 308L filler metal. Weldments were activated twice during each exposure by contact with mild steel wool.

TABLE 9.9. *Nionel and 304L Stainless Steel Corrosion in Sulfate-Containing Melter Condensate from Phosphate Glass Process*

Conditions: Five 48-hour exposures to boiling solutions.

Condensate Composition: 4.2M H₂SO₄, 2.1M HNO₃, 0.2M H₃PO₄.

Material	Average Corrosion Rate, in./year	
	Liquid	Vapor
Ti	0.066	0.0005
Zircalloy-2	0.0001	0.0001

In WSEP, the feed pump supplies feed (Purex Waste) over the range of 5 to 60 liters/hr to the three solidification processes. In a large plant this rate would be increased considerably. The feed pump is designed to circulate feed from the bottom of the feed tank back to the tank at a rate of 40 to 80 liters/min. This minimizes solids settling in the feed loop and allows use of a standard centrifugal pump. By using a pump recirculation loop as used in WSEP, the feed rate to the process can be varied over an extremely wide range (5 liters/hr to more than 1000 liters/hr) by changing the feed control valve trim while using the pump.

Feed from the processes is drawn off from the recirculation loop through a control valve. In WSEP, difficulty with solids plugging of the feed control valve was experienced when a tapered plug trim was used. This difficulty was eliminated by using a control valve with a spline type of trim. The pumping pressure requirements for both the pot calciner and phosphate glass processes are not critical. However, the spray solidifier internal mixing nozzle requires a relatively narrow range of pump pressure for a given atomizing air pressure. For the nozzle used in WSEP, a pump pressure range of about 30 to 40 psig is required for an atomizing gas pressure of 45 psig.

Line sizing between the pump and the process should be done with great care so that solids do not readily settle in the lines.

Flushing of the feed lines to the process is an absolute necessity before starting feed and after any termination of the feed. If not flushed, solids will settle in the lines, and the high temperature at the process

discharge will calcine the feed in the lines to form plugs. A pumping system is required to provide flush water at rates equal to feed rates to the solidifier. In WSEP a submerged canned rotor pump in the final condensate from the process is used to pump condensate through a small flush tank from which the liquid may be metered into the feed lines for flushing. A pressure in excess of the feed pump is maintained on the flush tank at all times to prevent contamination of the condensate with feed. Since this pump requires no special features, a centrifugal pump outside the condensate tank could be used, and any source of water or dilute nitric acid could be used.

The pump used for circulating caustic solution through the scrubber tower is a submerged pump identical to the one used for feed line flushing in WSEP. This pump also does not require any special features and could be mounted outside of the caustic tank.

Metering pumps are used in various parts of the WSEP to add liquid chemicals to the processes. For these pumps a maximum capacity about the same as the feed rate is desired. A high pressure pump and spray system may also be used to pump chemicals at sufficient pressure to clean selected process equipment through spray nozzles. A pump with an output pressure of 100 psig would generally serve this purpose.

9.5.2 Agitation Requirements

Because the wastes and final feeds contain gross solids, it is essential that these wastes are almost constantly agitated to provide uniform delivery of feed solids to the processes and to prevent solids plugging and caking difficulties.

While some of the final phosphate mixes have gelatinous, slow settling precipitates which will not immediately cause problems, other solutions may have only sodium rare earth sulfates, which if allowed to settle will form hard cakes. Air sparging as a method of agitation is not suitable for continuous use since volatile ruthenium is removed from the solution. Spargers are also susceptible to plugging by solids that settle to the bottom of tanks.

9.5.3 Flow Metering

Flowmeters are required to measure feed rates to the processes. In WSEP, magnetic flowmeters have been used. Both radiation and nonradiation resistant meters have been tested. The radiation resistant meters have radiation resistant wiring which is potted in silicone rubber to keep the wires separated. Performance of both types of meters has not always been satisfactory. Problems include loss of signal, frequent shifts in calibration, and wire failure. The wire failures are described below. An additional problem with magnetic flowmeters for metering waste are the small hole size required for accurate metering of the small flow rates used in WSEP (5 to 25 liters/hr).

9.5.4 Electrical and Instrument Wiring

Neoprene rubber has been a satisfactory wire covering in WSEP. It has a useful life of at least two years. The more expensive linear polyethylene is classified as radiation resistant, but has a useful life of only one year in WSEP. The linear polyethylene becomes brittle and causes wire breakage when the cables are moved. Glass covered thermocouple wiring is also better than linear

polyethylene. In general, in areas where the wiring will be contacted or moved, the combination of inexpensive neoprene-covered wiring and easy remote replacement appears to provide good service.

9.6 FURNACE AND MELTER REQUIREMENTS

Since the solidification processes are high temperature operations, specific furnaces and melters are required for each process. The added complexity of internal heat generation in the solidified wastes creates the need for cooling integrated with the heating requirements in some cases. When internal heat generation rates are very high, cooling requirements may exceed air-cooling capabilities, and pots may have to be filled while immersed in water. Special heating and cooling requirements are further discussed below.

9.6.1 Pot Calciner Furnace

A multiple-zoned furnace is required because the heating and cooling needs are different for each vertical portion of the pot at any given time. Some of the sludge and scale formed during calcination and solids from the feed fall to the bottom of the pot. Thus, solids accumulate faster from the bottom upward than from the walls inward. 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 and may be superfluous. (31) Maximum furnace heating requirements are based on pot diameter. For 8- and 12-inch diameter pots, approximately 35 and 70 kilowatts of net heating capacity are needed, respectively, during the period of maximum boilup rates.

Cooling is also required in the furnace to remove the heat of radioactive decay from the calcine after all material has been calcined. Zone cooling is required for the same reasons zone heating is needed. Design of furnaces with zone heating is relatively straight-forward, while design for zone cooling presents a major problem to the designer. The walls of pots containing 1.5 kW/linear foot of pot of radioactive decay heat have been cooled to 400 °C, using air indirectly on the outside of a second container surrounding the pot. (31)

9.6.2 Spray Calciner and Melter Furnaces

The furnace for heating the spray calciner must have multiple zones for heating to temperatures of 800 °C to provide heat flux which varies slightly with the vertical position of the drier. The top portion of the spray tower (the part above the point where the atomized waste would impinge on the walls of the tower, i.e., 25 to 30% of the total length of the tower) consumes 35 to 40% of the heat. The heat requirement for the lower 70% of the tower is nearly uniform. Approximately 1 kilowatt of net heat for each liter per hour of liquid feed rate is required.

The furnace for heating the continuous melter must be capable of providing 2 to 3 kilowatts of heat for each liter per hour of melt formed at furnace temperatures up to 1300 °C. Modifications of standard resistance-heated electrical furnaces or induction-heated furnaces have performed satisfactorily in this service.

The receiver furnace requirements are similar to those in pot calcination except that total heating requirements depend only upon the natural heat losses from the furnace

to maintain the solidified waste at a temperature near its slump or melting point (up to 950 °C). Multiple heating zones are required because it is necessary to cool a zone which is full of melt at the same time that a zone which is filling with melt must be heated. Zone heights of 13 inches have proven to be satisfactory in WSEP. Cooling requirements of the pots are similar to those for pot calcination: increased heat density is attainable in the product, and proportionally increased cooling capacity is needed.

9.6.3 Phosphate Glass Furnace and Melter Requirements

The continuous melter and furnace requirements are essentially the same as those discussed previously for the spray solidifier. Exceptions are that in the phosphate glass melter the net heat transfer requirements are 50 to 100% higher, primarily because of the added evaporation load, and the desired freeboard requirements above the melt level are somewhat higher because of the foaming tendency in the melter.⁽³³⁾ The capacity of a platinum melter that is 10 inches in diameter and has a 14 inch-high heated section is 1.2 liters/hr of glass, or about 3 liters/hr of slurry feed.^(34,35) The vapor stream from the melter is hot (400 to 600 °C) and corrosive⁽³⁶⁾ and must be routed through platinum piping until the temperature is reduced to about 120 °C.

The furnace for heating the melter is similar to that for the spray solidifier, except that the net heat load requirement is about 7 kilowatts for each liter/hr of melt formed at temperatures up to 1300 °C.

The receiver furnace requirements are the same as those in spray solidification, except that the temperature requirement is reduced to about 700 °C for phosphate glass solidification.

9.7 SAMPLING AND ANALYTICAL REQUIREMENTS

Samples of the waste solidification process streams are needed for process control and for monitoring the process effluents for radioactivity. Liquid samples provide most of the information necessary for the operation of the waste solidification process and also comprise the bulk of the samples taken to monitor radioactivity in the auxiliary process equipment used to decontaminate the solidifier effluents. Samples of the liquid feed to the solidifiers are generally adequate to describe the composition of the solidified waste product. Consequently, samples of the solid wastes are needed primarily where product quality information (such as leachability) is desired. The final aqueous and gaseous effluents leaving the auxiliaries and entering man's environment must be continuously monitored to show that the levels of radioactivity released to the environment are well below the limits set by the federal government for the effluents from a nuclear processing plant.⁽⁴⁸⁾

The analytical results for all samples (liquid, gas or solid) must be qualified to establish the reliability of the data. The reliability of any analytical data is dependent upon the accuracy of the analytical procedure and upon obtaining representative samples from the process. The estimated accuracies for the analytical procedures used to analyze the WSEP aqueous samples are given in Table 11.6. The analytical accuracy for the major chemical and radiochemical constituents in the WSEP wastes are all within the 5 to 15% error range.

9.7.1 Aqueous Samples

Special care is required to obtain representative samples of aqueous waste solutions because they often contain suspended (undissolved) solids, they cover a wide range of levels of radioactivity, and the location of the process equipment and its construction usually limits accessibility for the ideal "dip" or "grab" sample. Because the vessels used for radioactive waste solutions are usually constructed with a minimum of bottom outlets to minimize the chance for leaks, it is common practice to use top-entering dip legs for solution transfers, including sampling. Steam- or air-operated jets are popularly used for batch transfer of solutions because pumps are less reliable for lifting solutions which contain suspended solids out of tanks, and pumps require more maintenance. In the WSEP system, steam-operated jets are used for all solution transfers between tanks, and air-operated jets are normally used only for sampling. The air-operated jet is used to obtain undiluted (representative) sample of the process solution. A more detailed description of the WSEP sampling equipment is available in Reference 44. The requirements for obtaining representative samples of aqueous process solutions for all sampling mechanisms will include: (1) adequate agitation of the process solution to assure good suspension of solids, (2) adequate recirculation of the sampling train to displace trapped solutions, and (3) control of sample dilution or contamination .

Where nonrepresentative samples are obtained because of incomplete suspension of the undissolved solids, it may be necessary to match the mixing pattern in the tank (upflow at the sampler dip tube) and the local solution velocity

(at the dip tube) with the recirculation rate in the sampling lines (i.e. isokinetic sampling). A minimum of 5 to 10 line volumes is necessary in most systems to displace the stagnant solutions in the sample lines and dip legs. The recirculation rate must be sufficient to prevent suspended solids from settling out of solution. The sampling device should not dilute or otherwise contaminate the sample or the process solution being sampled. Also, the sample device must prevent the contamination of the sample by the environment. This is particularly a problem with sampling solutions containing low levels of radioactivity in a shielded facility which frequently has a high concentration of radioactivity in the cell air. The aqueous sampler must be able to handle the solids present in some streams (the basis of up to 0.1 inch diameter solid particles was used for the WSEP samplers). The air-operated jet, recirculation type of sampler has performed very well during the WSEP work, even for the feed solutions which contain from 20 to 90 vol% suspended solids.

The size of the aqueous sample is dependent upon the number of analyses needed per sample, and the sample volume required per analysis. The analytical methods and techniques used to analyze the WSEP samples require 0.5 to 1.0 milliliters of sample for most of the analyses. The aqueous samples in WSEP, therefore, contain about 20 milliliters of solution which includes about a 10% excess for the 10 to 15 analyses requested for a feed sample and a large excess for the 3 to 7 analyses requested for a condensate sample. Smaller condensate samples are not taken because it is more convenient to use one size of sample bottle, and the 20 milliliter sample bottle is easier to handle in the remote facility than smaller bottles.

For solutions encountered in solidification, the concentrations of radioactivity normally range from 2000 to 20,000 Ci/liter for the feed down to as low as 0.01 μ Ci/liter for the condensate. All of the WSEP aqueous samples are transferred to the analytical laboratory in shielded sample carriers except for the fractionator condensate and the scrubber samples (i.e. the solutions representing the "decontaminated" effluents from the auxiliary equipment; radionuclide concentrations in these samples are usually 100 to 1000 μ Ci/liter). About half of the samples, including the feed samples, have direct gamma dose readings greater than 2 rad/hr at the surface of the 20 milliliter sample bottles. These samples must be analyzed in a high level radiochemistry cell using remotable equipment which adds appreciably to the time required to perform each analysis, but does not interfere with the accuracy. In general, the analytical accuracies given in Table 11.6 are mostly a measure of the inaccuracies induced in the results by the presence of undissolved solids in the aqueous samples.

In the WSEP program, duplicate samples are taken of aqueous solutions which contain visible quantities of undissolved solids or where erratic analytical results indicate that non-representative samples were obtained. Since the samples of feed to the solidification process provide a major fraction of the process information for a WSEP demonstration, it is common practice to take duplicate feed samples at the start and the end of each demonstration. On the average, about 3 out of 4 WSEP feed samples (containing 20 to 90 vol% suspended solids) are analyzed with the same results (within 10%) for the major constituents. About one out of four samples, however, have salt and radioactivity concentrations which differ significantly (greater than 50%) from the average of the other three. The high

percentage (~25%) of nonrepresentative feed samples or analyses indicates that periodic duplicate sampling is necessary to provide a representative sample of aqueous waste solutions which contain appreciable quantities of undissolved solids.

The analyses required to characterize an aqueous waste solution for waste solidification fall into two categories: (1) the analyses for reactor-produced materials (i.e. fission products) and (2) the analyses for materials added during fuel reprocessing. The chemical reprocessing materials may include chemical neutron (fission) poisons (such as boron or cadmium), chemical reductants and salting agents (such as ferrous sulfamate and aluminum nitrate), corrosion products and fuel cladding materials (such as iron), and chemicals used to adjust the acidity or basicity of the aqueous waste solutions (usually nitric acid and sodium hydroxide). The principal reactor-related analyses include total ruthenium, total rare earths, strontium-90, promethium-147, total beta, and gamma emission analysis (GEA). The GEA is used to measure the concentrations of the major gamma emitting radionuclides in the aqueous waste solutions including cerium-praseodymium-144, cesium-137, cerium-141, ruthenium-103, ruthenium-rhodium-106, and zirconium-niobium-95.

Other chemicals and radiochemicals which are expected to become important in high level wastes in the future include tritium, technetium, fluorine, tellurium, antimony, tin, and vanadium. Most of these materials are potentially volatile, and will require additional efforts to either contain them in the solidified waste or remove them from the solidifier effluents. Vanadium and other high temperature metals are expected to be used in increased quantities for cladding material for future nuclear power fuels. The

accuracy to which the waste composition must be known is largely dependent upon the type of solidification process being used.

The major constituents in feed to the spray and phosphate glass processes are iron, aluminum, sulfate, rare earths, and alkali metals; to the pot calcination system are the alkali metals and sulfate. In general, a 10 to 15% error (high or low) in the analytical determination of these major constituents in the waste solutions will not significantly influence the operability of the three solidifiers, and appreciably larger analytical errors can be tolerated for the minor constituents.

9.7.2 Gas Sampling

Liquid samples from each successive off-gas decontamination step (evaporation-condensation) can be used to determine the approximate concentration of radioactivity in the preceding off-gases. Gas samples are not normally essential to the operation of the auxiliary equipment for the waste solidifier, and the need for samples of the noncondensable gases from the waste solidification process are mainly to ensure conformance to established emission limits. Non-routine samples may be desirable to assist in determining the efficiency of a piece of equipment for the removal of volatile or entrained radionuclides from the gas stream. The most desirable monitoring system for a continuous process is an in-line system to warn, immediately, the operator of excessive levels of radioactivity in the auxiliary off-gas train.

Representative gas samples are usually difficult to obtain and difficult to analyze, primarily because most of

the radioactivity found in the gas streams exists as entrained liquid and solid particles. Because of the heterogeneous nature of the radioactivity in the off-gas streams, the "total trap" type of gas sampler is best suited for gas stream analysis. A "total trap" sampler removes all radioactivity from the gas sample stream and confines the activity in either a liquid (absorption) or on a solid (filtration and adsorption). Some of the methods which have been used to selectively trap the ruthenium from a gas stream include absorption-adsorption on silica gel saturated with formaldehyde, ^(25,43) adsorption on polyethylene ⁽⁴⁰⁾ beads near their softening point (about 80 °C), adsorption on beds of ferric oxide, ^(41,42) and absorption-adsorption in solutions of ferrous hydroxide. ^(45,46) Each of these methods is suitable for monitoring the efficiency of auxiliary process equipment for the removal of ruthenium. Where the total radioactivity must be trapped from a gas sample stream, some combination of filtration, adsorption, and absorption method are normally used to trap gases and aerosols. The stack gases (about 3,000,000 liters/min) containing the WSEP off-gases (about 300 liters/min) and other process gases are continuously sampled with a total trap sampler which consists of a high efficiency filter followed by a caustic scrubber. Each week the filter is changed and counted for total beta and total alpha radioactivity. The scrubber solution is also changed weekly and counted for total gamma radioactivity.

The radionuclides in the gaseous effluents are the primary reason for taking gas samples, but other noncondensable gases may require monitoring as well. The oxides of nitrogen in the solidifier off-gases represent a potential pollution problem because they are difficult to scrub completely from

the gas stream and they represent a chemistry problem because they influence the ruthenium chemistry in the off-gas stream. To characterize the process off-gases, it may be desirable to monitor the gases for the oxides of nitrogen. Nitrogen oxides can be analyzed directly by colorimetric methods if greater than 1% NO_2 at 1 atmosphere or by colorimetric analysis of Saltzman reagent for less than 1% NO_2 in the gas. (49,50,51) Gas chromatography is difficult due to the high reactivity of NO_2 in air-water mixtures.

9.7.3 Solid Sampling

Samples of the solidified waste are not expected to be necessary to the routine operation of a waste solidification plant. However, the actual solid sampling may be desirable to determine the quality of the solidified waste. For example, leachability measurements on product samples may be desired before shipment or storage of the solidified waste. Solid sampling may occasionally be desirable to obtain material balance information.

The size of the solid sample is limited by the analytical requirements to provide accurate data. The analytical requirements are the same as the requirements for liquid samples, since the solid must be dissolved in aqueous solutions prior to analysis by most standard analytical procedures.

The molten waste from the continuous melters (for the spray and phosphate glass solidifiers) were not "true" solid solutions. Occluded solid particles on the order of 1 millimeter in diameter were observed in both the spray

and the phosphate glass solidified wastes. Consequently, special care is required to obtain representative samples for dissolution and analysis.

Most of the solid samples taken during the WSEP program contain between 1 and 3 milliliters of melt (about 3 to 10 grams) with 40 to 100 Ci/ml of melt. The resultant gamma radiation dose rates are 1 to 10 Rad/hr through about 2 inches of lead.

In general the analyses needed to characterize the solid wastes and the aqueous wastes are the same. The most difficult analytical problem with the solid samples is obtaining complete dissolution of the solids for analysis. The WSEP solidified melt samples are quite insoluble in all known reagents. In general, the accuracy of the analyses for a solid sample constituent is a function of the leachability of the constituent from the solid. Consequently, sodium, phosphate, and cesium are usually the most accurate analyses, and the concentrations of the more insoluble rare earths are generally less accurate. The composition of the solid wastes can best be determined from the total feed composition and analyses of the effluent stream from the solidifier. Analysis of the volatile constituents in the solid samples may also be helpful.

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10.0 ABSTRACT OF SAFETY ANALYSES

(by W. K. Winegardner)

Safety analyses have been performed for the WSEP program to assure that (1) potential major hazards of the WSEP have been identified, and (2) sufficient safeguards have been incorporated to minimize the consequences and the probability of an incident that could result in the release of radionuclides to the environs. The primary consideration in these studies was that in event of such an incident, exposure of persons and contamination of property would be minimal.

These safety analyses were reviewed in detail and approved by a council of Battelle-Northwest staff members who are recognized experts in a broad range of technical-safety areas and hold responsible positions within the Battelle-Northwest organization. A safety analysis and a council review of the WSEP equipment, facility, and program plans were completed before the WSEP radioactive demonstrations began. The overall conclusion from the safety studies was that the large number of safeguards included make the possibility extremely low for any of the postulated incidents to occur. Furthermore, even if the large number of safeguards failed and the incidents did occur, significant amounts of radioactivity would not be released from the building. Although the safety analyses were specific to the WSEP program and systems, the relative safety in the WSEP systems confirms the fact that solidification of high-level wastes and their interim storage can indeed be done safely. These factors will be further confirmed for general situations involving solidification of high level wastes in later safety analysis studies in the waste solidification program.

The three hypothetical accidents which were determined to have the most potential for causing hazardous situations are listed in descending order of importance:

- "Red-oil"* reaction.
- Waste pot failure
- Melter failure.

Other conceivable incidents which were investigated and found to result in lesser releases of radionuclides than the aforementioned three included:

- Coolant failure to in-cell storage rack for pots full of solidified waste.
- Potential hydrogen explosion.
- Loss of pot furnace cooling.
- Failure of services (air, water, steam, electricity).
- Load-in and load-out hazards.
- Flooding of B-Cell.
- Excessive cell heat load.
- Cell pressurization from failed air supply line.
- Welding hazards.
- Radioiodine in waste solutions.
- Criticality incident.

The inventory of fission products with the maximum hazard potential in any one pot was estimated to include 4.6, 2.5, 0.3, and 0.3 megacuries of total radioactivity, cerium-rare earths, strontium-89 and strontium-90, respectively. The heat rate from a pot of solidified waste containing this inventory is 23 kilowatts. Storage of 14 of these pots in B-Cell was assumed.

* A "red-oil" reaction is one in which Purex-type of organic solvent is rapidly oxidized by the nitrate in solution, with the evolution of large quantities of gases and energy.

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(by M. R. Schwab)

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11.0 APPENDIX

(by M. R. Schwab)

11.1 DEFINITIONS

The definitions in this section are those used throughout this report and the Waste Solidification Program performed by Battelle-Northwest for the AEC. The definitions are also generally consistent with normally used terminology in the nuclear fuel reprocessing industry. The definitions are presented in alphabetical order below.

Auxiliaries

The auxiliary equipment is that equipment used to decontaminate and separate the nitric acid, water, and noncondensable effluents in the solidifier off-gases (i.e., condensers, evaporator, fractionator, scrubber, and filters).

BNW

Battelle-Northwest (BNW) is the Pacific Northwest Laboratory of the Battelle Memorial Institute whose headquarters are in Columbus, Ohio. BNW operates the Pacific Northwest Laboratory in Richland, Washington for the AEC, and performs private contract research and development work at the same site.

Calcine

The dry solid formed from high temperature (300 to 900 °C) drying of wastes (pot calcination) or feeds (spray calcination). The calcine is a porous, friable solid of mixed metallic oxides from which most of the volatile

constituents (nitrates and water) have been removed. Melt-forming chemicals may be added to the calcine at high temperature to produce a molten ceramic or glass.

Ceramic

A solidified waste whose structure is basically micro-crystalline. A ceramic has a dull nonglassy (or sometimes partly glassy) appearance and is a monolithic solid.

Concentration Factor (or Volume Reduction Factor)

The volume reduction of the salt-bearing waste that is achieved in an evaporation or solidification step. The term is used in the WSEP program to compare volumes of original aqueous wastes to the volumes of the final solids or to intermediate concentrated wastes (such as the denitrator bottoms in the phosphate glass process).

Decontamination Factor (DF)

The ratio of the amount of a material (usually radioactive) initially present to the amount remaining after a suitable processing step has been completed.⁽¹⁹⁾

1. Cumulative DF: The ratio of the total material (usually radionuclides) that is in or has accumulated at a point in the process or effluent chain to the total material that has left that point for the duration of the manufacture of one pot full of solidified waste. Measurements are frequently taken from liquid samples at successive, adjacent points in the effluent chain. For example, the total

radioactivity in the evaporator (fractionator) at the end of a solidifier demonstration run divided by the net gain in radioactivity in the fractionator (fractionator condensate) is taken as the Cumulative DF for the evaporator (fractionator).

2. Instantaneous DF: The ratio of the concentration of a material (usually radionuclides) at a process point (such as in the solidifier, evaporator, or fractionator) to the concentration of the material in the effluents from that equipment (usually the condensed vapor), measured at the same time.

Distribution of Radioactivity

A material balance on the total radioactivity fed to the solidification equipment involves measuring the fraction of the radioactivity present in the feed to the solidification equipment which accumulated in the product pot and in the effluent treatment equipment. A material balance is usually made for each of the principal gamma-emitting radionuclides, ZrNb-95, Ru-103, RuRh-106, Cs-137, Ce-141, CePr-144 and for the principal beta emitters Sr-90 and Pm-147. In general, only the radionuclides of ruthenium are volatile and therefore appear in significant quantity in the auxiliaries. The nonvolatile materials are carried downstream in the process effluent by physical entrainment.

Effective Thermal Conductivity

The effective thermal conductivity for a solidified waste is calculated from the basic equation for steady-state heat transfer

through a cylindrical solid with a uniform internal heat generation rate and a thermal conductivity which is constant over the temperature range for the solidified waste:

$$k_{\text{eff}} = \frac{(P/V) (10^3) (r^2)}{4\Delta T}$$

where: k_{eff} = thermal conductivity, W/(m) (°C)

P = total power in solid waste, watts

V = total volume of solid waste, liters, P/V = power density, W/liter

r = radius of pot receiver, (solid cylinder), meters

ΔT = temperature difference from pot centerline to pot wall, °C

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

Equivalent Aging Time

The specific fission product heat generation rate, or power, (W/tonne) of the waste from a nuclear fuel decays at a known rate from the time of discharge from the reactor. In the WSEP program, two thermal reactor fuels are used as bases: (1) 20,000 MWd/tonne at 15 MW/tonne, and (2) 45,000 MWd/tonne at 30 MW/tonne. The basis for core fuels from fast reactors is 100,000 MWd/tonne at 200 MW/tonne. The radioactive wastes solidified during the WSEP program were prepared from cold chemicals and concentrated wastes from low-exposure reactor fuels. The "equivalent" aging time of a WSEP solidified waste is determined as the time required for the fission product power (W/tonne) in the spent, base fuel (at the time of discharge) to decay to the level of the fission product power (W/tonne) in the solidified waste.

Freeze Valve

Each of the continuous melters (for the spray and phosphate glass solidification processes) has a drain tube which is sealed by freezing melt and is opened by remelting the solidified melt in the tube. The drain tube is called the freeze valve or the dump valve. In WSEP, the drain tube will permit the complete drainage of the melter.

Fuel Processing Plant

A chemical plant for processing (or sometimes called reprocessing) partially spent nuclear fuel from a power reactor to purify and separate valuable fissionable materials from nonradioactive and other radioactive materials.

Glass

A solidified waste which has primarily an amorphous, or noncrystalline structure. The solid has a glassy, lustrous appearance. With few exceptions, the only glassy solid wastes from the WSEP program are phosphate glasses.

Heat Generation Rate

The rate at which heat is generated by radionuclide decay in the waste material in Btu/hr or watts; equivalent to power.

Liters/Tonne

A concentration term common to the WSEP work. The volume of aqueous or solid waste containing the fission products and inert

chemicals from one metric ton (tonne) of spent nuclear fuel from a nuclear reactor. A standard aqueous waste concentration of 378.5 liters/tonne (100 gal/tonne) was selected for the WSEP program.

Melt

The waste form in the melter of the phosphate glass or spray solidification processes in the WSEP. Some of the waste from these processes may also be molten in the receiver or storage containers.

Melter Weir (Overflow)

Each of the continuous melters for the spray and phosphate glass processes have overflow tubes by which melt can continuously flow to the receiver pot while still maintaining a nearly constant melt volume in the melter. These overflow tubes are designated as weirs.

Percent Denitration

The percent of the nitrate in the feed to the solidification equipment which is volatilized. The term is normally applied only to the denitrator-evaporator in the phosphate glass process.

PC

The WSEP abbreviation for pot calcination. In pot calcination at Oak Ridge National Laboratory, the liquid waste is added to a pot that is heated in a multiple-zone heating and cooling furnace. The waste is concentrated at constant volume until the buildup of scale (salt cake) restricts heat transfer to

a point that the feed rate has been gradually reduced to one that is unprofitably low. The feed is then discontinued and the pot deposits are dried to a calcine after which the pot is cooled in the furnace, removed, sealed, and taken to storage.

The pot calcine product is a friable, porous calcine (see Calcine); a mixture of oxides with a low bulk density, a low thermal conductivity, and a relatively high solubility in aqueous solutions.

PG

The WSEP designation for phosphate glass solidification. In phosphate glass solidification at the Brookhaven National Laboratory, liquid waste is continuously concentrated to a thick slurry in an evaporator from which the slurry is drawn off for conversion to a glass in a continuous melter. The molten glass flows into a receiver-storage pot below the melter. After the pot is filled, it is cooled in the furnace, sealed, and taken to storage.

The phosphate glass solid is a monolithic glass that is characterized by its low solubility in aqueous solutions, a good thermal conductivity (i.e., moderately high), and a dark black-green color.

PNL

The Pacific Northwest Laboratory (PNL) is that part of the laboratory at Richland, Washington which is owned by the Atomic Energy Commission and operated by Battelle-Northwest. At PNL, research and development work is done on nearly all of the facets of atomic energy.

Pot

The pot is the container used to store the solidified waste. The solidified waste is either received in the pot as a molten solid from a continuous melter (spray and phosphate glass melts) or it is formed directly in the pot where the pot is also the processing vessel (pot solidification). The WSEP pots are usually either 8 or 12 inches in diameter but 6-inch diameter pots may also be used. All of the WSEP pots are 8 feet long and made of either mild steel, type 304L stainless steel or type 310 stainless steel.

Pot Cooling Time

The time required for cooling a pot full of completely processed, solidified waste to the point that the pot wall temperature will not exceed 427 °C (800 °F). The pot wall temperature limit was selected as a reasonable maximum for protection of in-cell equipment during the transfer of a pot within the cell.

Pot Temperatures

1. Centerline Temperature: A thermocouple measured temperature inside a thermowell pipe positioned in the center of the receiver pot for the solidified wastes at the midpoint of a furnace heating or cooling zone.
2. Wall Temperature: A reading via a thermocouple welded to the outside of the pot receiver at the midpoint of a furnace heating or cooling zone.

3. In "Cool" Furnace: The temperatures at steady-state with maximum air cooling in the furnace.
4. In "Warm" Furnace: The pot temperatures at steady-state (without cooling air) in the insulated, unheated furnace.
5. In Air: The pot temperatures at steady-state with the pot hanging in ambient air in a hot cell.
6. In Water: The pot temperatures at steady-state with the filled portion of the pot submerged in water. The temperatures of the water may be as low as the ambient air or as high as 100 °C.

Power

The rate at which heat is generated by radionuclide decay in the waste solutions and solids. (It is also called the heat generation rate.)

Power Density

The rate of internal heat generation per unit volume of waste (W/liter), especially for solid waste.

Processing Rate

In WSEP, processing rate is normally expressed as liter/hour of aqueous waste processed, or as waste processed from so many metric tons of fuel per day (tonnes/day). It is determined for each WSEP run from a feed material balance over the "steady-state" operating period with an allowance for or measurement of final pot cooling time. For the phosphate glass and spray

solidification processes, four hours are allowed as an average for the pot cooling time. The pot solidification operating period includes a drying and cooling time as part of the cycle, and no additional cooling time is necessary prior to pot changeout. A pot changeout time is not included in the WSEP processing rate because the pot changeout time and techniques may vary significantly in different production facilities. However, pot changeout time may be a significant part of the total pot filling cycle (estimated at 2 to 10 hours).

Product

The product is the solidified waste and its receiver-storage pot.

PW-1

The WSEP abbreviation for Purex Waste number 1. It is one of the 5 standard base waste formulations established in the waste solidification program for thermal reactor fuels. PW-1 is an aqueous waste discharged by a fuel processing plant using a Purex flowsheet to process a spent nuclear power fuel with an exposure history of 20,000 MWd/tonne at 15 MW/tonne. See Tables 2.3 and 2.4 for waste composition. The basis for the PW-1 waste was the waste stream generated by a Purex process from the first cycle of the fuel reprocessing scheme wherein an iron fuel container is dissolved with the fuel. The distinguishing characteristics of the PW-1 waste include high iron, low sodium, no sulfate, and no aluminum.

PW-2

The WSEP abbreviation for Purex Waste number 2. It is one of the 5 base waste compositions established in the waste

solidification program for thermal reactor fuels. PW-2 is an aqueous waste discharged by a fuel processing plant using a Purex flowsheet to process spent nuclear power fuel with an exposure history of 20,000 MWd/tonne at 15 MW/tonne. The basis for the PW-2 waste was the waste stream generated by a Purex process which includes a mixture of first and second cycle process wastes where iron and sulfamate ions are used as reductants for partitioning uranium from plutonium. The distinguishing characteristics of the PW-2 waste include medium level iron, high sodium, high sulfate, and no aluminum.

PW-3

The WSEP abbreviation for Purex Waste number 3. It is one of the 5 base waste compositions established in the waste solidification program for thermal reactor fuels. PW-3 is a sulfate-containing aqueous waste discharged by a fuel processing plant using a Purex flowsheet to process spent nuclear power fuel with an exposure history of 20,000 MWd/tonne at 15 MW/tonne. PW-3 waste is the same as the acidic PW-2 waste which has been neutralized with sodium hydroxide. The normally acidic Purex waste is sometimes made slightly basic for storage in underground vaults with mild steel liners. The distinguishing characteristics of the PW-3 waste include medium level iron, very high sodium, high sulfate, and no aluminum.

PW-4

The WSEP abbreviation for Purex Waste number 4. It is one of the 5 base waste compositions established in the waste solidification program for thermal reactor fuels. PW-4 is an aqueous waste discharged by a fuel processing plant using a Purex flowsheet to process spent nuclear power fuel with

an exposure history of 20,000 MWd/tonne at 15 MW/tonne. PW-4 waste is that generated by a Purex reprocessing scheme wherein essentially no chemical salts are added during reprocessing. The resultant waste is a chemically "clean" fission product waste. The distinguishing characteristics of the PW-4 waste include low iron, low sodium, no sulfate, and no aluminum.

PW-4m

The WSEP abbreviation for Purex Waste number 4 modified. The PW-4m waste is the same as PW-4 waste except for the reactor exposure history for the fuel. PW-4m is an aqueous waste discharged by a fuel processing plant using a Purex flowsheet to process spent nuclear power fuel with an exposure history of 45,000 MWd/tonne at 30 MW/tonne. PW-4m waste is that generated by a Purex scheme wherein essentially no chemical salts are added during reprocessing. The resultant waste is a chemically "clean" fission product waste. The distinguishing characteristics of the PW-4m waste include low iron, low sodium, no sulfate, and no aluminum.

PW-5

The WSEP abbreviation for Purex Waste number 5. It is one of the 5 base waste compositions established in the waste solidification program for thermal reactor fuels. PW-5 is an aqueous waste high in aluminum content discharged by a fuel processing plant whose process flowsheet uses aluminum as a salting agent for solvent extraction. The TBP-25 and the Redox processes are two such processes which discharge a high aluminum waste. PW-5 contains fission products from a nuclear power fuel with an exposure history of 20,000 MWd/tonne at 15 MW/tonne.

Purex

Purex, an acronym which stands for Plutonium-Uranium-Rare Earth-Extraction, is a solvent extraction process for the separation of uranium, plutonium, and fission products from a nitric acid solution of the spent nuclear fuel. The solvent used is tributyl phosphate (TBP) diluted with a straight-chain organic. The fission products leave the solvent extraction system as an acidic, aqueous waste stream.

Shutdown Time

The WSEP phosphate glass demonstrations require a 10 to 15 hour shutdown period to dilute the denitrator-evaporator bottoms for removal of the concentrated waste slurry. About half of the concentrate in the denitrator-evaporator at the end of a WSEP demonstration is processed to a solid in the melter during the dilution and shutdown period. About 10 to 20% of the 60 liters of solidified waste in an 8-inch diameter pot receiver is accumulated during the dilution period. In a production facility, such shutdowns would occur very seldom, and would not significantly affect overall processing rates as they do in the WSEP system.

Slump Point

The temperature at which the solid ceramic or glass begins to soften as seen by a rounding of irregular edges, by the sagging in the middle of a thin plate supported at each end, or by the solid surface of freshly formed calcine "slumping" and becoming smooth.

SS

The WSEP designation for spray solidification. In spray solidification, developed by Battelle-Northwest, liquid waste is fed through a pneumatic atomizing nozzle into the top of a heated cylindrical tower. The atomized waste is sequentially evaporated, dried, and calcined into a powder as it falls through the tower into a continuous melter below the calciner where it is melted at temperatures of 800 to 1200 °C. The molten calcine flows into a receiver-storage pot below the melter. After the pot is filled, it is cooled in the furnace, sealed, and taken to storage.

The spray solidification product is a monolithic, tough, solid ceramic which has a moderately low solubility in aqueous solutions and a good thermal conductivity.

Solidifier

The solidifier is the equipment used to convert the high-level radioactive aqueous waste (1000 to 20,000 Ci/liter) to a solid waste (10,000 to 100,000 Ci/liter). The basic elements of equipment in the WSEP spray solidifier include: (a) an atomizing nozzle and a spray tower for atomizing and drying-calcining the feed; (b) a multiple-zone furnace for heating the spray tower; (c) porous stainless steel filters adjacent to the spray tower to remove the bulk of the entrained calcine dust from the off-gases; (d) a continuous melter for melting the powdered calcine; (e) a furnace for heating the melter; (f) a pot for receiving the molten waste; and (g) a multiple-zoned furnace for heating and cooling the receiver pot.

The basic elements of equipment in the WSEP phosphate glass solidifier include: (a) a continuous evaporator to denitrate and concentrate the feed to a syrupy consistency; (b) an airlift recirculation pot for controlled transfer of the syrupy concentrate to the melter; (c) a continuous melter for final evaporation and melting of the waste; (d) a furnace for heating the melter; (e) a pot for receiving the molten waste; and (f) a multiple-zoned furnace for heating and cooling the receiver pot.

The basic elements of equipment in the WSEP pot solidifier include: (a) a multiple-zone furnace for heating and cooling the calcine; (b) a pot for calcining the waste; and (c) an off-gas line from the pot to the first process condenser which can be washed down continually.

Startup Time

Only the phosphate glass solidifier has a startup time during which feed is being processed but not converted to a solid. The denitrator-evaporator has an operating volume of about 50 liters of concentrated feed, or about 150 to 200 liters of unconcentrated feed. Approximately 10 hours are required to fill the denitrator to its operating level prior to the transfer of concentrated waste to the melter. The startup time for the phosphate glass solidifier is the time period between feed-on to the solidifier and the start of feed (concentrate) to the melter. In a production facility, such startups would occur very seldom, and would not significantly affect overall processing rates as they do in the WSEP system.

Steady-State

The steady-state operating period for a WSEP demonstration is the total time period for a continuous solidifier during

which the processing rate is insensitive to startup and shutdown conditions. For the spray solidifier, the steady-state time is the same as the feed-on time. For the phosphate glass solidifier, the total time at steady-state is the total feed-on time less the startup time required to accumulate an operating volume in the denitrator-evaporator. Although pot solidification is not a steady-state process, the total feed-on time and the drying-cooling time are used for the operating period to determine the average processing rate.

Stick Point

The temperature at which calcine powder becomes sufficiently softened to stick to a stainless steel rod when the rod is inserted, then removed, from a pile of powder. The furnace temperature in the spray calciner is maintained below the stick point to prevent the coating of heat transfer surfaces with calcine.

TBP

The abbreviation of tributyl phosphate. Tributyl phosphate is the extractant in the Purex solvent extraction process used for the recovery of uranium and plutonium from spent nuclear fuels. TBP can degrade to dibutyl phosphate (DBP) and monobutyl phosphate (MBP). The DBP causes excessive foaming during the concentration of Purex waste solutions.

Thermal Maximum

Thermal maximum is a WSEP term for the heat rate (power) density in a solidified waste for which one or more of the following steady-state limits are exceeded:

1. A pot receiver centerline temperature of 900 °C.
2. A receiver wall temperature of 427 °C in ambient air (25 to 40 °C).

The bases for the above limits are, respectively:

1.
 - a. The nominal maximum processing temperatures for the solidification products are all at or near 900 °C.
 - b. The centerline thermowell is made of type 310 stainless steel for which the corrosion rate can become excessive above 900 °C.
2. The limit of 427 °C (800 °F) was selected as a reasonable temperature to minimize potential heat damage to other in-cell equipment during transfer of the filled pot receivers in the hot cells. Also, corrosion of mild steel can become an important factor at temperatures above 427 °C.

Tonne

A metric ton is 1000 kilograms or 2204.6 pounds. The metric tonne of nuclear fuel (uranium plus plutonium) is commonly used in describing such fuels. Waste/tonne of nuclear fuel is commonly used in this report and in the WSEP program.

Waste

Waste in the WSEP program is generally the high radioactivity level liquid wastes resulting from the reprocessing of spent nuclear fuels. Such wastes are sometimes designated as feeds to the solidification devices. The high level aqueous wastes in WSEP contain up to about 20,000 Ci/liter of radionuclides.

WSEP

Waste Solidification Engineering Prototypes, the fully radioactive pilot plant demonstration of the solidification of high level radioactive waste solutions, and the supporting nonradioactive studies. The scale of operation is generally waste from 0.5 to 1.0 tonne/day of nuclear fuel.

10CFR20

Code of Federal Regulations, Title 10, Part 20. In particular, Appendix B, Table 2, Columns 1 and 2 are used for the maximum permissible concentration of radionuclides in liquid and gaseous effluents.

1WW

The abbreviation for the concentrated, acidic, aqueous waste from the evaporation of the raffinate (waste) from the first solvent extraction cycle of the Purex process. The 1WW stream contains essentially all of the nonvolatile fission products from the spent nuclear fuels in a nitric acid solution.

 $\Sigma M_T^+ / P$

The sum of the metallic cation gram equivalents (ΣM_T^+) divided by the gram moles of phosphate in the waste stream. For example, a solution of $1M$ Fe^{+3} and $1M$ Na^+ and $2M$ H_3PO_4 has an M/P of $(3 \times 1 + 1 \times 1) / 2 \times 1$, or 2.0. Metallic anionic material (e.g., MoO_4^{-2}) are not included in the ratio.

FIGURE 11.1. Vapor Phase Equilibria for Aqueous Solutions of Nitric Acid^(8,9)

FIGURE 11.2. Boiling Point Diagram for Aqueous Solutions of Nitric Acid (5,6,11)

FIGURE 11.3. Specific Gravity of Aqueous Solutions of Nitric Acid(10,11)

FIGURE 11.4. Specific Heat of Aqueous Solutions of Nitric Acid (10)

FIGURE 11.5. Viscosity of Aqueous Solutions of Nitric Acid⁽¹⁰⁾

FIGURE 11.6. Specific Gravity of Aqueous Solutions of Phosphoric Acid (3,16)

FIGURE 11.7. Boiling Point Diagram for Aqueous Solutions of Phosphoric Acid(6,16,20)

FIGURE 11.8. *Specific Gravity of Aqueous Solutions of Sodium Hydroxide (5)*

FIGURE 11.9. Vapor Pressure of Water over Aqueous Solutions of Sodium Hydroxide⁽⁵⁾

FIGURE 11.10. Viscosity of Aqueous Solutions of Sodium Hydroxide (5)

FIGURE 11.11. Specific Gravity of Aqueous Solutions of Sulfuric Acid (1,10)

FIGURE 11.12. Specific Heat of Aqueous Solutions of Sulfuric Acid (1,10)

FIGURE 11.13. Ternary Boiling Point Diagrams for the Sulfuric Acid-Nitric Acid-Water System(3)

a) Specific gravity of H_2SO_4 - H_3PO_4 - H_2O system at 14.88 mole% H_2O .

b) Specific gravity of H_2SO_4 - H_3PO_4 - H_2O system at 7.0 mole% H_2O .

c) Specific gravity, g/ml at 25 °C

d) Specific gravity, g/ml at 45 °C

e) Specific gravity, g/ml at 75 °C

f) Specific gravity, g/ml at 95 °C

FIGURE 11.14. Specific Gravities for the Ternary System of Sulfuric Acid-Phosphoric Acid-Water⁽⁴⁾

FIGURE 11.14. Specific Gravities for the Ternary System of Sulfuric Acid-Phosphoric Acid-Water⁽⁴⁾

FIGURE 11.15. Specific Gravity Correction Factors for Salts in High Level Waste Solutions(6)

FIGURE 11.16. Boiling Points of High Level Waste Salt Solutions(6)

FIGURE 11.17. Nitric Acid Volatility from Waste Solutions⁽⁶⁾

TABLE 11.1. *Selected Radioisotope Data Pertinent to High Level Waste Solidification(14,15)*

Nuclide	Half Life ^(a)	Particles			Photons		Watts/Kilocurie		Total
		Max. E, MeV	Avg E, MeV	Abund., %	E, MeV	Abund., %	Beta	Gamma	
Sr-89	50.6 d	1.463 ^(c)	0.582	100	0.913	0.01	3.45	0.0005	3.45
Sr-90	28 y	0.544 ^(c)	0.201	100	--		1.19		1.19
Y-90	64 h	2.27 ^(c)	0.942	100	0.511 pair	0.0045	5.58	0.0001	
		0.52 ^(c)	0.191	0.017	0.016 Kx	0.011	0.0001	0.00001	
		1.74 ce	1.74	0.017			0.0017		5.58
Y-91	59 d	1.54 ^(c)	0.615	99.7	1.208	0.3	3.63	0.0214	
		0.33	0.097	0.3			0.0017		3.65
Zr-95 (Nb-95m)	65 d (90 h)	1.13 ^(c)	0.437	0.4	0.760	43	0.0103	1.937	
		0.885 ^(c)	0.335	2	0.726	55	0.0397	2.367	
		0.396	0.120	55	0.235	0.8	0.3913	0.0111	
		0.360	0.107	43	0.017 Kx	0.7	0.2728	0.0007	5.03 ^(d)
Nb-95	35 d	0.93 ^(c)	0.352	1	0.768	99	0.0208	4.5086	
		0.16	0.044	99			0.2583		
		0.748 ce	0.748	0.2			0.0088		4.80
Tc-99	2.1 × 10 ⁵ y	0.292 ^(c)	0.107	100	--		0.6345		0.63
Ru-103 (Rh-103m)	40 d (57m)	0.71	0.234	3	0.610	7	0.0416	0.2532	
		0.39	0.117	1	0.498	89	0.0069	2.6282	
		0.212	0.059	89	0.362	0.3	0.3113	0.0064	
		0.10	0.026	7	0.297	0.4	0.0107	0.0070	
		0.475 ce	0.475	0.6	0.040	0.25	0.0169	0.0006	
		0.037 ce	0.037	91			0.1996		3.48 ^(d)
Ru-106 (Rh-106)	1.0 y (30 s)	0.0394	0.010	100	2.9 M	0.012	0.0593	0.0020	
		3.54	1.51	78	2.4 M	0.026	6.9843	0.0037	
		3.0	1.26	8	2.0 M	0.09	0.5977	0.0106	
		2.4	0.977	11	1.6 M	0.27	0.6372	0.0256	
		2.0	0.792	2	1.1 M	2.4	0.0939	0.1565	
		1.5	0.564	0.5	0.9 M	0.7	0.0167	0.0373	
		1.3	0.477	0.2	0.624	9.9	0.0056	0.3663	
		1.2	0.434	0.4	0.612	1	0.0102	0.0362	
		1.0	0.351	0.09	0.513	20.5	0.0018	0.6236	9.67 ^(d)
Te-125m	58 d	0.105 ce	0.105	47	0.1096	0.3	0.2926	0.0019	
		0.078 ce	0.078	53	0.0353	7.5	0.2457	0.0156	
		0.030 ce	0.030	13	0.027 Kx	114	0.0231	0.1825	0.76
Te-127m (Te-127)	105 d (9.3 h)	0.73 ^(c)	0.268	1.5	0.665	0.013	0.0238	0.0005	
		0.695	0.226	97.5	0.418	0.83	1.306	0.0205	
		0.27	0.077	1	0.360	0.12	0.0045	0.0025	
		0.054	0.014	0.013	0.21 M	0.1	0.00001	0.0012	
		0.084 ce	0.084	56	0.089	0.1	0.2789	0.0005	
		0.057 ce	0.057	42	0.059	0.5	0.1419	0.0017	
Te-129m (Te-129)	33 d (67 m)				0.027 Kx	37		0.0592	1.84 ^(d)
		1.59	0.601	5	1.12	1	0.1781	0.0664	
		1.453	0.542	76	0.72	1	2.442	0.0426	
		0.99	0.343	15	0.475	16	0.3050	0.4506	
		0.7	0.23	3	0.211	2	0.0409	0.0250	
		0.3	0.09	1	0.106	0.3	0.0053	0.0018	
		0.101 ce	0.101	47	0.027	25	0.2814	0.0400	
		0.074 ce	0.074	48	0.027 Kx	41	0.2106	0.0656	4.16 ^(d)
Cs-134	2.1 y	1.453 ^(c)	0.561	0.2	1.57	0.1	0.0066	0.0093	
		0.892 ^(c)	0.329	1.5	1.365	5	.0293	0.4047	
		0.658	0.211	61	1.0 M	8	0.7632	0.4744	
		0.410	0.122	9	0.800 M	83	0.0651	3.9375	
		0.282	0.080	0.5	0.605	98	0.0023	3.5158	
		0.086	0.022	27	0.566 M	25	0.0352	0.8390	
					0.475	4		0.1126	10.16

TABLE 11.1. Contd

Nuclide	Half Life ^(a)	Particles			Photons		Watts/Kilocurie	
		Max. E, MeV	Avg E. MeV	Abund., %	E, MeV	Abund., %	Beta	Gamma
Cs-137	30 y	1.18 ^(c)	0.446	5	0.6616	85	0.1322	3.3347
(Ba-137 m)	(2.6 m)	0.514 ^(c)	0.185	95	0.032 Kx	9	1.0421	0.0170
		0.625 ce	0.625	10			0.3706	4.90 ^(d)
Ce-141	32.5 d	0.580	0.183	30	0.145	48	0.3255	0.4127
		0.435	0.131	70	0.036 Kx	17	0.5437	0.0363
		0.138 ce	0.138	3			0.0245	
		0.103 ce	0.103	19			0.1160	1.46
Ce-144	285 d	2.98	1.222	97.7	2.18	0.8	7.080	0.103
(Pr-144)	(17 m)	2.29 ^(c)	0.918	1.3	1.49	0.25	0.071	0.022
		0.80	0.263	1	0.691	1.6	0.016	0.066
		0.32	0.092	76	0.134	10.5	0.415	0.083
		0.24	0.067	4	0.100	0.1	0.016	0.001
		0.186	0.051	20	0.080	2	0.060	0.010 7.94 ^(d)
Pm-147	2.62 y	0.225	0.0605	100	0.121	0.004	0.3587	0.00003
		0.104	0.027	0.01			0.00001	0.36
Sm-151	90 y	0.0759	0.020	98.4	0.0216	0.08	0.1167	0.0010
		0.0543	0.014	1.6	0.007 Lx	0.5	0.0013	0.0002
		0.020 ce	0.020	0.5			0.0006	
		0.014 ce	0.014	1.0			0.0008	0.197
Eu-155	1.8 y	0.247	0.069	15	0.1053	21	0.0613	0.1311
		0.185	0.050	10	0.0865	33	0.0296	0.1692
		0.158	0.043	32	0.0600	1.7	0.2998	0.0060
		0.140	0.037	43	0.0453	0.8	0.0943	0.0021
		0.097 ce	0.097	0.8	0.0265	1	0.0046	0.0016
		0.078 ce	0.078	2	0.0188	0.03	0.0092	0.00003
		0.055 ce	0.055	8			0.0260	
		0.036 ce	0.036	13	0.043 Kx	32	0.0277	0.0815
		0.010 ce	0.010	40	0.007 Lx	10	0.0237	0.0041 0.972
Eu-156	15 d	2.447	0.069	32	2.18 M	5.3	0.1309	0.6851
		1.21	0.419	11	2.05 M	11.5	0.2733	1.3979
		0.48	0.145	34	1.90 M	5	0.2923	0.5633
		0.30	0.085	23	1.25 M	33	0.1159	2.4461
					1.0 M	13		0.7709
					0.86 M	2		0.1019
					0.812	9.5		0.4574
					0.65 M	11		0.4239 7.659

a. d = days, y = years, h = hours, m = minutes, s = seconds

b. Nuclide identification and half lives in parenthesis refer to short-lived daughters included in equilibrium with long-lived parent.

c. Beta with unique first forbidden shape. Others have allowed shape.

ce Conversion electron instead of beta particle.

M Multiple gammas near the listed photon energy.

Kx K X-rays from internal conversion or K capture.

Lx L X-rays from internal conversion or L capture.

Pair Annihilation radiation resulting from internal conversion by positron-electron pair creation.

d. The total W/kCi for the combined parent-daughter decay is given.

TABLE 11.2. *Solubility of Chemicals Used in Waste Solidification (1,2,7)*

	Formula Weight	Solubility in 100 parts of: (a) (b)			Reference
		Cold Water	Hot Water	Acidic Solution	
AgNO ₃	169.89	122 ⁰	952 ¹⁰⁰	s	1
Al(NO ₃) ₃ ·9H ₂ O	375.15	63.7 ²⁵	vsd	s	7
Al(NO ₃) ₃ ·xH ₂ O	2.6M	vs	vsd	s	
B ₂ O ₃	69.64	1.1 ⁰	15.7 ¹⁰⁰	s	1,2
Ba(NO ₃) ₂	261.38	8.7 ²⁰	34.2 ¹⁰⁰	sl s	1,2,7
Ca(NO ₃) ₂ ·4H ₂ O	236.16	266 ⁰	660 ³⁰	s	7
Cd(NO ₃) ₂	236.43	109 ⁰	326 ⁶⁰	vs	7
Co(NO ₃) ₂ ·6H ₂ O	291.05	133.8 ⁰	217 ⁸⁰	s	7
Cr(NO ₃) ₃ ·9H ₂ O	400.18	s	s	s	7
CuSO ₄ ·5H ₂ O	249.69	31.6 ⁰	203.3 ¹⁰⁰	s	7
Fe(NO ₃) ₃ ·9H ₂ O	404.02	s	s	sl s	7
Fe(SO ₄)·7H ₂ O	278.03	15.65 ⁰	48.6 ⁵⁰	s	7
HNO ₃	12.2M	∞	∞	∞	
H ₃ PO ₄	12.1M	2340 ²⁶	vs	∞	2
H ₂ SO ₄	17.45M	∞	∞	∞	
KNO ₃	101.1	13.3 ⁰	247 ¹⁰⁰		7
LiNO ₃ ·3H ₂ O	123.0	34.8 ⁰	57.5 ^{29.6}	s	7
LiOH·H ₂ O	41.96	22.3 ¹⁰	26.8 ⁸⁰		7
Na ₂ MoO ₄ ·2H ₂ O	241.96	56.2 ⁰	115.5 ¹⁰⁰		2,7
Na ₂ SiO ₃ ·9H ₂ O	284.22	vs	vs	i	2,7
NaNO ₃	85	92.1 ²⁵	180 ¹⁰⁰		7
NaOH	40	42 ⁰	347 ¹⁰⁰	d	7
NaOH	10M			d	7
NaPO ₃	101.97	21	vs	i	2
Ni(NO ₃) ₂ ·6H ₂ O	290.8	238.5 ⁰	vs	s	7
R.E. (NO ₃) ₃ ·6H ₂ O ^(c)	434	vs	vs		
Ru(NO ₃) ₃ ·xH ₂ O	10 wt% Ru	vs			
Sr(NO ₃) ₂	211.65	70.9 ¹⁸	100 ⁹⁰		1,7
ZrO(NO ₃) ₂ ·2H ₂ O	267.3	s	d		2

(a) Superscript numbers are temperatures in °C.

(b) s = soluble; vsd = very soluble, decomposes;
vs = very soluble; sl s = slightly soluble
∞ = soluble in all proportions; i = insoluble;
d = decomposes

(c) Lindsay Chemical Company, Code No. 350, trivalent rare earth nitrates with average molecular weight of 434.

TABLE 11.3. *Thermal Stability of Selected Salts (1,2,7,22)*

Element	NITRATES		SULFATES		PHOSPHATES		Reference	Remarks
	M.P., °C(a)	D, °C(b)	M.P., °C	D, °C	M.P., °C	D, °C		
Ag	212	444	652	1085	482(m) 585(p) 849(o)	--	2,7	Meta, pyro, and ortho phosphates
Al	73.5	150	770	--	>1500(o)	--	7	Ortho phosphate $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$
Ba	592	--	--	1580	--	--	1,2	BaSO_4
Ca	561	--	1450(mn)	1193(tr)	975(m) 1230(p)	--	2,7	mn is monoclinic, tr from rhombic to monoclinic
Ce	150, -3H ₂ O	200-250	195	--	--	--	7	
Cd	350	--	1000	108, -H ₂ O	900(p)	--	2	Pyrophosphate
Co	56	55, -3H ₂ O	735	880	--	--	2,7	
Cr	100	100-130	100	100, -10H ₂ O	--	--	2,7	
Cs	414	400-600	1010	600(tr to hex)	--	--	2,7	Transition to hexagonal
Fe	35	125-165	64	90, -6H ₂ O	--	--	2,7	
H	86(B.P.)	--	10.5	330	42.35(o)	213, -1/2H ₂ O(o)	2	Boiling Point
Li	264	600	130, -H ₂ O	860	837(o)	--	2,7	
Mn	25.8	129.5	700	850	1196(p)	--	7	
Na	306.8	380	884	--	628(m) 988(p)	--	2,7	
Ni	56.7	136.7	760	848, -SO ₃	--	--	7	
Sr	570	645	1605	1580	--	--	2,7	
Th	--	180-290	--	--	--	--	22	
U	60.2	200-300	--	100	--	--	7	Uranyl nitrate, uranyl sulfate
Zr	100	200	380	410	--	--	2,7	

a. M.P. is melting point temperature

b. D is decomposition temperature

TABLE 11.4. *General Properties of Aqueous Solutions of Phosphoric Acid at 20 °C (6,3,16,20)*

H_3PO_4 , wt %	P_2O_5 , mole %	H_3PO_4 , <u>M</u>	<u>Sp. Gr.</u>	Viscosity, centi- poise
1	0.09	0.10	1.0038	
4	0.38	0.42	1.0200	
8	0.76	0.85	1.0420	
10	0.98	1.07	1.0532	1.166
14	1.41	1.54	1.0764	
18	1.86	2.02	1.1008	
20	2.11	2.27	1.1134	1.576
22	2.34	2.53	1.1263	
26	2.86	3.06	1.1529	
30	3.39	3.61	1.1805	2.254
35	4.12	4.34	1.216	2.728
40	4.92	5.12	1.254	3.329
45	5.78	5.94	1.293	4.094
50	6.71	6.81	1.335	5.090
55	7.75	7.74	1.379	6.378
60	8.87	8.73	1.426	8.105
65	10.13	9.78	1.475	10.48
70	11.54	10.89	1.526	13.90
75	13.10	12.08	1.579	19.08
80	14.86	13.32	1.633	27.60
85	16.87	14.65	1.689	~45
90	19.17	16.02	1.746	
92	20.22	16.60	1.770	
94	21.30	17.20	1.794	
96	22.43	17.81	1.819	
98	23.68	18.43	1.844	~125
100	25.00	19.07	1.870	~200
	26.3		1.89	
	28.0		1.91	~700
	29.5		1.94	
	31.4		1.97	~2700
	33.2		1.99	~5000

TABLE 11.5. *Conversion Factors and Useful Constants (12,14,15,19)*

Radionuclide	Half Life	Energy, W/kCi		Total, W/kCi	10 CFR 20 Limits, Appendix B, Table II	
		Gamma	Beta		Air, $\mu\text{Ci/ml}$	Water, $\mu\text{Ci/ml}$
H-3	12.3 y	none	0.0186	0.11	2×10^{-7}	3×10^{-3}
Sr-89	50.6 d	0.0005	3.45	3.5	8×10^{-10}	3×10^{-5}
Sr-90	28 y	none	1.19	1.2	3×10^{-11}	3×10^{-7}
Y-90	64 h	0.0001	5.581	5.6	3×10^{-9}	2×10^{-3}
Nb-95	35 d	4.509	0.288	4.8	2×10^{-9}	1×10^{-4}
ZrNb-95	65 d	2.157	0.357	2.5	1×10^{-9}	6×10^{-5}
RuRh-103	40 d	1.448	0.293	1.7	2×10^{-10}	8×10^{-5}
RuRh-106	1.0 y	0.631	4.203	4.8	2×10^{-10}	1×10^{-5}
Cs-134	2.1 y	9.293	0.901	10.2	4×10^{-10}	9×10^{-4}
CsBa-137	30 y	1.676	0.772	2.4	5×10^{-10}	2×10^{-5}
Ce-141	32.5 d	0.449	1.010	1.9	2×10^{-9}	9×10^{-5}
CePr-144	285 d	0.142	3.829	4.0	2×10^{-10}	1×10^{-5}
Pm-147	2.62 y	0.0003	0.359	0.36	2×10^{-9}	2×10^{-4}

$N = \text{No exp } (-0.693t/t_{1/2})$

$\text{dis/min/ml} \times 4.5 \times 10^{-10} = \text{Ci/l}$

$\text{dis/min/mg} \times 4.5 \times 10^{-10} = \text{Ci/g}$

$\text{Btu/hr} \times 3.413 = \text{W}$

$\text{Btu/(hr)} (\text{ft}^3) \times 0.01035 = \text{W/l}$

$\text{Btu/(hr)} (\text{ft}^2) (^{\circ}\text{F}) \times 5.66 = \text{W/(m}^2) (^{\circ}\text{C})$ - or - $\text{W/(m}^2) (^{\circ}\text{C}) \times 0.176 = \text{Btu/(hr)} (\text{ft}^2) (^{\circ}\text{F})$

$\text{Btu/(hr)} (\text{ft}^2) (^{\circ}\text{F/ft}) \times 1.73 = \text{W/(m)} (^{\circ}\text{C})$ - or - $\text{W/(M)} (^{\circ}\text{C}) \times 0.578 = \text{Btu/(hr)} (\text{ft}^2) (^{\circ}\text{F/ft})$

$K_{\text{eff}} = \frac{Q}{4\pi L\Delta T} = \frac{Sr^2}{4\Delta T}$ For K_{eff} in units of $\text{W/(m)} (^{\circ}\text{C})$, use T in $^{\circ}\text{C}$; L, r in meters; Q in watts; S in W/m^3

H_2 generation due to radiolysis = $\sim 7 \text{ cm}^3/(\text{hr})(\text{kCi})$ (assuming 4 W/kCi)

1 l/hr water boilup $\sim 1 \text{ ft}^3/\text{min}$ vapor at 100°C

TABLE 11.6. *Analytical Chemistry Methods in Support of the WSEP Program (13)*

Analysis Made and Description of Method	Estimated Accuracy and Precision		Detection Limit
Aluminum: Aluminum is determined spectrophotometrically by measuring the colored complex formed with sodium mercaptoacetate and chromoxane cyanine RA. Iron and high concentrations of phosphate or fluoride interfere.	±15%	±7%	5 ppm
Beta Emitters: "Total beta" activity is determined by counting a sample aliquot with a thin window, gas flow, proportional counter. A counting efficiency of 50% is used to convert counts per minute to disintegrations per minute. Although this counting efficiency is estimated to be close to the actual counting efficiency for the mixture of beta emitters present in normal WSEP samples, a large uncertainty exists because of the possible variations in sample composition.	±25%	±5%	10^{-3} $\mu\text{Ci}/\text{ml}$
Carbonate: Water soluble carbonates are titrated directly with standard acid. Insoluble carbonates are separated by treating the sample with sulfuric acid and distilling the carbon dioxide liberated into a measured volume of standard sodium hydroxide. The carbon dioxide trapped as soluble sodium carbonate is titrated with standard acid.	±10%	±5%	3000 ppm
Density (Solids): The density of solid samples is determined from its weight in air and its weight while submerged in a liquid of known density. Carbon tetrachloride is the liquid normally used.	±5%	±2%	N.A. (a)
Fluoride: Fluoride is separated from the sample by pyrohydrolysis. The volatilized fluoride is absorbed in dilute sodium hydroxide and determined spectrophotometrically using a lanthanum alizarin complexone indicator.	±10%	±5%	5 ppm
Gamma Emitters: Radionuclides for which gamma ray emission is a significant factor in radioactive decay are determined by counting a sample aliquot on a high resolution gamma spectrometer using a Ge(Li) detector. Radionuclides determined include: Nb-95, Zr-95, Cs-137, Cs-134, Ru-106/Rh, Ru-103, Ce-141, and Ce-144/Pr. The accuracy and precision of reported concentrations depend on the relative concentrations present. Major constituents are determined to an accuracy of about ±5%. The uncertainty in the determination of minor constituents may be as high as ±50%.	See Description		10^{-4} $\mu\text{Ci}/\text{ml}$ (for major constituents)
Hydroxide Ion (Basicity): Hydroxide ion concentration is determined by adding a small amount of sample to a 4% ammonium oxalate solution adjusted to pH7, adding an excess of standard acid and back titrating with standard sodium hydroxide to a pH7. High concentrations of hydrolysable ions will have an adverse effect. Carbonates would have an additive effect.	±5%	±2%	N.A.
Hydrogen Ion (Acidity): Hydrogen ion concentration is determined by adding a small amount of sample to a 4% ammonium oxalate solution adjusted to pH7 and titrating with standard sodium hydroxide to a pH7. High concentrations of hydrolysable ions give a positive interference. High concentrations of U_2 uranium have an erratic additive effect. HPO_4 cannot be determined by this method. In the presence of sufficient quantities of the above, precision is adversely affected, and accuracy may be destroyed.	±5%	±2%	N.A.
Iron: Iron is determined spectrophotometrically as an iron (II)-ortho-phenanthraline complex. Iron (III) is reduced with hydroxylamine hydrochloride before analysis.	±10%	±5%	20 ppm

TABLE 11.6. *Contd*

Analysis Made and Description of Method	Estimated Accuracy and Precision		Detection Limit
Mercury: Mercury is extracted into carbon tetrachloride as a dithizone complex and determined spectrophotometrically.	±10%	±5%	20 ppm
Nitrate: Nitrate is determined spectrophotometrically after reaction with phenoldisulfonic acid to form a colored nitro-phenoldisulfonic acid compound. Some of any nitrite present will be oxidized and determined as nitrate.	±10%	±5%	50 ppm
Nitrite: Nitrite in the sample is reacted with β-naphthylamine-6, 8-disulfonic acid (amino G acid) and α-naphthylamine to form a purple azo dye which is determined spectrophotometrically.	±10%	±5%	5 ppm
Nitrogen: Total nitrogen is determined by reducing the fixed nitrogen in the sample to ammonia with Devarda's alloy in a Kjeldahl flask, distilling into boric acid solution and titrating to a colorimetric end-point with standard acid using bromocresol green and methyl red indicators.	±10%	±5%	3 ppm
Phosphorus: Phosphorus present as orthophosphate is determined spectrophotometrically as the phosphovanadomolybdate complex. Phosphorus when present in forms other than orthophosphate is converted to orthophosphate before analysis.	±10%	±5%	5 ppm
Pm-147: Promethium-147 is separated by chromatographic elution from a cation exchange column with α-hydroxyisobutyric acid. The separated Pm-147 is measured by counting on a calibrated proportional beta counter.	±6%	±3%	10 ⁻³ μCi/ml
Rare Earths (Total): The total rare earths are determined gravimetrically after precipitation as the oxalates and ignition to the oxide. If the rare earths present are known to consist primarily of cerium, results are calculated assuming the dioxide is formed. If cerium is not the primary constituent the results are calculated assuming that sesquioxide is formed. Elements forming acid insoluble oxalates interfere.	±15%	±7%	2000 ppm
Ruthenium: Ruthenium is oxidized to ruthenium tetroxide with sodium bismuthate and distilled from sulfuric acid into a solution of sodium hydroxide and sodium hypochlorite. The volatilized ruthenium is determined spectrophotometrically.	±20%	±10%	5 ppm
Sodium: Sodium is determined by flame emission spectrophotometry.	±10%	±5%	1 ppm
Solids (Percent): A sample aliquot is centrifuged in a calibrated centrifuge cone. The volume of the settled solids is read from the cone.	±20%	±10%	N.A.
Specific Gravity: Specific gravity is determined by weighing a measured volume aliquot of the sample solution at ambient temperature.	±2%	±1%	N.A.
Strontium-90: Strontium-90 is determined by separating the total strontium by chromatographic elution from a cation exchange column and measuring the yttrium-90 buildup with a proportional beta counter.	±10%	±5%	10 ⁻³ μCi/ml
Sulfur: Sulfur is oxidized to sulfur trioxide by combustion with vanadium pentoxide and trapped in dilute sodium hydroxide. The sulfate formed is precipitated as a barium sulfate suspension and determined photometrically using a Beckmen Model B spectrophotometer.	±10%	±5%	100 ppm

a. Not Available

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