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Pacific Northwest Laboratories
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AEC Research and Development Report

WASTE SOLIDIFICATION PROGRAM

VOLUME 10

EVALUATION OF SOLIDIFIED
WASTE PRODUCTS

JUNE 1972

BNWL-1666

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PACIFIC NORTHWEST LABORATORY

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U.S. ATOMIC ENERGY COMMISSION

Under Contract AT(45-1)-1830

Printed in the United States of America

Available from

National Technical Information Service

U.S. Department of Commerce

5285 Port Royal Road

Springfield, Virginia 22151

Price: Printed Copy \$3.00; Microfiche \$0.95

3 3679 00062 1377

BNWL-1666

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Waste Disposal
and Processing

WASTE SOLIDIFICATION PROGRAM
VOLUME 10
EVALUATION OF SOLIDIFIED WASTE PRODUCTS

By

J. E. Mendel and J. L. McElroy

Nuclear Waste Technology Department

July 1972

BATTELLE
PACIFIC NORTHWEST LABORATORIES
RICHLAND, WASHINGTON 99352

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WASTE SOLIDIFICATION PROGRAM
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ABSTRACT

Demonstrations of the solidification of high level radioactive wastes have been successfully conducted on an engineering scale in the Waste Solidification Engineering Prototypes (WSEP) at the Pacific Northwest Laboratory. The processes demonstrated in the WSEP produced highly radioactive solidified waste in the form of (1) oxide calcine, (2) phosphate micro-crystalline ceramic, (3) phosphate glass, and (4) borosilicate glass. A total of 4,930 kg of solidified waste, containing 51,800,000 curies initially, was encapsulated in 33 containers (pots). The mild steel, 304L and 310 stainless steel pots containing the solidified wastes, each 8 feet long, range from 6 to 12 inches in diameter, and are very representative of the solidified waste pots which will be produced by power reactor fuel reprocessors for many years to come. Nominal fission product oxide content of the solids ranges from 9 to highs of 47 and 82 weight percent in glass and calcine products, respectively.

The pots containing the solidified wastes have now been in interim storage from 2 to 6 years. Currently 23 are in air at ambient temperature, and 10 in the Solids Storage Engineering Test Facility (SSETF) in air or water at controlled temperatures. An evaluation program is being conducted to measure the properties of the highly radioactive solidified wastes during interim storage and to compare the properties with those measured on laboratory-prepared, nonradioactive solids of

comparable chemical composition. Properties being measured include pot pressurization and corrosion, and solidified product homogeneity, leachability, thermal conductivity, and dispersibility. Properties of the highly radioactive products have been found to be substantially those predicted from nonradioactive studies.

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1.0 INTRODUCTION

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

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

A considerable amount of development on techniques for solidification of high-level wastes has taken place in the past 17 years and is still progressing. Four processes for solidification of high-level liquid wastes have been developed in the USA to the point of radioactive demonstrations on an engineering scale. The four processes are pot calcination, spray solidification, phosphate glass solidification, and fluidized bed calcination. Waste solidification methods under development abroad include the FINGAL process in England,⁽¹⁾ the

Pot Vitrification process in France⁽²⁾ and a borosilicate glass fixation process in Germany.⁽³⁾

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

Fluidized bed calcination was the first solidification process placed in routine radioactive operation. In this application, aluminum and zirconium-bearing wastes from enriched uranium fuels have been processed at the Idaho Chemical Processing Plant (ICPP) by the Allied Chemical Corporation since 1963.⁽⁴⁾

Between November 1966 and October 1970, the pot calcination, spray solidification, and phosphate glass solidification processes, developed by Oak Ridge National Laboratory, Battelle-Northwest and Brookhaven National Laboratory, respectively, were demonstrated at the Pacific Northwest Laboratory for the Atomic Energy Commission on an engineering scale with full radioactivity levels.⁽⁵⁾

An important purpose of these waste solidification demonstrations was to assist in providing the technological bases for the establishment of a high level radioactive waste management policy in the United States. A policy was officially announced in the Federal Register, November 14, 1970.⁽⁶⁾ The regulations specify that high level radioactive wastes produced from the commercial reprocessing of irradiated power reactor fuel must be shipped to a Federally-owned repository for disposal, and that the wastes must be converted to a dry solid and placed in sealed containers prior to shipment in approved shipping casks. Up to 10 years interim storage of the wastes is permitted at the reprocessor's

site, however, the wastes must be solidified sometime during the first 5 years of onsite storage.

The pilot-plant operations which have been conducted in the WSEP have provided information for technical, economic, and safety evaluations of the pot, spray, and phosphate glass processes. Product properties, as they affect processing parameters, interim storage, shipping and final disposal, are of great importance in such evaluations.

Product evaluation, in the context of this report, considers both the solidified waste and the pot in which it is sealed at completion of the solidification process, since it is the properties of the integral "package" that are of primary concern.

Detailed descriptions of the WSEP, and the radioactive demonstration runs that were made in the facility, have been reported in the 10 other reports in this series.⁽⁷⁻¹⁶⁾ This report presents results and analyses of product evaluation measurements which were made during the WSEP runs, and during the interim storage period following solidification. Experimental data have been obtained from nonradioactive laboratory and pilot plant tests, from "grab" samples of the melt-formed WSEP products during radioactive processing, from core-drilled samples of the WSEP pots in interim storage, and from non-destructive testing and monitoring of the WSEP pots. A detailed description of the Solids Storage Engineering Test Facility (SSETF) in which some of the WSEP pots are being held in interim storage in controlled water or air environment at elevated temperatures is given in Reference 9. Many of the nonradioactive product evaluation data have been reported previously.⁽¹⁷⁾

2.0 SUMMARY

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2.0 SUMMARY

The properties of the solidified wastes prepared in the WSEP program have been assessed on the basis of tests made on nonradioactive samples and on highly radioactive engineering-scale containers (pots) of the solidified wastes. To date, twelve of the thirty-three radioactive WSEP pots have been sampled by core drilling.

Thirteen different solidified waste compositions have been prepared on an engineering-scale in the comprehensive radioactive WSEP program. Four fundamental solid forms for the incorporation of radioactive wastes were represented; calcined oxide, phosphate ceramic, phosphate glass, and borosilicate glass. Several different high level radioactive waste solutions, typifying the range of wastes which can be produced by the Purex solvent extraction process, were immobilized in the solids. Major conclusions from the evaluations of these solidified waste products were as follows:

- WSEP pots of calcine and phosphate products containing the maximum allowable amount of heat from radioactive decay* have been safely stored in air or water for periods of up to 5 1/2 years. Pots of borosilicate products containing the maximum allowable amount of radionuclide heat content have been safely stored for up to 2 years. The storage tests are continuing.

* The maximum limit of radionuclide heating in the WSEP program was set as that in which any one of the three following conditions existed for a pot air-cooled by natural convection.

1. A maximum centerline temperature of 900 °C.
2. A maximum temperature at the pot wall of 425 °C.
3. A minimum thickness of the solidified waste in contact with the container wall of no less than half the radius of the container when a partially molten core existed in the waste.

- There is no indication of significant pot wall corrosion on any of the 33 pots; internal thermowells in four of the pots have developed leaks, however. Thermowell leaks pose only minor problems since the thermowells can be seal-welded immediately after processing. In many instances, internal pot thermowells won't be used in commercial operations.
- Mild steel is a satisfactory material of construction for pots which are filled from a supplementary melter, such as used in the spray solidification and phosphate glass processes.
- Good correlation is being obtained between measurements made on nonradioactive and radioactive solidified wastes.
- Leachability of the most nonleachable product sampled from a WSEP pot to date was 5×10^{-5} g/cm²-day initially and less than 1×10^{-5} g/cm²-day after 36 weeks leaching.
- Satisfactory solidified waste pot handling techniques for remote welding, calorimetry, ultrasonic wall thickness scanning, and vacuum leak checking, have been demonstrated.

2.1 CHARACTERISTICS OF SOLIDIFIED WASTES

All of the WSEP melt-formed waste solidification processes filled the pots quite uniformly with homogeneous solidified product. There has been little indication of fission product segregation in the filled pots. Several techniques are being used to establish the homogeneity of the waste in the pots. Axial gross gamma radiation profiles, obtained on each pot soon after filling, serve as a rough indicator. More precise information comes from the axial and radial temperature profiles which are obtained from many thermocouples installed in each pot. Finally, core drilled samples, 0.75 inch in diameter, are being taken from three elevations on each WSEP pot. Fission product analyses are made along the length of the core-drilled samples. In two pots

containing phosphate product a slight migration of cesium from the hottest central region of the pots toward the upper and lower ends of the pots has occurred. The segregation was not sufficient to significantly perturb the temperature or radiation profile of the pots. Analyses of samples of the one pot calcine process pot which has been core-drilled to date indicate a small increase in concentration of cesium-137 toward the upper regions of the pot and of the rare earths toward the bottom of the pot.

The bulk specific gravity of the solidified wastes in the WSEP pots averaged 1.4, 3.0, 2.9, and 3.5 for the oxide calcine, phosphate ceramic, phosphate glass and borosilicate glass, respectively.

Effective thermal conductivity of the WSEP products, at an average temperature of 300 °C, was about 0.35, 1.2, 1.0, and 1.1 W/(m²)(°C/m) for the oxide calcine, phosphate ceramic, phosphate glass and borosilicate glass, respectively. The effective thermal conductivities of the radioactive WSEP products averaged about 15 percent higher than the thermal conductivity of non-radioactive specimens of similar chemical composition.

The coherence and physical strength of the WSEP solidified wastes have not been deleteriously affected to this date by the very intense long-term radiation bombardment (calculated to range from about 1×10^{11} to about 1×10^{12} R) encountered in interim storage. Physical properties of core-drilled samples are proving to be very similar to those predicted from examination of nonradioactive specimens. The oxide calcine product produced by the pot calcination process is in the form of a friable cake which crumbles to powder easily when handled. The phosphate ceramic product produced by the spray calciner-melter process is a tough microcrystalline product. Core-drilled samples obtained in some instances from the WSEP

phosphate ceramic pots are segmented because of circumferential cracks which apparently exist in the product within the pot.

→ Of the four phosphate glass pots which have been sampled all but one were almost completely devitrified. In one 8-inch phosphate glass pot, the outer 1.5 inches of product was glassy and brittle. The devitrified phosphate glass product is tough, and good core samples are obtained. Tests with nonradioactive phosphate glass have shown that devitrification occurs within a few hours at temperatures in the range of 550 to 750 °C. Most of the devitrification observed in the WSEP pots probably occurred during processing, as the temperature of the pots was in this range for much of the time during filling. Additional devitrification may have occurred during interim storage.

The radioactive borosilicate glass samples obtained by core drilling rising level glass and in-pot melting process pots 4 and 11 months after processing, respectively, were not devitrified. It was not possible to obtain complete core samples of the borosilicate glasses; the glasses shattered and some of the sample pieces were lost; thus the evidence is not conclusive that some devitrification has not occurred. Nonradioactive tests indicate that the devitrification temperatures of the WSEP borosilicate glasses are 50 to 100 °C higher than the phosphate glasses. Devitrification occurs within 24 hours in the temperature 700 to 750 °C. Preliminary tests indicate the increase in leachability is less marked than with phosphate glasses.

At the maximum centerline temperature limit set for storage of the WSEP pots, 900 °C, the melt-formed products are either molten or semi-fluid. Laboratory tests indicated some stratification of the phosphate ceramics into two layers would occur in the molten core during prolonged storage at 900 °C. In general the higher valent cations concentrated in the lower layer and the monovalent cations in the upper layer. None of the radioactive WSEP phosphate ceramic pots were stored with a molten core.

Some of the radioactive WSEP phosphate and borosilicate glass pots were stored with molten cores for up to 10 days. In laboratory tests the phosphate and borosilicate glasses did not stratify significantly at 900 °C and no evidence of stratification has been observed in the WSEP pots.

In all of the WSEP waste solidification processes the temperatures utilized during solidification processing were (1) as high, and in most cases higher, than the maximum allowed storage temperature, and (2) about 100 °C higher than the temperature of the "standard fire" used in evaluating shipping casks.* This was done to assist in avoiding the presence of volatile components which could cause pressurization of the sealed pots during interim storage or shipping. Pressure monitoring of many of the WSEP pots has corroborated the lack of significant pressurization.

Phosphate melts are much more corrosive than borosilicate melts, however phosphate melt corrosion doesn't become severe until temperatures are raised above approximately 875 °C. By WSEP criteria the wall temperature of the pots is limited to 425 °C during interim storage. Internal and external corrosion of WSEP stainless and mild steel pot walls has been negligible to this date as shown by ultrasonic wall thickness measurements and by examination of the wall disc specimens obtained during core sampling of the pots.

After processing, caps were welded on the pots and the pots were vacuum leak checked with a helium mass spectrometer. During leak checking the internal thermowells in four of the pots were found to contain leaks. Five samples of the thermowell have been obtained from various points within one of the pots, containing phosphate glass, in an attempt to locate and

* The flowsheet used when sulfate-containing waste was processed by the spray calciner melter process was a slight exception. This product contained 14 wt% SO₃ and processing temperatures were maintained below 875 °C to maximize retention of the SO₃.

study the leak. None of the thermowell samples was visibly corroded (viewed through magnifying periscope) indicating a very localized leak. In a commercial solidification facility, thermowells, if used, could be seal-welded at the same time the pots were cap-welded thus the effect of failed thermowells would not be serious.

A major purpose of the measurements made on the WSEP solidified wastes is to assist in safety analyses and comparisons of the behavior of the very hazardous materials in the event containment is lost and they are exposed to the environment. For this purpose, leachability, dispersibility, volatility, and stored energy in the waste products have been studied.

Leach rates (at 25 °C) of the highly radioactive core-drilled WSEP products ranged from 1×10^{-2} to 5×10^{-5} grams product/cm²-day initially. Most leach rates decreased by at least a factor of 10 after a few weeks leaching. In many instances these leach rates were higher than were measured on nonradioactive products of the same composition. The evidence indicates the increased leachability is due more to the prolonged high temperature to which the products have been exposed than to the effects of the intensely concentrated radiation. Devitrification, which was observed in most of the core-drilled phosphate glass products, resulted in an approximately thousand-fold increase in leachability.

An empirical dispersibility test in which samples of the solidified products are fractured under controlled conditions is demonstrating that the glassy phosphate and borosilicate products break to form more particles of a smaller size than do the phosphate ceramic and devitrified phosphate glass products. More refined tests will be required to fully evaluate mobility of the fractured particles in moving air.

Another potential mechanism for spread of contamination from exposed solidified waste is by the volatilization of fission

products. Slight, but measurable, volatility of cesium, the most volatile of the major fission products in the solidified waste, occurs at 800 °C. No large dependence of cesium volatility upon product form was noted in laboratory tests with tracer cesium, i.e., volatilization from phosphate glass, borosilicate glass, phosphate microcrystalline ceramic, and oxide calcine was of the same order of magnitude. In the temperature range 800 to 1200 °C cesium volatilization increased by approximately a factor of ten for every 150 °C rise in temperature to approximately 6% per hour at 1200 °C.

There exists a potential for the storage of energy in solidified radioactive waste due to the introduction of defects in the lattice structure by the intense radiation fields. A raise in temperature could release the stored energy in a burst.⁽¹⁸⁾ However, the presence of significant amounts of stored energy in solidified wastes has not been demonstrated. Energy storage did not occur in laboratory-prepared nonradioactive solidified wastes which were irradiated to dosages up to 10^{10} R. Techniques are being developed to measure stored energy in the radioactive WSEP products, some of which have had doses in excess of 10^{12} R, but no data are yet available.

2.2 HANDLING AND STORAGE OF FILLED POTS

Containers (pots) for the WSEP solidified wastes are 8 feet long cylinders 6, 8 or 12 inches in diameter constructed of Schedule 40 mild steel or 304L or 310 stainless steel pipe. After filling with solidified waste to a height of about 6 feet, a lid containing a tap for leak testing and pressure instrumentation has been welded on each pot at a remotely controlled welding station. Storage in a water environment (pot wall temperatures up to 80 °C) and in an air environment (pot wall temperatures up to 425 °C) is being demonstrated.

All of the pots, including several containing sufficient radioactive decay heat to produce a centerline temperature of 800 to 900 °C when the pots were hanging in air, have now been safely handled through several transfer operations without mishap. There has been no detectable bowing, warping or dimensional changes in the pots during processing or subsequent storage. In the same manner no significant pot wall corrosion, internal or external, has occurred during processing or subsequent storage.

Remote welding of the pots, even the making of patch welds after core drilling, has proven to be very feasible and amenable to routine operation. Vacuum leak testing of the pots is being done satisfactorily with a helium mass spectrometer, except with pots containing the pot calcine product which out-gas under vacuum for an exceedingly long time (days to weeks). Whole pot calorimetry was performed on all of the WSEP pots and was demonstrated as being a relatively simple technique for determining the amount of radioactive decay heat in pots of solidified waste.

Scouting decontamination tests performed on a WSEP pot indicated steam cleaning is a promising technique for reducing smearable contamination on the exterior of the pots. Steam cleaning reduced the smearable contamination by a factor of almost 200 to 80,000 $\beta\gamma$ counts/minute. Further decontamination tests on the WSEP pots are planned.

3.0 PROGRAM DESCRIPTION

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3.0 PROGRAM DESCRIPTION

3.1 WSEP PROGRAM

Four different forms of solidified waste products have been produced in the program conducted in the WSEP facility during the period November 1966 to October 1970. The forms were:

- Oxide calcine, produced by the Oak Ridge National Laboratory-developed pot calcination process.
- Phosphate ceramic, produced by the Hanford-developed spray calciner-melter process.
- Phosphate glass, produced by the Brookhaven National Laboratory-developed phosphate glass process.
- Borosilicate glass, produced by the rising level glass (RLG) and in-pot melting (IPM) processes, which are modifications of the pot calcination and spray calciner-melter processes, respectively.

A total of 589, 617, 656, and 120 liters of highly radioactive oxide calcine, phosphate ceramic, phosphate glass, and borosilicate glass, respectively, were produced in the 33 WSEP runs. Summaries of the processes and the WSEP runs are given in Figure 3.1 and Table 3.1. The previous reports in this series⁽⁷⁻¹⁶⁾ may be sought if more details on the WSEP solidification processes or the demonstration runs are desired. This report brings together the information which has been gathered to date concerning the properties of the WSEP solidified wastes and waste-pot combinations which have been prepared during the program.

3.2 POT DESIGN

The pots used to contain the WSEP solidified wastes were prototypical of those expected to be used for the containment

FIGURE 3.1. Outline of WSEP Waste Solidification Processes

TABLE 3.1. WSEP Radioactive Demonstration Runs

Run No.	Date of Run	Processing Summary			Pot Description		Filled Pot Summary							
		Waste Type PW	Average Feed Rate, liter/hr	Process Rate, tonne/day	Diam., inch	Material of Construction	Volume of Solid, liter	Bulk Density, kg/liter	Fill Height, inch	Total, MCi	Total Heat Rate, kW	Heat Rate Density, W/liter	E to Wall ΔT , (°C)	G Temp, (°C)
PC-1	Nov. 1966	2	13.8	0.73 ^(a)	12	304L	105 ^(b)	1.3	~72	0.09	0.60	5.7	70	140
PC-2	Feb. 1967	2	14.7	0.79	12	304L	105	1.2	~72	0.43	1.7	16.2	235	485 ^(d)
PC-3	Feb. 1967	2	12.3	0.72	8	304L	60	1.4	~72	0.38	1.8	30	220	410
PC-4	Jun. 1967	1	14.7	0.96	12	304L	110	1.3	~72	0.65	2.7	23.7	312	477
PC-5	Jul. 1967	1	13.2	0.78	8	304L	55	1.4	~72	1.15	4.3	78	495	725
PC-6	Sep. 1967	2	8.5	0.57	8	304L	60	1.3	~72	1.3	5.1	85	700	940
PC-7	Aug. 1970	1	10.7	0.64	8	304L	60	1.2	~72	1.4	5.6	93	753	1012
PC-8	Sep. 1970	4m	7.9	0.40	6	304L	34	1.3	~72	1.2	4.8	141	604	855
PC-9	Oct. 1970	4m	9.0	0.30	6	310	~16	3.5	35	1.4	5.6	310	370	635
(RLG)				Avg 0.65						28.00	232.2			
PG-1	Nov. 1967	2	14.6, 13 ^(e)	0.53	12	Mild Stl.	92	2.7	50	0.35	1.6	17	89	316 ^(d)
PG-2	Dec. 1967	2	14	0.38	8	304L	35	2.9	43	0.40	1.7	49	135	355
PG-3	Jan. 1968	2	16	0.21	8	Mild Stl.	35	2.8	43	0.60	3.3	95	255	655 ^(d)
PG-4	Mar. 1968	2	7.5	0.34	8	Mild Stl.	73	2.9	89	1.1	4.2	57	175	510 ^(d)
PG-5	Apr. 1968	1	10.0, 11.5 ^(e)	0.24	12	Mild Stl.	113	2.8	61	2.2	8.8	78	352	712
PG-6	May 1968	1	10.5	0.28	8	304L	62	2.8	75	2.4	9.6	155	380	780
PG-7	Jul. 1967	2	17.0	0.58	8	310	67	2.7	81	2.8	9.8	146	401	782
PG-8	Aug. 1969	4m	13.0	0.39	8	Mild Stl.	67	2.9	81	2.3	8.8	132	350	710
PG-9	Oct. 1969	4m	25.0	0.47	6	304L	27	2.8	58	1.0	4.2	158	204	566
PG-10	Oct. 1969	4m	22.0	0.34	6	304L	29	2.9	63	2.6	9.3	317	369	827
PG-11	Dec. 1969	LMFBR	18.0	0.20	8	304L	60	2.9	73	3.3	11.9	198	417	834
				Avg 0.36						219.1	273.2			
SS-1	Jan. 1967	1	16.3	0.84	12	304L	38	3.2	21	0.08	0.28	7.5	30	170
SS-2	Apr. 1967	1	13.8	0.72	8	304L	48	3.2	58	0.42	2.1	44	70	315
SS-3	Jul. 1968	2	11.3	0.46	12	304L	39	2.7	21	0.42	1.6	40	80	315
SS-4	Sep. 1968	2	12.3	0.53	8	Mild Stl.	56	2.9	68	1.4	5.1	93	220	505
SS-5	Oct. 1968	1	16.7	0.90	8	304L	66	3.2	80	2.5	8.2	127	270	633
SS-6	Nov. 1968	1	17.7	0.82	8	304L	65	3.2	79	3.0	10.0	168	305	767
SS-7	Dec. 1968	1	17.9	0.94	8	304L	62	3.2	75	3.6	12.7	204	453	928
SS-8	Feb. 1969	1	14.5	0.74	8	304L	59	2.9	72	1.8	7.2	120	210	605
SS-9	Mar. 1969	4m	15.2	0.58	8	310	68	2.9	83	2.0	7.2	107	242	594
SS-10	Apr. 1969	4m	13.5	0.46	8	Mild Stl.	56	3.1	68	2.6	7.9	141	262	610
SS-11	Mar. 1970	LMFBR	14.9	0.29	8	304L	60	3.1	73	3.1	10.5	175	353	754
SS-12	Apr. 1970	4m	10.8	0.46	8	304L	54	3.0	66	1.4	4.9	90	197	474
(IPM)														
SS-13	May 1970	4m	15.4	1.05	8	304L	50	3.0	61	2.8	10.0	200	404	824
(IPM)				Avg 0.68						225.1	287.3			
										225.2	281.93			

a. Based on feed time plus drying and cooling time for all pot calcine runs.

b. Present volume estimated from receiver pot temperature and feed consumption for all pot calcine runs.

c. Receiver Pot setting in furnace with cooling air on.

d. Receiver pot setting in furnace with cooling air off.

e. Two feed batches were used.

of solidified high-level power reactor waste, except for the large number of thermocouples which were added to collect experimental data. Each pot had two longitudinal internal thermowells and tack-welded external thermocouples. The pots were 8-foot long cylinders, 6, 8 or 12 inches in diameter constructed of mild steel or type 304L or 310 stainless steel. The pots were designed to be filled with solidified waste to a nominal height of 6 feet.

Insofar as possible, a standard design was used for the 33 pots. A narrow fillhead was used on the pot solidification process pots. Pots for the other processes had a wide fillhead. The fillheads were designed so that a cap could be welded on the pots after filling with waste. Details of the pot designs are shown in Appendix A.

3.3 PRE-FILL AND AFTER-FILL POT MEASUREMENTS

The pre-fill measurements made on each WSEP pot, which are listed below, served, (a) as a quality assurance function, and (b) as a basis for comparison with after-fill measurements to determine the magnitude of changes which might occur during processing or storage.

Pre-Fill Measurements:

1. Photographs (including a view of the identification number which was welded on each pot)
2. Dimensions between critical points
3. Weight
4. Ultrasonic wall thickness measurements at 680 points on the pot wall.

After-fill measurements were made on each WSEP pot in order to (a) detect any deterioration of the pot which might have

occurred during processing, (b) assure the pot was ready for interim storage, and (c) establish time-zero data for later measurements during interim storage.

After-Fill Measurements:

1. Temperature profile in air-cooled furnace or while hanging in open air
2. Visual inspection of the top surface of the solidified waste in the pot and measurement of freeboard
3. Dimensions between critical points to detect possible warpage, bulging, etc.
4. Weight
5. Heat generation rate
6. Ultrasonic wall thickness scan
7. Gross gamma radiation profile
8. Leak test with helium mass spectrometer leak detector (test done after pot lid was welded in place).

3.4 INTERIM STORAGE

Following after-fill measurements the pots were placed in temporary storage in facilities located within the processing cell. Provisions were made for both air and water storage. Cooling during air storage was by convection only; no forced air cooling was used (except for the initial cool-down while the pots were still in the processing furnace). The pots with higher radionuclide heat generation rates were stored for an initial period of six months or more in a water basin equipped with cooling coils which were used to maintain the water temperature at about 50 °C.

After varying periods of temporary storage in the processing cell the pots were transferred to an adjoining cell

which contains equipment for obtaining core samples from the pots. The Solids Storage Engineering Test Facility (SSETF) is also located in this cell. The SSETF consists of 10 environmental test pods in which WSEP pots of high level solidified waste can be studied in individually controlled environments (a SSETF pod is shown in Figure 3.2). Each pod is insulated. Provisions are made for heating and cooling environments of either air (max. temp., 600 °C) or water (max. temp., ~95 °C) in the test pods. Pots not scheduled for study in the SSETF are being interim-stored in racks at ambient air temperature on the floor of the same cell. Specific design details of the SSETF and the other WSEP pot handling facilities have been published.⁽⁹⁾ Figure 3.3 shows the interim storage conditions for the 33 WSEP pots. It is planned that the pots will be maintained under surveillance and study during an interim storage period of approximately 10 years, corresponding to the maximum period presently permitted under U. S. regulations governing the handling of high level wastes.

3.5 PRODUCT MEASUREMENTS

Monitoring data obtained from the WSEP pots and analyses of samples of the highly radioactive products, obtained by core drilling through the side walls of the pots, are the major sources of data on the characteristics of the WSEP products. An example of the 3/4-inch diameter core-drilled samples being obtained is shown in Figure 3.4. All of the WSEP pots will be sampled at least once during the 10-year interim storage period (those in the SSETF will be sampled at least 3 times, as shown in Figure 3.3). The core-drilled samples from the WSEP pots are unique, coming as they do from the first full-sized pots of solidified high level waste containing radioactivity levels typical of those that will result from the reprocessing of power reactor fuels. Corollary measurements on nonradioactive

FIGURE 3.2. Environmental Test Pod

FIGURE 3.3. WSEP Pot Interim Storage Program Schedule

FIGURE 3.4. Core Drill Sampling of a Waste Storage Pot

solids of the same chemical composition have been, and are being, made to assist in defining the properties, or changes in the properties, of the WSEP solidified high level wastes. ^(17,19)

4.0 COMPOSITION OF SOLIDIFIED WASTES

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4.0 COMPOSITION OF SOLIDIFIED WASTES

4.1 COMPOSITION OF HIGH LEVEL RADIOACTIVE WASTES

The four aqueous waste solutions, designated PW-1, PW-2, PW-4m and LMFBR, (Table 4.1) which have been incorporated in the WSEP solidified wastes were chosen to cover a range of typical acidic nitrate high level waste compositions which can be generated by Purex solvent extraction plants reprocessing power reactor fuels with integrated burnups ranging from 20,000 to 100,000 MWd/MT. The PW-1 and PW-2 waste compositions were representative of those generated from relatively low burnup fuels reprocessed by conventional solvent extraction techniques. The PW-1 waste composition contained considerable ferric nitrate to correspond with that derived from dissolution of chopped-fuel dissolver basket liners. The PW-2 waste simulated a combined first and second cycle waste containing ferric, sulfate, and sodium ions from plutonium valence adjustment steps. The PW-4m waste composition was designed to be representative of that derived from high burnup fuels reprocessed by "clean" techniques of the future (e.g., no metal salt additives). The LMFBR waste was representative of that from clean processing of LMFBR fuel.

The total waste processed in the WSEP program was equivalent to that which would have been produced in the reprocessing of 40 tonnes of power reactor fuel which had been irradiated to an integrated exposure of over 20,000 MWd/Te. Since such quantities of power reactor fuel wastes were not available the wastes used in the WSEP program were manufactured by combining:

TABLE 4.1. Chemical Compositions of High-Level Liquid Wastes for WSEP Demonstrations

Constituent	Concentration, Molarity at 378 liters/tonne			
	PW-1 (a)	PW-2 (a)	PW-4m (b)	LMFBR (c)
<u>Nonfission Products</u>				
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	--
<u>Fission Products</u> (d)				
Mo	0.065	0.065	0.130	0.24
Tc(Mo)	0.014	0.014	0.031	0.060
Sr	0.015	0.015	0.036	0.040
Ba	0.019	0.019	0.041	0.068
Cs(K)	0.035	0.035	0.078	0.21
Rb(K)	0.007	0.007	0.014	0.019
Y+RE	0.12	0.12	0.27	0.53
Zr	0.065	0.065	0.14	0.22
Ru(Fe for 0.9 Ru)	0.032	0.032	0.082	0.22
Rh(Co)	0.007	0.007	0.013	0.060
Pd(Ni)	0.017	0.017	0.043	0.16
Ag(Cu)	0.0008	0.0008	0.0016	0.019
Cd(Cu)	0.0008	0.0008	0.0025	0.010
Te	--	--	--	0.034
Sn	--	--	--	0.010
Sb	--	--	--	0.003
Se	--	--	--	0.005
<u>Oxide Weight, Kg/tonne</u>				
<u>Inerts</u>	31.7	55.1	4.6	9.7
<u>Fission Products</u>	22.0	22.0	49.0	101.1
<u>Total</u>	53.7	77.1	53.6	110.8

- a. Fission product content corresponds to thermal reactor fuel exposures of 20,000 MWd/tonne at 15 MW/tonne.
- b. Fission product content corresponds to thermal reactor fuel exposures of 45,000 MWd/tonne at 30 MW/tonne.
- c. Fission product content corresponds to fast reactor core fuel exposures of 100,000 MWd/tonne at 200 MW/tonne.
- d. Elements in parentheses were used as chemical standins in WSEP demonstration runs.

<u>Constituent</u>	<u>Purpose</u>
1. Hanford Purex Plant IWW specially prepared to have a low sulfate content	Provide radioactive fission product spectrum, albeit at lower concentrations than in the nominal power reactor wastes, and typical nonradioactive Purex waste constituents, such as solvent degradation products.
2. Fission product rare-earth concentrate, principally ^{144}Ce	Provide radionuclide decay heat equivalent to power reactor wastes.
3. Inert chemicals	Increase chemical composition as required to equal nominal WSEP waste compositions shown in Table 4.1.

The WSEP wastes, while not being actual high exposure power reactor fuel wastes, are considered to have been good approximations for the study of solidification processing and interim storage for periods up to at least 10 years. The chemical standins (Table 4.1) that were used in the WSEP wastes for some of the more expensive fission products and did not amount to more than 5.9 mole percent of the content of any of the final melt-formed solidified products. No effects attributable to the use of the chemical standins were found in laboratory tests.

The predominant radioactive isotope in the WSEP wastes was relatively short-lived ^{144}Ce , whereas a large proportion of the fission product radioactive energy released in solidified high level wastes is due to longer-lived isotopes, principally ^{90}Sr and ^{137}Cs (Table 4.2). The decay of ^{144}Ce produces mainly beta energy, and the amount of beta decay energy which will be released in the WSEP pots in the first 10 years of their lives (the time period currently under study) is comparable to that

TABLE 4.2. Lifetime Radioactive Energy Released
in a Pot of Solidified High Level Waste
due to Fission Product Decay(a)

Isotope	Half-Life	Gm-Atoms Initially in Pot(b)	Lifetime Energy Release			
			Beta		Gamma	
			kW-hr	%	kW-hr	%
⁸⁹ Sr	51 days	0.01996	311	0.07	--	--
⁹⁰ SrY	28.8 years	8.02	246,000	56.07	--	--
⁹¹ Y	59 days	0.0435	723	0.16	--	--
⁹⁵ Zr	65 days	0.089	286	0.07	1,730	0.63
⁹⁵ Nb	35 days	0.1829	226	0.05	3,750	1.36
¹⁰³ Ru	40 days	0.0138	27	0.01	181	0.07
¹⁰⁶ RuRh	1.0 year	1.117	41,500	9.47	6,070	2.20
¹²⁵ Sb	2.7 years	0.076	234	0.05	881	0.32
¹³⁴ Cs	2.1 years	1.549	6,240	1.42	64,800	23.44
¹³⁷ Cs	30 years	12.21	85,200	19.45	183,000	66.00
¹⁴¹ Ce	33 days	0.00651	31	0.01	12	--
¹⁴⁴ CePr	285 days	1.50	53,500	12.21	1,960	0.71
¹⁴⁷ Pm	2.6 years	0.863	1,400	0.32	--	--
¹⁵¹ Sm	90 years	0.150	81	0.02	--	--
¹⁵⁴ Eu	16 years	0.422	2,600	0.59	14,500	5.25
¹⁵⁵ Eu	1.8 years	0.0424	113	0.03	59	0.02

- a. Assuming the pot contains the high level waste from processing 1 tonne of irradiated uranium, exposure = 46,000 MWd/tonne at 30 MW/tonne (Reference 20).
- b. Cooled 180 days at time of solidification in pot.

for pots of radioactive waste from highly irradiated power reactor fuels (Figure 4.1). The gamma activity in the WSEP pots is lower by a factor of more than 10 in relation to highly irradiated power reactor fuels. Radiation effects due to fission product decay, if the decay has any detectable influence on solidified waste properties, should become apparent within 10 years because a very significant fraction of the total fission products present will decay in this period (Figure 4.1). The other major source of radiation effects in solidified wastes, the transuranic isotopes, decay at a much slower rate, consequently their effects may be expected to be comparatively insignificant in the initial years of solidified radioactive waste storage.

4.2 COMPOSITION OF SOLIDIFIED HIGH LEVEL RADIOACTIVE PRODUCTS

The four types of solid product produced from the WSEP prototypical high level wastes were:

1. Oxide calcine	Small quantities of phosphate or sulfate added to suppress alkali metal volatility.
2. Phosphate Ceramic	Phosphate* added sufficient to convert all cations present to a mixture of ortho and pyrophosphates.
3. Phosphate Glass	Phosphate* added sufficient to convert all cations present to metaphosphates.
4. Borosilicate Glass	Borate and silica added individually or as glass frit.*

* Cations also added to obtain desired product properties.

FIGURE 4.1. Cumulative Radioactive Energy Generation in Solidified Wastes Due to Fission Product Decay

Solidified wastes of 13 different compositions were prepared in the WSEP radioactive demonstration program (Table 4.3). The 13 different compositions represent most of the possible combinations of the incorporation of the four prototypical high level waste compositions into four types of solid product.

4.2.1 Concentration Factors Achievable by Solidification

The ultimate minimum volume achievable in a waste solidification product is determined by many factors, including fuel exposure, proportion of nonfission product constituents (added either during reprocessing or solidification) and porosity of the product. The specific volumes (volume per tonne of U processed) of the radioactive WSEP solidified waste products are shown in Table 4.4. Assuming a nominal 378 liters of liquid waste per tonne of uranium the concentration factors achieved by solidification ranged from 2.4 to 11.8 and averaged about 7 for PW-4m, the waste considered most typical of future reprocessing plants.

4.2.2 Heat Generation in Solidified Waste

A major consideration in the operation of a high level waste solidification process is the removal of fission product heat (Table 4.5) from the solidified product. In certain cases it may not even be possible to take full advantage of the concentration factors available in solidification. A detailed discussion of the effect of fission product heat upon waste solidification processing parameters is given in Section 8 of Reference 16.

TABLE 4.3. Nominal Composition of WSEP Solidified Wastes^(a)

Product Type	Oxide Calcine			Phosphate Ceramic				Phosphate Glass				Borosilicate Glass	
Waste Solidification Process	Pot Calcination (PC)			Spray Solidification (SS)				Phosphate Glass (PG)				RLG	IPM
Waste Type	PW-1	PW-2	PW-4m	PW-1	PW-2	PW-4m	LMFBR	PW-1	PW-2	PW-4m	LMFBR	PW-4m	PW-4m
WSEP demonstrations with given composition, run number	PC-4 PC-5 PC-7	PC-1 PC-2 PC-3 PC-6	PC-8	SS-1 SS-2 SS-5 SS-6 SS-7 SS-8	SS-3 SS-4 SS-10	SS-9 SS-10	SS-11	PG-5 PG-6	PG-1 PG-2 PG-3 PG-4 PG-7	PG-8 PG-9 PG-10	PG-11	PC-9	SS-12 SS-13
Composition, wt%													
P ₂ O ₅	--	--	5.6	44.2	41.0	46.1	44.2	67.8	67.9	63.8	65.4	--	--
SiO ₂	0.4	0.3	0.4	0.2	0.1	0.1	--	0.1	0.2	0.1	--	17.6	22.5
B ₂ O ₃	--	--	--	--	--	--	--	--	--	--	--	22.3	25.2
Na ₂ O	3.4	13.2	7.2	7.2	13.7	7.7	10.0	12.4	4.4	8.2	8.1	13.8	5.9
K ₂ O	1.4	0.9	3.2	0.7	0.4	1.0	1.2	0.3	0.6	0.8	0.9	1.7	4.5
Li ₂ O	--	--	--	2.7	3.5	2.6	--	--	--	--	--	--	--
Fe ₂ O ₃	53.6	17.3	6.9	27.2	7.6	18.7	22.6	11.7	11.5	8.8	8.5	3.8	2.3
Al ₂ O ₃ ^(b)	(4.5)	(7.4)	(4.4)	(2.3)	2.6 (3.2)	(2.0)	(2.5)	(3.3)	(2.9)	(4.0)	(3.2)	(3.1)	(3.7)
Cr ₂ O ₃	0.6	0.8	0.7	0.3	0.4	0.2	0.4	0.1	0.5	0.2	0.3	0.4	0.2
NiO	1.2	0.9	2.8	0.6	0.4	0.9	1.5	0.3	0.6	0.7	1.2	1.5	0.9
ZnO	--	--	--	--	--	--	--	--	--	--	--	--	10.5
CaO	--	12.8	--	--	6.8	--	--	--	--	--	--	--	1.4
MgO	--	--	--	--	--	--	--	--	--	--	--	--	0.7
SO ₃	6.1	31.8	--	--	14.0	--	--	--	--	--	--	--	--
U ₃ O ₈	2.0	1.3	2.4	1.0	0.6	0.6	--	0.4	0.8	--	--	1.1	0.6
RE ₂ O ₃	13.8	9.0	32.4	7.0	4.0	10.2	9.5	3.0	5.9	8.0	7.5	17.4	10.3
ZrO ₂	5.6	3.7	12.7	2.9	1.6	4.0	3.0	1.2	2.5	3.1	2.4	6.8	4.0
MoO ₃	7.9	5.2	16.7	4.0	2.3	5.2	4.8	1.7	3.5	4.1	3.8	9.0	5.3
RuO ₂	0.3	0.2	0.8	0.2	0.1	0.2	0.1	0.1	0.1	0.2	0.1	0.4	0.2
Co ₃ O ₄	0.4	0.3	0.8	0.2	0.1	0.2	0.5	0.1	0.2	0.2	0.4	0.4	0.2
CuO	0.1	0.1	0.2	--	--	0.1	0.3	--	--	0.1	0.2	0.1	0.1
SrO	1.1	0.7	2.7	0.6	0.3	0.8	0.5	0.2	0.5	0.6	0.4	1.4	2.3
BaO	2.0	1.4	4.5	1.1	0.6	1.4	1.2	0.5	0.9	1.1	0.9	2.4	2.9
SnO ₂	--	--	--	--	--	--	0.2	--	--	--	0.1	--	--
Theo. wt% Fission Product Oxides ^(c)	38.3	25.5	82.4	20.0	11.5	28.3	28.8	8.8	17.3	22.2	22.8	46.7	28.5
Bulk Specific Gravity	1.4	1.35	1.3	3.2	2.8	3.0	3.0	2.8	2.8	2.9	2.9	3.5	3.0

- a. Chemical standins were used for some fission products. See Table 4.1.
- b. Representative Al₂O₃ concentrations in the radioactive products are shown in parenthesis. The Al₂O₃, nontypical of power reactor wastes, resulted from the small and variable amounts of aluminum unavoidably present in the Hanford Purex plant HLW used in preparing the WSEP wastes. In preparing the wastes for the WSEP radioactive runs the iron concentration was reduced in proportion to the aluminum present.
- c. Calculated on a no substitution basis.

TABLE 4.4. Specific Volume of Solidified Wastes in WSEP Demonstration Runs

Waste Type	Nominal Fuel Exposure	Solidified Waste Volume, Liter/Tonne of Uranium Processed			
		Oxide Calcine	Phosphate Ceramic	Phosphate Glass	Borosilicate Glass
PW-1	20,000 MWd/Te at 15 MW/Te	41,43,46	34,28,33,34,34,35	108,94	
PW-2	20,000 MWd/Te at 15 MW/Te	50,45,47,50	64,63	42,40,51,59,64 ^(a)	
PW-4m	45,000 MWd/Te at 30 MW/Te	46	54,52	79,65,84	32,100, ^(b) 57
LMFBR	100,000 MWd/Te at 200 MW/Te	--	111,100	158	

a. Does not include volume of sulfate waste, which appears as a side stream in this process.

b. Large volume is due to calcium and zinc added during one demonstration, but subsequently shown to be unnecessary.

TABLE 4.5. Heat Generation Rates in Fuel Reprocessing Plant Waste as a Function of Cooling Time

Years From Reactor Discharge	Watts/Tonne of Fuel Processed ^(a)	
	20,400 MWd/tonne	46,600 MWd/tonne
0.5	8380	19,210
1	4800	11,680
2	2490	6,370
3	1550	4,150
4	1120	3,000
5	890	2,440
6	710	2,100
7	670	1,870
8	630	1,700
9	600	1,580
10	570	1,480
15	490	1,200
20	420	1,060
35	290	720

a. Includes heat generation rate from actinide elements not removed by separations processing (100% of the americium, curium, and neptunium radioactivity plus 0.3% of the plutonium radioactivity).

5.0 CHARACTERISTICS OF
SOLIDIFIED WASTES

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5.0 CHARACTERISTICS OF SOLIDIFIED WASTES

Solidification converts high level wastes to a compact form which can be shipped safely so that over the long-term large inventories of radionuclides can be isolated at only a few carefully chosen locations. The properties of the solidified wastes can significantly affect the design of the solidified waste containers, the interim storage facilities, the equipment used for shipping, and the ultimate waste repository.

5.1 PHYSICAL STRUCTURE AND MELTING POINT

5.1.1 Oxide Calcine (Pot Calcine Product)

The pot calcine product was formed in the pots as a porous cake of friable calcine with an irregular cone-shaped void at the top center. The calcine was laid down in a somewhat layered fashion on the pot walls and bottom as the runs progressed. During the final stages of processing the temperature was raised to 900 °C to assure complete decomposition of the nitrates present. At this temperature the alkali metal salts of the small amount of sulfate or phosphate present (see compositions in Table 4.3) melted, which helped to bind together the high melting oxides in the remainder of the calcine product. A photograph of radioactive pot calcine removed with a spatula through a hole drilled in the wall of the PC-7 pot is shown in Figure 5.1. The chunks of calcine visible in the photograph could be crushed easily with only gentle force.

5.1.2 Phosphate Ceramic (Spray Calciner-Melter Product)

The phosphate ceramic produced by the spray calciner-melter process is a rock-like microcrystalline solid with a chemical composition equivalent to a mixture, in approximately equal proportions, of the pyro and ortho phosphates of all of the cations present. The ceramic, which has a relatively sharp melting point at about 950 °C, (800 °C for the sulfate-containing PW-2 ceramic) was cast in the pots by pouring from a platinum melter

FIGURE 5.1. Radioactive Pot Calcine Product

above the pot. In part of the first WSEP run, SS-1, the melter was allowed to overflow in a continuous drop-wise fashion. Batch dumping in 4 to 6 liter batches, which eliminated the problem of stalagmite formation in the pots, was used thereafter.

A photograph of a typical phosphate ceramic core-drilled sample (from SS-4 pot) is shown in Figure 5.2. It was impossible to obtain whole cores from the phosphate ceramic pots SS-6, SS-8 and SS-10. Apparently the product in these pots contained one or two circumferential cracks which extended most of the length of the pots. The cracks were possibly due to thermal contraction of the product as the pots cooled. Whole cores were obtained from the SS-2 and SS-4 pots.

FIGURE 5.2. Core-Drilled Sample of Radioactive Phosphate Ceramic Product from Pot SS-4 (Circular object is pot wall sample.)

5.1.3 Phosphate Glass (Phosphate Glass Process Product)

The phosphate glass products were originally homogeneous black glasses with a chemical composition equivalent to the metaphosphates of all of the cations present. The glass melts flowed readily at 900 °C, and slumped slowly at temperatures as low as 600 °C. During all but the latter part of Run PG-11, during which batch-dumping was used, melt was discharged to the pots in a continuous dropwise manner while the pot was heated. Photographs of typical phosphate glass core-drilled samples are shown in Figure 5.3. Four phosphate glass pots have been core sampled to date. All but one, PG-8, have been found to be almost completely devitrified. Devitrification of phosphate glass products is discussed in Section 5.2.1.

a. Completely devitrified sample from PG-7 pot.

b. Partially devitrified sample from PG-8 pot.

c. View of hole in PG-8 pot showing devitrification toward center.

FIGURE 5.3. Core-Drilled Samples of Radioactive Phosphate Glass Product

5.1.4 Borosilicate Glasses (Rising Level Glass and Spray In-Pot Melting Process Products)

The WSEP borosilicate glasses were black glasses containing nonhomogeneities of two general types:

1. Occlusions of waste oxide suspended in the glassy matrix.
2. A separate microcrystalline phase which collected at the melt surface or as globules suspended within the melt.

The amount of both types of nonhomogeneity was very dependent upon thermal history and is discussed in more detail in Section 5.2.2. The WSEP borosilicate glasses were formed in-place in the receiver pots at 900-950 °C. The IPM glass slumps slowly at 600 °C whereas the RLG glass (see Table 4.3 for compositions) does not slump in a similar manner until 800 °C, probably due to its higher metal oxide content.

It has not been possible to obtain coherent core samples of the glassy WSEP products. The samples shatter into many small pieces as shown in the photographs of IPM process borosilicate glass in Figure 5.4.

5.2 EFFECT OF TEMPERATURE

Three time periods must be examined when considering the effects of temperature upon solidified high level wastes:

(a) processing, (b) cool-down, and (c) handling and storage.

Processing--The high temperatures during processing serve to decompose nitrates in the waste and, in the case of the melt-formed products, to allow the chemical rearrangements to occur which are necessary to produce the desired product characteristics. As a general rule product quality is enhanced by increased temperatures during processing. Nonradioactive studies indicated phosphate glass process products were improved by processing at 1200 °C vs 1000 °C.⁽¹⁷⁾ Borosilicate glass homogeneity is improved by increased processing temperature, as discussed below.

FIGURE 5.4. Core-Drilled Sample of IPM Borosilicate Glass Product from Pot SS-12

Cool-Down--The transition from processing to storage temperatures can be rapid, e.g. water quenching, or slow in varying degrees. Because of a relatively rapid devitrification rate, phosphate glasses benefit from fast cool-downs. Other effects such as the relative amounts of fracturing due to thermal shock at various cooling rates have not been evaluated.

Handling and Storage--Maximum allowable temperatures must be established for pots of solidified wastes to assure safety during handling and storage of the pots. For the WSEP pots the limiting case was considered to be when the pots were hanging in air, cooled only by convection currents. The temperature limits imposed for this case are given on page 2.1. The WSEP limits permit a 900 °C centerline temperature in the pots. Since both the phosphate and borosilicate glasses are fluid at this temperature, the WSEP molten core storage limit is imposed

so that the molten, or soft, center does not exceed one-half the pot diameter. Eight WSEP pots actually contained sufficient radioactive heat to maintain a molten core while hanging in air. The temperature history of these pots is shown in Table 5.1.

5.2.1 Devitrification

Devitrification of phosphate glasses increases their leachability by a factor of approximately 1000. The products are

TABLE 5.1. Temperature History of WSEP
Molten Core Pots

<u>Run No.</u>	<u>Product Form</u>	<u>Waste Type</u>	<u>Total Time During Which Molten Core Existed (a)</u>
SS-7	Phosphate Ceramic	PW-1	Approx. 24 hours
PG-5	Phosphate Glass	PW-1	Approx. 10 days
PG-6	Phosphate Glass	PW-1	Less than 24 hours
PG-7	Phosphate Glass	PW-2	Approx. 10 days
PG-8	Phosphate Glass	PW-4m	Approx. 4 days
PG-10	Phosphate Glass	PW-4m	Approx. 16 days
PG-11	Phosphate Glass	LMFBR	Approx. 4 days
SS-13	Borosilicate Glass	PW-4m	Approx. 5 days

- a. WSEP pots with potential molten cores were stored in water except when measurements were being made. In most cases the pots were cooled in water and then allowed to reheat to the molten core condition for the time periods shown while hanging in air.

changed from the most nonleachable of WSEP products to some of the most readily leachable. Most of the phosphate glass products in the four WSEP phosphate glass pots which have been core drilled to date have been devitrified.

No devitrification has been found in samples of the two borosilicate pots which have been drilled. This is not absolute proof that devitrification has not occurred since the borosilicate glass samples shattered during drilling and only incomplete samples were obtained (some of the particles were entrained in the drill cooling air).

Devitrification of WSEP phosphate glass occurs between 550 and 750 °C, and is most rapid at about 650 °C, as shown in Figure 5.5. An accelerated leach test was used to evaluate the degree of devitrification which had occurred in glass specimens held for varying lengths of time at the temperatures of interest. The leach data show that significant devitrification occurred within 2 hours at 650 °C and that approximately 50% devitrification had occurred within 24 hours. The temperatures of the WSEP phosphate glass pots were within the devitrification temperature range for many hours while being filled (see Figures 4.18 and 4.19 in Reference 16) and it is probable that much of the devitrification observed in the WSEP pots occurred during processing.

Devitrification of WSEP IPM borosilicate glass occurs between 650 and 850 °C. It is most rapid between 700 and 750 °C, where samples are almost completely converted to crystalline form in less than 24 hours. Preliminary data indicate that leachability of IPM borosilicate glass is not increased by devitrification in the marked manner of phosphate glass (Figure 5.6), however more measurements are required.

5.2.2 Potential for Phase Separation

Only macroscale phase separation is considered in this discussion. Separate phases on a microscale are to be expected in the oxide and phosphate ceramic products, and to some extent in the glassy products, e.g., undissolved oxide particles suspended in the glassy matrix. Generally these nonhomogeneities

FIGURE 5.5. Phosphate Glass (PW-2) Devitrification Temperature

FIGURE 5.6. IPM Borosilicate Glass (PW-4m) Devitrification Temperature

are evenly distributed and affect product characteristics uniformly. When the distribution is uneven however, the macro-scale differences in product characteristics which may result can become significant. Undesirable changes in many properties, such as melting point, corrosivity, thermal conductivity, and leachability, may occur in portions of the product. Hot spots due to enrichment of heat-producing radioisotopes can be formed. Thus it is essential to assure that macroscale phase separation does not occur during the filling of solidified waste pots or during their storage.

In the WSEP Program, several methods are being used to determine the homogeneity of the solidified waste in the storage pots. Thermocouples spaced longitudinally along the centerline, midway between centerline and wall, and at the pot wall surface, are used to detect the presence of hot spots. Longitudinal gamma scans were made on most pots after processing to determine if the radioactive profile was uniform. Core samples are being taken from near the top, the center and the bottom of the product in each WSEP pot. The gamma activity along the length of each core sample is measured, thus the analyses yield information on axial and radial fission product distribution in the pots. In addition laboratory measurements were made to determine the effects of off-standard processing and storage conditions. Most of the discussion on nonhomogeneity in solidified wastes which follows is based on results of the laboratory studies since the products in the WSEP pots have been found to be quite homogeneous.

Calcine Product

In the pot calcine process, containment of the radioisotopes in the high level waste is provided by the pot; the additional protection provided by physical properties of the calcine is insignificant, thus no attempt was made to define the physical structure of the pot calcine product with sufficient precision so that changes due to thermal treatment or radiation could be identified.

Phosphate Ceramic

Homogeneous phosphate melts are formed readily but they tend to divide into separate phases when held for long periods at high temperatures. The results of tests in which WSEP-type phosphate melts were held at a series of elevated temperatures for two months are depicted in Figure 5.7.

High temperature storage caused the spray solidifier melts to separate into two layers, the upper layer amounting to 10 to 50 percent of the whole. The upper layer became somewhat richer in phosphate than was the original melt; in some cases sufficient phosphate segregation occurred to produce a glass in the upper layer. The melting point of the lower layer increased by as much as 300 °C over that of the original melt. Considerable fission product segregation between the two phases occurred. In general, the mono- and di-valent cations tended to concentrate in the upper layer and the high valence cations in the lower layer, as shown by the data in Table 5.2.

It is noteworthy that the phase separation illustrated in Figure 5.7 occurred at temperatures up to 200 °C below the operating temperature of the process melter, however the separation illustrated is that observed after 8 weeks at temperature. Other tests indicated that the rate at which phase separation occurred was sufficiently slow to assure unimpaired melter operation. For example, spray solidified PW-4m melts held at 1150 °C began to show the first signs of major phase separation after about 8 hours at temperature. Holdup time in the WSEP melter was about 3 hours and the operating temperature was generally lower, about 1050 °C. Thus, there is good assurance that phase separation of phosphate melts will not occur in normal melter operation, and that the product discharged into the pot will be homogeneous. However, phase separation is certainly to be expected above certain maximum temperatures in "molten core" storage of phosphate products. The approximate maximum centerline temperatures which can be permitted

PRODUCT FORM	WASTE	550 °C	650 °C	750 °C	850 °C	950 °C
PHOSPHATE CERAMIC	PW-1			HOMOGENEOUS SLATE-GREY MICROCRYSTALLINE	SLATE-GREY MICROCRYSTALLINE (WITH VOIDS)	YELLOW-GREY CRYSTALLINE SLATE-GREY MICROCRYSTALLINE
	PW-2	MICROCRYSTALLINE (WITH VOIDS)	GREY CERAMIC MICROCRYSTALLINE (WITH VOIDS)	DARK GREEN GLASS DEVITRIFIED GLASS MICROCRYSTALLINE (WITH VOIDS)		
	PW-4m			SLATE-GREY MICROCRYSTALLINE	YELLOW-GREY CRYSTALLINE SLATE-GREY MICROCRYSTALLINE	YELLOW CRYSTALLINE GREY CRYSTALLINE SLATE-GREY MICROCRYSTALLINE
	LMFBR			SLATE-GREY MICROCRYSTALLINE	YELLOW-BROWN CRYSTALLINE SLATE-GREY MICROCRYSTALLINE (WITH VOIDS)	BROWNISH YELLOW NEEDLE-SHAPED CRYSTALS SLATE-GREY MICROCRYSTALLINE
PHOSPHATE GLASS	PW-1				BLACK GLASS BROWN DEVITRIFIED	BLACK GLASS COARSE BROWN, YELLOW, GREEN CRYSTALS
	PW-2			BROWN DEVITRIFIED INDISTINCT STREAKS OF FINE POROSITY	BROWN DEVITRIFIED INDISTINCT LAYERING	HOMOGENEOUS PARTIALLY DEVITRIFIED GLASS
	PW-4m				HOMOGENEOUS PARTIALLY DEVITRIFIED GLASS	BLACK GLASS FINE CRYSTALS INTERSPERSED IN ~ 50 VOL % GLASS
	LMFBR				HOMOGENEOUS BROWN DEVITRIFIED	BLACK GLASS GRADUAL CHANGE TO FINE CRYSTALLINE ~10 VOL % GLASS
BOROSILICATE GLASS (IPM)	PW-4m				BLACK GLASS BLACK GLASS WITH DARK GREEN SUSPENSION MOTTLED GREEN IN GREY CERAMIC	BLACK GLASS OFF-WHITE CERAMIC OCCLUSIONS

(a) APPEARANCE OF NONRADIOACTIVE SIMULATED SOLIDIFIED WASTES AFTER TWO MONTHS AT GIVEN TEMPERATURES.

FIGURE 5.7. Thermally-Induced Phase Separation in Solidified Wastes ^(a)

during storage of phosphate products without the occurrence of phase separation are shown in Table 5.3.

TABLE 5.2. Melt Constituent Segregation Resulting from Thermally-Induced Phase Separation

Melt Constituent	Concentration Ratio, Upper Layer/Lower Layer		
	Phosphate Ceramic		Phosphate Glass
	PW-2 Melt (a)	PW-4m Melt (b)	PW-4m Melt (b)
Cs	--	1.8	1.1
Sr	1.3	--	1.5
Ni	1.5	--	--
Fe	0.9	--	--
Cr	0.5	--	--
Rare Earths	0.1	0.3	0.7
Zr	0.4	--	--
Ru	--	0.06	0.4

a. 8 weeks at 750 °C.

b. 8 weeks at 950 °C.

TABLE 5.3. Permissible "Molten Core" Storage Temperatures for Phosphate-Based Solidified Wastes

Waste Type	Maximum Stable Melt Temperature	
	Phosphate Ceramic	Phosphate Glass
PW-1	Approx. 900 °C	Undefined, but <800 °C
PW-2	Approx. 600 °C	Above 950 °C
PW-4m	Approx. 800 °C	Approx. 900 °C
LMFBR	Approx. 800 °C	Approx. 900 °C

It is believed that some phase separation is permissible; for instance, using the WSEP criteria of permitting the molten core to extend one half way from the centerline to the wall, less than 25 percent of the volume would be subject to fission product segregation of the type described in Table 5.2.

Phosphate Glass

The phosphate glass melts are considerably more stable toward phase separation during prolonged high temperature treatment than are the phosphate ceramic melts (Figure 5.7). Phase separation in the phosphate glass melts is apparently due to a precipitation phenomenon. Finely divided crystals (coarse crystals in the case of the PW-1 melt) collected in the lower portions of the melt. While some fission product segregation occurred, the separation was much less marked than in the spray solidifier melts (Table 5.2).

Borosilicate Glass

In contrast to phosphate melts, which tend to be metastable and partition into separate phases if held in the molten state for long periods of time, the homogeneity of borosilicate melts is benefited by long term molten storage. (See IPM PW-4m results, Figure 5.7). The WSEP borosilicate products exhibited two types of nonhomogeneities:

1. Occlusions of waste oxide suspended in the glassy matrix.
2. A separate microcrystalline phase which collected at the melt surface or as globules suspended within the melt.

The amount of both types of homogeneity was very dependent upon thermal history. Either higher temperatures or increased duration of thermal treatment decreased the nonhomogeneity.

The waste oxide occlusions tend to segregate toward the bottom of the melt before dissolving. There is also a small amount of slag at the top surface. Photographs taken of core-drilled

samples of the WSEP Rising Level Glass product illustrate that some oxide material remained undissolved in the lower portions of the pot (Figure 5.8). Gamma analyses of the core-drilled samples indicated no significant partitioning of cesium and cerium in the RLG glass. It may be concluded that the presence of the occluded oxide material does not affect product quality significantly. The presence of the other type of borosilicate nonhomogeneity, the separate microcrystalline phase, is undesirable however, because it is more water soluble and more corrosive than the bulk melt, and is enriched in certain fission products, cesium, in particular.

FIGURE 5.8. Core Drilled Samples of Radioactive RLG Borosilicate Glass Product

The separate microcrystalline phase encountered in the WSEP tests was yellow. The composition of the yellow phase was quite complex, but its presence in borosilicate waste melts was traced to one element, molybdenum, a high yield fission product. The yellow phase was not observed in either borate or phosphate waste melts, thus it can be concluded that silicate concentration in the melt is an important factor. The borosilicate composition used in the WSEP runs contain relatively large proportions of borate. They represent a compromise between the higher leach rates resulting from more borate and less yellow phase resulting from reduced silicate.

The quantity of yellow phase in the WSEP IPM pots is probably quite small. Actually no yellow phase was found in the core-drilled samples from the SS-12 pot; however, this is not conclusive evidence since the yellow phase tends to collect at the very top and bottom of the melt. To predict the amount probably present in the radioactive runs the yellow phase was physically separated from the glassy product from one prototypical nonradioactive pilot plant IPM run. About 150 grams (1/3 at the top and 2/3 at the bottom) were found in 84.1 kg of product. Some important characteristics of the yellow phase are given in Table 5.4.

No chemical additive has been found that will solubilize molybdenum in the WSEP borosilicate melts at 900 to 950 °C, the WSEP borosilicate operating temperature. The yellow phase dissolves in the melts completely at 1050 °C, however, and there would appear to be an incentive to operate waste solidification processes utilizing borosilicates at 1050 °C.

5.2.3 Fission Product Distribution in WSEP Pots

The initial fission product distribution within the WSEP pots was determined from gamma radiation profiles of each pot shortly after filling. The profiles were obtained by positioning an ionization chamber about 6 inches from the pot wall

TABLE 5.4. Characteristics of the "Yellow Phase" in the Borosilicate Products

	<u>Top Yellow Phase</u>	<u>Bulk Melt</u>	<u>Bottom Yellow Phase</u>
304L SS Corrosion rate at 950 °C, in./yr	0.44	0.02	0.44
Melting points, °C	700	950	975
Density, g/cm ³	3.116	3.102	3.731
Accelerated Leach Test at 95 °C			
%Weight Loss			
First 24 hr	78.2	1.4	22.8
Second 24 hr	4.4	1.1	1.1
Third 24 hr	3.8	1.1	0.68
Overall % wt loss	79.8	3.6	24.2
Composition, wt% (a)			
Nd	<1	0.8	1
Ce	<0.1	3	0.5
La	<0.1	3	1
Ba	6	3	5
Mo	7	0.3	8
Sr	0.8	3	5
Fe	1	1	0.05
Cr	1	0.1	0.2
Ca	1	20	10
K	6	0.7	5
Si	<1	8	<0.05
Na	60	30	20
B	0.07	3	0.4

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

and recording the radiation level at 12-inch intervals along the length of the pot. No collimation was attempted. In general the radiation profiles corresponded to the temperature profiles, and both maximum radiation and temperature readings were measured 2.5 to 3 feet above the bottom of the pot, as would be expected. Details of the gamma radiation profiles have been published:

<u>Product Type</u>	<u>Run Numbers</u>	<u>WSEP Report</u>	<u>Pages</u>
Calcine	PC-1 through PC-6	BNWL-814	6.11-6.13
	PC-7 and PC-8	BNWL-1628	6.4 -6.6
Phosphate Ceramic	SS-1 through SS-6	BNWL-1391	6.15-6.17
	SS-7 through SS-11	BNWL-1583	6.6 -6.9
Phosphate Glass	PG-1 through PG-6	BNWL-1185	6.12-6.14
	PG-7 through PG-11	BNWL-1541	6.5 -6.8
Borosilicate Glass	PC-9	BNWL-1628	6.4 -6.6
	SS-12 and SS-13	BNWL-1583	6.6 -6.9

More detailed information on the distribution of fission products within the pots is being obtained from gamma spectrometry of the core drilled samples. Nominally the core drilled samples are 3/4-inches in diameter and about 3-1/2 inches long and are taken at three elevations so that samples from the midpoint, and near the top and bottom, of the solidified waste in each pot are obtained. The core samples are sawed into sections so that analysis of the individual sections yields information on the radial distribution of fission products at each elevation.

The dominant activities in the samples are due to ^{137}Cs and $^{144}\text{CePr}$; this is convenient because the chemistry of cesium and cerium is sufficiently different that even minor phase partitioning may be expected to involve some segregation of these isotopes. The gamma spectrometry results, expressed as the

activity ratio, $d|m|g^{137}\text{Cs}/d|m|g^{144}\text{Ce}$, for core-drilled samples from nine WSEP pots are shown in Figure 5.9. Most core drillings did not yield a full length core sample, therefore the data are not complete.

Only two samples of pot calcine product have been analyzed to date, from the 13.5 and 46 inch levels of the PC-7 pot. The samples were not coherent so it was not possible to determine radial fission product distribution, however a significant difference in fission product distribution at the two different heights in the pot was noted. The Cs/Ce distribution ratio was higher in the upper sample, in agreement with expected behavior. Cerium is less soluble than cesium and tends to precipitate first, i.e., lower in the pot.

The radial fission product distribution was quite uniform in all of the six phosphate products drilled, but in two of the products (SS-6 and PG-6) significant axial variations in fission product distribution were observed. In both cases the Cs/Ce ratios were lowest at the midpoint of the pots and were higher toward the two ends of the pots.

The borosilicate samples were completely fragmented so the radial location of the individual sample pieces could not be pinpointed, however this proved to be of little consequence since the fission product distribution in the borosilicate glass samples was found to be very homogeneous.

5.3 THERMAL CONDUCTIVITY

Thermal output due to radioactive decay can assume values of 400 W/liter or higher when short-cooled high level radioactive wastes are concentrated in the solid form. This heat must be dissipated sufficiently to maintain temperatures of the solidified wastes and pot walls low enough to prevent deleterious effects at any time in the handling and disposal of the waste pots, thus there is a considerable advantage in obtaining a relatively high thermal conductivity in the solid forms used for immobilization

FIGURE 5.9. Radial and Axial Activity Distribution in WSEP Pots

of the wastes. The effective thermal conductivity (k_{eff}) of the melt-formed WSEP solids was in the range 0.8 to 1.3 W/(m²) (°C/m) while the k_{eff} of the porous pot calcine product was in the range 0.3 to 0.4 W/(m²) (°C/m) (Figure 5.10).

Effective thermal conductivity of the WSEP pots was obtained by use of the following relationship:

$$\Delta T = \frac{Q}{4\pi k_{\text{eff}} L}$$

where:

$\Delta T = T_c - T_w$ (T_c is the maximum internal temperature and T_w is the wall temperature in the same zone. See Figures 7.1 and 7.2 for location of thermocouples.

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

L = length of heat generating cylinder (meters).

Power generated in the pots, Q , was obtained by whole pot calorimetry^(8,9) and by knowledge of heat producing isotopes in the feed solution.

Effective thermal conductivities measured on the WSEP pots are arranged according to product form and shown graphically in Figures 5.11, 5.12, 5.13 and 5.14. In most cases the k_{eff} of the highly radioactive solids in the pots was slightly higher than the thermal conductivity of nonradioactive solids of the same nominal composition. The k_{eff} of solidified wastes increased with temperature in the range 100 to 600 °C, except for the phosphate ceramic which had an essentially constant k_{eff} over this temperature range. Above 600 °C the k_{eff} of the glassy solids increased markedly. These low-melting products begin to soften at about 600 °C and the increase in k_{eff} which was noted above 600 °C is mostly due to convection currents. (Note that the temperature plotted as the abscissa in Figures 5.11 to 5.14 is $(T_c - T_w)/2$,

FIGURE 5.10. Effective Thermal Conductivity of WSEP Solidified Wastes

FIGURE 5.11. Effective Thermal Conductivity of Oxide Calcine Products

FIGURE 5.12. Effective Thermal Conductivity of Phosphate Ceramic Products

FIGURE 5.13. Effective Thermal Conductivity of Phosphate Glass Products

FIGURE 5.14. Effective Thermal Conductivity of Borosilicate Glass Products

thus the central area in the pots was considerably above 600 °C at the onset of the marked increase in k_{eff} as a function of temperature.)

The effective thermal conductivities shown in Figures 5.11 to 5.14 were measured within hours or, at most, a few days after the pots were filled. Measurements of k_{eff} as a function of time in interim storage, as obtained on pots representative of the different WSEP product forms, are shown in Table 5.5. There is no indication of appreciable change in thermal conductivity during interim storage for periods of up to three years.

5.4 VOLATILE COMPONENTS

5.4.1 Pot Pressurization

A primary requirement in the current regulations governing the solidification of high-level radioactive wastes in the United States is that the solid shall be "chemically, thermally, and radiolytically stable to the extent that the equilibrium pressure in the sealed container will not exceed the safe operating pressure for that container during the period from canning through a minimum of 90 days after receipt (transfer of physical custody) at the Federal repository". Pressure has been monitored on selected radioactive WSEP pots during interim storage and only minor pressurization has been observed.

Bourdon tube gauges were installed on most of the pots as soon as their caps were seal-welded. The gauges used proved to be not mechanically rugged enough for the crowded in-cell remote handling conditions. As the filled pots were transferred from one storage condition to another and the gauges were jarred and vibrated, the pressure-vacuum readings changed. Representative pressure readings are given in Table 5.6. The highest reading observed was 6.5 psig on the pot of run PG-4 and this was believed to be a false reading from a damaged gauge.

TABLE 5.5. Effective Thermal Conductivity of Solidified Wastes During SSETF Storage

Solidified Form	Waste Type	Run No.	Initial		6 Months		1 Year		1.5 Years		2 Years (d)		2.5 (d) Years		3 Years (d)		3.5 (d) Years	
			T _{ave} (a)	k _{eff} (b)	T _{ave}	k _{eff}	T _{ave}	k _{eff}	T _{ave}	k _{eff}	T _{ave}	k _{eff}	T _{ave}	k _{eff}	T _{ave}	k _{eff}	T _{ave}	k _{eff}
Oxide	PW-2	PC-6	590	0.32	B Cell Storage (c)								548	0.22	520	0.38	517	0.38
Calcine	PW-4m	PC-8	593	0.37			630	0.30	595	0.28								
Phosphate Ceramic	PW-2	SS-4	395	1.1			120	1.03	130	0.97	107	1.25	88	1.23	88	1.23		
	PW-1	SS-8	500	1.4			578	1.23	523	1.16	513	1.07	477	0.96				
	PW-4m	SS-9	473	1.14					556	1.06	514	1.04	477	1.02	493	1.02		
	PW-4m	SS-10	480	1.39			102	1.02	141	1.0	NA	NA	NA	NA	79	0.93		
Phosphate Glass	PW-1	PG-6	590	1.07					129	1.11	102	1.06	110	1.0				
	PW-2	PG-7	582	0.9			366	0.86	NA	NA	431	0.72	457	0.68				
	PW-4m	PG-8	535	0.87			189	0.79	NA	NA	287	0.88	78	0.68				
Borosilicate Glass	PW-4m	PC-9	571	1.36			600	1.22										
	PW-4m	SS-13	622	1.28					124	0.90	100	0.87						

NA Not available

a. $T_{ave} = \frac{\text{Centerline Temperature} + \text{Wall Temperature}}{2}$

b. k_{eff} = Effective Thermal Conductivity, W/(m²) (°C/m).

c. No thermal conductivity measurements were made during storage in B Cell, the processing cell.

d. The k_{eff} variations are primarily due to the reduced accuracy obtained as ΔT decreased with time.

TABLE 5.6. Pressure Measurements on Solidified Waste Pots

Run No.	Solidified Waste Type	Pot Environment	Time from Weld Date to Date of Pressure Reading, Months	Pressure, psig
PC-1	Oxide Calcine	Water Storage, B Cell	5	+ 2.0
PC-2	"	Water Storage, B Cell	8	- 5.0
PC-3	"	Water Storage, B Cell	11.5	-14.0 (a)
PC-4	"	Water Storage, B Cell	13	- 2.7
PC-5	"	Water Storage, B Cell	8	- 1.0
PC-6	"	Water Storage, B Cell	6	- 5.5
SS-1	Phosphate Ceramic	Water Storage, B Cell	9.5	0
SS-2	"	Water Storage, B Cell	15	+ 2
SS-4	"	Water Storage, B Cell	1	+ 3
SS-6	"	Water Storage, B Cell	1	- 1
PG-1	Phosphate Glass	Air Storage, B Cell	11	- 9.8
PG-2	"	Water Storage, B Cell	3	-14.7 (a)
PG-3	"	Air Storage, B Cell	2	-14.2 (a)
PG-4	"	Air Storage, B Cell	7	+ 6.5
PG-6	"	Water Storage, B Cell	3	- 2.5
PG-7	"	Water Storage, B Cell	8	+ 1
PG-8	"	Water Storage, B Cell	7	- 0.5
PG-9	"	Water Storage, B Cell	6	+ 5

a. Pots were sealed with the vacuum from the vacuum leak checking.

Pressure is monitored continuously on the pots undergoing interim storage studies in the SSETF. The pressures measured on the water-stored SSETF pots generally have been slightly below atmospheric pressure; the pressures measured on the pots stored in air at elevated temperatures have not been greater than that pressure due to the increase in temperature when the pots are placed in the controlled environment.

The absence of any significant pressure buildup in the sealed pots indicates that the residual level of nitrate and other unstable or volatile constituents is as low as would be expected from the processing temperatures used in the WSEP processes. The lowest processing temperature was 875 °C, used for the sulfate-retaining spray calciner-melter PW-2 flowsheet. All other processing temperatures were at least 900 °C.

5.4.2 Fission Product Volatility

The potential for atmospheric release of fission products by volatilization from WSEP-type solidified wastes was examined briefly in laboratory studies. High temperature excursions in solidified waste can be postulated, for instance, a situation could occur in which a shipment of radioactive waste is involved in a high temperature fire and the container integrity is lost. Although such temperature excursions are a very remote possibility it is important that sufficient data exist to predict the effects of such an eventuality.

Vapor pressure data⁽²¹⁾ indicate, and previous studies^(22,23) verify, that cesium is the fission product with the most significant volatility. Cesium volatilization from all of the WSEP solidified waste types was determined in the temperature range 800 to 1000 °C (Table 5.7). In a few instances the temperature was increased to 1100 and 1200 °C.

The volatility data in Table 5.7 were obtained by spiking powdered specimens of each waste type with aqueous tracer

TABLE 5.7. High Temperature Volatility of WSEP Solidified WastesTABLE 5.7. High Temperature Volatility of WSEP Solidified Wastes

Loss per Hour, %	Temperature, °C	Oxide			Phosphate						Borosilicate	
		Pot Calcination			Spray Calciner- Melter			Phosphate Glass			RLG PW-4m	IPM PW-4m
		PW-1	PW-2	PW-4m	PW-1	PW-2	PW-4m	PW-1	PW-2	PW-4m		
Weight	800	0.004	0.005	0.071	0.001	0.12	0.004	0.008	0.001	0.001	ND	ND
	900	0.053	0.14	0.11	0.009	0.16	0.080	0.014	0.010	0.007	0.002	0.002
	1000	0.095	0.27	0.23	--	0.21	0.17	0.061	0.056	0.098	0.004	0.012
	1100						0.29			0.23		
	1200						0.47			1.23		
Cs	800	0.016	ND	0.024	0.012	0.10		0.001	0.015	ND	0.12	0.018
	900	0.038	ND	0.12	0.11	0.28		0.050	0.059	--	0.40	0.030
	1000	0.36	ND	0.090	0.12	0.51	0.65	0.14	0.26	0.82	0.61	0.33
	1100					2.0	1.2	0.96		1.2		
	1200						2.9			--		

ND - Not Determined

solutions of ^{137}Cs . The spiked specimens were dried, mixed and melted in 25 mm ID alumina crucibles for one hour at 1000 °C. Initial weight and radioactivity were obtained at this point. Volatility was determined by reinserting the crucibles into a furnace held at progressively higher temperatures and measuring weight loss and the radioactivity level after each temperature step. Thus the cesium remaining, rather than that volatilized, was actually measured. Time at each temperature varied from up to 112 hours at 800 °C to 1 hour at 1200 °C. Duplicate runs were in the range 800 to 1000 °C and the results are averaged in the table. Individual runs were made to 1100 or 1200 °C in some instances. Initial sample weights averaged about 3 grams.

No large trends due to the effects of product type, i.e. calcine, phosphate or borosilicate melt, were found. Temperature had the largest effect, as shown in Figure 5.15, where the cesium volatility from products formed from PW-4m wastes by all of the WSEP solidification processes is compared. Cesium

FIGURE 5.15. Cesium Volatility from Solidified PW-4m Wastes

volatility doubled for every 150 °C rise in temperature over the range 800 to 1200 °C.

The volatility data in Table 5.7 and Figure 5.15 are given as fraction released per hour. This fraction is dependent upon surface:volume ratio. In the laboratory tests the surface:volume ration was approximately 5. In the WSEP continuous melters the ratio was approximately 0.04 and the fractional release rate, as measured by the cesium volatilized during WSEP processing, was lower by a factor of almost 10 (see Figure 5.15). In the WSEP runs in which the melt was formed in the pots, i.e., the IPM and RLG runs, the surface:volume ratio was even lower, in the range of 0.01, and the fraction volatilized was decreased by over a factor of 10.

The cesium volatility data obtained on the WSEP products agree quite well with those obtained by Albrethson.⁽²²⁾ However, the values are significantly lower than those reported for the FINGAL glasses.⁽²³⁾ The discrepancy may be due to differences in product composition or experimental procedure. In the WSEP and some of Albrethson's studies, cesium tracer was added to powdered glass and the glass was remelted, whereas in the FINGAL studies cesium tracer was added prior to the initial melting. Further investigation of the volatility of fission products from solidified wastes would be desirable.

5.5 CORROSION

Corrosion of stainless steel (Type 304L or 310) is uniformly low in borosilicate and phosphate melts up to about 875 °C. Above this temperature corrosion by borosilicate melts increases in a regular manner with temperature; corrosion by phosphate melts, however, can become abruptly catastrophic. The different corrosive behavior of the two types of melt is illustrated by the laboratory-measured corrosion rates shown in Figure 5.16. The very rapid corrosion of stainless steel at higher temperatures in phosphate melts occurred in an unpredictable manner

FIGURE 5.16. Corrosion of Stainless Steel in Solidified Waste Melts

and is apparently due to a depassivation phenomenon that does not occur in borosilicate melts.

Because of potential corrosion, the walls of the pots receiving phosphate melts were not allowed to exceed 800 °C during WSEP processing and these high temperatures were experienced only for periods of a few minutes when the melts were batch-dumped. The average wall temperature during the overall duration of a typical 50 hour run was about 625 °C, or less if the receiver pot was not heated. The borosilicate processes required that melting of the products be done in the pots, thus pot wall temperatures were higher, averaging about 925 °C when melting was occurring in that vicinity in the pot, and about 800 °C during the remainder of the run. The pot wall corrosion which occurred during the WSEP runs was minimal as shown by ultrasonic wall thickness measurements (Table 5.8). The afterfill wall thickness measurements agreed within ± 0.02 inches with the prefill wall thickness measurements and indicate that in all cases the pot wall corrosion was less than 0.02 inches, as predicted by the laboratory data. The variations in the measurements shown in Table 5.8 reflect the precision obtainable in practice with the remotely-operated wall thickness scanning technique being utilized. ⁽¹⁹⁾

Mild steel pots were used to contain the product from two spray calciner-melter runs (SS-4 and 10) and five phosphate glass runs (PG-1, 3, 4, 5 and 8). Corrosion of the mild steel pots, as of the stainless steel pots, was minimal. Laboratory measurements indicated a slightly higher, but very acceptable, corrosion rate for mild steel at receiving temperatures, as shown in Table 5.9. At these temperatures the corrosion rate of mild steel in the phosphate melts is much less than the air oxidation rates at the same temperature, which are reported to be 0.1 and 0.3 in./yr at 600 and 700 °C, respectively. ⁽²⁴⁾

TABLE 5.8. Ultrasonic Wall Thickness Measurements on WSEP Pots

Run No.	Pot Material	Pot Dia. in.	Initial Wall Thickness, in.	Change in Wall Thickness After Fill, mils (0.001 in.)											
				3.5 in. (a)	7 in.	13.5 in.	20 in.	26.5 in.	33 in.	39.5 in.	46 in.	52.5 in.	59 in.	65.5 in.	72 in.
PC-1	304L SS	12	0.338	-18	-11	-14	-11	-6	-12	-2	0	-3	(-2) ^(b)	-5	-3
PC-2	304L SS	12	0.334	-9	-2	-10	-2	-3	0	-2	-1	-3	(-4)	-6	-5
PC-3	304L SS	8	0.310	NA	-1	0	0	+2	0	+2	+2	+4	+2	+4	(+5)
PC-4	304L SS	12	0.328	NA	-7	-2	+2	0	+3	+8	+8	+11	(+12)	+11	+8
PC-5	304L SS	8	0.320	0	+1	+1	+2	-2	-2	0	0	+3	0	(+2)	+3
PC-6	304L SS	8	0.320	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	(NA)
PC-7	304L SS	8	0.319	+6	+6	+8	+4	+8	+10	+10	+6	+7	+7	+9	(+7)
PC-8	304L SS	6	0.272	+3	+5	-1	-1	+3	+3	+1	+1	0	0	0	(+2)
PC-9	310 SS	6	0.305	-3	-3	-5	-2	-3	(-5)	-2	-2	-5	-3	-3	-3
SS-1	304L SS	12	0.331	NA	-18	-16	(-11)	-11	-4	-4	+1	0	-2	-1	-16
SS-2	304L SS	8	0.321	-4	-6	-5	-2	-5	-5	-7	-7	-7	(-2)	-5	-1
SS-3	304L SS	8	0.318	+2	-3	-4	-2	-1	+2	-2	(-2)	-3	-8	-4	-6
SS-4	mild steel	8	0.324	+18	+18	+15	+10	+10	+8	+10	+10	+7	+7	(+10)	+13
SS-5	304L SS	8	0.315	-3	-5	-1	-5	-3	-6	-3	-7	-10	-7	0	(+17)
SS-6	304L SS	8	0.324	-15	-15	-13	-16	-16	-14	-18	-17	-14	-14	-13	(-15)
SS-7	304L SS	8	0.312	-2	-8	-3	-2	-5	-4	-2	-8	-8	-4	-8	(-2)
SS-8	304L SS	8	0.323	+7	+7	+7	+9	+8	+9	+9	+11	+12	+8	+10	(+8)
SS-9	310 SS	8	0.357	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	(NA)
SS-10	mild steel	8	0.313	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	(NA)	NA
SS-11	304L SS	8	0.323	-6	-5	-4	-6	-7	-4	-7	-4	-4	+2	+2	(-6)
SS-12	304L SS	8	0.333	-4	-1	-2	-1	-1	-5	-7	-4	-10	-6	(-6)	-8
SS-13	304L SS	8	0.305	-1	-1	+1	-2	0	-3	-2	+1	+3	(-10)	0	+1
PG-1	mild steel	12	0.300	-1	+10	+3	+4	+8	+7	+6	+4	(+9)	+10	+6	+8
PG-2	304L SS	8	0.317	+1	+1	0	-5	-4	-3	-2	(-5)	-3	-2	-2	-6
PG-3	mild steel	8	0.315	-12	-5	-2	+13	NA	-8	-2	(+3)	+8	0	+3	0
PG-4	mild steel	8	0.330	-5	-23	-10	-11	-5	-3	+2	-15	-12	+5	-16	(-4)
PG-5	mild steel	12	0.295	-5	+8	+7	+5	-2	0	+3	+8	+1	(+3)	+7	+9
PG-6	304L SS	8	0.310	NA	+11	+11	+15	+13	+18	+17	+19	+20	+17	+20	(+13)
PG-7	310 SS	8	0.316	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	(NA)
PG-8	mild steel	8	0.309	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	(NA)
PG-9	304L SS	6	0.316	-10	-11	-12	-12	-14	-10	-8	-11	-9	(-11)	+3	+2
PG-10	304L SS	6	0.312	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	(NA)	NA
PG-11	304L SS	8	0.335	+8	+6	+8	+6	+4	+9	+8	+7	+2	+6	+6	(+8)

NA = Not Available

a. Height from bottom of pot. Many measurements were made around the circumference at each height.

The values shown were obtained from an average of these measurements.

b. Reading at approximate level of solidified waste within pot is shown in parentheses.

TABLE 5.9. Corrosion Rates of Storage Vessels
at Melt Receiving Temperature

Process	Melt Type	Temp., °C	Exposure Time, hr	Corrosion Rate, in./yr		
				Mild Steel	304L SS	310 SS
Spray Calciner-Melter	PW-1	600	1000	0.0035	0.00055	0.0004
Spray Calciner-Melter	PW-1	700	1000	0.007	0.002	0.002
Phosphate Glass	PW-1	600	1000	0.0019	0.0004	0.0004
Phosphate Glass	PW-1	700	1000	0.007	0.0023	0.002

After the melt has cooled upon completion of processing, the pot wall contacts only solidified melt and the potential for further corrosion at the melt-pot wall interface is greatly reduced. Long-term external corrosion then becomes a major consideration. External corrosion of the pot walls can be controlled by maintaining the wall temperature below certain limits and by controlling the environment. The environment during handling and interim storage of pots of solidified high level waste will be ambient air and, in many cases, water. The WSEP pots were exposed to both environments. The only precautions taken were to maintain the water containing mild steel pots at $0.01M \text{ Cr}_2\text{O}_7$ and the pH above 5.0. *Note*

Wall temperatures of the WSEP pots, both mild steel and stainless steel, were maintained below 425 °C in ambient air by limiting the amount of fission product heat encapsulated in the pots. (See Section 6.2.1 for further details.)

Although no significant corrosion of the WSEP pot walls has occurred, internal thermowell failures have occurred. In a nonradioactive developmental spray solidifier-melter run, using a flowsheet quite similar to that used in the WSEP to process PW-4m waste, a 1 foot long section of internal thermowell was completely dissolved after a melt-batch was dumped into the pot. ⁽²⁵⁾ The maximum pot centerline temperature ranged between 950 and 1000 °C for about an hour during this time.

When the WSEP PG-6 pot was core-drilled after 32 months of water storage it was found to contain water.⁽²⁶⁾ Both the centerline and intermediate thermowells had failed. (It was possible to pressurize the pot by applying air to the end of the thermowells.) The thermowells were made of 1/2 and 3/4-inch Schedule 80 Type 310 stainless steel (about 0.15-inch wall thickness). Five samples of the thermowells have been retrieved from the pot by core-drilling and none of these shows significant corrosion (Figure 5.17). It is concluded that accelerated corrosion occurred preferentially at an isolated spot(s) on the thermowell. The PG-6 failure mechanism is not yet fully understood. As stated above the potential for corrosion is greatest during processing. Yet in the PG-6 case the leak rate of the pot was measured to be very low, 8.3×10^{-8} to 1.5×10^{-7} atm cm²/sec, 16 months after processing. The thermowell leak apparently developed in the period 16 to 32 months after processing. The PG-7 pot has shown a somewhat similar behavior in that the pot leak checked satisfactorily 0.4 months after processing, yet a leak was found in a subsequent check 10 months after processing.

The centerline thermowell in the pot from run SS-5 was found to have a leak when the pot was leak checked after welding the cap in place. Indications are that the borosilicate glass containing pot, SS-12, also has a leaky thermowell, however more testing is required to establish this fact with certainty.

The WSEP experience has identified pot thermowells as a potential "weak" point in the waste solidification system. Unless assurance against failures of the type encountered in the WSEP runs can be designed into waste solidification processes, the use of pot thermocouples should be avoided where possible. If used, provisions should be made to seal off or remove the thermowells after the pots are filled.

Neg 715245-3

Neg 722407-6

Neg 722407-8

Neg 715686-1

FIGURE 5.17. Thermowell Samples from PG-6 Pot

5.6 LEACHABILITY

The leachability of solidified high level waste specimens is a prime concern when potential mechanisms by which radioactivity can be released to the biosphere are being considered. To determine the leaching behavior of the WSEP solidified wastes three types of samples have been leached:

1. Nonradioactive samples. Samples were cubes of approximately 30 cm^2 geometrical surface area sawed from larger specimens. These nonradioactive specimens were used to study the effects of thermal history upon product characteristics, as described in Reference 17.
2. Radioactive "grab" samples. "Grab" samples were obtained by filling small stainless steel vials, approximately 5/8 inch diameter and 1-1/2 inches long, from the stream of melt as it was being transferred from the melter to the receiving pot. The product in the "grab" sample vials cooled rapidly, thus these samples represent the most rapidly quenched samples which were leached. Wafers approximately 1/4-inch long were cut from the "grab" sample vials and the two exposed ends, having a surface area of about 4.5 cm^2 , were leached.
3. Radioactive core-drilled samples. The core-drilled samples are nominally 3/4-inch in diameter. Wafers about 1/2-inch long are cut from these for leaching. In practice many of the core-drilled samples are somewhat fragmented and more irregular-shaped samples, on which the surface area can only be estimated, have to be used for the leach tests.

The experimental apparatus being used to measure the leachability of WSEP products is similar to that described by Paige⁽²⁷⁾ and is shown in Figure 5.18. The measurements were made at ambient temperature, approximately 25 °C, using 500 ml of

FIGURE 5.18. Apparatus for Measuring Leachability of Highly Radioactive Samples

distilled water as leachant. The leach water was sampled and replaced on a weekly schedule initially, and on a monthly schedule later.

Leach rates were calculated from analysis of one or more constituents in the leach water as follows:

$$\begin{aligned} & \frac{\text{Quantity Constituent A leached/day}}{\text{Quantity Constituent A initially present}} \times \frac{\text{Sample weight}}{\text{Sample surface area}} \\ &= \frac{(\text{Fraction Constituent A leached})}{\text{day}} \times \frac{\text{Sample wt, gms}}{\text{Sample area, cm}^2} \\ &= \text{gms sample leached/cm}^2 \text{ day.} \end{aligned}$$

The leach rates calculated in this manner are directly dependent upon the relative leachability of the constituent analyzed in the leach water and will represent the actual grams of sample leached only if all constituents leach from the sample at a uniform rate. In actuality there are large variations in the relative leachability of different ions from solidified wastes. When using leach data for accident analyses, etc., the most precise results are of course obtained by using leach rates calculated from measurements of the specific ion in question, however knowledge of relative leachabilities allows some extrapolations to be made. The radioactive leach data plotted in Figures 5.19 to 5.23 are based upon analyses of ^{137}Cs in the leach water; the nonradioactive leach data shown in the same figures for comparison are based upon analyses of sodium in the leach water.

When the radioactive samples were weighed at the end of the leaching period the overall weight loss was found to be less than that calculated from the cesium-based leach data, generally by a factor of 2 to 4 (see Table 5.10). The weight loss calculated from sodium analyses usually exceeded the actual weight loss only by a factor of 1.5 to 2. Leach rates

FIGURE 5.19. Leachability of Phosphate Ceramic PW-1, PW-2 and PW-4m Products at 25 °C

FIGURE 5.20. Leachability of Phosphate Glass PW-1 Products at 25 °C

FIGURE 5.21. Leachability of Phosphate Glass PW-2 Products at 25 °C

FIGURE 5.22. Leachability of Phosphate Glass PW-4m Products at 25 °C

FIGURE 5.23. Leachability of IPM Borosilicate Glass PW-4m Product at 25 °C

of the radioactive samples based upon ^{144}Ce and, in a few cases, ^{106}Ru activity in the leach water are also shown in Table 5.10. The cerium leachability is approximately a factor of 1000 lower than the cesium leachability. The scattered ruthenium leach rate data indicate a leachability which is intermediate between that of cerium and cesium. Measurements made on nonradioactive WSEP samples indicate strontium leachability corresponds to that of sodium within a factor of 10 (Figure 5.24). In general the strontium leach rate was found to be lower than that of sodium in the borosilicate glasses but was actually higher in some of the phosphate products.

Other workers have also compared the relative leachability of ions from solidified wastes with results quite similar to this work:

TABLE 5.10. Weight Loss During Leaching of Radioactive Products

WSEP Run No.	Sample Type	Isotope Analyzed	Leach Rate, gm Samples/cm ² -day				Surface Area, cm ²	Initial Weight, gms	Weight Loss, gms			Loss Ratio	
			1 week	4 weeks	24 weeks	40 weeks			Actual	Based on Cs Data	Based on Ce Data	Cs/Total	Ce/Total
SS-6 (Phosphate Ceramic, PW-1 Waste)	Grab	¹³⁷ Cs	2.9×10^{-4}	2.0×10^{-5}	3.9×10^{-6}	2.5×10^{-6}	12.3	9.919	0.204	2.4	~0.0023	12	~0.01
		¹⁴⁴ Ce	4.5×10^{-6}	6.1×10^{-8}	5.1×10^{-9}	5.5×10^{-9}							
	Core	¹³⁷ Cs	1.5×10^{-2}	7.3×10^{-4}	2.3×10^{-4}	1.7×10^{-4}	13.1	11.115	0.108	0.94	~0.00059	9	~0.005
		¹⁴⁴ Ce	1.5×10^{-5}	6.6×10^{-7}	4.4×10^{-8}	4.4×10^{-8}							
	Core	¹³⁷ Cs	2.5×10^{-3}	2.5×10^{-4}	2.5×10^{-4}	1.3×10^{-4}							
		¹⁴⁴ Ce	4.5×10^{-7}	5.5×10^{-7}	1.6×10^{-7}	$<5 \times 10^{-8}$							
SS-10 (Phosphate Ceramic, PW-4m Waste)	Grab	¹³⁷ Cs	6.0×10^{-3}	3.2×10^{-3}	1.1×10^{-3}	4.4×10^{-4}	14.7	13.386	1.121	1.87	0.0005	1.7	0.0005
		¹⁴⁴ Ce	1.0×10^{-7}	8.1×10^{-8}	3.0×10^{-8}	2.0×10^{-8}							
	Core	¹⁰⁶ Ru	ND	4.7×10^{-6}	5.4×10^{-6}	ND							
		¹³⁷ Cs	4.0×10^{-3}	1.5×10^{-3}	6.4×10^{-4}	--							
		¹⁴⁴ Ce	1.5×10^{-6}	1.2×10^{-7}	2.8×10^{-7}	--							
		¹⁰⁶ Ru	7.3×10^{-5}	1.4×10^{-5}	$<1 \times 10^{-5}$	--							
PG-6 (Phosphate Glass, PW-1 Waste)	Grab	¹³⁷ Cs	8.9×10^{-6}	5.7×10^{-6}	5.7×10^{-6}	7.4×10^{-6}	13.6	10.379	1.624	6.6	~0.006	4.1	~0.004
		¹⁴⁴ Ce	1.1×10^{-6}	2.3×10^{-6}	1.9×10^{-6}	5.0×10^{-7}							
	Core	¹³⁷ Cs	4.7×10^{-2}	3.3×10^{-4}	4.3×10^{-4}	2.3×10^{-4}	12.0	8.570	2.476	6.3	0.023	2.5	0.009
		¹⁴⁴ Ce	3.5×10^{-5}	1.5×10^{-6}	$<5 \times 10^{-7}$	$<5 \times 10^{-7}$							
	Core	¹³⁷ Cs	5.2×10^{-2}	2.9×10^{-3}	3.0×10^{-4}	2.1×10^{-4}							
		¹⁴⁴ Ce	1.8×10^{-4}	5.8×10^{-6}	1.4×10^{-6}	1.1×10^{-6}							
PG-7 (Phosphate Glass, PW-2 Waste)	Grab	¹³⁷ Cs	NA	4.3×10^{-6}	1.4×10^{-5}	2.9×10^{-6}	13.6	10.2	1.6	4.6	0.0039	2.9	0.003
		¹⁴⁴ Ce	NA	1.4×10^{-6}	2.2×10^{-6}	1.4×10^{-6}							
	Core	¹⁰⁶ Ru	NA	4.3×10^{-6}	1.9×10^{-6}	8.1×10^{-7}							
		¹³⁷ Cs	2.4×10^{-2}	4.0×10^{-3}	5.2×10^{-4}	--							
		¹⁴⁴ Ce	5.0×10^{-5}	2.6×10^{-6}	7.0×10^{-7}	--							
		¹⁰⁶ Ru	3.3×10^{-3}	9.1×10^{-5}	3.3×10^{-5}	--							
PG-8 (Phosphate Glass, PW-4m Waste)	Grab	¹³⁷ Cs	2.2×10^{-3}	7.2×10^{-4}	2.0×10^{-4}	--	14.4	11.141	0.44	0.88	0.0069	2.0	0.02
		¹⁴⁴ Ce	2.7×10^{-5}	6.0×10^{-6}	3.2×10^{-6}	--							
	Core	¹⁰⁶ Ru	2.9×10^{-3}	7.2×10^{-4}	1.3×10^{-4}	--							
		¹³⁷ Cs	8.6×10^{-5}	1.5×10^{-6}	4.8×10^{-7}	7.3×10^{-6}							
		¹⁴⁴ Ce	1.5×10^{-6}	4.8×10^{-7}	2.0×10^{-7}	2.0×10^{-7}							
		¹³⁷ Cs	2.4×10^{-5}	5.4×10^{-6}	4.8×10^{-7}	2.0×10^{-7}	5.1	1.989	Test in Progress				
PG-10 (Phosphate Glass, PW-4m Waste)	Grab	¹³⁷ Cs	6.8×10^{-7}	6.1×10^{-7}	4.8×10^{-7}	2.0×10^{-7}	7.6	6.141	Test in Progress				
		¹⁴⁴ Ce	3.1×10^{-5}	4.2×10^{-6}	1.3×10^{-5}	4.4×10^{-7}							
	Core	¹³⁷ Cs	1.6×10^{-3}	1.3×10^{-3}	5.1×10^{-4}	4.1×10^{-4}	11.0	6.935	0.440	2.0	0.0047	4.5	0.01
		¹⁴⁴ Ce	1.8×10^{-5}	2.6×10^{-6}	5.6×10^{-7}	2.9×10^{-7}							
		¹³⁷ Cs	2.7×10^{-3}	5.1×10^{-3}	6.6×10^{-4}	4.1×10^{-4}							
		¹⁴⁴ Ce	1.5×10^{-5}	1.0×10^{-6}	5.1×10^{-7}	5.7×10^{-7}							
PC-9 (RLG Borosilicate Glass, PW-4m Waste)	Grab	¹³⁷ Cs	4.7×10^{-4}	3.0×10^{-4}	1.0×10^{-4}	8.4×10^{-5}	5.7	5.613	0.064	0.29	~0.000014	4.5	~0.0002
		¹⁴⁴ Ce	1.6×10^{-8}	1.0×10^{-8}	ND	ND							
	Core	¹³⁷ Cs	2.0×10^{-4}	1.6×10^{-4}	6.5×10^{-5}	6.7×10^{-5}	5.2	3.107	0.055	0.13	0.000014	2.4	0.0003
		¹⁴⁴ Ce	2.5×10^{-8}	1.4×10^{-8}	$<5 \times 10^{-9}$	5.8×10^{-9}							
	Core	¹³⁷ Cs	6.6×10^{-5}	3.7×10^{-5}	1.5×10^{-5}	7.4×10^{-6}	23	14.456	0.054	0.11	0.0001	2.0	0.002
		¹⁴⁴ Ce	4.5×10^{-8}	4.0×10^{-8}	ND	8.6×10^{-9}							
SS-12 IPM Borosilicate Glass, PW-4m Waste)	Core	¹³⁷ Cs	4.4×10^{-5}	3.1×10^{-5}	9.5×10^{-6}	1.2×10^{-5}	17	9.137	0.047	0.08	0.00006	1.7	0.001
		¹⁴⁴ Ce	1.4×10^{-8}	9.0×10^{-9}	1.2×10^{-8}	1.1×10^{-8}							

ND Not Determined

FIGURE 5.24. Comparison of Leachability of Sodium and Strontium in WSEP Solidified Waste Products

<u>Order of Leachability</u>	<u>Reference</u>
Cs > Na, Sr > Ru > Ce	This Work
Cs > Al > Pb, Sr, Ce	27
Cs, Sr > Na > Zr-Nb > Ru, Ce	28
Na > S: > B > Cs > Sr > Ce > Tb	29
Cs, Sr > Ru, Ce, Al (from a calcine)	30

Generally cations of low valence tend to be less tightly bound and are able to diffuse through a stable skeletal matrix in which the higher valence cations are tightly bound. By chemical analogy to cerium, it is probable that plutonium is bound in the matrix or skeletal network of solidified wastes, and is therefore comparatively nonleachable. No measurements of plutonium leachability have been made, however.

The long-lived fission products of interest, ^{137}Cs and ^{90}Sr , belong to the more leachable group of ions which can diffuse to the surface of the solid for release to the leachant. They tend to exhibit a leach rate which decreases with time, as the diffusion paths through the less soluble constituents become progressively longer. The leaching of silicate glasser can often be described by the expression,

$$Q = at^{1/2} + bt$$

where Q is the quantity extracted in time t , and a and b are empirical constants.^(31,32) The leaching of some of the WSEP phosphate glasses and ceramics was also found to be described by this expression. The expression indicates that, as leaching is continued, a gradual transition occurs from a diffusion-controlled process to a linear process. WSEP findings indicated that very long leaching periods (years) would probably be required in most cases to adequately define the constant, b .

5.6.2 Leach Rates of Coherent WSEP Products

The curves describing the leachability of the WSEP products (Figures 5.19 through 5.23) are smoothed curves representing the best fit of a large amount of data.

Phosphate Ceramic (Figure 5.19). The phosphate ceramic products are relatively leachable, particularly during the first few weeks of leaching. Initial leach rates can exceed 1×10^{-2} gm/cm²-day but decrease within 4 to 8 weeks to approximately 1×10^{-3} gm/cm²-day. The phosphate ceramic formulation used to process PW-1 wastes was the most leach resistant, reaching a leach rate below 1×10^{-4} gm/cm²-day in about 4 months.

The leachability of the radioactive phosphate ceramic products was consistently higher than that of nonradioactive products, sometimes by a factor of 10 or more. In the other solidified waste forms the radioactive products were generally more leachable than the nonradioactive products, but the difference in leachability was less marked.

Phosphate Glass (Figures 5.20, 5.21 and 5.22). The principal feature in the leachability characteristics of the phosphate glasses is the large increase in leachability which occurs when the glasses devitrify. The leach rate of the WSEP phosphate glasses in the vitreous state was between 1×10^{-5} and 1×10^{-6} gm/cm²-day. In contrast to the phosphate ceramic products the leach curves for the vitreous phosphate glasses did not show a large variation as a function of time. After devitrification, however, the leachability characteristics of the phosphate glasses were very similar to the phosphate ceramics. The initial leachability of the devitrified glasses exceeded 1×10^{-2} gm/cm²-day but decreased within a few weeks to values between 1×10^{-3} and 1×10^{-4} gm/cm²-day.

As described previously, most of the radioactive core drilled samples of phosphate glass have been found to be completely

devitrified. Their leachability characteristics resemble those of nonradioactive phosphate glasses which have been devitrified by a thermal treatment at 600 °C for 8 weeks.

Borosilicate Glass (Figure 5.23). The leachability of the radioactive WSEP borosilicate glasses corresponded very closely to that of nonradioactive glasses of the same chemical composition. Leach rates for the most nonleachable of the two WSEP borosilicate glasses, the IPM product, were about 5×10^{-5} gm/cm²-day initially and decreased to 9×10^{-6} gm/cm²-day in about 8 months. Leach rates of the other WSEP borosilicate glass, the RLG product, were a factor of 8 to 10 higher.

The leach rates of the WSEP borosilicate products are somewhat higher than those which have been reported for some other borosilicate glasses being used as a media for radioactive waste encapsulation. This is because the WSEP processing techniques required a low melting point (below 900 °C), hence the formulations contain more B₂O₃ than is desirable from the standpoint of achieving an optimum low leachability.

5.6.3 Leach Rates of Calcine Product

One pot of radioactive calcine product has been sampled by core drilling the wall and pushing in a sharpened tube in an attempt to remove a plug of calcine. Coherent plugs were not obtained because the caked calcine crumbled into fragments (Figure 5.1).

Leach data on the radioactive calcine product were obtained in a modified Paige apparatus wherein the sample was supported on fritted glass and leach water was circulated upward over the sample by an airlift recirculator. Representative seven gram samples, taken from two elevations in the pot, were leached and the results, expressed as cumulative percent leached, are shown in Table 5.11.

TABLE 5.11. Leachability of Radioactive WSEP
Pot Calcine Product at 25 °C

Elapsed Time	Cumulative Percent Leached			
	Sample 46 inches from Pot Bottom		Sample 13.5 inches from Pot Bottom	
	<u>137Cs</u>	<u>144Ce</u>	<u>137Cs</u>	<u>144Ce</u>
1 day	17.7	0.005	24.7	0.015
2 days	21.3	0.011	27.2	0.027
3 days	21.8	0.0126	27.6	0.036
1.5 weeks	22.0	0.0147	27.7	0.042
2.5 weeks	22.1	0.0157	27.8	0.0434
3.5 weeks	22.13	0.0159	27.84	0.0437
7.5 weeks	22.22	0.0160	27.89	0.0439

About 1/4 of the cesium present in the calcine was readily leached; the remainder was relatively nonleachable. Somewhat similar results were obtained in studies on radioactive zirconia calcine produced by fluidized bed calcination in the Idaho Waste Calcining Facility.^(33,34) Higher calcining temperatures apparently reduce the proportion of readily leachable cesium in the calcine. In the Idaho WCF studies it was found that about 60 percent of the cesium in calcine processed in the standard manner (operating temperature = 400 to 600 °C) was readily leached,⁽³³⁾ whereas only a little over 20 percent of the cesium in calcine heat-treated at 1200 °C was readily leachable.⁽³⁴⁾ Maximum operating temperature of the pot calcination process was 900 °C and about 25 percent of the cesium was readily leachable.

Cerium was approximately a thousand-fold less leachable from the calcine than was cesium. This difference is of the same order of magnitude as that observed in the coherent solid products.

5.7 RADIATION EFFECTS

Cumulative radiation doses to the WSEP products have been calculated to be in the range of 1×10^{11} to 1×10^{12} R to date. The quantity of radiation generated in the WSEP products during the first few years will be quite similar to that generated in typical solidified power reactor high level wastes during a similar time period (Figure 4.1). Areas of concern are the effect that the intense radioactive bombardment may have upon the physical strength of initially coherent solidified wastes and the possibility of storing radiation energy in the waste solids.

5.7.1 Dispersibility Tests

Changes in physical structure of the WSEP products are being evaluated by a dispersibility test. The empirical test, which is described in detail in Reference 19, involves breaking a standard sized sample by impacting with a 2.9 pound weight which is dropped 5 feet and measuring the size distribution of the fragments. In general the rock-like phosphate ceramics break into fewer and larger fragments than glass samples. Devitrified phosphate glass behaves similarly to phosphate ceramic. The results of dispersibility tests performed on highly radioactive WSEP pot samples and nonradioactive samples with similar chemical composition are given in Table 5.12. Good correspondence was obtained between the radioactive and nonradioactive samples indicating that radiation has not greatly changed the physical structure of the phosphate-based solidified wastes. Such comparisons have not been possible with the borosilicate glasses. As described earlier, the radioactive borosilicate glasses have not devitrified and it has not been possible to obtain core drill samples of these products of sufficient size to make a standard dispersibility test.

TABLE 5.12. Solidified Waste Product Dispersibility,^(a)
Comparison of Radioactive and Nonradioactive
Products

Solidified Product Type	Waste Type	Specimen	Crushed Sample Particle Size Distribution, wt%		
			>0.1 inch	0.02-0.1 inch	>0.02 inch
Phosphate Ceramic	PW-1	SS-6 Core drill	70.0	20.0	10.0
	PW-1	Nonradioactive, 100 °C storage	86.4	7.9	5.7
	PW-1	Nonradioactive, 600 °C storage	95.7	2.6	1.7
	PW-2	SS-4 Core drill	61.0	21.0	18.0
	PW-2	Nonradioactive, 100 °C storage	64.0	24.5	11.5
	PW-4m	SS-10 Core drill	98.4	0.8	0.8
	PW-4m	Nonradioactive, 100 °C storage	78.7	11.0	10.3
	PW-4m	Nonradioactive, 600 °C storage	70.4	20.1	9.4
Phosphate Glass	PW-1	PG-6 Core drill ^(b)	95.7	1.1	3.2
	PW-1	PG-6 Core drill ^(b)	91.0	6.7	2.3
	PW-1	Nonradioactive, 100 °C storage	34.6	41.1	24.6
	PW-1	Nonradioactive, 600 °C storage ^(b)	91.7	5.1	3.2
	PW-2	PG-7 Core drill ^(b)	90.9	5.4	3.6
	PW-2	PG-7 Core drill ^(b)	95.2	2.3	1.2
	PW-2	PG-7 Core drill ^(b)	93.2	4.2	1.4
	PW-2	Nonradioactive, 100 °C storage	46.8	36.2	16.9
	PW-2	Nonradioactive, 600 °C storage ^(b)	97.4	1.5	1.1
	PW-4m	PG-10 Core drill ^(b)	92.5	5.3	2.1
	PW-4m	Nonradioactive, 100 °C storage	58.8	28.6	12.6
	PW-4m	Nonradioactive, 600 °C storage ^(b)	94.6	3.7	1.7

TABLE 5.12. (Contd)

Solidified Product Type	Waste Type	Specimen	Crushed Sample Particle Size Distribution, wt%		
			>0.1 inch	0.02-0.1 inch	>0.02 inch
Borosilicate Glass (RLG) ↓	PW-4m	Nonradioactive, 100 °C storage	56.2	30.8	13.0
	PW-4m	Nonradioactive, 600 °C storage	44.7	37.5	17.8
Borosilicate Glass (IPM) ↓	PW-4m	Nonradioactive, 100 °C storage	56.2	31.1	12.7
	PW-4m	Nonradioactive, 600 °C storage	53.3	33.6	13.1

- a. Test procedure described on Page 5.55.
- b. These phosphate glass samples were completely devitrified.

5.7.2 Stored Energy

Energy storage, due to irradiation-formed lattice defects, occurs in many materials and is potentially possible in solidified radioactive waste. Analyses performed at ORNL indicate the phenomenon will present no serious problems at the salt mine repository.⁽¹⁸⁾ The analyses were based on theory and correlations with other materials; no data on solidified waste were available so a maximum saturation value of 200 cal/g was assumed. Additional work is required to establish upper-limit values for energy storage in actual solidified wastes, and the conditions under which it can be released.

Some stored energy measurements have been made on nonradioactive solidified wastes of the following WSEP types:

<u>Waste Type</u>	<u>Solidified Form</u>
PW-1	Phosphate Glass
PW-2	Phosphate Glass
PW-2	Phosphate Ceramic
PW-4m	Phosphate Glass
PW-4m	Phosphate Ceramic
PW-4m	Borosilicate (IPM and RLG)

Stored energy measurements were made with a differential scanning calorimeter after the solidified waste samples had been irradiated with a ^{60}Co source to doses of 1×10^9 R, 5×10^9 R and 1×10^{10} R at 50 °C. No detectable energy was released when the samples were heated to 500 °C. In contrast, NaCl irradiated to 5×10^9 R under the same conditions, released 12 cal/g of stored energy when heated.

The total irradiation achieved in these tests was much lower than will be received by actual solidified wastes. Only gamma radiation was used, which is much less effective in producing the lattice defects which cause stored energy than is the beta and alpha particle and neutron radiation to which the actual solidified wastes will also be subjected. Further stored energy tests are planned, utilizing first core-drilled radioactive samples of WSEP solidified wastes and perhaps ultimately whole pots of radioactive waste.

6.0 HANDLING AND STORAGE
OF FILLED POTS

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6.0 HANDLING AND STORAGE OF FILLED POTS

All of the WSEP pots, including several containing sufficient radioactive decay heat to produce a centerline temperature of 800 to 900 °C when the pots were hanging in air (see Table 3.1 for centerline temperatures), have now been safely handled through several transfer operations without mishap. Handling operations included those involved in the afterfill measurements (page 3.2), cap welding, inter-cell transfer, and a core-drilling. Some of the operations were done only to obtain experimental data, e.g. temperature monitoring to measure effective thermal conductivity and core-drilling to obtain samples of the solidified wastes for study, but most of the operations were prototypical of those which will be done routinely in a commercial waste solidification facility. Not

6.1 OPERATIONS ON FILLED SOLIDIFIED WASTE POTS

The criteria governing acceptance of pots of solidified waste by the Federal repository for ultimate disposal have not been established but will probably include:

- Dimensional limits
- Specifications for contained radionuclide heat generation
- Pot wall thickness limits
- Specifications for tightness of pot seal
- Specifications for verification of product dryness and lack of pressurization
- Surface contamination limits.

The regulations in force require that the pots be sealed before shipment to the repository.⁽⁶⁾ The WSEP pots are being used to obtain practical experience in the handling required to seal the pots and collect the above information.

6.1.1 Pot Dimensions

Remote in-cell measurements were made on each WSEP pot at completion of the processing cycle to determine if any pot deformation (swelling, bowing or warping) had occurred. The measurements were made with straight edge rulers and calipers. Within the accuracy of the measurements ($\pm 1/4$ inch), no deformation of any of the pots was detected.

6.1.2 Pot Calorimetry

The heat generation rate in each pot must be known to assure that the limits of the heat removal capabilities of the various storage facilities, shipping casks, and ultimate disposal site are not exceeded. A flowing water calorimeter, described in References 8 and 9, was used to obtain the heat generation rate in the WSEP pots. (This is the "total heat rate", shown in Table 3.1, which ranged up to 12.7 kW/pot). Calorimetry of a pot required about 4 hours. It should be noted that measurement of the pot wall temperature while hanging in air indirectly provided an approximation of the heat generation rate in each pot.

6.1.3 Wall Thickness Measurements

Maintenance of the integrity of the pots containing solidified waste until ultimate disposal is a major premise of the high level waste disposal program. Assurance that pot integrity has not been jeopardized by corrosion must be obtained by non-destructive means such as the ultrasonic wall thickness measurements made on the WSEP pots. Ultrasonic wall thickness scanning of a WSEP pot typically required about 3 hours to obtain approximately 50 measurements. The results obtained were described in Section 5.5.

6.1.4 Pot Welding

Remote welding of pot caps on the WSEP pots was successfully accomplished using press-in pot caps with a raised weld

joint, a pot rotating turntable and an automatic tungsten inert gas (TIG) welding torch mounted on a self-centering jig in the top center of the pot. (Design details of the caps of the pots are described in Appendix A.)

Remote welding first required chucking the pot in the turntable and cleaning the pot lip with a damp swab. The pot cap with a raised step weld joint was pressed in place and a plug (with a 2-inch conoseal flange for test purposes) was then threaded into the center of the pot cap. The pot head runout* was checked by a dial indicator. The arc-head and torch were then positioned above the pot head using a self-centering jig. A weld test specimen was placed under the torch. Welding parameters were selected and set on the remote console, and a test weld was made to verify system operability. (This operability test was required because normally only one pot was welded per month.) The torch was positioned over the weld joint at an angle of about 30 degrees to vertical, and the automatic weld cycle was started. Welding arc and weld puddle were continuously monitored through a spotting scope, and minor adjustments were made in torch position, as required, by operator control with a manipulator.

The pot cap and pot plug welds were inspected visually for cracks or other flaws. A helium leak check was then made using a mass spectrometer leak tester. Leak rates in the range of 10^{-7} atm-cm³/sec demonstrated successful welds.

Lids were welded on 33 WSEP pots and only two unacceptable welds were encountered. These were due to welding equipment failures, such as loss of argon flow. These welds were ground down and free hand repaired using 308 stainless steel filler rod.

With a 1/8 inch diameter electrode (2 percent thoriated tungsten) and an argon flow rate of 20 SCFH, weld parameters

* Runout is the deviation from perfect form of a circle, detected by full rotation of the part on a datum axis.

were generally: 180 amps, 12 volts and a weld speed of 4.6 in./min. Lids were approximately 4 and 8 inches in diameter. Typically cap-welding of a WSEP pot, including set-up at the welding station, has been done in 4 hours.

This same technique (only with a rotating torch, instead of rotating the item being welded) has been used to remotely weld 1-1/8 inch diameter plugs into WSEP pots, and is being developed for plugging 1/2 and 3/4 inch thermowell pipe ends and plugging the 2-inch conoseal flange on top of the pots. An experienced manipulator operator can also do some free hand welding of short sections using the raised step weld joint. The size of the raised metal in the step weld joint has been varied from about 0.06 x 0.06 inches for the 1-1/4 inch plugs to about 0.15 x 0.15 inches for most of the other lids and plugs used in the WSEP.

6.1.5 Leak Testing

After welding the pots were leak tested using a helium-traced mass spectrometer leak tester.⁽⁹⁾ The technique is quite time consuming but achieves the detection and location of very small leaks; it also serves as a convenient method to certify "dryness" of the solidified product, which is a criterion which has been established for the solidified high level wastes prepared in the United States.⁽⁶⁾ Water present would interfere with obtaining the required high vacuum and would show up in the cold trap.

Use of the helium-traced mass spectrometer leak tester requires that the pots be pumped down to an extremely low pressure (0.2 microns or less) which typically requires 3 hours for ceramic or glass-containing WSEP pots. However, experience has shown that vacuum leak checking is one of the most time-consuming operations being done on the WSEP pots due to the difficulty of maintaining a leak-free system. The difficulties are

*Leak rate
10⁻⁹, 10⁻⁸ atm cc/sec*

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increased because part of the system is in-cell and must be maintained remotely.

The results of typical leak checks performed on the WSEP pots are shown in Table 6.1. It has not proven practical to vacuum leak check the pots containing the oxide calcine formed by the pot calcination process due to excessive off-gasing. Several of these pots were vacuum-pumped for over 48 hours and pressures lower than about 120 microns were not achieved.

6.1.6 Pot Decontamination

Very shortly after filling, waste pots will be sealed shut and then stored in an interim storage location--most likely under water. It will be desirable but probably not practical, to prevent the pots from becoming excessively contaminated so that decontamination will be simplified and the interim storage location can be maintained as contamination free as possible. The pot handling and welding station should be isolated from the solidification equipment.

Pots that are highly oxidized may be the most difficult to decontaminate. Thus stainless steel exposed to greater than 800 °C or mild steel exposed to greater than about 600 °C for several hours may have an oxide scale that contains embedded radioactive particles but that may later flake off. Most scale on the WSEP pots appears to be strongly attached so that flaking may not be a problem.

Removal of loose contamination can be predominantly accomplished by steam cleaning. Two oxidized WSEP waste pots, one stainless and one mild steel, exposed to highly contaminated cell conditions were cleaned by steam cleaning. Smears of a 100 cm² surface area were reduced in radioactivity from approximately 5 R/hr (at 6 inches) to about 30 mrad/hr (80,000 counts/min) with less than 1 mrad/hr of gamma activity after steaming for

TABLE 6.1. Summary of Leak Test Results on WSEP Pots

Run No.	Leak Rate, atm cm ³ /sec	Run No.	Leak Rate, atm cm ³ /sec
PC-1	Pot not leak checked (a)	SS-9	2.1×10^{-7}
PC-2	"	SS-10	5.4×10^{-7}
PC-3	"	SS-11	1.7×10^{-7}
PC-4	"	SS-12	8.0×10^{-7}
PC-5	"	SS-13	4.1×10^{-7}
PC-6	5×10^{-8} (b)	PG-1	1.2×10^{-8}
PC-7	Pot not leak checked	PG-2	2.4×10^{-8}
PC-8	"	PG-3	4.6×10^{-8}
PC-9	NA	PG-4	NA
SS-1	NA	PG-5	NA
SS-2	NA	PG-6	1.5×10^{-7}
SS-3	NA	PG-7	4.1×10^{-7}
SS-4	5.1×10^{-8}	PG-8	5.4×10^{-7}
SS-5	(c)	PG-9	2.6×10^{-7}
SS-6	2.5×10^{-7}	PG-10	7.0×10^{-7}
SS-7	NA	PG-11	3.8×10^{-7}
SS-8	5.3×10^{-7}		

- a. Excessive and prolonged outgassing occurred under vacuum.
b. Vacuum pumping for approximately 3 weeks was required to reduce off-gassing sufficiently for leak check.
c. Attempt to leak check revealed leak in thermowell.

about 1 min/ft² of pot surface area. A jet type water-steam cleaner should produce better results than steam alone.⁽³⁵⁾

Complete removal of the pot oxide scale would be more difficult and may require soaking of the pots. However, soaking is considerably less efficient than jet type cleaning (larger solution volumes required and blast action on the surface is not possible).⁽³⁵⁾ Nonradioactive laboratory tests have shown that a solution of 80 g/liter of ammonium citrate (at 90 °C) will effectively remove the oxide scale from mild steel and leave the surface unsmearable, however the required soak time is several hours. In similar tests with stainless steel, 0.1M KMnO₄ in 1.3M NaOH followed by 0.1M HF-0.5M HNO₃ gave good results. A 10 minute soak at 90 °C in each solution, with a water rinse in between, removed nearly all of the oxide scale. Use of fluoride increases the waste disposal problems.

Some surface contamination is inevitable. This can be countered during interim water storage by continuously recirculating the water through ion exchangers. During interim air storage, the storage cell air will be filtered before discharge to the stack.

6.2 STORAGE OF SOLIDIFIED WASTE POTS

The WSEP pots ranged from 6 to 12-inches in diameter. The diameter restriction was imposed by problems of heat removal. The size of the pots and the amounts of radioactive waste which can be placed in them depend on: (1) bulk density and heat generating rate of the waste, (2) thermal conductivity of the waste, (3) temperature limits imposed by safety considerations, (4) pot design, and (5) heat dissipation properties of the pot storage media. The first two items are properties inherent to a given waste composition and were discussed in Sections 4 and 5. The latter items are discussed in the following sections.

6.2.1 Temperature Limits Imposed by Safety Considerations, WSEP Criteria

The radioactive decay heat generation rate allowed in any WSEP pot was limited so that none of the following criteria were exceeded:

1. A maximum centerline temperature of 900 °C for all products except the sulfate-containing spray calciner-melter product, for which the maximum was placed at 700 °C. (The centerline temperature restriction assured that product temperatures in the sealed pots did not exceed temperatures to which the product had already been exposed during processing, thus the possibility of volatilization of any components was minimized. A more stringent restriction was applied to the sulfate-containing melt because some SO₃ volatilization occurred at processing temperatures. The centerline temperature restriction was also imposed to minimize corrosion of the thermowells in the WSEP pots. Additionally, as discussed in Section 5.0, the restriction was required in some cases to prevent excessive phase segregation.)
2. A maximum temperature at the pot wall of 425 °C. (This restriction was imposed to limit oxidative corrosion of the external pot surfaces and to allow normal handling.)
3. A thickness of the solidified waste in contact with the pot wall of no less than half the radius of the pot if a partially molten core existed in the waste. (This restriction was imposed to protect the pots from internal corrosion.)

The WSEP program was designed to produce a sequence of pots by each solidification process containing gradually increasing quantities of decay heat until one or more of these criteria was approached when the pots were hanging in air. (See Table 3.1.) The maximum heat-rate values achieved in the WSEP solidified wastes were:

	W/liter	
	<u>6-inch Pot</u>	<u>8-inch Pot</u>
Oxide Calcine	141	93
Phosphate Ceramic	--	204
Phosphate Glass	317	198
Borosilicate Glass	310	200

Generally the 900 °C centerline criterion was limiting for the ceramic product while the molten core criterion was limiting for the low-melting glassy products. At 93 W/liter the centerline temperature of the 8-inch pot calcine pot was 1012 °C in air, well in excess of the WSEP criteria. Although this pot was handled successfully, the basic concept of maintaining the storage temperature below the processing temperature seems prudent until further information is available.

The WSEP criteria were designed to assure safe containment of calcine and melt-formed solidified wastes in the pots. Considerations of maintaining optimized solidified waste properties within the pots could make more restrictive limits desirable. For instance, centerline temperature limits which were 300 to 400 °C lower would have had to be imposed to prevent devitrification of the WSEP solidified wastes which were incorporated in glasses. This condition can be attained readily without severely restricting the heat rate density if the pots are water cooled, either during or immediately after filling.

6.2.2 Effect of Pot Design on Heat Dissipation

The WSEP pots were simple right cylinders and are representative of the most economical pot to construct. Studies have indicated that alternative designs can greatly increase the quantities of radioactive heat which can be contained in a given diameter pot without exceeding any of the criteria given in Section 6.2.1. In many instances it is possible that the advantages accruing from the dissipation of additional fission product heat may outweigh the additional costs of the more complicated pot designs.

Heat removal aspects of several alternative designs of containers for solid radioactive waste are described in Reference 16. For maximizing the heat removal from a single container, containers with multiple internal cooling ports are the most effective, with improvements up to a factor of 10 possible with no change in outer pot diameter. Heat removal from annular containers can be increased by factors greater than three times that for simple cylinders at constant cylinder diameter. For pots with internal fins, layered waste-metal systems, or mixed waste-metal systems, increased heat removal from a pot by factors of about two are possible in the ranges of practical conditions.

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7.0 APPENDIX A

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DESCRIPTION OF WSEP POTS

The pots for the WSEP solidified wastes were 8 feet long with diameters of 6, 8, or 12 inches, and were constructed of Type 304L or 310 stainless steel or mild steel. The pots were of a common design except for some relatively minor differences associated with the fill heads and thermowell configurations (Figures 7.1 and 7.2). The pot fill heads were designed to be clamped (pot calcination and RLG processes) or pressed against (spray calcination and phosphate glass processes) a fill head assembly during processing. Details of the coupling to the fill head assemblies may be found in Reference 8.

After processing, the pots were uncoupled and lids were placed on the pots. The lids for the pot calcination and RLG process pots were designed so that crane hooks could be attached. All lifting and moving of these pots was done with the lids, so the lids were screwed in place. Two types of lid were used, the first was a simple closure type for use during initial in-cell handling after processing. The second, illustrated in Figure 7.1, contained a flange for the connection of monitoring equipment and was welded in place. Subsequent pot handling utilized a bail attached above the Conoseal connection.

Handling of the spray solidifier and phosphate glass pots was done by means of two large ears welded on the sides of the pots, therefore the lids were not threaded. The lids and the ID at the tops of the pots were machined to close tolerances and essentially a press fit was obtained by cooling the lids in liquid nitrogen before they were set in the tops of the pots.

Each WSEP pot contained thermocouples attached to the surface of the pot and inserted in two thermowells, one located along the centerline of the pot, the other intermediate between

FIGURE 7.1. Pot Calciner and RLG Process Pot Description

FIGURE 7.2. Spray Solidifier and Phosphate Glass Pot Description

the centerline and the wall. Thermocouples were located in the thermowells and on the pot walls at mid-points of each zone of the six-zoned pot furnaces used in processing (Figures 7.1 and 7.2). The thermocouples were used during processing and remained in the filled pots to be used for monitoring temperatures in the highly radioactive pots. Thermocouple failure has been a frequent occurrence in the WSEP program. At this time more than half of the original thermocouples have failed. Most of the failures are associated with the thermocouple connectors at the top of the pots rather than the actual thermocouples.

Two configurations were used for the centerline thermowells. In the pots used for pot calcination and RLG processing the thermowell extended to the centerline immediately at the top of the pot. The centerline thermowell was actually a processing aid in the RLG process where increased rates were achieved by directing the incoming feed solution onto the thermowell to give film flow down the thermowell and more efficient heat transfer into the feed solution. On the other hand the centerline thermowell in the spray solidifier and phosphate glass pots was not extended to the centerline until approximately halfway down the pot. This was done to prevent incoming melt from solidifying on the relatively cold thermowell at the top of the pot and blocking access to the remainder of the pot.

8.0 ACKNOWLEDGMENTS

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This report represents the collected effort of many people, too many to be individually acknowledged. Everyone who participated in the successful WSEP demonstrations contributed. However, the authors do wish to especially acknowledge the excellent contributions of the individuals who have been directly involved in the WSEP product evaluation effort, R. J. Thompson, F. P. Roberts, E. O. Badgett, C. E. Bigelow, C. E. Saari, L. H. Williams, H. H. Irby, Sr., W. K. Winegardner, and J. H. Kleinpeter.

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