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Pacific Northwest Laboratories
Richland, Washington 99352

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AEC Research and Development Report

QUARTERLY PROGRESS REPORT
RESEARCH AND DEVELOPMENT
ACTIVITIES
WASTE FIXATION PROGRAM
JULY THROUGH NOVEMBER, 1972

DECEMBER 1972

BNWL-1699

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Waste Disposal
and Processing

QUARTERLY PROGRESS REPORT
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WASTE FIXATION PROGRAM
July through November, 1972

Compiled by
A. M. Platt
Nuclear Waste Technology Department

December 1972

BATTELLE
PACIFIC NORTHWEST LABORATORIES
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	<u>1972</u>	
*		HEDL-TME-72-3
*		HEDL-TME-72-6

* Waste program results were reported in Hanford Engineering Development Laboratory Monthly Technical Progress Reports during this period. These reports have a limited distribution.

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QUARTERLY PROGRESS REPORT
RESEARCH AND DEVELOPMENT ACTIVITIES
WASTE FIXATION PROGRAM

July through November, 1972

INTRODUCTION

This progress report reinitiates and is the fiftieth in a series that presents research and development activities in the field of radioactive wastes. Reports covering the period April 1970 to July 1972 are not included in this series.*

SUMMARY

The Waste Fixation Program (WFP), initiated by the United States Atomic Energy Commission, has the primary objective of providing technology to assure that suitable processes and solidified waste forms are available for fixation of high-level radioactive waste to permit their safe interim and long-term storage and their final disposal.

Two waste compositions have been selected for study during the WFP. A low-salt, or "clean" waste, designated PW-4b, represents a waste from a fuel reprocessing plant wherein no chemical salts are added during processing. A high-salt or "dirty" waste, designated PW-6, represents a waste which is modestly high in chemical salts which are added during processing.

Preliminary tests indicate up to 35 wt% PW-6, as oxide, can be incorporated in homogeneous borosilicate glasses which have low leach rates and low viscosities and which are

* See previous quarterly report list in the front of this report.

relatively noncorrosive to high chromium-high nickel alloys. Up to about 20 wt% PW-4b, as oxide, has been incorporated in a lead silicate glass which is even more leach resistant.

In corrosion tests to select a metal for a melter material, 10 commercial alloys corroded at rates of ≤ 10 mils/month during 425 hours in a selected PW-6 borosilicate melt held at 1150 °C.

The solidification facility that contained the WSEP equipment is being reactivated for WFP radioactive demonstrations. Manipulators have been reinstalled and work is in progress to clean out unusable material from the cell and to reconnect and recondition the remaining solidification equipment and auxiliaries.

Of the five WSEP phosphate glass pots that have been core drilled, three were found to be almost completely devitrified while two were only partially devitrified. When devitrification of phosphate glass occurs, the leachability of cesium increases by a factor of approximately 10^3 but the leachability of cerium increases by only a factor of approximately 10.

WASTE FIXATION PROGRAM

J. L. McElroy

The Waste Fixation Program (WFP) is being initiated by the United States Atomic Energy Commission's Division of Waste Management and Transportation. The primary objective of the program is to provide technology to assure that suitable processes and solidified waste forms are available for fixation of high-level radioactive wastes to permit their safe interim and long-term storage and their final disposal.

BACKGROUND

The previous Waste Solidification Demonstration Program associated with the Waste Solidification Engineering Prototypes (WSEP) was terminated in July 1971 after radioactive demonstrations were completed with the pot, spray, and phosphate glass solidification processes.

Following the completion of the WSEP demonstrations the solidification facility (B-cell in 324 Building) was placed in a safe-standby condition. The 33 pots of solidified waste from WSEP were stored in A-cell of the 324 Building where 10 selected pots were placed in the Solids Storage Engineering Test Facility (SSETF) environmental waste pot storage pods. During the ensuing year, work was continued to evaluate the WSEP radioactive waste products in the SSETF and to prepare two formal reports (WSEP Volumes 10 and 11)* summarizing the findings from the WSEP program.

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

J. L. McElroy, K. J. Schneider, J. N. Hartley, J. E. Mendel, G. L. Richardson, R. W. McKee, and A. G. Blasewitz, Waste Solidification Program Summary Report, Volume 11, Evaluation of WSEP High-Level Waste Solidification Processes, BNWL-1667, Battelle-Northwest, July 1972.

During the WSEP program the national high-level waste disposal plan was to convert the aqueous wastes to solids and store the solids for up to 10 years before delivery to a federal salt mine repository. At the salt mine the product was to be disposed of permanently. The container needed only survive an additional 90 days after which the salt would become the permanent container. There were no specific criteria for the type of solids other than requiring a dry, stable solid.

Recently, it has become evident that the product may be stored for as long as 100 years in engineered storage systems before permanent disposal. For such storage, an improved product form is believed desirable. There is also greater interest in establishing improved solid product forms to further minimize the possibility for dispersal to the environment during interim storage, shipping, engineered storage, and disposal. Improved product forms are the primary basis for establishing the Waste Fixation Program.] At present the most favored form of solidified high-level waste is a silicate glass.

Several incentives exist for making improved silicate-based products. Silicate glasses are much less leachable and dispersible than calcines and are generally more stable than phosphate glasses and ceramics. In addition, silicate products are less corrosive to processing and storage vessels than phosphates and appear to be less sensitive to changes in waste composition. Economic evaluation in the WSEP program also indicated that processes making consolidated products such as the silicates will have an economic advantage since solidification will be possible without interim liquid storage. (Such a management scheme should thereby have further improvements in safety compared to those presently used.)

Solidification systems which are more amenable to commercial use can be developed by combining the advantages of various

solidification techniques (developed in the United States and abroad). These improved high-level waste solidification systems would involve two steps:

- 1) a continuous, reliable, high-capacity system for dehydrating and denitrating the liquid waste, and
- 2) a continuous nonplatinum melter system to produce a high-integrity silicate-based product.

The product would then be discharged in the molten state into the final container where it is cooled and resolidified into a glass for storage.

The Waste Fixation Program (WFP) will be comprised of five tasks. Briefly these are as follows.

1. Improved Solidification Systems. This task will provide industry with an engineering-scale nonradioactive evaluation and demonstration of improved and reliable waste solidification systems and products. Initial efforts will be on production of silicate glass products in a continuous calciner-melter system. Engineering-scale nonradioactive equipment development is also required to test and refine process flow sheets and equipment to be used during subsequent radioactive demonstrations. Current plans call for the spray and fluidized bed calciners to be tested [with the development effort for the fluidized bed calciner to be done at the Idaho Chemical Processing Plant (ICPP)]. Both metallic (nonplatinum) and ceramic materials are being considered for construction of the continuous melter.

2. AEC Waste Studies. The objective of this task is to design, construct, and perform design verification tests on engineering-scale equipment and processes for conversion of Hanford high-level waste residues to a high integrity solid form suitable for storage on-site or shipment to a federal repository. The processes and technology will be developed in

cooperation with Atlantic Richfield Hanford Company (ARHCO) at Hanford and will utilize technical and experimental data provided by ARHCO. Radioactive demonstrations in the WFP using equipment developed in this task will demonstrate solidification of Hanford wastes in a manner which will provide data for ARHCO's detailed design of full-scale facilities for the solidification of the production waste inventories at Hanford.

3. Radioactive Demonstrations. Full-scale radioactive demonstrations will establish the process and equipment technology of improved solidification systems for commercial high-level waste. These systems will be comprised of continuous calciner:nonplatinum melter combinations to make silicate glasses. Advanced concepts for the solidification of Hanford AEC high-level wastes will be demonstrated on a pilot plant scale. A major objective of this task is the production of large-scale specimens of solidified waste for studies pertinent to the definition of the physical properties and characteristics which affect product safety.

4. Product Evaluation. The product evaluation task will evaluate the large-scale solidified waste specimens produced in the prior WSEP program and during the WFP. The properties of the solidified waste must be measured as a function of time and environmental conditions in order to assess the relative safety of differing modes of solidification and handling of high-level wastes during storage, shipment, and final disposition. The waste properties are being measured on engineering-scale pots of fully radioactive waste. These data are augmented by measurements on laboratory-scale preparations as required.

5. Waste Management Analysis. This task will define and investigate safety parameters of waste management systems in relation to the containment, immobilization, and isolation of hazardous wastes and will evaluate the radiological safety implications of these systems. The scope of the work will range

from the investigation of complex solidified wastes and the relative merits of different solid forms to the evaluation of containment requirements and interactions between the waste container and its environment. Prior to final disposition of the solidified wastes, waste management systems are expected to include interim storage of liquids and solids, partitioning, solidification processing, and transportation. The variety of environments that waste products will encounter must be considered along with the physical-chemical properties related to immobilization in these environments (e.g., waste form leachability and volatility and engineered and geologic containment barriers).

SOLIDIFICATION STUDIESREFERENCE WASTE COMPOSITIONS FOR THE WASTE FIXATION PROGRAM -
K. J. Schneider and J. E. Mendel

In the new Waste Fixation Program (WFP) the conversion of highly radioactive liquid wastes to solids having low leach rates will be demonstrated. The WFP is currently aimed at high-level wastes from reprocessing of commercial power reactor fuels. Because of the variety of schemes by which a reprocessor may design and operate his plant, a variety of high-level waste compositions will be generated at the various plants. The studies in the WFP will attempt to be as responsive as practical to the potential myriad of waste compositions which industry will have.

As a primary basis for the studies, the reference waste compositions designated as PW-4b and PW-6 in Table 1 are to be used. Two reference waste compositions are to be used, with the attempt to bracket in most of the anticipated compositions. For comparisons, compositions of reference wastes from LWR fuels used in the previous Waste Solidification Engineering Prototypic Program (WSEP) are also shown in Table 1. The new reference compositions represent an updating of the range of wastes as indicated by current trends. Shown in Table 2 is a more detailed breakdown of the actinides and fission products to be in the new reference wastes, with the chemical substitutions.

The low-salt, or "clean" waste, designated PW-4b, represents a waste from a reprocessing plant wherein no chemical salts are added during processing. The waste salts are almost totally fission product salts.

The high-salt, or "dirty" waste, designated PW-6, represents a waste which is modestly high in chemical salts which

TABLE 1. Reference Waste Compositions for WFP
and Comparisons with WSEP Compositions

	Concentration, <u>M</u> , at 378 liter/MT				
	Low-Salt Waste		High-salt Waste		
	PW-4m (used in WSEP)	PW-4b for WFP	PW-1 (used in WSEP)	PW-2 (used in WSEP)	PW-6 for WFP
H	0.5	1.0	3.7	3.9	3.0
Na	0.10	--	0.14	0.93	2.0
Fe	{ 0.05	0.05	{ 0.93	{ 0.44	0.5
Al		--			--
Cr	0.012	0.012	0.012	0.024	0.045
Ni	0.005	0.005	0.005	0.01	0.020
Actinides	0.01	0.022	0.01	0.01	0.065
NO ₃	2.4	~2.8 (to bal)	7.5	5.4	7.8 (to bal)
SO ₄	--	--	--	0.87	--
PO ₄	0.003	0.025	0.003	0.006	0.025
SiO ₃	0.01	--	0.01	0.01	--
F, Hg, Zr, I, Li, Soluble poisons	--	--	--	--	--
Fuel	en. U LWR	en. U LWR	en. U LWR	en. U LWR	en. U LWR
Fuel exposure, Mwd/MT	46,600	33,000	20,400	20,400	33,000
MW/MT	31	30	15	15	30
Out-of-reactor, years	0.5	0.5	0.5	0.5	0.5
Spent fuel code	ISOGEN	ORIGEN	ISOGEN	ISOGEN	ORIGEN

are added during processing. Extremes of wastes with higher salt content than this are certainly possible, but it is believed that this is near the upper range of those currently anticipated.

The bases for the amounts of constituents in the two new waste compositions are discussed below.

TABLE 2. Fission Product and Actinide Compositions
in Reference Wastes for WFP

	Constituent ⁽¹⁾	Concentration, M, at 378 liter/MT ⁻	
		PW-4b	PW-6
Fission Products ⁽²⁾	Mo	0.095	0.095
	Tc (Mo)	0.022	0.022
	Sr	0.027	0.027
	Ba	0.027	0.027
	Cs (K)	0.054	0.054
	Rb (K)	0.010	0.010
	Y + Re (RE mix) ⁽³⁾	0.208	0.208
	Zr	0.106	0.106
	Ru (Fe)	0.059	0.059
	Rh (Co)	0.010	0.010
	Pd (Ni)	0.032	0.032
	Te	0.012	0.012
	Ag	0.002	0.002
	Cd	0.002	0.002
Actinides	Np (U)	0.0085	0.0085
	U + Pu (U)	0.011	0.054
	Am + Cm (RE mix)	0.0022	0.0022

1. Chemical stand-ins used are shown in parentheses.
2. Concentrations obtained from Table 3.8, Siting of Fuel Reprocessing Plants and Waste Management Facilities, USAEC Report ORNL-4451, compiled by ORNL staff, July 1970, for LWR fuel, burnup = 33,000 MWd/MT; power level - 30 MW/MT, 150 days out of reactor.
3. For instance Lindsay mixed rare earth nitrate mixture No. 350.

Fuel

A light water reactor fuel enriched with ^{235}U is used as the reference source of waste. Such LWR's are projected to be by far the most prevalent nuclear power source until around 1990. Some LWR's fueled with recycled plutonium will exist during that time period, but the waste from these LWR's should be essentially the same as the reference wastes. The actinide content from plutonium recycle fuels may be a factor of 2 to 3 higher than those shown, but the effects on waste processing should be negligible. A possible significant chemical effect of plutonium recycle fuels could result if the fluoride ion is needed to dissolve the spent fuels.

The fuel exposure was selected to be typical of the high end of the exposure range as currently projected. The reference age of the fuel was kept the same as before at six months, because that age appears to be typical of the expected time of reprocessing. The changes in waste solidification chemistry from the first few years of aging time will be minor in any event.

Wastes from LMFBR's or HTGR's are not shown and are not planned to be studied in the initial period of the WFP. It is believed, however, that there will be significant chemical differences in these wastes. A few comments about some of these differences are mentioned in the discussions below.

Spent Fuel Code

ORIGEN was used because it has been continually updated since the previous WSEP program began, and is believed to be current with existing nuclear technology. No attempts have been made to keep the ISOGEN program current for a number of years.

Waste Volume

There is no apparent reason to change the base volume from 100 gal/MT, or 378 liters/MT, as it was in the WSEP program. However, the actual unit volumes used may be different. For example, the PW-4b waste should be reasonably stable chemically at about one-third that volume; on the other hand, significant chemical additives to either waste could render the waste chemically unstable unless it is diluted to a larger unit volume.

Acid Concentration

The concentrations selected are believed to be near the low and the high ends of the range of acid concentrations to be expected in plant operations. No neutralized wastes are anticipated in commercial plants.

Sodium

No sodium will be in the waste unless it is added as a chemical additive during reprocessing. Technology exists for plant flow sheets which do not use sodium. At the other extreme, significant sodium could be present from additives such as NaNO_2 for plutonium valence control, from combining the spent Na_2CO_3 from organic washing with high-level wastes, from combining spent caustic from off-gas scrubbing with high-level wastes, from combining laboratory and decontaminating solution wastes with high-level wastes, etc. The potential sodium content from all these sources could be perhaps five times the quantity selected for PW-6. However, that quantity is believed to be on the high side of most situations.

Iron

The trend in reprocessing is not to use iron as an additive. That shown in PW-4b is an estimate of iron from corrosion in a plant which has reasonably low corrosion of

stainless-steel equipment. That shown in PW-6 is a high-scale estimate of iron from corrosion plus significant iron present as springs in some LWR fuel elements. Current data indicate that dissolution of the stainless-steel cladding of LMFBR fuels could add up to about 0.1M iron. Higher quantities of corrosion iron than that shown in PW-6 are projected to be present in HTGR wastes.

Aluminum

Essentially no aluminum is expected to be present from LWR fuels under most conditions. However, processing of plutonium-enriched fuels and LMFBR fuels could result in aluminum in waste from passivating the fluoride which may be used for dissolution of the fuels. Also, aluminum oxide will likely be present in the wastes from HTGR fuels. A possible exception could be the use of aluminum nitrate if fluoride is used to aid dissolution of plutonium fuels. Also, small amounts could be present from alumina spacers used in some fuel elements.

Chromium and Nickel

These are only present from corrosion of stainless-steel equipment.

Actinides

The quantities are those from transuranic and transplutonic elements (approximately 0.01M) plus uranium and plutonium waste losses of 0.1 percent for PW-4b and 0.5 percent for PW-6. These waste losses represent near-low and near-high ends of the expected range. Plutonium recycle fuels could result in an additional increase of transuranic and transplutonic elements of up to about 0.03M.

Nitrate

The nitrate is shown as approximate only. It is present in stoichiometric quantities with other constituents.

Sulfate

No sulfate is expected to be used in currently designed or future reprocessing plants for LWR or LMFBR fuels. Sulfate may be present in significant quantities in wastes from reprocessing HTGR fuels.

Phosphate

The phosphate is derived from degradation and entrainment of the TBP solvent. The value used is that developed in WSEP Volume 11, Report BNWL-1667.*

Silicate

Essentially no silicate is expected to be present in the LWR and LMFBR wastes. However, small amounts could be present where silica is used in some fuel elements in the form of a boron-containing glass, used as a nuclear poison. Also, silica will be present in wastes from HTGR fuels.

Other Constituents

Fluoride is assumed to be absent. It is possible, however, that it could be present from dissolution of plutonium recycle fuels, and it is likely to be present from dissolution of LMFBR and HTGR fuels.

Mercury is expected to be absent under most conditions. The primary potential source appears to be from $\text{Hg}(\text{NO}_3)_2\text{-HNO}_3$ scrubbing of vent gases for radioiodine removal.

Significant quantities of nonfission product zirconium are not expected to be present. The amount of zirconium which is dissolved during leaching of the fuel from the zirconium cladding should be negligible, but we know of no data on the subject.

* J. L. McElroy, K. J. Schneider, J. N. Harlety, J. E. Mendel, G. L. Richardson, R. W. McKee, and A. G. Blasewitz, Waste Solidification Program Summary Report, Volume 11, Evaluation of WSEP High-Level Waste Solidification Processes, BNWL-1667, Battelle-Northwest, July 1972.

Fission product iodine and bromine are assumed to be removed from the fuel during head-end and therefore should be absent in the waste. Iodine is present in the spent fuel at a quantity equivalent to 0.0055M in the waste.

Up to about 0.4M lithium is expected in HTGR wastes, but is assumed to be absent here.

Soluble poisons are not included in the reference waste compositions, even though they are expected to be present in many cases. It is believed that use of such poisons will be specific to the individual reprocessing plant; therefore, the major responsibility for R&D for these constituents should reside with each fuel reprocessor for his case. Soluble poisons which have been proposed for use are gadolinium, cadmium, and boron. Any of these may be used. Although it does not present the same processing problems as if it were in the aqueous waste, boron will be added to the wastes in the WFP in the borosilicate glass. Boron is expected to be present in HTGR fuels and their wastes.

LABORATORY STUDIES

Melt Development - J. E. Mendel

The goals of the Waste Fixation Program are to develop silicate-based glasses for the incorporation of reference waste compositions PW-4b and PW-6 (Tables 1 and 2) which have the following properties:

- Minimum possible leach rate
- Homogeneous
- Viscosity of less than 500 poises at 1150 °C
- Relatively noncorrosive to high nickel-high chromium alloys, or other candidate materials of construction for continuous melters, at 1150 °C.

Preliminary tests indicate up to 35 wt% PW-6, as oxide, can be incorporated in borosilicate glasses which possess most of the desired properties. Up to about 20 wt% PW-4b, as oxide, has been incorporated in a lead silicate glass which is even more leach resistant.

Emphasis in the preliminary tests has been on achieving the lowest practical leach rate. Recently it was found that the leaching mechanism of the waste glass melts differs from that of commercial glass in the standard accelerated leach test (described below) and the initial conclusion, that the waste glasses were about as leach resistant as commercial soda lime bottle glass, is having to be revised.

Experimental Procedure. Two large batches of calcined simulated PW-4b and PW-6 have been prepared. Aliquots of calcined waste are dry mixed with additives and held at 1150 °C in Al_2O_3 or unglazed procelain crucibles for 3 hours to form the melts for study. The melts are cooled in the furnace at a rate averaging about 50 °C/hour.

Leachability of the glasses is being evaluated by the accelerated leach test procedure used in the WSEP development program.* In this test the sample is powdered and sieved. The -45 +60 mesh fraction (250 to 354 microns) is washed free of fines with acetone and a 1 gram aliquot is enclosed in a stainless steel screen envelope. The sample is suspended in 150 ml of distilled water at 95 °C for 24 hours and the loss in weight is determined. The procedure is repeated two or more times with fresh water so that each sample is in contact with water at 95 °C for a total of 72 hours. The test is valuable for rapid comparisons of the leach resistance of glasses which can have widely varying compositions. Typical

* R. J. Thompson, J. E. Mendel, and J. H. Kleinpeter, Waste Solidification Demonstration Program: Characterization of Nonradioactive Samples of Solidified High-Level Waste, BNWL-1393, Battelle-Northwest, June 1970.

accelerated leach rates measured on laboratory Pyrex glass and laboratory "soft" bottle glass are shown in Table 3.

TABLE 3. Typical Accelerated Leach Rates of Commercial Glasses

	Accelerated Leach Rate, % wt loss			Overall, 72 hr
	1st 24 hr	2nd 24 hr	3rd 24 hr	
Pyrex glass	0.08	0.06	0.03	0.17
Pyrex glass	0.05	0.04	0.09	0.18
Bottle glass	0.52	0.27	0.50	1.19
Bottle glass	0.52	0.36	0.46	1.35

If the surface area of the sieved sample is assumed to be $200 \text{ cm}^2/\text{g}$ (Barton* measured 135, 200 and $213 \text{ cm}^2/\text{g}$ on three of his samples by the BET method), then a 1 percent total weight loss for the 72-hour period corresponds to a leach rate of $1.7 \times 10^{-5} \text{ g/cm}^2\text{-day}$. The accelerated leach rates for Pyrex and bottle glass thus correspond to bulk leach rates of 2.9×10^{-6} and $2.2 \times 10^{-5} \text{ grams glass/cm}^3\text{-day}$ at 95°C , respectively. In Figure 1 these values are compared with leach data found in the literature. The agreement is fairly good. The data in Figure 1 also illustrate the very large dependence of glass leachability upon temperature. Furthermore the lower line on Figure 1 probably delineates fairly accurately the lower limits of leachability that one can reasonably hope to attain with a glassy solid incorporating radioactive wastes.

Borosilicate Glass Melts. A series of borosilicate glass melts incorporating PW-6 were made of which those shown in Table 4 are representative. In the first six melts three mole ratios of B/Si, 0.75, 1.50 and 2.25, and two levels of Pw-6 content, 35 and 50 wt% oxide, were tested. None of the melts

* G. B. Barton, Solidification of High-Level Wastes, Part IV. Phosphate Melts for Fixation of Radioactive Residues from Purex Type Wastes, Three to Fifty Percent Fission Product Oxides, BNWL-80, Battelle-Northwest, July 1965.

FIGURE 1. Rate of Attack of Distilled Water on Industrial Glasses as a Function of Temperature

* W. C. Taylor and R. D. Smith, "Solubility Characteristics of Glasses Basically Different in Composition," J. Am. Ceramic Soc., Vol. 19, pp 331-335, 1936.

** U. L. Upson, personal communication from Corning Glass Works, reported in Fixation of High-Level Radioactive Wastes in Phosphate Glass-Hot Cell Glass Experiment, BNWL-200, Battelle-Northwest, January 1966.

*** J. D. Cauwood, S. English and W. E. S. Turner, J. Soc. Glass Technol., Vol. 1, 153 (1917), as described on p. 128, G. W. Morey, The Properties of Glass, 2nd Edition.

TABLE 4. Melt Development for Improved Solidification Systems

	Melt No.	Melt Composition, wt%									Homogeneity	Estimated Viscosity Poises @ 1150 °C	Leachability, % wt Loss @ 95 °C			
		SiO ₂	B ₂ O ₃	Al ₂ O ₃	CaO	Misc.	Na ₂ O	Fe ₂ O ₃	FP Oxides	Others ⁽¹⁾			1st 24 hr	2nd 24 hr	3rd 24 hr	Overall 72 hr
A.	72-1	25.0	10.9	5.3	8.8	0	13.6	11.5	18.3	6.6	Yellow microcrystalline 2nd phase	<500	0.31	0.37	0.38	1.06
	72-2	18.7	16.3	5.6	9.4	0	13.6	11.5	18.3	6.6	Undissolved sediment	<500	1.02	0.81	0.55	2.36
	72-3	14.9	19.5	5.9	9.7	0	13.6	11.5	18.3	6.6	Undissolved sediment	<500	2.85	1.64	1.00	5.40
	72-4	32.5	14.2	6.9	11.4	0	9.5	8.1	12.8	4.6	Homogeneous	<500	0.32	0.33	0.36	1.01
	72-5	24.4	21.1	7.3	12.2	0	9.5	8.1	12.8	4.6	Homogeneous	<<500	0.70	0.57	0.48	1.75
	72-6	19.5	25.3	7.6	12.6	0	9.5	8.1	12.8	4.6	Homogeneous	<<500	0.47	0.78	0.72	1.96
	72-7	39.8	17.4	0	0	0	11.6	9.9	15.7	5.6	Homogeneous	<500	1.48	1.54	1.62	4.56
	72-9	34.0	10.3	7.2	11.9	0	9.9	8.5	13.4	4.8	Homogeneous	<500	0.40	0.31	0.36	1.07
	72-10	35.0	15.2	0	12.2	0	10.2	8.7	13.8	4.9	Homogeneous	<500	0.41	0.42	0.56	1.38
	72-12	34.8	8.3	7.3	12.2	0	10.2	8.6	13.7	4.9	Homogeneous	<500	0.40	0.34	0.40	1.13
	72-13	30.8	13.4	6.5	16.2	0	9.0	7.6	12.1	4.4	Homogeneous	<500	0.40	0.36		
	72-14	36.8	16.0	7.8	0	0	10.7	9.1	14.4	5.2	Homogeneous	>500	0.42	0.27		
	72-15	38.0	0	8.0	13.3	0	11.0	9.4	14.9	5.4	Yellow microcrystalline 2nd phase	<500		Not determined		
	72-16	29.1	14.9	7.2	12.0	0	10.0	8.5	13.5	4.8	Homogeneous	>500	0.43	0.46		
	72-17	31.5	13.7	10.0	11.0	0	9.2	7.8	12.4	4.4	Homogeneous	<500	0.38	0.40		
	72-20	31.8	16.5	6.7	11.0	0	9.2	7.8	12.5	4.5	Homogeneous		0.43			
	72-21	36.8	13.3	6.4	10.7	0	8.9	7.6	12.0	4.3	Homogeneous		0.49			
	72-26	35.8	15.6	7.5	12.5	0	10.7	9.2	7.0	1.7	Homogeneous	~500	0.48	0.43	0.42	1.32
	72-27	36.2	15.7	7.6	12.7	0	0.5	9.6	14.3	3.4	Nonhomogeneous (slag)		0.36	0.42	0.39	1.16
	72-28	35.7	15.5	7.5	12.4	0	10.7	0.7	14.1	3.4	Homogeneous	<500	0.48	0.52	0.48	1.47
	72-29	28.0	12.2	5.9	9.7	0	8.9	7.9	22.1	5.3	Undissolved sediment	<500	0.38	0.45	0.36	1.19
	72-30	39.8	17.3	8.4	13.8	0	0.6	0.7	15.7	3.7	Homogeneous	>500	0.39	0.35	0.36	1.20
B.	72-42 ⁽²⁾	61.7	0	0	5.1	0	5.6	1.3	23.4 ⁽³⁾	2.9	Homogeneous	>>500	0.10	0.0	0.05	0.15
C.	72-51	28.1	0	0	0	5.6 K ₂ O 46.5 PbO	0.5	0.7	15.0	3.6	Homogeneous	~500	0.10	0.05	0.04	0.20

1. Mainly U₃O₈, plus traces of Cr₂O₃, NiO and P₂O₅
2. 1400 °C for 3 hours, furnace cooled
3. Did not contain molybdenum

containing 50 wt% PW-6 were homogeneous while all of those containing 35 wt% were homogeneous. As expected, leachability increased with B/Si ratio and melt 72-4 with the lowest B/Si ratio and 35 wt% PW-6 was selected for further testing.

The remainder of the compositions in Table 4 represent variations of the "base" melt 72-4 composition. Individual constituent concentrations were varied while other melt constituent concentrations were maintained constant at the "base" melt composition. Although this work is continuing, the conclusion after preparation of melt 72-30 was that a really significant improvement in leachability would only be achieved by a large perturbation of the "base" melt composition. Subsequent tests have examined melts which 1) contain much higher silica concentrations than the "base" melt, or 2) contain appreciable concentrations of cations of proven value in enamel formulations such as lead, zinc and copper.

High Silica Melts. The potential improvement in leach resistance inherent in high silica melts is shown by melt 72-42 in Table 4B. A relatively high proportion of fission products (23.4 wt%) was incorporated in a homogeneous glass having a leach resistance comparable to that of Pyrex glass. Presently, the major drawback to high silica melts is that fission product molybdenum separates out as a soluble second phase. Although fission product molybdenum is nonradioactive, the second phase also contains significant amounts of radioactive fission products, such as ^{137}Cs .

High silica formulations have melting points well above 1150 °C, considered the maximum operating temperature for a metallic melter; therefore, a ceramic melter would be required.

Enamel-Type Melts. About 18 silicate melts, with and without boron, containing relatively large amounts of lead, zinc or copper have been prepared, but data collection is not complete. They will be described in the next quarterly report.

A promising formulation of the enamel type, incorporating PW-4b in a high-lead glass, is melt 72-51 (Table 4C), which has a leach resistance quite close to that of Pyrex glass. Initial tests indicate that this lead glass composition is more corrosive to Cr-Ni-Fe alloys than is the "base" borosilicate formulation; however, with proper alloy selection lead glasses may be usable.

Leaching Mechanism of Waste Glasses. A fundamental difference in the leaching mechanism of the "base" glass (melt composition 72-4) and commercial soda-lime bottle glass is apparent from the data shown in Figure 2. According to the accelerated leach test, the two glasses have comparable leachability when 1 gram samples are used in the test, which is the standard procedure. However when the sample size is decreased, the measured leach rates diverge rapidly. The measured leach rate of the "base" glass increases while that of the commercial glass remains the same or may actually decrease.

These results apparently indicate that the "base" glass is actually much less leach resistant than initially thought. The reason for the divergent leach behavior of the "base" glass and that of commercial soda-lime silica glass is being sought.

Melter Materials Corrosion Studies - R. F. Maness

Corrosion tests were initiated with the "base" melt (Melt 72-4, Table 4). Initial tests were run in alumina crucibles at 1150 °C for 425 hours with 15 commercial alloys. Alloy compositions are given in Table 5. Melt composition and corrosion test results are given in Table 6. Corronel 230 and 20-45-5 alloy (an Armco product) appeared to offer the best resistance. However, ten of the alloys evaluated corroded at rates ≥ 10 mils/month as determined by weight loss. No appreciable preferential attack at the melt-vapor interface was noted in any case. Tests to determine the corrosion resistance of most of these ten alloys at 1100 and at 1200 °C are planned.

FIGURE 2. Variation of Measured Leach Rate as Function of Sample Size

Table 5. Nominal Composition of Candidate Melter Alloys

Alloy	Weight Percent				
	Cr	Ni	Mo	Fe	Others
Corronel 230	35	65	--	--	
316 SS	16	12	3	bal	
329 SS	25	5	2	bal	
309 SS	22	13	--	bal	
E-Brite 26-1	25	--	--	bal	
Owens-Corning Alloy	26	bal	--	3	6 W
20-45-5 Alloy	20	45	5	bal	
Inconel 601	23	60	--	14	1 Al
Inconel 617	22	54	9	--	1 Al, 12.5 Cr
Inconel 690	30	60	--	10	
Inconel X	15	bal	--	8	2 Ti, 1 Al, 1 Nb
RA 333	25	45	3	bal	3 W, 3 Co
Hastelloy X	22	bal	9	18	1 W, 2 Co
18-18-2 Alloy	18	18	--	bal	2 Si
Supertherm	25	35	--	bal	14 Co, 5 W
Udimet 710	18	bal	3	--	15 Co, 1.5 W, 5 Ti, 2.5 Al

TABLE 6. Corrosiveness of Waste Melt to Candidate Melter Alloys at 1150 °C

Melt Composition: 100 g calcine, 64 g SiO₂,
 42 g H₃BO₃, 100 g Al(NO₃)₃,
 40 g CaCO₃
 425 hour exposures in alumina crucibles

Alloy	Corrosion Rate, mils/mo	
	Liquid	Interface
Corronel 230	2.1	2.3
316 SS	dissolved	dissolved
329 SS	6.7	--
309 SS	7.4	10.6
E-Brite 26-1	6.7	--
Owens Corning Alloy	4.9	6.1
20-45-5 Alloy	2.7	2.9
Inconel 601	6.5	5.6
Inconel 617	6.3	5.3
Inconel X	5.5	6.7
RA 333	9.9	13.0
Hastelloy X	5.4	6.0
18-18-2 Alloy	20.6	62.4
Supertherm	19.8	--
Udimet 710	27.4	32.3

Ruthenium is the only fission product judged likely to accelerate corrosion; therefore a melt of the composition given in Table 6 but containing 1 wt% ruthenium (added as $\text{Ru}(\text{OH})_3$) was prepared. Corrosion tests are in progress with this melt at 1150 °C using Corronel 230, 20-45-5 alloy and Inconel 690 as test materials.

Corrosion tests have also been initiated with a lead-bearing waste glass (melt 72-51, Table 4) which has demonstrated a low leach rate. This glass was prepared from PW-4b waste, PbSiO_3 , KNO_3 and SiO_2 . These tests are still in progress.

ENGINEERING STUDIES

Nonradioactive Spray Calciner and Melter - J. D. Kaser

A spray-calciner and continuous melter assembly is being installed in Engineering Development Laboratory-102 in 324 Building. This equipment will be used to experimentally study aspects of spray-calciner and melter operation that can be more economically and thoroughly studied by nonradioactive than by radioactive experimentation. These aspects include long-term equipment reliability, effects of chemical composition changes, wall deposition, atomization efficiency, quench scrubbing, and throughput capacities.

Construction design is nearly complete and equipment is being obtained. Installation of the spray calciner and calciner-melter support structure is scheduled to begin in December 1972. The solidification facility is expected to be operable by May 1973.

RADIOACTIVE DEMONSTRATIONSSOLIDIFICATION CELL (B-CELL) REACTIVATION - B. O. Kahle
and J. L. McElroy

The B-cell solidification facility that contained the WSEP equipment is being reactivated for Waste Fixation Program radioactive demonstrations. Manipulators have been reinstalled and work is in progress to clean out unusable material from the cell and to reconnect and recondition the remaining solidification equipment and auxiliaries.

Approximately 400 ft³ of hardware and solid dry waste have been removed from B-cell and buried. The hardware consists of unrepairable equipment such as furnaces, pumps, and service jumpers with maximum radiation readings of approximately 100 R/hr at 1 foot. The equipment is removed from the cell to the airlock where it is placed in a 1.5-inch thick mild steel box (4 × 4 × 8 feet). This box is then placed in a plywood box to contain the contamination which accumulates on the steel box during loading. Maximum localized radiation readings through the boxes after they are filled are approximately 2 R/hr at 1 foot.

SOLIDIFICATION EQUIPMENT REACTIVATION - W. F. Bonner
and D. H. Siemens

Reactivation of B-cell is providing an opportunity for evaluation and improvement of operating methods and equipment designs. Much of the equipment being replaced in the cell is newly designed to allow more efficient cell operation during the WFP radioactive demonstrations. Some of the recent developments are presented here.

Process Off-Gas Filters

The process off-gas filters have been redesigned to allow more efficient replacement. The new filter assemblies will

each utilize a disposable 8 × 8 × 6 inch, 50 cfm absolute filter and be equipped with sample taps for isokinetic gas sampling. The previous filter design utilized expensive reusable canisters and remote changeout of the filters was very time consuming.

Spray Solidifier Top Flange and Spray Nozzle

A simplified top flange arrangement for the spray solidifier has been designed. The new design provides two 2-inch holes in the flange to allow inspection and cleaning of the calciner interior without removing the feed nozzle. A simpler method of installing the feed nozzle is also incorporated in the design. The improved atomizing feed nozzle design utilizes a cleanout needle, flange mounting adapter, and nozzle body that are commercially available.

Spray Calciner Furnace

Initial resistance checks of the spray calciner furnace showed a high resistance across one of the heating elements. Inspection of the interior wiring required removing the calciner chamber and transporting it to the cell window where the power panel could be disassembled. Tightening the internal connectors to the suspect element restored the normal resistance. The furnace can therefore be used in the WFP program. Inspection of the furnace wiring revealed the asbestos insulation to be in good condition.

With the calciner chamber removed, the interior of both the calciner barrel and the lower cone could be examined. A layer of grey scale covered about half the internal surface of the calciner barrel. The scale was about 1/2-inch thick midway up the barrel but very thin near the top and bottom. This amount of scaling is not believed excessive for the number of hours the calciner had been operated (>600 hours) and may be typical of the steady state scale deposit (the loose powder

was flushed from the barrel prior to putting the cell in standby). It should be noted however, that the calciner feed rate capacity was reduced below normal during the last two WSEP runs. This could be due to the 1/2-inch thick band of scale around the center of the calciner barrel. Both the loss of rate capacity and the scale deposit could have been caused by the loose heating element connection, which was also associated with the middle zone of the three zone furnace.

The cone wall at the bottom of the calciner and directly beneath the spray nozzle was covered with a very nonuniform deposit as much as 1-inch thick. It is postulated that at least part of the cone wall scale formed during feed nozzle failure when aqueous feed dripped from the nozzle onto the hot cone wall.

EVALUATION OF SOLIDIFIED WASTE PRODUCTS

J. E. Mendel

The purpose of the product evaluation task is to define the properties of typical solidified high-level waste products.* Regulations permit the solidified wastes to be stored for up to ten years at the fuel reprocessor's plant before transfer to a government-operated repository, where retrievable storage for up to 100 years is planned. Thus potential alterations in product properties which may occur under storage conditions for a period of over 100 years are of concern.

The interim storage period is being studied by monitoring and periodically sampling, the actual full-scale highly-radioactive solidified waste products from the WSEP program (and later from the WFP program) for a period of at least ten years. Extrapolation of the interim storage data, plus laboratory-scale studies using rate accelerating techniques, will be used to study the potential changes in product properties which may occur during longer term storage.

INTERIM PRODUCT STORAGE DEMONSTRATION - J. E. Mendel

Thirty-three prototypical containers (pots) of solidified highly radioactive waste were prepared during the WSEP demonstrations of the pot calcination, phosphate glass and spray solidification processes for the solidification of high-level wastes. Each pot contains, on an average, the amount of waste that would be generated during the reprocessing of 1.2 tonnes of irradiated uranium.

The pots containing the solidified wastes have now been in interim storage from 2.5 to 6 years. Currently 23 are in

* Product, in this usage, includes both the solid waste and its container, or pot.

air at ambient temperature, and 10 are in the Solids Storage Engineering Test Facility (SSETF)* in air or water at controlled temperatures (Table 7).

A major portion of the experimental program centers around the 10 pots in SSETF, where the storage conditions can be controlled accurately and pot temperature and pressure can be monitored continuously. Many factors were considered in selecting the SSETF pots in order to assure that maximum useful information would be gained during the course of the program. The pots were chosen to assure that all of the major variables would be represented in the SSETF test program, as is shown in Table 8.

The LMFBR waste type used in WSEP runs SS-11 and PG-11 was not included because the final melts used to incorporate this waste had compositions essentially identical to the PW-4m melts.

Additional considerations, such as age and radioactivity content, also entered into final selection of the specific pots used for the SSETF program. Thus, the pots selected tend to come from the latter portions of the series for each process in WSEP (Table 7). It is for this reason that no 12-inch pots, which were used only in the earlier WSEP runs, were included in the test program.

As new improved products from the WFP become available they will displace WSEP pots in the SSETF.

Data are being obtained on the stability of the WSEP products, as a function of time and conditions of interim storage, by two types of measurements: 1) measurements made on the pots, and 2) measurements made on samples of solidified waste removed from the pots (Table 9). The waste samples are obtained by core drilling through the walls of the pots, with a 3/4-inch

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

TABLE 7. Description of WSEP Pots and Interim Storage Status

Run No.	Date of Run	Waste Type PW	Pot Description		Volume of Solid, liter	Bulk Density, kg/liter	Heat Rate Density, W/liter	Q _L to Wall ΔT, (c) °C	Q _L Temp., (b) °C	Interim Storage				Core-Drilling	
			Diam., in.	Material of Construction						SSETF Storage Mode(d)	Max. Temp., °C(e)			Age at Core-Drilling, yr	Number of Core Samples Taken
											Pod	Pot Wall	°C		
PC-1	Nov. 1966	2	12	304L	105 (a)	1.3	5.7	70	140						
PC-2	Feb. 1967	2	12	304L	105	1.2	16.2	235	485 (c)						
PC-3	Feb. 1967	2	8	304L	60	1.4	30	220	410						
PC-4	Jun. 1967	1	12	304L	110	1.3	23.7	312	477						
PC-5	Jul. 1967	1	8	304L	55	1.4	78	495	725						
PC-6	Sep. 1967	2	8	304L	60	1.3	85	700	940	Air	475	--	--		
PC-7	Aug. 1970	1	8	304L	60	1.2	93	753	1012					1.3	2
PC-8	Sep. 1970	4m	6	304L	34	1.3	141	604	855	Air	420	400	--		
PC-9 (RLG)	Oct. 1970	4m	6	310	~16	3.5	310	370	635	Air	390	430	460	1.2, 1.4	6
PG-1	Nov. 1967	2	12	Mild Stl.	92	2.7	17	89	316 (c)						
PG-2	Dec. 1967	2	8	304L	35	2.9	49	135	355						
PG-3	Jan. 1968	2	8	Mild Stl.	35	2.8	95	255	655 (c)						
PG-4	Mar. 1968	2	8	Mild Stl.	73	2.9	57	175	510 (c)					4.3	3
PG-5	Apr. 1968	1	12	Mild Stl.	113	2.8	78	352	712						
PG-6	May 1968	1	8	304L	62	2.8	155	380	780	Water				1.7, 2.5	11
PG-7	Jul. 1967	2	8	310	67	2.7	146	401	782	Air	460	--	500	1.3	6
PG-8	Aug. 1969	4m	8	Mild Stl.	67	2.9	132	350	710	Water	52	52	88	2.2	4
PG-9	Oct. 1969	4m	6	304L	27	2.8	158	204	566						
PG-10	Oct. 1969	4m	6	304L	29	2.9	317	369	827					1.2	4
PG-11	Dec. 1969	LMFBR	8	304L	60	2.9	198	417	834						
SS-1	Jan. 1967	1	12	304L	38	3.2	7.5	30	170						
SS-2	Apr. 1967	1	8	304L	48	3.2	44	70	315					5.0	3
SS-3	Jul. 1968	2	12	304L	39	2.7	40	80	315						
SS-4	Sep. 1968	2	8	Mild Stl.	56	2.9	93	220	505	Water	38	--	45	3.5	3
SS-5	Oct. 1968	1	8	304L	66	3.2	127	270	633						
SS-6	Nov. 1968	1	8	304L	65	3.2	168	305	767					2.1	4
SS-7	Dec. 1968	1	8	304L	62	3.2	204	453	928						
SS-8	Feb. 1969	1	8	304L	59	2.9	120	210	605	Air	460	--	478	1.9	3
SS-9	Mar. 1969	4m	8	310	68	2.9	107	242	594	Air	510	500	503		
SS-10	Apr. 1969	4m	8	Mild Stl.	56	3.1	141	262	610	Water	52	--	72	1.6	4
SS-11	Mar. 1970	LMFBR	8	304L	60	3.1	175	353	754						
SS-12 (1PM)	Apr. 1970	4m	8	304L	54	3.0	90	197	474					1.7, 1.9	6
SS-13 (1PM)	May 1970	4m	8	304L	50	3.0	200	404	824	Water	62	66	120		

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

b. Receiver pot setting in furnace with cooling air on.

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

d. Pots not in SSETF are stored in open racks on A-cell floor.

e. Current temperatures. Some thermocouples are inoperative.

TABLE 8. SSETF Storage Program

Variable	Distribution in SSETF Test Program	
Solidification Process	Pot Calcination	2 pots, PC-6, PC-8
	Spray Solidifier	4 pots, SS-4, SS-8, SS-9, SS-10
	Phosphate Glass	3 pots, PG-6, (a) PG-7, PG-8
	In-Pot Melting	1 pot, SS-13
	Rising Level Glass	1 pot, PC-9
Waste Type	PW-1	2 pots, SS-8, PG-6(a)
	PW-2	3 pots, PC-6, SS-4, PG-7
	PW-4m	6 pots, PC-8, SS-9, SS-10, PG-8, SS-13, PC-9
Pot Diameter	6 inches	2 pots, PC-8, PC-9
	8 inches	9 pots, PC-6, (a) SS-4, SS-8, SS-9, SS-10, PG-6, PG-7, PG-8, SS-13
Pot Material	Mild Steel	3 pots, PG-8, SS-4, SS-10
	304L Stainless Steel	5 pots, PG-6, PC-8, PG-6, (a) SS-8, SS-13
	310 Stainless Steel	3 pots, PG-7, SS-9, PC-9
Environment	Air	6 pots, PC-6, SS-8, SS-9, PG-7, PC-8, PC-9
	Water	5 pots, PG-8, SS-4, SS-10, PG-6, (a) SS-13
Potential for Molten Core		4 pots, PG-6, (a) PG-7, PG-8, PC-9

a. After discovery of leak, water storage of PG-6 pot in SSETF was discontinued.
The pot is now in A-cell atmospheric storage rack.

TABLE 9. Product Property Measurements Being Made During Product Interim Storage

	Measurement*	Purpose	Findings to Date
A. Measurements on Filled Pots	Temperature, by 3 sets of thermocouples arranged longitudinally, 1) in thermowell at pot centerline, 2) in thermowell midway between pot centerline and pot wall, and 3) tack-welded to external pot wall.	1. Record storage conditions. 2. Determine effective thermal conductivity.	With one exception no significant change in effective thermal conductivity has been found.
	Pressure, by pressure transducer on SSETF pots, by Bourdon tube pressure gauge on selected remaining pots.	Measure any pressure increase due to thermal decomposition or radiolysis.	No significant pressurization. Pressurization of pots placed in SSETF hot air storage did not exceed that due to thermal effects.
	Leak Tests, by vacuum helium mass spectrometry.	1. Check weld closures. 2. Detect leaks due to other causes.	1. About 90% of core drill holes have been welded closed and leak checked, special circumstances prevented either welding or leak checking of other 10%. 2. 4 pots have been found to have leaks in the internal thermowells.
	Wall Thickness Measurements, by ultrasonic scanning.	Detect corrosion of the pot wall.	Pot wall corrosion is less than 0.02 in. for all pots, both mild steel and stainless steel.
B. Measurements on Core-Drilled Samples	Leachability from sample of known surface area suspended in slowly recirculating water at 25 °C. Water analyzed for radioisotopes.	Obtain data for hazards evaluations.	Products vary widely in leachability. See WSEP Volume 10 report for details.
	Homogeneity by gamma spectrometry. Ratio of $^{137}\text{Cs}/^{144}\text{Ce}$ is obtained. Analysis of core sample increments gives radial variation. Core samples are taken at 3 elevations to give axial variation.	Obtain data on uniformity of product composition, and detect possible fission product segregation.	Slight enrichment of ^{137}Cs towards the upper and lower end of two pots has been found. Data are not yet sufficient to determine if this is statistically significant.
	Dispersibility, by determining relative amounts of small and large particles formed during impact.	Obtain data for hazards evaluations.	1. In the few direct comparisons made so far, behavior of highly irradiated products has been very similar to non-radioactive products with the same thermal history, indicating radiation has not greatly affected physical integrity of products. 2. Glasses tend to shatter into many small particles, ceramics into fewer larger particles.
	Devitrification, by visual inspection.	Determine potential change of glasses to crystalline solids.	1. Most phosphate glasses have devitrified. See text, this report. 2. To date there is no evidence of devitrification of the borosilicate glasses.
	Corrosion, by examination of circular pot wall segment removed prior to core drilling.	Corroborate external ultrasonic wall thickness scans and examine for fine pitting or cracking.	No evidence of significant corrosion of any pot wall segment.

* R. J. Thompson, J. E. Mendel, C. Hampton, Jr., and H. H. Irby, Sr., Waste Solidification Demonstration Program: Experimental Techniques for Characterization of High-Level Radioactive Solidified Waste, BNWL-1425, Battelle-Northwest, June 1970.

diameter bit. After the sample is removed, a stainless steel plug is inserted in the hole and it is welded closed.

To date 59 core drill samples have been taken from 13 WSEP pots. Standard procedure is to take three samples from each pot, at elevations near the top, bottom and center of the product column. However, as shown in Table 7, more samples have been taken from several pots, usually to obtain better sample specimens. This has been true especially of the borosilicate glass pots where the samples have often been ground to small bits of glass during drilling. A large number of core samples were taken from the PG-6 pot in an effort to pinpoint the location of corrosion, thought to be the cause of a leak in the thermowell of that pot. In this case, several samples of the thermowell were satisfactorily obtained. In summary, with the exception of the borosilicate glass pots, the core drilling technique has proven a very satisfactory means of obtaining representative samples of the highly radioactive solidified waste after storage in pots for varying lengths of time.

The data obtained on the WSEP products to the beginning of this report period are reported in the WSEP Volume 10 report.*

Current storage conditions are shown in Table 7. There has been no significant change in this report period. Temperature and pressure monitoring of the SSETF pots is continuing.

MEASUREMENTS ON CORE-DRILLED SAMPLES - J. E. Mendel

Five out of the 11 WSEP phosphate glass pots have now been core drilled. Three were found to be almost completely devitrified (pots from runs PG-6, PG-7 and PG-10) while two were only partially devitrified (pots from runs PG-4 and PG-8). Leach

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

rates, based on ^{137}Cs analyses, measured on 8 core-drilled samples from PG-6, PG-7 and PG-10 pots were all in the range 5×10^{-2} to 2×10^{-4} g/cm²-day, typical of devitrified phosphate glass. The samples from PG-4 pot have not been analyzed but 4 samples, 2 glassy and 2 devitrified, from PG-8 pot have now been leached for 40 weeks and the data are plotted in Figure 3.

The PG-8 pot contained PW-4m waste incorporated in phosphate glass and was core drilled 26 months after filling. During most of this time the pot was stored in water. The pot initially contained 2.3 MCi, mostly $^{144}\text{Ce-Pr}$. The resultant radiation exposure to the phosphate glass exceeded 10^{11} R before the core samples were taken.

Analysis of the leach data from the PG-8 samples indicates:

- 1) Phosphate glass can absorb over 10^{11} R without devitrification and with only a slight decrease in leach resistance, if stored under the proper thermal conditions.
- 2) When devitrification of phosphate glass occurs, the leachability of cesium increases by a factor of approximately 10^3 but the leachability of cerium increases by only a factor of approximately 10. (It is thought that the leaching behavior of plutonium and the other transuranics will resemble that of cerium, but this remains to be established.)

FIGURE 3. Leach Rate of Core-Drilled Samples of WSEP Run PG-8 Product, based on ¹³⁷Cs and ¹⁴⁴Ce Analyses

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