BNWL-1083
UC-70

3 -
6-69

INTERIM STATUS REPORT ON THE WASTE
SOLIDIFICATION DEMONSTRATION PROGRAM

June 1969

AEC RESEARCH &
DEVELOPMENT REPORT

ROUTE TO	P.N.W.	LOCATION	FILES	ROUTE	DATE
J.P. Roberts	30976	325	AUG 5		1970

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

PACIFIC NORTHWEST LABORATORY

RICHLAND, WASHINGTON

operated by

BATTELLE MEMORIAL INSTITUTE

for the

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

3 3679 00061 4406

BNWL-1083

UC-70, Waste
Disposal and Processing

INTERIM STATUS REPORT ON THE WASTE
SOLIDIFICATION DEMONSTRATION PROGRAM

Prepared for presentation to the National Academy of Sciences
Committee on Radioactive Waste Management at Richland,
Washington, June 23 and 24, 1969

By

A. G. Blasewitz

J. E. Mendel

K. J. Schneider

R. J. Thompson

Chemical Technology Department
Chemistry and Metallurgy Division

June 1969

FIRST UNRESTRICTED
DISTRIBUTION MADE

JUN 5 '69

BATTELLE MEMORIAL INSTITUTE
PACIFIC NORTHWEST LABORATORY
RICHLAND, WASHINGTON

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

INTERIM STATUS REPORT ON THE WASTE
SOLIDIFICATION DEMONSTRATION PROGRAM

ABSTRACT

The Waste Solidification Demonstration Program is a cooperative program involving the Pacific Northwest Laboratory, the Brookhaven National Laboratory, and the Oak Ridge National Laboratory to provide the technological bases which will enable industry to convert the high-level liquid waste from the reprocessing of nuclear fuel to a safer solid form. The work has reached its culmination with the operation of the Waste Solidification Engineering Prototypes by Battelle-Northwest wherein engineering-scale radioactive demonstrations are being conducted with three alternative solidification systems: phosphate glass, spray solidification, and pot calcination. Approximately 60% of the radioactive demonstrations have been completed and have shown that the processes are feasible and essentially ready for commercial application.

Another major activity is the determination of the behavior of the solidified waste products and evaluation of the safety and economic aspects of this behavior as related to the management of high level wastes.

The radioactive demonstrations will be completed in late 1970. Although a few of the containers of solidified waste will be monitored for approximately five years to observe possible long term effects, the majority of the product evaluation data will be available within two years. Evaluation and reporting of the results of various phases of the program is being done on a continuing basis. Overall technical, safety, and economic evaluations for industrial applications will be completed in 1972.

TABLE OF CONTENTS

LIST OF FIGURES.	vii
LIST OF TABLES	ix
1.0 INTRODUCTION	1.1
2.0 SUMMARY.	2.1
3.0 WASTE SOLIDIFICATION DEMONSTRATION PROGRAM . . .	3.1
3.1 Program Scope	3.1
3.2 Waste Solidification Engineering Prototypes	3.3
3.3 Product Evaluation	3.12
3.4 Major Milestones in the Waste Solidification Demonstration Program	3.14
4.0 PROCESS AND PRODUCT CHEMISTRY	4.1
4.1 Purposes of the Laboratory Program	4.1
4.2 WSEP Waste Compositions.	4.1
4.3 Solution Stability Considerations	4.3
4.4 Pot Calcination Process.	4.5
4.5 Melt Formation from High Level Radioactive Wastes	4.5
4.6 Characteristics of Phosphate Melts	4.7
4.7 Future Process and Product Chemistry Requirements	4.10
5.0 RADIOACTIVE ENGINEERING DEMONSTRATIONS IN THE WASTE SOLIDIFICATION ENGINEERING PROTOTYPES. . .	5.1
5.1 Program Description	5.1
5.2 Overall Status of WSEP Demonstrations	5.2
5.3 Overall Comparison of the Three Processes.	5.4
5.4 Significant Findings to Date for the Solidification Processes	5.6
5.5 Significant Findings to Date for Effluents from WSEP	5.10
5.6 General Solidification Technology To Be Developed in WSEP.	5.13
5.7 Specific Solidifier Technology To Be Developed in WSEP.	5.15
5.8 Schedule of Remaining Program.	5.16

6.0	PRODUCT EVALUATION PROGRAM	6.1
6.1	Overall Program Description	6.1
6.2	Nonradioactive Studies	6.2
6.3	Radioactive Studies	6.6
6.4	Solids Storage Engineering Test Facility (SSETF)	6.8
6.5	Pertinent Characteristics of WSEP Solidified Wastes	6.10
6.6	Discussion of Maximum Heat Content	6.12
6.7	Status of the Product Evaluation Program	6.13
	ACKNOWLEDGEMENTS	6.15
	BIBLIOGRAPHY.	6.17
	General.	6.17
	Spray Solidification	6.18
	Pot Solidification	6.19
	Phosphate Glass Solidification	6.19
	APPENDIX	A-1

LIST OF FIGURES

3.1	Process Features of the Waste Solidification Engineering Prototypes	3.4
3.2	Phosphate Glass Solidification System	3.6
3.3	Spray Solidification System	3.7
3.4	Pot Solidification System	3.8
3.5	Waste Solidification Product Evaluation Program	3.13
3.6	Solids Storage Engineering Test Facility	3.15
6.1	Typical Nonradioactive Laboratory Thermal Conductivity for Phosphate Glass Melt	6.3
6.2	Typical Leach Rates for Solidified Wastes from Spray Solidifier and Phosphate Glass Processes	6.4
6.3	Effect of Thermal Conductivity upon Maximum Heat Which May Be Stored in Container of Solidified Waste	6.13
A.1	Solidified High Level Waste Samples from WSEP	A-1
A.2	Floor Plan of the Chemical and Materials Engineering Laboratory	A-2
A.3	Plan View of B Cell Equipment Arrangements	A-3
A.4	WSEP Evaporator and Fractionator Rack Before Installation	A-4
A.5	Looking into WSEP Equipment Cell	A-5
A.6	Looking Down on WSEP Equipment in Cell	A-6
A.7	WSEP Containers for Solidified Waste	A-7
A.8	Environmental Test Pods Before Installation in SSETF	A-8

LIST OF TABLES

3.1	Chemical Compositions of High-Level Liquid Wastes for WSEP Demonstration	3.11
3.2	Waste Solidification Demonstration Program Milestones	3.16
3.3	Waste Solidification Demonstration Program: Analysis and Formal Reporting	3.18
4.1	Precipitates Potentially Present in Radioactive Wastes	4.3
4.2	WSEP Waste Solutions at Reference Concentration of 100 gal/tonne	4.4
4.3	Phosphate Melt Compositions Used in the WSEP Demonstrations	4.9
5.1	Overall Status WSEP Radioactive Demonstrations	5.3
5.2	Comparison of Pot, Spray, and Phosphate Glass Solidification Processes	5.5
5.3	Significant Findings to Date for Pot, Spray, and Phosphate Glass Solidification Processes in WSEP	5.7
5.4	Significant Findings to Date for Effluents from Pot, Spray, and Phosphate Glass Solidification Processes in WSEP	5.11
5.5	General Technology Development Remaining for Solidification Processing in WSEP Program	5.14
5.6	Technology To Be Developed for the Pot, Spray, and Phosphate Glass Solidification Processes	5.15
6.1	Characteristics of Solidified High Level Waste	6.11

INTERIM STATUS REPORT ON THE WASTE SOLIDIFICATION DEMONSTRATION PROGRAM

1.0 INTRODUCTION

This document provides an interim status report of the Waste Solidification Demonstration Program. It describes the objectives and scope of the program, the method of conducting the work, the significant findings to date, and the work which remains to bring it to a successful conclusion. Supplementary illustrations and descriptions are provided in the Appendix.*

The purpose of the Waste Solidification Demonstration Program is to provide the technological bases which will lead industry to adopt at the earliest possible time the practice of solidifying the high level liquid waste which results from the reprocessing of nuclear fuel. It is generally recognized that converting this intensely radioactive liquid waste to a solid, less mobile form is safer, and therefore highly desirable. The establishment of soundly based conversion (solidification) operations has, however, required significant technical advances in the areas of process and equipment development, product and container evaluation, and the development of techniques to assure the safe and economic handling of the secondary waste streams associated with the solidification process. It could not be expected that industry would incorporate this admittedly desirable step into their operations until the engineering feasibility, reliability, safety, and economics had been established.

A cooperative program involving the Pacific Northwest Laboratory, the Brookhaven National Laboratory, and the

* A particular reason for compiling the material at this time is to provide background material for discussions of the program during the forthcoming visit to Hanford (June 23 and 24, 1969) by the Committee on Radioactive Waste Management of the National Academy of Sciences.

Oak Ridge National Laboratory has therefore been established to provide the required technology. The program has reached its culmination with the operation of the Waste Solidification Engineering Prototypes (WSEP) by Battelle-Northwest at the Pacific Northwest Laboratory. In this facility, pilot plant demonstrations are being conducted with three alternative solidification systems: phosphate glass solidification, spray solidification, and pot calcination. The demonstrations are performed with solutions that have chemical compositions and radioactivity levels comparable to those which will exist in the commercial plants. Studies are also being conducted in the important areas of evaluating the solidified waste product and its container, and determining practical and economic methods of treating the secondary waste streams to assure that they will present no hazard to the environment.

2.0 SUMMARY

The waste solidification demonstration program has been progressing very satisfactorily. Approximately 60% of the radioactive demonstrations and their associated effort have been completed. More than 29 million curies of radionuclides have been solidified and encapsulated in the 22 demonstration runs completed thus far. Six of the demonstrations were by pot calcination, 10 by spray solidification, and 6 by phosphate glass solidification. An additional 25 million curies of radionuclides will have been solidified and encapsulated when the remaining 14 demonstration runs are completed late in 1970.

Solidification of wastes typical of fuels from thermal reactors exposed to 20,000 MWd/tonne is nearly complete, and solidification of wastes from advanced thermal reactor fuels exposed to 45,000 MWd/tonne has begun. Similar demonstrations on wastes from fast reactor core fuels will have been demonstrated by late 1970.

The major current technology for the pot, spray, and phosphate glass solidification processes and the design features of the WSEP and the associated solidified waste evaluation facilities have been formally reported. Evaluation and reporting of the results of the radioactive demonstrations with individual solidification processes is being done on a continuing basis. Overall technical, safety, and economic evaluations from the total program for direct applications by commercial fuel reprocessors will be completed in 1972.

Although evaluations are far from complete, the major conclusion from the program to date is that solidification of high level aqueous wastes by the pot, spray, and phosphate glass processes is feasible and essentially ready for application by commercial processors of spent nuclear fuels.

No "winner" from among the three processes has evolved, nor is a universal "winner" expected. Each process and its solidified waste has advantages and disadvantages which must be weighed carefully for each specific application.

Cleanup of the gaseous effluents from solidification with a WSEP type of cleanup system has been demonstrated to readily meet requirements in 10CFR20* for gases. The aqueous effluents from the WSEP system contain up to one million times the allowable radionuclide content for drinking water, but these effluents should be readily returnable to similar but larger systems required in fuel reprocessing plants for treating other similar effluents.

Wastes containing up to 12.7 kilowatts of self-generating heat from decay of 3.7 megacuries of radionuclides have been converted to 60 liters of solid in one 8-inch diameter by 8-foot long container. Such heat rate levels represent total out-of-reactor times of approximately six months for 20,000 MWd/tonne fuel.

Radioactive and nonradioactive laboratory studies have provided much information regarding the characterization of the solidified wastes. Extensive engineering-scale tests wherein up to 16 large containers of solidified wastes will be evaluated under controlled environmental storage conditions for up to 5 years have recently been activated. Most of the results from characterizations of these solidified wastes will be available shortly after completion of radioactive demonstrations with the solidification processes. Evaluation of the data relative to the safety and economic aspects of the characteristics and management of these solidified wastes will be reported in 1972.

* *"Standards for Protection Against Radiation," U.S. Atomic Energy Commission. August 9, 1966.*

Limited results from evaluations of these solidified wastes have generally corroborated nonradioactive tests. Specifically, the results are:

- No pressurization has occurred during pot storage.
- High-integrity, hermetically-sealed containers result after processing and capping.
- Effective thermal conductivity for the spray ceramic solid is as expected [1.0 to 1.7 W/(m) (°C)], but is slightly lower than anticipated for pot calcine [0.3 to 0.5 W/(m)(°C)] and phosphate glass [0.8 to 1.3 W/(m)(°C)].
- Leachability of the spray ceramic solid [10^{-3} to 10^{-5} g/(cm²)(day)] and the phosphate glass [10^{-4} to 10^{-6} g/(cm²)(day)] are as expected.
- Mild steel is satisfactory for containers for the spray and phosphate glass solids.
- The phosphate glass tends to devitrify to a crystalline solid upon extended storage at high temperatures.

The solidified wastes from the spray and phosphate glass processes are monolithic melt-formed phosphate ceramics. Compared to silicate and borate melts, phosphate melts have the advantages of simple, all-liquid chemical adjustment of the waste solutions before solidification, easily handled hydrous precipitates in the chemically adjusted wastes, flexibility for a wide variety of waste compositions, and solid products with relatively low melting points. The disadvantages of phosphate melts are the high corrosion rates at temperatures greater than 875 °C, and the approximately one order of magnitude higher leach rates.

The crystalline, rock-like ceramic formed by spray solidification has an average composition between ortho- and pyrophosphates. Homogeneous solids containing up to 25 wt% (19 mole%) fission product oxide are readily prepared. The

glass formed by phosphate glass solidification is a mixture of metaphosphates and may contain at least 18 wt% (13 mole%) fission product oxides. The fission product content of the friable, somewhat powdery, post calcination product is limited only by the "cleanness" achieved in the reprocessing plant and by the need for addition of sulfate to decrease the volatility of cesium and rubidium. A fission product content of about 76 wt% (62 mole%) will be demonstrated in the waste solidification program.

3.0 WASTE SOLIDIFICATION DEMONSTRATION PROGRAM

A. G. Blasewitz

3.1 PROGRAM SCOPE

The overall scope and content of the Waste Solidification Demonstration Program can best be described by considering the principal activities which are involved.

a. Waste Solidification Demonstration

Pilot plant operation of three alternative solidification systems to establish the required process and equipment technology. This phase of the work involves the following items:

1. Establishing the comparative flexibility, reliability, and operability of engineering-scale solidification equipment.
2. Identifying (and resolving, wherever possible) the problems associated with large scale radioactive operation of each of the solidification processes.
3. Producing of solidified waste specimens (production scale) for studies pertinent to a definition of the criteria and limitations regarding the short term storage, shipping, and long term storage of the contained product.

b. Effluent Decontamination Demonstration

Pilot plant operation of decontamination equipment located downstream of the solidification systems. The purpose of this work is to investigate the parameters affecting the performance of the decontamination equipment. It involves the following items:

1. Providing data regarding the decontamination of the off-gases from the solidification processes prior to their discharge.

2. Characterizing the secondary liquid waste streams resulting from the solidification processing methods.
3. Evaluating alternative methods for treating the secondary waste streams.
4. Establishing the performance characteristics of the individual decontamination equipment pieces, i.e., evaporator, acid fractionator, filters, and scrubber.

c. Product Evaluation

Determination of the behavior of the products (the containers and their contents) from the WSEP solidification processes, and determination of the safety and economic aspects of this behavior as related to the management of high level wastes. Two primary areas of technology are involved in this work:

1. Characterization of the pertinent physical and chemical properties of the products from the three solidification processes demonstrated in the program.
2. Engineering and safety analysis of the product characteristics for direct application to the industrial reprocessors of nuclear fuels.

d. Supporting Laboratory and Engineering Studies

Conducting supporting laboratory or engineering studies.

Information in the following areas is provided.

1. Chemical flowsheet development.
2. Process chemistry as it affects the solidification systems or the products.
3. Establishing firm operating conditions for the radioactive demonstrations.
4. Improving the operational reliability of the solidification systems.

5. Providing sound bases for scaleup factors.
6. Investigating advanced methods for high level waste solidification.

e. Analysis and Reporting

Performing engineering-scale analyses of the data from the waste solidification demonstration program and translating these analyses into reports which provide industry with the basic technical, safety, and economic information which they need to design and operate a solidification facility for high activity wastes. This work involves the preparation of fifteen major formal documents. It also involves the preparation of numerous interim and topical reports.

3.2 WASTE SOLIDIFICATION ENGINEERING PROTOTYPES

The Waste Solidification Engineering Prototypes (WSEP) represent the major operational activity in the program. It is the facility wherein the prototypic waste solidification and decontamination equipment are operated. It is an engineering scale pilot plant (capable of handling the high level liquid waste from a one ton per day fuel reprocessing plant) and is located in the Chemical and Materials Engineering Laboratory at the Pacific Northwest Laboratory. The main process features of the WSEP are shown in Figure 3.1.

The liquid waste is loaded into a cask and brought to the WSEP facility from the Hanford separations plant operated by the Atlantic Richfield Hanford Company. The waste is chemically adjusted in a feed tank to reproduce a variety of reactor fuel processing waste solutions. In addition, purified and concentrated fission product solutions are similarly brought into the plant from the Hanford fission product separations facility and added to the feed tank to reproduce feeds with varying fission product distributions and heat generation rates. (If

Neg 0691648-3

FIGURE 3.1. Process Features of the Waste Solidification Engineering Prototypes

necessary, digestion can be done in the feed tank to aid feed preparation or to decompose organic residue. The wastes can also be fed to the evaporator for volume reduction and the elimination of gross quantities of nitric acid.) From the feed tank or the evaporator, the wastes are fed directly to one of the three solidification processes.

The vapors from the solidification processes are routed through a single off-gas system common to all processes. These vapors are first routed through a condenser to the evaporator. The condensates are reconcentrated in the evaporator (along with incoming waste in some cases). The vapors from the evaporator are decontaminated from entrained aerosols first in the evaporator tower and again during condensation and scrubbing in an acid fractionator. The vapors from the fractionator are again condensed and collected for disposal as a low-radioactivity-level waste stream. The remaining gases are treated by high efficiency filtration, scrubbing, and additional backup filtration before discharge to the atmosphere. The recovered acid is recycled to the production separations plant.

The solidified waste is collected in "pots" 8 or 12 inches (and possibly 6 inches) in diameter and 8 feet long. The pots are sealed by welding a lid in place.

Schematic diagrams of the phosphate glass solidification system (originally developed at the Brookhaven National Laboratory), the spray solidification system (developed at Hanford), and the pot solidification system (originally developed at the Oak Ridge National Laboratory) are presented in Figures 3.2, 3.3, and 3.4, respectively. The main process functions for the three solidification techniques are:

- In continuous phosphate glass solidification, liquid waste is mixed with glass-forming chemicals (normally phosphoric acid) and concentrated by a factor of about five to a thick

Neg 0682348-1

FIGURE 3.2. Phosphate Glass Solidification System

Neg 0682456-2

FIGURE 3.3. Spray Solidification System

Neg 0682456-3

FIGURE 3.4. Pot Solidification System

slurry in an evaporator. The slurry is fed to a continuous melter where final evaporation and glass formation occur at temperatures of 900 to 1200 °C. The molten glass flows into the heated receiver-storage pot. The pot is then cooled and sealed for storage. The product from the phosphate glass process is a monolithic, moderately brittle glass formed after cooling the melt. The glass has fairly good thermal conductivity and low solubility in aqueous solutions.

- In spray solidification, liquid waste is fed into the top of a heated tower through a pneumatic atomizing nozzle. The spray is progressively dried and calcined to powder as it travels downward inside the reactor. The powder falls directly into the melter, while the process gas flows into the filter chamber, carrying along some of the finer waste powder as dust. The dust collects on porous metal filters and is periodically blown off the filters and into the melter by puffs of high pressure steam or air directed backward through the filters by small nozzles at the outlets of the filters. In the melter, the powder is melted at 700 to 1200 °C. The molten waste then flows through an overflow weir tube or freeze valve into the receiver storage pot. The pot is then cooled and sealed for 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 fairly good thermal conductivity and moderately low solubility in aqueous solutions.
- The pot solidification process is a batch system, and the principal processing vessel is the permanent storage pot. In pot calcination, liquid waste is added to a heated pot held at a nearly constant liquid level. After the waste is boiled for 5 to 10 hours, calcine scale begins

to form on the pot wall. The calcine deposit grows inward and causes increased resistance to heat transfer, which in turn requires gradual reduction in feed rate until the pot is full of calcine except for a small core of thick sludge. At that time, feeding is stopped, and heating is continued until all the waste is converted into a calcine at about 900 °C. The pot is then cooled and sealed for storage. The product for pot solidification is a mixture of oxides (and sulfate, if sulfate is present in the waste) of the metallic constituents in the original liquid waste. The product is a porous, friable calcine with low thermal conductivity and relatively high solubility in aqueous solutions.

Four waste compositions have been selected for demonstration in the program. These are shown in Table 3.1. The four compositions bracket the range of high-level waste compositions from Purex flowsheets for aqueous fuel reprocessing. PW-1 represents a Purex waste solution high only in iron salt content and void of sulfate. PW-2 represents a Purex sulfate-containing waste solution high in sodium content and low in other salts. PW-4m represents a relatively "clean" Purex waste stream without sulfate that has low concentrations of all salts except fission products. This waste is expected to be typical of future wastes resulting from the reprocessing of fuel from advanced thermal reactors. The Liquid Metal Fast Breeder Reactor (LMFBR) waste is likewise a relatively "clean" Purex waste stream based upon the reprocessing of the fuel from the core of a fast breeder reactor. Although it is quite likely that the fuel from the core and blanket regions of a fast reactor will be combined before reprocessing, a waste composition based upon the core material alone has been selected for the few demonstration runs which will be performed in WSEP with LMFBR

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

Concentration, Molarity at 378 liters/tonne(a)				
Constituent	PW-1	PW-2	PW-4m	LMFBR
General Chemical Composition of Inert Materials				
Na	low	high	low	low
Fe	high	med	low	low
SO ₄	0	high	0	0
Actual Chemical Composition of Inert Materials				
H	3.70	3.90	0.50	0.50
Fe	0.93	0.44	0.050	0.16
Cr	0.012	0.024	0.012	0.046
Ni	0.005	0.010	0.008	0.023
Al	0.001	0.001	0.001	--
Na	0.14	0.93	0.10	0.10
U	0.010	0.010	0.010	0.010
Hg	<0.001	<0.001	<0.001	--
NO ₃	7.5	5.4	2.4	4.7
SO ₄	--	0.87	--	--
PO ₄	0.003	0.006	0.003	0.060
SiO ₃	0.010	0.010	0.010	--
F	<0.001	<0.001	<0.001	--
$\Sigma M_{chem}^{+ (b)}$	3.03	2.48	0.37	0.83
kg oxide/ tonne	31.7	28.1 ^(c)	4.6	9.7
Chemical Composition of Major Materials from Nuclear Fission				
	Fuel Exposure in Thermal Reactors		Core Fuel	
	20,000 MWd/tonne	45,000 MWd/tonne	Exposure in LMFBR	
Constituent	at 15 MW/tonne	at 30 MW/tonne	100,000 MWd/tonne at 200 MW/tonne	
Mo	0.065	0.130	0.24	
Tc	0.014	0.031	0.060	
Sr	0.015	0.036	0.040	
Ba	0.019	0.041	0.068	
Cs	0.035	0.078	0.21	
Rb	0.007	0.014	0.019	
Y+RE ^(d)	0.12	0.27	0.53	
Zr	0.065	0.14	0.22	
Ru	0.032	0.082	0.22	
Rh	0.007	0.013	0.060	
Pd	0.017	0.043	0.16	
Ag	0.0008	0.0016	0.019	
Cd	0.0008	0.0025	0.010	
Te	0.006	0.014	0.034	
Sn	0.0007	0.0016	0.010	
Sb	0.0002	0.0004	0.003	
$\Sigma M_{fp}^{+ (b)}$	0.91	1.73	4.10	
kg oxide/ tonne	22.0	49.0	101.1	

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

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

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

(d) RE is rare earth elements.

type wastes. This has been done to emphasize and facilitate a definition of the effects of the greatly increased quantity of fission products and the significant differences in fission product distribution associated with fast reactor fuels.

3.3 PRODUCT EVALUATION

The product evaluation studies constitute the second major operational activity in the Waste Solidification Demonstration Program. The broad scope of this phase of the work is presented pictorially in Figure 3.5. As shown, the waste pots are measured, leak checked, and radiographed after fabrication and before processing to provide a base for correlating subsequent evaluation data. Grab samples can be taken of the material during the filling of the receiver pot for the two processes wherein the product is in a molten condition at the time it is placed in the receiver. These samples can be taken to a shielded chemical laboratory cell for measurements of leachability, crystallinity, and dispersibility. When filled with solidified waste, the pots are sealed, weighed, dimensionally checked, leak tested, ultrasonically scanned for pot wall thickness, and calorimetry checked. The pots are then placed in interim storage; temperature and pressure data are periodically monitored during this period.

Some of the receiver pots will be placed into controlled environment storage. This involves placing the receiver pot in an environmental storage pod wherein different storage media can be used and different storage temperatures can be maintained. Data will be monitored continuously regarding the environmental storage conditions, temperature distribution throughout the solidified waste, and pressure within the receiver pot. Samples can also be taken from the vapor space above the solidified waste. The capability will exist to periodically remove the pot from the environmental pod, drill into the pot and remove a sample of the solidified waste. These samples will be taken

Neg 0681892-1

FIGURE 3.5. Waste Solidification Product Evaluation Program

to the shielded cell for measurements to determine whether pertinent characteristics are changing as a function of the storage conditions and time.

The controlled environmental storage will be conducted in a separate cell which has been prepared for this purpose and which is known as the Solids Storage Engineering Test Facility (SSETF). A schematic diagram of a portion of this facility is shown in Figure 3.6.

The facility can accommodate up to 16 of the environmental pods with each having its individually controlled environmental storage conditions.

3.4 MAJOR MILESTONES IN THE WASTE SOLIDIFICATION DEMONSTRATION PROGRAM

A helpful technique in the development of a perspective regarding the overall Waste Solidification Demonstration Program and its current status is to consider the major milestones in the program. These are presented in Table 3.2. The listing shows that the majority of the milestones associated with the radioactive demonstrations has been reached and that these activities have entered their final phase (22 demonstration runs have been completed and 14 more are currently scheduled). The processing of wastes typical of fuels having an irradiation history of 20,000 MWd/tonne and a demonstration of thermal maximum have been completed for the pot and spray solidification systems; one run remains to complete this phase of the work for the phosphate glass system. The demonstration of the processing of waste from advanced thermal reactor fuel (involving irradiation conditions of 45,000 MWd/tonne at a specific power of 30 MW/tonne) has been initiated for the spray solidification system and will be completed for all processes in approximately one year. The radioactive testing will be concluded with the demonstration of the processing of LMFBR waste.

Neg 0671892-3

FIGURE 3.6. Solids Storage Engineering Test Facility

TABLE 3.2. *Waste Solidification Demonstration Program Milestones*

Date	Event
1962 September	Design of WSEP started
1965 December	Design and construction completed
1966 November	First radioactive demonstration Nonradioactive tests completed
1967 September	Thermal maximum demonstrated for pot calcination with 20,000 MWd/tonne waste compositions First series of six pot calcination demonstrations completed
1968 May	First series of six phosphate glass solidification demonstrations completed
December	Thermal maximum demonstrated for spray solidification with 20,000 MWd/tonne waste compositions
1969 January	Controlled environmental pot storage facility (SSETF) activated
April	First series of 10 spray solidification demonstrations completed
June	Thermal maximum demonstrated for phosphate glass solidification with 20,000 MWd/tonne waste compositions
September	Phosphate glass solidification demonstrations with 45,000 MWd/tonne wastes completed
December	Spray solidification demonstrations with 45,000 MWd/tonne wastes completed Spray calciner in pot melting demonstrations complete
1970 April	Pot solidification demonstrations with 45,000 MWd/tonne wastes completed
May	Pot solidification demonstrations on LMFBR-type wastes completed
July	All pot solidification demonstrations completed
August	Spray solidification demonstrations on LMFBR-type wastes completed All spray solidification demonstrations completed
September	Phosphate glass solidification demonstrations on LMFBR-type wastes completed All phosphate glass solidification demonstrations completed All WSEP processing demonstrations completed
1972 January	Major engineering evaluation of solidified waste properties completed and reported (See Table 3.3)
June	All major analyses and reporting of WSEP information completed (See Table 3.3) WSEP pots moved to long-term storage facility for storage and long-term evaluation

In the area of product evaluation, laboratory tests have been in progress for some time, while the engineering-scale tests in the SSETF facility have begun only recently. Operation of the SSETF will continue for some time after conclusion of the WSEP demonstrations. Although a few of the containers will be stored in SSETF for up to five years to examine long term effects, it is anticipated that the major portion of the information will be available within the next one to two years.

The final analyses and reporting of the data from the Waste Solidification Demonstration Program represent very significant activities, both from the viewpoint of the effort which remains and the importance of documenting and distributing the information for industrial use. Because of the importance of this phase of the work and the fact that the formal reporting arrangement provides an encapsulation of the content of the program, the full listing of the formal reporting plan is presented in Table 3.3.

The major current technology for the pot, spray, and phosphate glass processes and the design features of the WSEP and product evaluation facilities have been formally reported. Evaluation and reporting of the results of blocks of radioactive demonstrations with individual solidification processes is being documented on a continuing basis. Overall technical, economic, and safety evaluations from the total program for use in direct applications will be completed within two years after demonstrations are completed.

As stated previously, the purpose of the program is to provide information which will enable 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. The subjects of the accomplishments

**TABLE 3.3. Waste Solidification Demonstration Program:
Analysis and Formal Reporting**

Category		Report Volumes	
No.	Description	No.	Release Date
1	Process Technology	1	May, 1969
			Process Technology-Pot, Spray and Phosphate Glass Solidification Processes
2	Design and Equipment Information	2	March, 1969
			Design Features of WSEP
		3	December, 1968
			Design Features of Facilities and Equipment for WSEP Product Evaluation Program
		14	April, 1972
			Design Criteria of High Level Waste Solidification Equipment
3	Performance of Solidification Processes	4	December, 1968
			Pot Solidification Performance During the First Radioactive Tests in WSEP
		5	June, 1969
			Phosphate Glass Solidification Performance During the First Radioactive Tests in WSEP
		6	February, 1970
			Spray Solidification Performance During the First Radioactive Tests in WSEP
		7	May, 1970
			Phosphate Glass Solidification Performance During the Last Series of Radioactive Tests in WSEP
		8	December, 1970
			Spray Solidification Performance During the Last Series of Radioactive Tests in WSEP
		9	April, 1971
			Pot Solidification Performance During the Last Series of Radioactive Tests in WSEP
		10	April, 1971
			Pot, Spray, and Phosphate Glass Solidification Performance During Radioactive Tests on Fast Reactor and Advanced Wastes in WSEP
4	Product Characteristics	11	June, 1971
			Product Evaluation Results from WSEP
		13	January, 1972
			Engineering Evaluation of Solidified Waste Products from WSEP
5	Overall Evaluations	12	February, 1972
			Evaluation of High Activity Waste Solidification Processes and Products in WSEP
		15	June, 1972
			Engineering, Economic, and Waste Management Evaluation of High Activity Waste Solidification Processes in WSEP

to date, and the remaining requirements to meet this objective successfully, will be discussed in further detail in the remaining sections of this interim status report concerning the Waste Solidification Demonstration Program.

4.0 PROCESS AND PRODUCT CHEMISTRY

J. E. Mendel

4.1 PURPOSES OF THE LABORATORY PROGRAM

The primary purposes of the laboratory process and product chemistry program associated with the Waste Solidification Demonstration Program are:

1. Definition of the solution characteristics of the wastes during storage and handling.
2. Definition of operating parameters during solidification processing, with particular attention to the effects of the various chemical additives.
3. Correlation of the quality of the solidified product with feed composition and processing parameters. (This portion of the laboratory program will be discussed in Section 6.0.)

The solution characteristic of most concern is precipitation behavior. The quantity and behavior of precipitates in the wastes are being studied by simulating the complex mixtures in the laboratory.

Laboratory measurements which assist in defining operating parameters are principally melting point, remelt temperature, melt viscosity, melt homogeneity, and volatility. These measurements also are being made on nonradioactive simulated wastes. Radioactive tracers are being used in some of the volatility studies.

4.2 WSEP WASTE COMPOSITIONS

Early in the Waste Solidification Demonstration Program it was recognized that because of the great diversity in possible waste solutions, it would be possible to study only a few of the most typical in detail. The compositions chosen for detailed study, shown in Table 3.1, are representative of four widely different waste types.

Diverse processing modes, fuel exposure levels, and fuel types were incorporated in the choices. Aqueous reprocessing in a Purex plant was assumed in all cases; the wastes are all nitrate solutions. PW-1 is a high salt content waste, as would result if the fuel processor dissolved iron fuel transport containers along with the fuel cores. PW-2 is also a high salt content waste containing sulfate, of the type that would result from combining the first and second cycle wastes from a reprocessing plant using ferrous sulfamate as a reducing agent. PW-4m is a "clean" waste with a low nonradioactive salt content as would be produced by optimum operation of a Purex plant using a reductant such as tetravalent uranium in place of ferrous sulfamate. PW-1 and PW-2 are wastes from moderately exposed fuels, 20,000 MWd/tonne at 15 MW/tonne, while PW-4m is waste from a higher exposure fuel, 45,000 MWd/tonne at 30 MW/tonne. PW-1, PW-2, and PW-4m contain the fission product spectrum from uranium fission. The LMFBR waste contains the fission product spectrum from fission of a mixed uranium-plutonium fuel after an exposure of 100,000 MWd/tonne at an exposure level of 200 MW/tonne. "Clean" processing is assumed. It should be noted that work with LMFBR waste is just now starting.

In both the laboratory studies and WSEP, chemical substitutions are being used for several of the fission products wherein use of the actual elements would be too expensive, or impossible, to obtain in the amounts required. Molybdenum is substituted for technetium, nickel for palladium, and cobalt for rhodium. Although the process behavior of ruthenium is of extreme importance, it is impractical to use the full amounts present in the nominal waste compositions shown in Table 3.1. Approximately 10% of the nominal concentration is added as inert $\text{Ru}(\text{NO}_3)_3$; iron is substituted for the remainder of the ruthenium.

4.3 SOLUTION STABILITY CONSIDERATIONS

Some precipitate is always present in the complex mixtures of radioactive wastes. As a rule of thumb, the concentration and acidity are adjusted, when possible, to keep the volume of precipitate below 10 to 15% and to keep the precipitate "friendly". A "friendly" precipitate is one that is easily suspended by agitation, and that settles slowly when agitation is stopped. Precipitates of this type can be easily transferred remotely by the standard techniques.

Some of the precipitates which occur in radioactive waste solutions are shown in Table 4.1. In general, the quantity of the unfriendly crystalline precipitates can be controlled by dilution and/or acidity adjustment. The hydrous precipitates are less subject to control by dilution but react to changes in acidity. Most of the hydrous precipitates are subject to aging, which is accelerated by heat. As the hydrous precipitates age, they become heavier and more unfriendly.

*TABLE 4.1. Precipitates Potentially Present
in Radioactive Wastes*

<u>Precipitate Constituents</u>	<u>Physical Character</u>	<u>Processing Influence</u>
Nitrates, Ba, Sr, Na	Crystalline	Unfriendly
Sulfates, Ba, Sr, Na-RE		
Silicic Acid		
Molybdic Acid (Complex heteropoly acids)	Amorphous	Friendly, or at least Tolerable
Phosphates, Zr, Fe, RE		
Hydroxides		

As standard practice, it is inadvisable to allow the metal ion equivalent concentration in radioactive waste to exceed about 6N. The allowable metal ion concentration decreases as nitric acid concentration increases above about 4N.

A standard reference concentration of 100 gal/tonne was adopted for PW-1, 2, and 4m in the WSEP studies as shown in Table 4.2. No problems have occurred in handling the solutions at these concentrations except for some severe caking of a mixed sodium rare earth sulfate compound in PW-2. It was found that the caking could be largely prevented by dilution to 200 gal/tonne.

TABLE 4.2. *WSEP Waste Solutions at Reference Concentration of 100 gal/tonne*

	<u>PW-1</u>	<u>PW-2</u>	<u>PW-4m</u>
Metal Ion Equivalents, <u>N</u>	3.9	3.4	2.2
"Free" Nitric Acid, <u>N</u>	3.7	3.9	0.5
Total Nitrate, <u>M</u>	7.5	5.4	2.4
Solids Content, vol%	3	10	10

Precipitate cakes of varying degrees of firmness have been observed in many laboratory-simulated waste solutions, even those with initially "friendly" precipitates, after standing several months. Periodic agitation prevents firm cakes from forming. In the event interim storage periods of weeks or months occur between processing and solidification of the wastes, provision for semicontinuous agitation of the solutions should be made.

The solution stability considerations are further complicated at the solidification plant where chemical additions are made in order to obtain desired qualities in the final product. In the pot calcination process, the adjustments are minor, although, as is discussed later, sulfate is a possible additive, producing a precipitate which requires care in handling.

Large chemical additions are made to the waste in preparing feed solutions to the Spray Solidifier and Phosphate Glass processes, yet feed solution handling problems in WSEP have been

minor. This is because the principal additive in these processes, phosphoric acid, forms bulky but amorphous precipitates. Feed solutions to both processes may contain over 40 vol% solids at concentrations of 140 gal/tonne.

4.4 POT CALCINATION PROCESS

The chemistry of the Pot Calcination process is simple and straight-forward; nitrates are converted to oxides by heating. A temperature of at least 800 °C must be attained to assure that denitration is complete. Otherwise, radiolysis will decompose residual nitrate and release gases. All of the oxides formed are stable at the maximum operating temperature, 900 °C, except those of the alkali metals. These are converted to the more stable sulfates by adding stoichiometric amounts of sulfuric acid prior to calcination. Conversely, if the waste contains sulfate, alkali metals, or alkaline earths may have to be added to stabilize the sulfate.

4.5 MELT FORMATION FROM HIGH LEVEL RADIOACTIVE WASTES

Two-thirds of the WSEP products will be solidified melts prepared by adding fluxing agents to the wastes. The melt processes are more complicated, but the products have significant advantages as compared to the product of a calcination process. The potential hazards in handling an essentially monolithic block of product are less than encountered in handling a powdery calcine, even though it is recognized that the main protection in both cases is the container itself. The higher thermal conductivity permits more heat-producing isotopes to be stored in a pot of solidified melt than in a pot of calcine. Stainless steel containers must be used in the calcination process, whereas cheaper carbon steel containers can be used in most melt processes.

The melt systems which are being considered for waste solidification are all based on one or more of the glass

formers, silicon, boron, or phosphorus. Phosphate melts were chosen for the WSEP processes. Workers in Europe are emphasizing the borosilicate system, sometimes including small amounts of phosphate, in their studies.

Generally, the phosphate system is more flexible and trouble-free than the silicon or boron-containing melt systems. Both boron and silicon cause precipitation problems in the acidic waste solutions. Silicon, in fact, is often added as solid SiO_2 . Special handling of the feeds, which are essentially slurries, often with abrasive solids, is required. In contrast, phosphate is easily metered into the waste solution as orthophosphoric acid, and any resulting phosphate precipitates are easily suspended and relatively noncaking.

A great many cations are compatible in phosphate melts. As much as 25 wt% fission product oxide can be incorporated in a low melting phosphate melt. The flexibility of the phosphate system is illustrated by the fact that it is also possible to retain at least 15 wt% sulfate in a relatively stable, homogeneous product. Sulfate is not compatible with either borate or silicate melts; a second phase is formed which floats on the bulk borate or silicate melt.

A most necessary characteristic of the phosphate system for the WSEP processes is that low melting products (melting points of 950 °C or less) can be obtained quite readily. The low melting products permit relatively high throughputs through the continuous platinum melters.

A disadvantage of the phosphate system is that the melts are quite corrosive at temperatures above 900 °C.

Phosphate glasses are somewhat more leachable in water than are borosilicate glasses. The difference in leachability of the phosphate and borosilicate glasses used for waste solidification has generally been less than a factor of ten. (Typical phosphate product leach rates are given in Section 6.0.)

4.6 CHARACTERISTICS OF PHOSPHATE MELTS

Satisfactory melts cannot be made from most high level radioactive wastes by the addition of phosphate alone. The resulting melting points are too high. Modifying cations must be added along with phosphate to lower the melting point.

A combination of three additives, phosphate plus sodium and iron, in the proper amounts has been found sufficient to prepare satisfactory melts from most wastes. Phosphate acts as the fluxing agent. Sodium, being monovalent, reduces the crosslinkages in the phosphate network and hence lowers the viscosity and melting points. Iron has a homogenizing influence, and helps minimize the tendency of some cations, particularly the rare earths, to separate out of the melt as a heavy phase.

Melts can be formed over a wide range of phosphate concentrations. Melt characteristics change markedly with phosphate concentration and these variations have important process significance. The relative quantities of cations (expressed as cation monoequivalents) and phosphate ions control melt properties. By convention, this ratio is known as the M/P ratio in the WSEP program and it is used routinely. An M/P ratio of 3 corresponds to an orthophosphate compound, 2 to a pyrophosphate, and 1 to a metaphosphate. At M/P ratios above 3, free oxide exists, and the melts become nonhomogeneous. When the M/P ratio is less than 1, ultraphosphates are formed. The ultraphosphates tend to evolve P_2O_5 at high temperatures, and the products are somewhat water soluble, both undesirable properties. The working range is perforce between an M/P ratio of 3 and 1.

At an M/P ratio of 1, metaphosphate chains and rings are formed which may be crosslinked in a very complicated manner. Because of the complicated crosslinking, the melts are viscous

and do not crystallize on cooling. Instead, glasses are formed. As the M/P ratio increases, the glassy character diminishes, and it is difficult to form glasses from melts with an M/P ratio above about 2.25, even with the most rapid quenching.

The crystalline products with M/P ratios of 2.5 to 2.75 have the most desirable properties for the spray solidifier process. A rather sharp melting point, which is not present at lower M/P ratios, is required. The calcine must be a dry, free-flowing powder at 700 °C, the desired operating temperature for the spray calciner, so that sticky deposits do not build up in the calciner. Yet the product must melt and flow at about 900 °C so that stalagmites do not form as the storage container is filled.

The products of the other melt-forming WSEP process, the phosphate glass process, are prepared with an M/P ratio of 1. The phosphate-rich feed remains relatively homogeneous even when concentrated by a factor of 5, to a specific gravity of about 1.9 in the evaporator-denitrator. If higher M/P ratios were used, the evaporator-denitrator solution would contain heavy solids that would prohibit liquid transfer to the continuous melter by an airlift circulator, as is now done.

As has been described, the choice of the M/P ratios used in the spray solidifier and phosphate glass processes is dictated by requirements in solution and melt characteristics which mainly hinge on the degree of glassiness. Other melt and product characteristics also vary in a somewhat systematic manner with M/P ratio. In general, the melting point increases with M/P ratio, when other compositional factors remain constant. The physical toughness of the rock-like products formed at the higher M/P ratios is greater than that of the brittle glasses formed at an M/P ratio of 1. In contrast, the chemical durability, as measured by leach tests in water, increases with glassiness. Sulfate retention increases with

M/P ratio; thus sulfate is completely volatilized in the phosphate glass process while it has been possible to retain the sulfate in PW-2 while processing via the spray solidifier process.

Although guidelines have been developed, the choice of the exact amount of additives to be used with a specific waste solution to form the most desirable product is still being made empirically. The additives which have been used in the WSEP tests to date are shown in Table 4.3.

TABLE 4.3. *Phosphate Melt Compositions Used in the WSEP Demonstrations*

Additives, Moles per Liter of Waste at 100 gal/tonne	Spray Solidifier Process			Phosphate Glass Process		
	PW-1	PW-2	PW-4m	PW-1	PW-2	PW-4m
Na	0.5	--	0.75	2.45	--	1.5
Li	0.5	1.17	0.75	--	--	--
Fe	--	--	1.1	--	--	0.5
Ca	--	0.6	--	--	--	--
Al	--	0.25	--	--	--	--
H ₃ PO ₄	1.74	1.61	2.80	6.23	3.36	5.7
NaPO ₃	--	1.27 (in melter)	--	--	--	--
	(M/P = 2.75)	(M/P = 2.7)	(M/P = 2.50)	(M/P = 1.0)	(M/P = 1.0)	(M/P = 1.0)
Product Composition, Oxide wt%						
Fission Products	18	10	25	8	14	18
Waste Inerts	30	28	4	13	21	3
Melt Forming Additives	52	62	71	79	65	79

The basic goal is to keep the fission product content of the product as high as possible. Therefore, the additives must be kept to the minimum that permits proper operation of the solidification equipment and yields a satisfactory product. The additives are basically sodium, iron, and phosphate. In the spray solidifier process, substitution of lithium for half the sodium has been found to decrease the melting point slightly. Iron is already present in PW-1 and PW-2 in sufficient quantity that more is not needed. The spray solidifier PW-2 additive

formulation is markedly different from the others because this flowsheet is designed to retain sulfate. Calcium and lithium are added to form more stable sulfates. Since sulfate volatility is a function of melt temperature, the lowest possible melt temperature is desirable. Therefore, additional flux and alkali metal are added directly to the melter as NaPO_3 , which allows a melter operating temperature of only 850 °C.

The maximum fission product content that has been demonstrated as obtainable in melt-formed solidified waste is the 25 wt% in the spray solidifier PW-4m product. It is believed that this approaches the maximum that can be obtained in a homogeneous phosphate product which has a low enough melting point and viscosity to be processed through a continuous platinum melter.

4.7 FUTURE PROCESS AND PRODUCT CHEMISTRY REQUIREMENTS

One method of assessing the current state of the chemical technology of waste solidification is to attempt to predict the amount of process chemistry assistance that an independent waste solidifier would require if starting operation today. To a large extent, the process chemistry requirements would hinge upon the composition (and the amount of variation in the composition) of the waste solutions coming to the solidification plant. If the wastes to be solidified had a fairly constant composition (changes of up to $\pm 10\%$ in even major waste components can be accommodated without adjustments in the amount of fluxing chemicals used), and if that composition did not contain significant amounts of constituents not included in the WSEP wastes, the process chemistry assistance effort would not be large. It could easily be incorporated into the process assistance program for the reprocessing plant with which the solidification facility would likely be associated. The process chemistry assistance requirements would escalate as the number of batches

of nonroutine waste went up or if the waste contained significant quantities of constituents which have not been studied in the WSEP, such as fluoride or mercury.

Even when the techniques of solidification have been perfected, there will be an ongoing process and product chemistry effort in every solidification plant to optimize the quality of the solid product and to increase decontamination efficiency in the solidification process effluents.

5.0 RADIOACTIVE ENGINEERING DEMONSTRATIONS IN THE WASTE SOLIDIFICATION ENGINEERING PROTOTYPES

K. J. Schneider

5.1 PROGRAM DESCRIPTION

The engineering demonstration studies in the Waste Solidification Program include the radioactive demonstrations with the WSEP solidification processes and equipment to the point that the pots filled with solidified waste are removed from the processing equipment for evaluation of the solidified wastes. The studies also include the demonstrations with the processes and equipment which decontaminate the primary effluents from the solidification equipment. In addition, supporting laboratory and engineering development studies are performed in direct support of the radioactive demonstration studies.

These fully radioactive demonstrations with the engineering-scale WSEP equipment in B-Cell of the Chemical and Materials Engineering Laboratory are the culmination of a large AEC program for the development of improved storage of high level wastes. These demonstrations are planned to consist of 36 runs wherein one container is filled with solidified waste in each run. The cylindrical containers are 6, 8, and 12 inches in diameter, are 8 feet long, and each is filled to the 6 foot level. Wastes from 0.6 to 2 tonnes of reactor fuel are contained in an 8-inch container (or pot) depending on the reprocessing scheme and solidification process. Approximately twice this amount of waste is contained in each 12-inch pot, and 55% is contained in each 6-inch pot. At the WSEP operating rates of 0.3 to 1.0 tonnes/day, the processing time required to fill an 8-inch pot is 40 to 70 hours. When the immediate startup and shutdown times are considered, performance of a demonstration run requires a week. Pre-run preparations and post-run cleanup require approximately one week each.

Equipment modifications, other facility operating requirements, and initial evaluations take an additional one to four weeks. The resultant schedule is an average of one demonstration run every 4 to 6 weeks. The 36 demonstrations now planned will require a total time of less than 4 years (from November 1966 to September 1970).

The demonstration program for each of the three WSEP solidification processes is divided into two nearly equal halves: (1) gradual escalation of radionuclide content in each test run with the two standard waste compositions (sulfate-free and sulfate-containing wastes from fuels with 20,000 MWd/tonne exposure) to determine overall effects of radioactivity and heat content, and overall process and equipment performance under remote operating conditions, and (2) demonstrations with wastes simulating those from thermal and fast reactors which have a higher content of fission products (up to 45,000 MWd/tonne exposure in thermal reactors and 100,000 MWd/tonne core exposure in fast reactors). We have just passed the 60% point in the demonstrations. We have completed the first phase and have entered the second phase of these demonstrations. The overall conclusion to date is that conversion to solids is indeed feasible for commercial application.

5.2 OVERALL STATUS OF WSEP DEMONSTRATIONS

Table 5.1 shows the overall status of the radioactive demonstrations in WSEP as of April 1, 1969. A total of 22 demonstrations have been completed, 6 in each of the pot and phosphate glass solidification processes, and 10 with the spray solidification process. Approximately 30 megacuries of mixed radionuclides representing waste from about 232,000 MWd of electrical power^(a) have been converted to solids. This amount

a. Assuming 33% thermal efficiency and 20,000 MWd/tonne.

of waste represents 88 days of all the nuclear power capacity in the United States as of March 1, 1969, about 5 days of all the nuclear power contracted to be on line by the end of 1973, and about 1.6 days of all the nuclear power anticipated in 1980. The total on-line processing time for solidification of these wastes was 56 days. The average on-line processing rates vary from 0.3 to 1.0 tonnes/day of fuel, depending upon the waste composition, the process, and the chemical flowsheet used.

TABLE 5.1. Overall Status WSEP Radioactive Demonstrations

	Solidification Method			Total
	Pot	Spray	Phosphate Glass	
Runs Completed	6	10	6	22
Megacuries Solidified	4.0	17.5	8.2	30
Equivalent Tonnes ^(a) Processed	11.3	14.6	9.0	35
MWd _e Represented by Waste ^(b)	75,000	98,000	59,000	232,000
Tonne/Day Rate ^(a)	0.6 to 1.0	0.5 to 0.9	0.3 to 0.7	--
Maximum kW in One Pot	5.1	12.7	9.8 ^(c)	108 ^(e)
Maximum W/l in Pot	85	205	160 ^(d)	--
Maximum Centerline Temperature in Pot, °C	940	930	780	--
Liters Solid/Tonne ^(a)	40 to 50	30 to 65	50 to 100	--
Runs to Complete	6	3	5	14

- a. Tonne is a metric tonne (1000 kilograms, or 2205 pounds) of original fuel.
- b. Assuming 33% thermal efficiency and 20,000 MWd/tonne.
- c. True maximum has not yet been demonstrated. Calculated maximum is 11.5 kilowatts.
- d. True maximum has not yet been demonstrated. Calculated maximum is ~~100 kilowatts~~ 190 Watts/Liter.
- e. Total kilowatts encapsulated to date.

The maximum amount of heat from radionuclide decay that can be incorporated into 8-inch diameter pots which are air-cooled^(a) by natural convection has been demonstrated for the spray and pot processes. The heat-rate values in the solidified wastes range from the highest of 205 W/liter for the spray solid to 85 W/liter for pot calcine. The out-of-reactor time represented by these maximum heat rates is less than half a year. Fourteen demonstration runs are currently planned to complete the remainder of the program.

5.3 OVERALL COMPARISON OF THE THREE PROCESSES

Table 5.2 shows a very brief and qualitative comparison of the three solidification processes and their solidified wastes. The major conclusion that can be drawn from this information is that no one method provides the best answer to all problems, but that each fuel reprocessing situation will determine largely what waste processing technique is optimum.

Pot calcination requires the simplest system and supporting development studies for nearly any application. It has good flexibility for a wide variety of waste compositions. However, it produces a relatively leachable and dispersable solidified waste which has poor heat transfer characteristics. Also, since it is a batch system, its amenability to scale-up is limited. The spray solidification process is a continuous process with a low in-process inventory. It produces a tough, rock-like solid with low leachability and good heat transfer characteristics. However, it requires a relatively complex

a. *The maximum limit of heat-rate in WSEP is that in which any one or more of the three following conditions exist:*

- 1. The temperature at the center of the pot is 900 °C or higher.*
- 2. The temperature at the wall of the pot is 425 °C or higher.*
- 3. The thickness of the "frozen wall" is a solidified waste which is partially molten is no less than half the radius of the containers.*

TABLE 5.2. Comparison of Pot, Spray, and Phosphate Glass Solidification Processes

	Advantages		Disadvantages	
	Pot	Spray	Pot	Spray
1. System	Simple			
2. Type —Amenability to Scale Up		Continuous Good	Batch Limited	Complex
3. Flexibility for Waste Variations	Good	Continuous Good		Limited
4. R&D Required for New Wastes	Minimum			Moderate
5. In-Process Inventory	Low	Lowest		Moderate
6. Specific Restrictions				Requires Platinum Melter
				Requires Good Waste Flow Control
				Requires Good Concentrate Flow Control
				Does Not Retain Sulfate in Solid
7. Product Leachability	Low	Lowest if Glass	High	
8. Thermal Conductivity	Highest	Good	Poor	
9. Toughness	Tough		Friable	
10. Storage Container	Mild Steel	Mild Steel	Stainless Steel	Brittle

system, and may require moderate development for wide variations in chemical waste compositions. The phosphate glass process is a continuous process which produces a glass with very low leachability and moderately good heat transfer characteristics. However, it requires a relatively complex system, it may require moderate development for wide variations in chemical waste compositions, and it does not retain sulfate in the solid if sulfate is present in the waste.

5.4 SIGNIFICANT FINDINGS TO DATE FOR THE SOLIDIFICATION PROCESSES

Highlights of the information obtained to date from the engineering demonstrations with the three solidification processes are shown in Table 5.3. Volatilization of the fission product ruthenium is important because: (1) It is highly desirable ultimately to retain all the ruthenium in the solidified waste, or an extra waste stream may result; (2) relatively large quantities of ruthenium may be recycled through the effluent treatment steps which could cause problems with buildup of ruthenium scale on equipment or could result in undesirably large ruthenium inventories; and (3) ruthenium is likely to be the limiting radionuclide in the effluents from solidification,^(a) and high volatilization rates will further complicate this cleanup problem. The amount of ruthenium volatilized from the pot and phosphate glass processes appears to be reasonably low, while that from the spray solidification process is frequently greater than 50% of the total, which is undesirably high. Recent demonstrations have shown that ruthenium volatilization from the spray process can be reduced to about 30% by reducing the acidity of the aqueous waste before solidification. Studies on methods for further

a. *Tritium may be the limiting isotope if it has not been removed during fuel reprocessing.*

reduction of the ruthenium volatilization from spray solidification are in progress. Volatilization of all other radionuclides is held to insignificant levels.

TABLE 5.3. *Significant Findings to Date for Pot, Spray, and Phosphate Glass Solidification Processes in WSEP*

	Pot	Spray	Phosphate Glass
1. Ruthenium Volatilization	5 to 30%	10 to 80%	3 to 15%
2. Primary Entrainment	<1%	<0.1%	<4%
3. Sulfate Wastes	Readily Processed	Reasonably Processed But Can Foam in Pot	Readily Processed Form Separate Waste
4. Sulfate-Free Wastes	Readily Processed	Readily Processed	Troublesome Sludge
5. Aluminum in Waste	Readily Processed	Limited Processability	Readily Processed
6. Foaming in Waste	Sometimes	No	Yes
7. Pot Temperatures	Temperature Control Good	Fill Unheated Pots	Fill Unheated Pots

Low entrainment from the solidification process is desirable to reduce the amount and handling problems during recycle of the entrainment, and to minimize the additional decontamination required for the effluent streams from solidification. The entrainment from all of the three solidification processes is acceptably low, although that from the spray process is better than from the pot or phosphate glass processes by an order of magnitude.

Wastes will contain large amounts of sulfates if ferrous sulfamate is used as a chemical reducing agent during fuel reprocessing. When this is done (as it is currently done at the two AEC production fuel reprocessing sites and at the Nuclear Fuel Services fuel reprocessing plant), the sulfate can require that significant changes be made in the solidification procedures. The heavy precipitate in sulfate-containing wastes can cause severe materials handling problems with pumps,

instruments, pipes, etc. Minimization of this problem has been demonstrated by dilution of the waste with water, and other methods are being investigated. Sulfate-containing wastes are readily solidified with the pot calcination process. Sulfate-containing wastes are processable with the spray process under moderately narrow chemical flowsheet and operating conditions, and they can cause foaming in the container for the solidified waste with certain deviations from normal operating conditions. Sulfate-containing wastes are readily processed with the phosphate glass process, but the sulfate is quantitatively volatilized from the molten glass. This volatilized sulfate cannot be recycled for reuse in the fuel reprocessing step without significant decontamination and chemical conversion efforts. Consequently, it must be treated as an additional effluent stream.

Sulfate-free wastes are currently expected to be the most common in future fuel reprocessing schemes. These wastes are readily solidified with the pot and spray solidification processes if the wastes contain the normal chemicals present in high level wastes. Sulfate-free wastes are processable with some difficulty with the phosphate glass process due to heavy precipitates in the denitrator evaporator. Significant improvement in the phosphate glass processability of sulfate-free wastes would likely result from adaptation of an alternative type of denitrator-evaporator.

At the present time, major amounts of aluminum are not expected in wastes, except in some current production wastes or possibly in wastes which may contain the fluoride ion from fuel dissolution operations. Aluminum-containing wastes are readily processed with the pot and phosphate glass processes. Modest amounts of aluminum (up to approximately 15% of the total cationic normality) are processable with the spray process without significantly modifying the chemical additives presently used.

Dibutyl phosphate, which is one of the degradation products of the solvent from Purex solvent extraction reprocessing of fuels, has been shown to cause severe foaming in the denitrator-evaporator of the phosphate glass process. However, control of this foaming has been satisfactorily demonstrated in WSEP by the addition of antifoam agents. Similarly, the solvent degradation products are suspected to be causing occasional foaming during pot calcination, but this effect has not yet been confirmed. Aqueous solutions which foam during boiling do not affect the spray solidification process.

Filling containers full of solidified wastes which have significant heat generation rates from decay of the fission products imposes special considerations during the solidification processes. Satisfactory filling and cooling for all three processes has been demonstrated in WSEP.

In pot calcination, the calcine or scale grows inward from the pot wall and upward from the bottom. Consequently, the amount of heat generating material present at various vertical locations is different and varies with the time in the filling cycle. Furthermore, the temperature of the material in the center of the pot in any zone will exceed that desired if cooling of the pot wall is not started before this calcine in the center of the pot has reached its desired temperature. Reliable solutions to this problem have been demonstrated in WSEP by the use of six-zone heating-cooling furnace and a simple three-step reduction of furnace temperatures based upon pot wall and center temperatures.

In the spray and phosphate glass processes, uniform filling of unheated pots without appreciable voids in the final solids have been demonstrated at pot filling rates as low as 15 liters/hour (in 3 to 7 liter batches), or waste from 5 to 10 tonnes/day of fuel. Uniform filling at lower rates may be possible, but has not been demonstrated. However, uniform

filling of pots at about 10% of these rates cannot be accomplished unless the pot is maintained at the "slumping" point (25 to 200 °C below the melting point) of the solidified waste. Filling of pots where such heating is required restricts the amount of self-generating heat that can be put into a pot, and in some cases, requires the use of a stainless steel pot where otherwise a mild steel pot is usable.

5.5 SIGNIFICANT FINDINGS TO DATE FOR EFFLUENTS FROM WSEP

Conversion of high level aqueous wastes to solids results in one or more effluent streams with lower levels of radioactivity. The total benefits of solidification are therefore not truly realized until the radionuclide contents of these effluents are reduced to nontoxic levels. A significant part of the WSEP program is that of characterizing these effluents and evaluating the need and means for their cleanup. This part of the program has only recently been emphasized and relatively little information has been obtained to date.

However, three broad generalizations can be made regarding the effluents from the WSEP processes:

1. The immediate effluent from the solidification step (i.e., the vapors or their condensed phase) have been decontaminated by factors of 10 to 500 so that they remain as intermediate level wastes.
2. The cleanup in the WSEP effluent treatment system is adequate for the final gaseous effluent stream, but is inadequate for the aqueous effluent stream by up to 6 orders of magnitude, based on limits in 10CFR20.
3. The volumes and radionuclide content of the immediate effluents from the solidification processes are relatively small compared to those associated with the "dilute" high level waste from the solvent extraction process during

fuel reprocessing. Consequently, such wastes can be reasonably recycled to facilities that a fuel reprocessing plant requires for an existing and larger scale problem.

A summary of the information from the Waste Solidification Program related to the first two generalizations above is presented in Table 5.4. The amount of ruthenium volatilized from the solidification steps is between 3 and 80%. The values for the pot and phosphate glass processes are considered to be reasonable and acceptable for cleanup and recycle; the higher values for the spray process are undesirable, and studies on control of acidity have recently shown that such volatilization can be reduced to an acceptable 30% or lower. The strontium (and other nonvolatile materials) in the initial effluent is acceptably low for all three processes and is normally a factor of about 5 lower than the maximum values shown.

TABLE 5.4. *Significant Findings to Date for Effluents from Pot, Spray, and Phosphate Glass Solidification Processes in WSEP(a)*

	Effluents From		
	Pot	Spray	Phosphate Glass
1. <u>Immediate Effluent Radioactivity Compared to Aqueous High Level Waste</u>			
A. Ruthenium	5 to 30%	10 to 80%	3 to 15% ^(b)
B. Strontium	<1%	<0.1%	<4% ^(b)
2. <u>Final Condensate Radioactivity Compared to 10CFR20 Limits</u>			
A. Ruthenium	20,000 to 500,000	300,000 to 3,000,000	100,000 to 500,000
B. Strontium	5,000 to 50,000	5,000 to 50,000	5,000 to 50,000
3. <u>Final Stack Effluent Radioactivity Compared to 10CFR20 Limits</u>			
A. Ruthenium	<1%	<1%	<1%
B. Strontium	<0.01%	<0.01%	<0.01%

a. Assuming operation at 1 tonne fuel/day with exposure of 45,000 MWd/tonne at 1 year.

b. For sulfate-containing waste, a separate sulfate effluent stream is obtained which contains 1 to 10% of the ruthenium and 0.3% of the strontium and other nonvolatile materials.

The radioruthenium content in the final WSEP condensate is a factor of 20,000 to 5,000,000 higher than allowable values in 10CFR20, with the condensate from the spray process being higher than from the other two processes. Consequently, additional cleanup by the factors shown in Table 5.4 would be required to convert this effluent to drinking water. The strontium and other nonvolatile material in the condensate is similar for all three processes, and requires considerably less cleanup than the ruthenium.

The radioruthenium in the final stack gas is less than detectable in all cases after dilution by a factor of 10,000 from building ventilation air.* All other remaining beta radioactivity in the building stack gas is assumed to be strontium-90. The values shown are at or near detection levels after the same factor of 10,000 dilution, and therefore are also probably higher than actual. Although ruthenium and other radionuclides present in the diluted process equipment effluents are known only as "less than detection limit" quantities at the present time (they will be defined for the direct, undiluted stream within a few months), they are sufficiently low to have demonstrated adequate overall cleanup.

Detailed studies on the cleanup needs of solidification effluents and the actual effects of integration of these cleanup needs with those of the total fuel reprocessing plant will be complete in a few months. However, as stated previously, the solidification effluents are not expected to add significantly

* The values shown are additionally conservative because they assume all radionuclides emitted to the air are from WSEP processing. Other sources of radionuclides in the facility are ventilation air from eight other high level radioactivity cells and process vent effluents from other in-cell activities.

to a technical problem that exists in any fuel reprocessing plant. Because the effluent treatment system in WSEP is similar to many used in fuel reprocessing, the resultant data should be very meaningful to commercial applications.

The discussion here is based upon having solidification processing capabilities with each fuel reprocessing plant. If the solidification capabilities were not integrated with but were remote from the fuel reprocessing plant, the solidification plant would need a complete, smaller-capacity version of effluent waste treatment facilities, and shipping of high level liquid waste and the reusable acid between the two processing plants would be required. These conditions are believed to be impractical and unsafe, and are not considered further.

5.6 GENERAL SOLIDIFICATION TECHNOLOGY TO BE DEVELOPED IN WSEP

Detailed technical, safety, and economic evaluations of the solidification processes, their effluents, and their solidified wastes will be the products of the WSEP program. These evaluations will be presented in a series of reports in concise and useful forms for use by fuel reprocessing and utility companies and by the government.

A summary of these remaining technology developments is presented in Table 5.5. Demonstrations with wastes from high exposure thermal reactor fuels are underway and will be completed in about one year. Paper and laboratory studies on wastes from fast reactor fuels are in progress, and demonstrations will be completed early in fiscal year 1971. Effects of various processing and waste management schemes will be evaluated after all the data from the demonstrations are available. Examples of variables which will be studied on both economic

and safety bases are interim liquid and solid storage, chemical flowsheet variations, transportation, and mixing of high level and other wastes.

TABLE 5.5. *General Technology Development Remaining For Solidification Processing in WSEP Program*

1. Effects of high exposure thermal reactor wastes.
2. Effects of fast reactor wastes.
3. Effects of various processing and waste management schemes.
4. Solidification equipment requirements.
5. Effluent processing requirements.
6. Economic factors.
7. Minimum solid waste container requirements.
8. Solidifier scale-up to 5 to 10 tonnes/day.

Detailed solidification equipment requirements will be established to provide most of the information that a competent, knowledgeable architect-engineering firm would need to design the equipment for a waste solidification plant. Characterization of the effluents from solidification and needs for processing these effluents will be defined and evaluated. Means for reducing contamination of effluents to sufficiently low levels for discharge to the environment will be evaluated, with emphasis on means for integration with the effluent treatment systems existing in fuel reprocessing plants.

Economic factors for solidification and storage of wastes, as well as all related activities, will be established. Operating and capital cost factors for a variety of processing schemes will

be developed. From limited cost analyses to date, it is known that the presently-conceived containers for solidified wastes will contribute up to half the total solidification plus storage costs. Consequently, alternative container shapes, sizes, and materials will be evaluated for safety and economic comparisons. Capacity scale-up factors for solidification equipment to the 5 to 10 tonnes of fuel per day range (processing plants currently planned to be on line after 1973 are sized at 5 tonnes/day) will be estimated in paper studies. WSEP and other demonstrated technology is in the capacity range of 0.5 to 1 tonne of fuel per day.

5.7 SPECIFIC SOLIDIFIER TECHNOLOGY TO BE DEVELOPED IN WSEP

A summary of the technology specific to the individual solidification processes that remains to be developed in the waste solidification program is shown in Table 5.6. The maximum amount of heat generating fission products that can be stored in a given pot geometry (or, the effective thermal conductivity) must be determined for the solids from the pot and phosphate glass processes as it has been for the spray process. (The value has been determined for the pot process, but because of experimental difficulties will be reconfirmed.)

TABLE 5.6. *Technology To Be Developed for the Pot, Spray, and Phosphate Glass Solidification Processes*

	<u>Technology Needs for Solidifier</u>		
	<u>Pot</u>	<u>Spray</u>	<u>Phosphate Glass</u>
Maximum Heat Rate in Pot	Confirm	--	Define
Ruthenium Volatilization	Control	Reduce	--
Less Expensive Equipment	Temperature Measurement	Melter	-- (a)
Operable Equipment	--	--	Slurry Handling; Melter Feed

a. *The same incentive exists here, as for the spray calciner, but development efforts are not being made in support of the WSEP program.*

Means for consistently limiting the volatilization of ruthenium during spray solidification to approximately half the total will be developed. Means for more consistent control of volatilization of ruthenium during pot calcination will be developed.

Because the container is also the processing vessel for the pot process, extra thermocouples in the pot (which are expensive) are currently used for controlling temperatures in the pot during solidification.

The platinum melters used in the spray and phosphate glass processes are very expensive and weak structural links in the chain of solidification process equipment. Alternative materials or means to eliminate the melter are being developed for the spray process. Similar studies are not being made for the phosphate glass process, but much of the technology developed for the spray process should spin off to the phosphate glass process.

The slurry handling capabilities and the melter feed control for the phosphate glass process are currently considered to be insufficiently reliable for commercial application. Solutions to these problems will be developed.

5.8 SCHEDULE OF REMAINING PROGRAM

Approximately 60% of the radioactive demonstrations planned in the WSEP and related programs have been completed, from which overall process and equipment performance have been confirmed. The final demonstrations are planned for completion in the fall of 1970. Developmental effort remaining for application at that time will be modest laboratory work pertinent to each specific case, which is not in the government-supported program. The work should readily be performed by the fuel reprocessors.

6.0 PRODUCT EVALUATION PROGRAM

R. J. Thompson

6.1 OVERALL PROGRAM DESCRIPTION

The objective of the product evaluation program is to determine the behavior of the product from the WSEP solidification processes, and to determine the safety and economic aspects of this product behavior as related to the management of high level wastes. "Product" in this context refers to the solidified waste and storage container, as prepared by any of the three waste solidification processes.

The main incentive for converting high level wastes to solid forms is for improved containment safety during the centuries that the material must be stored before the activity levels have decayed to nontoxic levels. A time period of great interest for these solidified wastes is the interim storage period before the waste is placed in a location for permanent storage where surveillance may be discontinued or greatly reduced. This time period is the first 10 to 30 years after solidification, when heat removal problems, product temperature, radioactivity, and rate of radiochemical changes are at their greatest. This program was undertaken to quantify the degree of improvement in safety and economics provided by storage of high level wastes as solids.

Two basic areas of technology are being investigated: (1) characterization of the pertinent physical and chemical properties of the products from the three solidification processes being demonstrated in the Waste Solidification Demonstration Program, and (2) engineering and safety analyses of the product characteristics for direct application to the industrial reprocessors of nuclear fuels. To provide the necessary data

to define the pertinent product properties and enable engineering and safety analyses of the product characteristics, three types of measurement data are being obtained: nonradioactive laboratory, radioactive laboratory, and engineering scale.

6.2 NONRADIOACTIVE STUDIES

The largest number of samples and measurements are being made in the nonradioactive laboratory. In general, the cost and experimental complications are at a minimum in this area, and a large number of samples can be used to study various effects exclusive of radiation. For example, the effects upon product quality of the processing parameters, melter operating temperature, residence time in melter, cooling rate (from melt to storage temperature), and storage temperature are being studied using laboratory-prepared nonradioactive product specimens. A detailed study, in which specimens were prepared using all 16 possible combinations of the above parameters at two levels, has been completed on phosphate glass PW-2. Similar studies with selected combinations of the parameters are underway with simulated specimens having compositions representative of the other WSEP products. The product characteristics being measured are thermal conductivity, density, heat capacity, linear coefficient of thermal expansion, leachability, dispersibility, crystallinity, thermal shock, and porosity. Ideally, known relationships will be evolved between laboratory and engineering-scale studies. There are obvious advantages to industry if nonradioactive laboratory results can be extrapolated to predict product properties.

Since thermal conductivity will be an important factor in determining the amount of heat that can be incorporated in a given container, efforts are being made to establish thermal conductivity values for the products of the three processes.

Results of the study of phosphate glass PW-2 product showed a significant increase in thermal conductivity when the glass devitrified. The thermal conductivity increased approximately 25% (Figure 6.1). Devitrification, or crystallization, of phosphate glass PW-2 product occurs at storage temperatures greater than 500 °C. Differences in thermal conductivity of the magnitude observed with the phosphate glass specimens are of importance to the industrial economics of waste solidification and are being given continuing attention in the nonradioactive testing.

FIGURE 6.1. Typical Nonradioactive Laboratory Thermal Conductivity for Phosphate Glass Melt

The integrity of the solidified waste becomes the only barrier to the dispersal of radionuclides once the primary container has been breached. Therefore, the leachability and dispersibility of the solidified wastes prepared by the three processes are being studied to determine the degree of safety provided by solidification. Leachability measurements on non-radioactive laboratory samples of phosphate glass and spray melt have been made; typical results are presented in Figure 6.2. In general, spray melt is an order of magnitude more leachable than the phosphate glass. However, it is significant to note that the spray melt products and phosphate glass products are several orders of magnitude "safer" than liquid wastes in this respect. Pot calcine is three to five orders of magnitude more leachable than the spray melt or phosphate glass.

FIGURE 6.2. Typical Leach Rates for Solidified Wastes from Spray Solidifier and Phosphate Glass Processes

Laboratory studies are also being conducted on the dispersibility of solidified wastes. The purpose of these studies is to provide data wherein the fraction of solid that would be readily dispersed under accident conditions can be estimated. A standard weight is dropped a specified distance on standard samples of product, and the resulting pieces are sized by screening. A relatively small percentage of the pieces from devitrified phosphate glass PW-2 samples were of a size for easy dispersion. Only 1 to 2 wt% of the shattered pieces were less than 500 microns in diameter while approximately 20 wt% of the shattered pieces from vitreous samples were less than 500 microns. Comparative data for the spray and pot products will be obtained.

Another series of laboratory investigations are aimed at predicting the affects of molten core storage before it is studied on an engineering scale. The maximum heat-rate permitted in the WSEP waste storage containers allows that a molten core can extend out from the center to half the radius of the containers (page 5.4). Only a few WSEP-filled waste containers are scheduled to be held at molten core conditions; the effect of molten core storage on other types of product will be studied in the laboratory. Two factors are of paramount importance: the potential for pressurization that can occur due to release of volatiles, and the possibility of fission product migration and accumulation to form "hot spots".

The pressurization potential is most severe in the sulfate-retaining spray solidifier melts. When these melts are heated to 750 °C in open laboratory containers, sulfur oxides are evolved slowly (essentially 100% of that present in a period of a few weeks). A test in which a container, designed to simulate a large closed storage container, was prepared and filled with sulfate-bearing waste to study the release of sulfur

oxides has been made. The sample, which was held with a temperature gradient of 800 °C centerline to 375 °C surface for seventeen weeks, did not show any container pressurization. Analysis is not complete, but it is believed that sulfur oxides were released from the hot zones (centerline) and reabsorbed or recombined in the colder zones.

Knowledge of the corrosion of the waste container by the primary melt or decomposition products is also very important and is being studied in the laboratory. Studies have been instituted to measure the corrosivity of the products of all three processes on container materials at storage conditions. Standard coupon samples of 304L and 310 stainless steel and mild steel have shown corrosion rates of a few tenths to a few mils per year at 600 to 700 °C.

6.3 RADIOACTIVE STUDIES

The real importance of the radioactive studies lies in providing to industry information and data on the properties and characteristics of actual solidified waste in volumes of industrial size. The measurements made in the radioactive portion of the Product Evaluation Program are being made principally on the filled containers, where emphasis is placed on the integrity of the solidified waste-container system. These measurements are supplemented by analyses made on actual samples of the solidified waste. ("Dip" samples of the product are taken as it is cast into the storage container, and core-drilled samples will be taken after the product has aged in the container). Special facilities have been provided for these measurements: the Solids Storage Engineering Test Facility (SSETF) for storage of the containers under carefully controlled conditions, and shielded hot cells devoted to measurements on the samples (see Figure 3.5).

The engineering-scale studies in product evaluation begin with prefill measurements on the WSEP container before the container is moved into the processing cell. These measurements form base reference points for later comparisons. The prefill measurements include the usual quality assurance measurements for fabrication (dimensions, tolerances, X-ray, etc.), and ultrasonic wall thickness scanning, leak testing, and general appearance photographs.

After the containers are filled with product, the basic dimensional measurements are repeated in the processing cell. No significant dimensional changes have been observed in measurements for "out-of-roundness" which are taken by dial-indicating micrometers. At this time, calorimetry and temperature profile measurements are also made to check the heat content of the container and to determine the effective thermal conductivity. The heat content measurement is helpful in making a material balance of heat-producing isotopes for each run in WSEP. The filled container is also weighed for material balance. The thermal conductivity is a highly important characteristic since it is the key factor in determining the amount of fission heat which can be placed in a container and the heat removal requirements at the storage locations. The thermal conductivity measurements are discussed in more detail in Section 6.7.

Other important after-fill measurements are an axial gamma scan, ultrasonic wall thickness, and helium leak test after the cap is welded in place. The gamma scan testing has shown a uniform axial distribution of fission products in filled containers for all three processes. The purpose of the gamma scans is to detect any gross axial migration of fission products and hence "hot spots" that might develop within the container. Adverse restrictions on the container heat load could result if severe "hot spots" are formed.

Reliable wall thickness data are not currently available but are expected within a few months. Actual corrosion measurements are important and will provide commercial reprocessors with valuable data on the integrity of the waste container.

Leak rates between 1×10^{-7} and 1×10^{-8} atmospheric cubic centimeters per second have been measured on sealed containers of phosphate glass and spray solidifier product with a helium leak detector. Leak testing of pot calcine-filled containers required higher capacity outgassing equipment which has just been obtained.

The pressure and temperatures of the waste containers are monitored routinely during storage. No pressurization of any container in the engineering studies has occurred.

6.4 SOLIDS STORAGE ENGINEERING TEST FACILITY (SSETF)

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

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

The variables involved in the test plan are:

- 3 processes (spray and phosphate glass solidification and pot calcination)
- 4 waste types (PW-1, PW-2, PW-4m, and LMFBR)

- 3 container materials (304L and 310 stainless steel and mild steel)
- 2 storage media (water and air).

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

Insight into product and container properties will be gained through this study. Specifically, the product will be studied for effective thermal conductivity and pressurization in the cell (nondestructive testing), and for crystallinity, leachability, and dispersibility in supporting laboratory studies (core drilled samples). Product conditions will include molten core storage for several waste containers. These molten core studies are designed to explore the behavior of the product at elevated storage conditions and will investigate factors such as fission product migration or segregation and chemical stability of the product. The data from the molten core studies have high potential significance in terms of the economics (the amount of fission heat which can be placed in a container) and/or the safety (assessing accident conditions) associated with the storing of solidified waste. The remainder of the environmental storage studies center about determining the effects of storage temperature (air or water), radiation, and feed type upon the physical and chemical properties of solidified waste products.

Periodically during the controlled environment storage of WSEP waste containers, the containers will be withdrawn and sampled by core drilling. The core-drilled samples will be transferred to the shielded chemical laboratory for measurements

of crystallinity, leachability, dispersability, and fission product migration. A cap will be welded over the hole and the container returned to its controlled environment storage. The wall plugs removed from the containers by core drilling will provide samples for corrosion studies on the container material following actual solidification processing and storage. Core drilling is expected to begin in late 1969.

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

6.5 PERTINENT CHARACTERISTICS OF WSEP SOLIDIFIED WASTES

A summary of the approximate characteristics of solidified high level waste from the three processes under development at the Pacific Northwest Laboratory is shown in Table 6.1. The products from the three processes can be described as calcine cake for the pot calcination process, microcrystalline or rock-like for the spray solidification process, and glass for the phosphate glass process. The pot calcine product has a high leach rate when compared with the spray solidifier and phosphate glass products. The pot calcine material may be more stable at elevated temperatures. The spray and phosphate glass melts can be stored in mild steel containers; stainless steel containers must be used in the pot calcination process. Because of the differences in heat conductivity, the maximum fission product heat per unit volume which can be stored in pot calcine product is less than half that which can be contained in the melt products.

TABLE 6.1. *Characteristics of Solidified High Level Waste*

	Pot Calcine	Spray Melt	Phosphate Glass
Form	Monolithic	Monolithic	<i>monolithic</i> Particulate
Description	Calcine Cake	Microcrystal- line	Glass
Chemical Composition, mole %			
Fission Product			
Oxides	up to ~80	up to 20	up to 25
Inert Metal Oxides	10 to 50	40 to 50	15 to 30
Sulfur Oxides (if in waste)	0 to 40	0 to 40	0
Phosphorous Oxides	~0	25 to 40	~60
Bulk Density, g/ml	1.1 to 1.5	2.7 to 3.2	2.7 to 3.0
Thermal Conductivity, W/m-°C	0.3 to 0.5	1.0 to 1.7	0.8 to 1.3
Maximum Heat, W/liter solid	85	205	190
Leachability in Cold Water, g/cm ² -day	10 ⁻¹ to 10 ⁻²	10 ⁻³ to 10 ⁻⁵	10 ⁻⁴ to 10 ⁻⁶
Hardness	Soft	Hard	Very Hard
Friability	Crumbly	Tough	Brittle
Residual Nitrate, wt% of product	≤0.05	≤0.005	≤0.005
Volume, liters/1000 MWd _{th}	1 to 2.5	1.2 to 3	1.5 to 5
Maximum Stable Tem- perature, °C	~900	Phase separa- tion at ~900	Devitrifies at ~500
Container Material	Stainless Steel	Mild or Stainless Steel	Mild or Stainless Steel

6.6 DISCUSSION OF MAXIMUM HEAT CONTENT

Good thermal conductivity is 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. The temperature difference from the center to the wall of a solid cylinder of self-generating heat varies as:

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

$k = \text{thermal conductivity}$
 $Q = \text{heat generation rate/unit volume}$
 $r = \text{radius of cylinder}$

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. This limitation could result in an undesirable increase 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 6.3 for values that are typical for wastes from high exposure thermal reactors or from fast reactors if core and blanket fuels are mixed.

The effective thermal conductivity of the products from the three WSEP processes has been found to vary between the following limits:

- Phosphate glass melt - 0.8 to 1.3 W/m-°C
- Spray solidifier melt - 1.0 to 1.7 W/m-°C
- Pot calciner product - 0.3 to 0.5 W/m-°C

FIGURE 6.3. *Effect of Thermal Conductivity upon Maximum Heat which May Be Stored in Container of Solidified Waste.*

6.7 STATUS OF THE PRODUCT EVALUATION PROGRAM

The contribution that the Waste Solidification Product Evaluation Program will provide is engineering, economic, and safety information for use by commercial fuel reprocessors.

The critical measurements to be supplied are:

- Thermal properties
- Container corrosion characteristics
- Chemical stability

- Leachability
- Dispersibility

To achieve this end, an integrated program of radioactive and nonradioactive studies is in progress.

In comparison to the demonstration and chemistry portions of the Waste Solidification Demonstration Program, the Product Evaluation Program is currently less complete. The nonradioactive measurements are approximately half complete and the radioactive measurements approximately one-quarter complete. It is anticipated that the major portion of the information from the engineering scale radioactive studies (SSETF) will be available within the next two years.

Full and final analyses cannot be accomplished on all phases of the program until the data are complete. Final engineering evaluation will present the data in practical form for use by fuel reprocessors in determining economics, safety, and engineering aspects of product storage and transportation.

ACKNOWLEDGEMENTS

This report represents the collected effort of a great many people, too many to be individually acknowledged. There has been excellent and gratifying cooperation among the three widely separated Laboratories involved, Brookhaven National Laboratory, Oak Ridge National Laboratory and the Pacific Northwest Laboratory. The authors wish to acknowledge in particular the assistance of all members of the Engineering Demonstration Section, who under the guidance of A. M. Platt, C. R. Cooley, and A. G. Blasewitz, have had primary responsibility for conducting the Waste Solidification Demonstration Program.

BIBLIOGRAPHYGENERAL

Symposium, Report of Working Meeting on Fixation of Radioactive Wastes in Stable, Solid, Media at the Johns Hopkins University, TID-7550. June 19-21, 1957.

Symposium, Report of the Second Working Meeting on Fixation of Radioactivity in Stable, Solid Media, Idaho Falls, Idaho, TID-7613. September 1960.

Symposium, Report of the Third Working Meeting on Calcination and/or Fixation of High-Level Wastes in Solid, Stable Media at Washington, D.C., TID-7646. February 1962.

Symposium, Treatment and Storage of High-Level Radioactive Wastes-Proceedings of the Symposium Held by the International Atomic Energy Agency in Vienna, Austria, October 1962.

Symposium, Report of the Fourth Working Committee Meeting - Waste Calcination and/or Fixation of High-Level Radioactive Wastes in Stable, Solid Media at Brookhaven National Laboratory, TID-7699. February 11, 1964.

Symposium, Solidification and Long-Term Storage of Highly Radioactive Wastes, Richland, Washington, CONF-660208. February 14-18, 1966.

W. G. Belter. "Advances in Radioactive Waste Management Technology-Its Effect on the Future U. S. Nuclear Power Industry," Third United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, A/Conf. 28/P/868, August 31-September 9, 1964.

R. T. Allemann, F. P. Roberts, and U. L. Upson. Hot Cell Studies of Solidification of Hanford High-Level Wastes - Radiant Heat Spray Calcination and Pot Calcination, HW-83896. General Electric Company, Richland, Washington, September 2, 1964.

C. R. Cooley and K. J. Schneider. "Unique Problems of Radioactive Waste Solidification," Presented at Joint AIChE-ICChE Meeting, London, England, June 13-17, 1965.

K. J. Schneider. Status of Technology in the United States for Solidification of Highly Radioactive Liquid Wastes, BNWL-820. Battelle-Northwest, Richland, Washington, October 1968.

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

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

D. W. Pearce or E. R. Irish or A. M. Platt, editors. Quarterly Progress Reports - Research and Development Activities - Fixation of Radioactive Residues,

1959 - HW-60584, HW-61635, HW-63048, and HW-63949

1960 - HW-65209, HW-66571, HW-67334, and HW-68193

1961 - HW-69176, HW-70517, HW-71374, and HW-72324

1962 - HW-73412, HW-74375, HW-75290, and HW-76262

1963 - HW-77288, HW-78188, HW-79140, and HW-76262

1964 - HW-81862, HW-83320, HW-34467, and HW-84603

General Electric Company, Richland, Washington.

1965 - BNWL-76, BNWL-139, BNWL-170, and BNWL-213

1966 - BNWL-276, BNWL-306, BNWL-365, and BNWL-410

1967 - BNWL-434, BNWL-507, BNWL-677, and BNWL-771

1968 - BNWL-824, BNWL-889, BNWL-923, and BNWL-1003

1969 - BNWL-1074. Battelle-Northwest, Richland, Washington.

SPRAY SOLIDIFICATION

B. M. Johnson. Heat Transfer in Radiant-Heat Spray Calcination, HW-58641. General Electric Company, Richland, Washington, February 1, 1959.

R. T. Alleman and B. M. Johnson. Continuous Calcination of Aqueous Radioactive Waste Solutions by Radiant-Heat Calcination, HW-63822. General Electric Company, Richland, Washington, March 16, 1960.

R. T. Alleman and B. M. Johnson. Radiant-Heat Spray Calcination Process for the Solid Fixation of Radioactive Waste, Part I: Non-Radioactive Pilot Unit, HW-65806 RD. General Electric Company, Richland, Washington, November 14, 1960.

J. D. Kaser and J. D. Moore. "Development of the Spray Calciner-Melter," Solidification and Long-Term Storage of Highly Radioactive Wastes, CONF-660208. Richland Symposium, February 1966.

POT SOLIDIFICATION

C. W. Hancher et al. "Solidification of Radioactive Liquid Waste by Pot Calcination," Presented at Meeting of ANS, Chicago, Illinois, CF-60-8-89. December 1960.

C. W. Hancher and J. C. Suddath. "Pot Calcination of Simulated Radioactive Waste with Continuous Evaporation," Presented at the National Meeting of the AIChE, Los Angeles, California, February 1, 1962.

C. W. Hancher, J. C. Suddath, and M. E. Whatley. Engineering Studies on Pot Calcination for Ultimate Disposal of Nuclear Waste from the TBP-25, Darex, and Purex Processes. Part I: The Systems Evaluation, ORNL-3277. Oak Ridge National Laboratory, September 23, 1963.

R. E. Blanco, J. O. Blomeke, W. E. Clark, E. J. Frederick, H. W. Goodbee, C. W. Hancher, J. M. Holmes, and J. C. Suddath. Status of the ORNL Potcal and Potglass Process for the Conversion of Highly Radioactive Wastes to Solids, ORNL-TM-857. Oak Ridge National Laboratory, May 8, 1964.

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

PHOSPHATE GLASS SOLIDIFICATION

L. P. Hatch, G. G. Weth, and E. J. Tuthill. "Ultimate Disposal of High-Level Radioactive Wastes-Fixation in Phosphate Glass with Emphasis on the Continuous Mode of Plant Operation," IAEA Symposium on Treatment and Storage of High-Level Radioactive Waste, Vienna, 1963.

U. L. Upson. Fixation of High-Level Radioactive Wastes in Phosphate Glass-Hot Cell Glass Experiment, BNWL-200. Battelle-Northwest, Richland, Washington, January 1966.

Gerald Strickland, E. J. Tuthill, and R. F. Drager. "Phosphate Glass Process: Evaporator Studies with Simulated Wastes," Solidification and Long-Term Storage of Highly Radioactive Wastes, CONF-660208. Richland Symposium, February 1966.

E. J. Tuthill, G. G. Weth, L. C. Emma, Gerald Strickland, and L. P. Hatch. "Phosphate Glass Process for Disposal of High-Level Radioactive Wastes," I & EC Process Design and Development, vol. 6, July 1967.

APPENDIX

Neg 0691648-1

FIGURE A.1. Solidified High Level Waste Samples from WSEP

FIGURE A.2. Floor Plan of the Chemical and Materials Engineering Laboratory

FIGURE A.3. Plan View of B Cell Equipment Arrangements

FIGURE A.4. WSEP Evaporator and Fractionator Rack before Installation

Neg 0662668-21

FIGURE A.5. Looking into WSEP Equipment Cell

Neg 0662668-7

FIGURE A.6. Looking Down on WSEP Equipment in Cell

Neg 41607-2

FIGURE A.7. WSEP Containers for Solidified Waste

Neg 0673128-6

FIGURE A.8. *Environmental Test Pods before Installation in SSETF*

DISTRIBUTIONNo. of
CopiesOFFSITE

1	<u>AEC Chicago Patent Group</u> G. H. Lee
1	<u>AEC Dayton Area Office</u> P. O. Box 66 Miamisburg, Ohio, 45342 Ed Walker, Chief Operations Branch
1	<u>AEC Division of Compliance</u> R. B. Chitwood
229	<u>AEC Division of Technical Information Extension</u>
1	<u>AEC Division of Materials Licensing</u> 4915 St. Elmo Avenue Bethesda, Maryland 20014 John A. McBride
1	<u>AEC Division of Naval Reactors</u> R. S. Brodsky
1	<u>AEC Division of Operational Safety</u> Alex F. Perge
1	<u>AEC Division of Production</u> W. L. Lennemann
5	<u>AEC Division of Reactor Development and Technology</u> C. N. Bartlett W. G. Belter W. H. McVey A. J. Pressesky W. H. Regan
1	<u>AEC Division of Space Nuclear Systems</u> F. C. Schwenk
2	<u>AEC Idaho Operations Office</u> P. O. Box 2108 Idaho Falls, Idaho 83401 K. K. Kennedy B. L. Schmalz

No. of
Copies

- 1 AEC Oak Ridge Operations Office
 C. S. Shoup
- 1 Allied Chemical Corporation
 Nuclear Fuels Department
 P. O. Box 70
 Morristown, New Jersey 07960
 R. L. Newman
- 3 Argonne National Laboratory
 S. Lawroski
 J. Loeding
 R. C. Vogel
- 1 Argonne National Laboratory
 East Area EBR - 2
 National Reactor Testing Station
 Scoville, Idaho
 P. Fineman
- 1 Atomic Energy Commission
 Minister of Defense
 Rehovoth, Israel
 Yehuda Feige
- 4 Atomic Energy of Canada Limited
 C. A. Mawson
 I. L. Ophel
 L. C. Watson
 J. Woolston
- 5 Atomic Energy Research Establishment
 Harwell, Didcot, Berks, England
 R. H. Burns
 H. J. Dunster
 W. H. Hardwick
 K. D. B. Johnson
 W. Wild
- 3 Australian Atomic Energy Commission
 Research Establishment
 Private Mail Bag
 Sutherland, New South Wales, Australia
 M. G. Bailie, Chemical Engineering Section
 R. C. P. Cairns
 L. Keher

No. of
Copies

- 3 Brookhaven National Laboratory
 L. P. Hatch
 E. J. Tuthill (2)
- 5 Center for Nuclear Studies
 P. O. Box 6, Fontenay-aux-Roses
 (Seine), France
 R. Bonniaud
 F. Laude
 J. Pomerola
 P. J. Regnaut
 J. Sauteron
- 1 Center for Nuclear Studies
 P. O. Box 269
 Grenoble (Isere), France
 M. G. Wormser, Chemistry Division
- 3 Center for Nuclear Studies
 P. O. Box 2, Saclay
 Gif-sur-Yvette
 (Seine-et-Oise), France
 C. Gailledreau
 A. Menoux
 Andre J. Raggenbass
- 2 Center for Study of Nuclear Energy (C.E.N.)
 Mol, Belgium
 L. Baetsle
 P. Dejonghe
- 1 Commissaire Boite
 Postale No. 149
 Paris (15 3m3), France
 F. Dumahel
- 1 Comitato Nazionale per l'Energia Nucleare
 Divisione di Protezione Sanitaria e Controlli
 Viale Regina Margherita 125
 Roma, Italy
 Ferruccio Gera
- 1 Commissariat a L' Energie Atomique
 Cadarache, France
 P. E. Pottier

No. of
Copies

1	<u>Dow Chemical Company (AEC)</u> D. L. Ziegler
6	<u>duPont Company, Aiken (AEC)</u> R. M. Girdler C. H. Ice L. H. Meyer C. M. Patterson E. B. Sheldon D. S. Webster
1	<u>duPont Company, Wilmington (AEC)</u> J. R. Thayer
1	<u>The E. F. MacDonald Company</u> Touramerica Division New York, New York Fred Herber-Oettgen
1	<u>EURATOM</u> Cassella Postale No. 1 Ispra, Italy M. Lindner
1	<u>EURATOM</u> 53 Rue Belliard Brussels, Belgium Pierre Kruys
2	<u>Eurochemic Library</u> Mol, Belgium
1	<u>European Nuclear Energy Agency</u> 38 Boulevard Suchet Paris 16, France I. G. K. Williams, Deputy Director
1	<u>General Electric Company</u> Fuel Recovery Operation 283 Brokaw Road Santa Clara, Calif. 95050 R. G. Barnes
2	<u>General Electric Company, Pleasanton, California</u> W. H. Reas

No. of
Copies

1	<u>General Electric Co.</u> Morris, Illinois S. G. Smolen
1	<u>George Washington University</u> Washington, D. C. C. R. Naeser
1	<u>Geotechnical Corporation</u> Box 28277, Dallas, Texas D. W. B. Heroy
1	<u>Grupo de Combustibles Irradiados</u> Junta de Energia Nucl. Div. de Mat, Civdat Univ. Madrid 3, Spain Federico de Lova Soria
1	<u>Gulf General Atomic</u> P. O. Box 608 San Diego, California 92112 J. J. Shefcik
1	<u>Hahn-Meitner Institut</u> 100 Glienicker Street 1 Berlin 39, Germany Hans W. Levi
1	<u>Harvard University</u> Cambridge, Massachusetts H. A. Thomas, Jr.
3	<u>Idaho Nuclear Corporation</u> J. A. Buckham C. M. Slansky B. R. Wheeler
1	<u>Illinois State Geological Survey Division</u> Urbana, Illinois J. C. Frye
3	<u>India Atomic Energy Establishment</u> Trombay Engineering Hall No. 5 Bombay 73, India Keshave Chandra Jitender D. Sehal K. T. Thomas

No. of
Copies

- 1 Jersey Enterprises, Inc.
Joseph Building
Richland, Washington
L. B. Torobin
- 3 Johns Hopkins University
513 Ames Hall
Baltimore, Md. 21218
J. Geyer
W. A. Patrick
A. Wolman
- 1 Kansas State Health Department
Topeka, Kansas 66601
S. J. Reno
- 1 Karlsruhe Nuclear Research Center
Decontamination Dept.
75 Karlsruhe
Siemensallee 83, West Germany
Helmut Krause
- 1 Karlsruhe Nuclear Research Center
Waste Storage Dept.
Leopoldshafen/Bd.
Max-Planck-Str. 12,
West Germany
H. F. Ramdohr
- 1 KFA
Director of Waste Treatment
Juelich, Germany
S. Rottay
- 1 Lawrence Radiation Laboratory, Berkeley (AEC)
Technical Information Division Library
- 1 Lawrence Radiation Laboratory, Livermore (AEC)
Technical Information Division Library
- 1 Los Alamos Scientific Laboratory (AEC)
C. W. Christenson
- 1 Mining Academy Clausthal
Petrology, Minerology
& Economics Geology, Dept.
Siemensalle, West Germany
H. F. A. Borchert

No. of
Copies

1	<u>Minister of Federal Property</u> Const. Dept Bad Godesberg, West Germany G. M. K. Klinke
2	<u>Mound Laboratory (AEC)</u> S. Freeman J. J. Goldin
1	<u>MPR Associates, Inc.</u> 815 Connecticut Avenue, N. W. Washington, D.C. 20006 Theodore Rockwell, III, Chairman, AIF Safety Task Force
1	<u>National Lead Company</u> 111 Broadway New York, New York 10006 Stephen Brown
1	<u>National Research Council</u> 2101 Constitution Avenue Washington, D.C. 20418 Dr. Cyrus Klingsberg Tech. Secretary National Academy of Scientists
1	<u>N. Y. State Atomic & Space Development Authority</u> 230 Park Ave. New York, N. Y. O. Townsend, Director
1	<u>William A. Nixon</u> 656 South Illinois Street Arlington, Virginia 22204
2	<u>Nuclear Fuel Services, Inc.</u> P. O. Box 124 West Valley, N. Y. 14171 J. P. Duckworth W. G. Urban
1	<u>Nuclear Materials and Equipment Corporation (AEC)</u> Nuclear Design and Development M. Selman, Manager

No. of
Copies

- 1 Nuclear Safety Associates
1055-R-Rockville Pike
Rockville, Md. 20852
W. A. Rodger
- 1 Nuclear Reactor Des. Sect.
Nuclear Power Plant Dept.
Hitachi, Ltd., Hitachi Works
Hitachi-Shi Ibaraki-Ken, Japan
A. Shimozato
- 4 Oak Ridge National Laboratory (AEC)
Central Research Library,
Document Reference Sect.
Central Research Library,
ORNL
Laboratory Records Dept.,
ORNL
Laboratory Records Dept.,
ORNL-RC
- 1 Phillips Petroleum Company
Water Reactor Safety Program Off.
P. O. Box 2067
Idaho Falls, Idaho 83401
W. Lyle Slagle
- 1 Plutonium Extraction Plant
Marccule, France
C. J. Jouannaud
- 1 Princeton University
Princeton, New Jersey 08540
H. H. Hess
- 2 Radiation Protection Dept.
Luisenstrasse 46,
Bad Godesberg, West Germany
H. M. Holtzem
G. Straimer
- 1 Tokai Refinery
At. Fuel Corp.
Tokai-Mura
Ibaraki-Ken, Japan
M. Ichikawa

No. of
Copies

8	<u>Union Carbide Corporation (ORNL)</u> P. S. Baker R. E. Blanco J. O. Blomeke W. C. Clark F. M. Empson H. B. Godbee J. C. Suddath M. E. Whatley
1	<u>University of Arizona</u> Tucson, Arizona E. S. Simpson, Professor of Geology
1	<u>University of Minnesota</u> Environmental Health Research and Training Center Room 1108, Mayo Building School of Public Health Minneapolis, Minnesota 55455 C. P. Straub
1	<u>University of North Carolina</u> Chapel Hill, North Carolina H. C. Thomas
1	<u>University of Texas</u> Austin, Texas 78712 E. R. Gloyna
1	<u>University of Wisconsin</u> Madison, Wisconsin 53715 H. Gladys Swope
2	<u>U. S. Bureau of Mines</u> Washington, D.C. J. E. Crawford J. W. Watkins
1	<u>U. S. Geological Survey</u> Washington, D. C. R. L. Nace
1	<u>U. S. Public Health Service</u> Winchester, Massachusetts D. Moeller

No. of
Copies

- 1 USDA National Agricultural Library
 Current Serial Record (G)
 Washington, D. C. 20250
- 1 Vanderbilt University
 Nashville, Tennessee
 P. A. Krenkel

ONSITE-HANFORD

- 1 AEC Chicago Patent Group
 R. K. Sharp (Richland)
- 6 AEC Richland Operations Office
 J. T. Christy
 O. J. Elgert (2)
 J. E. Goodwin
 C. L. Robinson
 W. E. Lotz
- 2 AEC RDT Site Rep., Richland
 P. G. Holsted
 A. D. Toth
- 2 Atlantic Richfield Company
 P. O. Box 370
 Richland, Washington 99352
 H. C. Rathvon
 L. L. Zahn
- 15 Atlantic Richfield Hanford Company
 M. H. Campbell
 J. B. Fecht
 W. M. Harty
 R. E. Isaacson
 H. H. Hopkins
 L. M. Knights
 W. P. McCue
 R. W. McCullough
 G. C. Oberg
 H. P. Shaw
 P. W. Smith
 R. E. Smith
 R. E. Tomlinson
 J. H. Warren
 File Copy

No. of
Copies

3	<u>Battelle Memorial Institute</u>
2	<u>Douglas United Nuclear, Inc.</u> T. W. Ambrose DJN File
145	<u>Battelle-Northwest</u> G. J. Alkire J. M. Atwood A. G. Blasewitz (102) W. R. Bond D. W. Brown R. E. Burns J. J. Cadwell C. R. Cooley E. A. Coppinger D. R. de Halas G. M. Dalen V. L. Hammond J. N. Hartley M. M. Hendrickson G. Jansen J. D. Kaser J. H. Kleinpeter F. J. Leitz J. L. McElroy (2) J. E. Mendel J. D. Moore R. L. Moore F. L. Mourich T. J. Owen P. C. Owzarski H. M. Parker D. W. Pearce A. M. Platt (2) K. J. Schneider M. R. Schwab R. J. Thompson C. J. Touhill E. E. Voiland W. K. Winegardner N. G. Wittenbrock Technical Information Files (5) Technical Publications (2)