Battelle

Pacific Northwest Laboratories
Richland, Washington 99352

BNWL-1578
UC-70

AEC Research and Development Report

QUARTERLY PROGRESS REPORT
RESEARCH AND DEVELOPMENT ACTIVITIES
FIXATION OF RADIOACTIVE RESIDUES
FEBRUARY, MARCH, AND APRIL 1971

May 1971

BNWL-1578

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately-owned rights.

PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE MEMORIAL INSTITUTE
for the
U. S. ATOMIC ENERGY COMMISSION
Under Contract AT(45-1) 1830

3 3679 00061 8001

BNWL-1578

UC-70, Waste
Disposal and Processing

QUARTERLY PROGRESS REPORT
RESEARCH AND DEVELOPMENT ACTIVITIES
FIXATION OF RADIOACTIVE RESIDUES
February, March, and April 1971

Edited by

K. J. Schneider
Chemical Technology Department

May 1971

BATTELLE
PACIFIC NORTHWEST LABORATORIES
RICHLAND, WASHINGTON 99352

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

PREVIOUS QUARTERLY REPORTS

<u>Quarter</u>	<u>Year</u>	<u>Report Number</u>	<u>Reference*</u>
	<u>1959</u>		
First		HW-60584	59-1
Second		HW-61635	59-2
Third		HW-63048	59-3
Fourth		HW-63949	59-4
	<u>1960</u>		
First		HW-65209	60-1
Second		HW-66571	60-2
Third		HW-67334	60-3
Fourth		HW-68193	60-4
	<u>1961</u>		
First		HW-69176	61-1
Second		HW-70517	61-2
Third		HW-71374	61-3
Fourth		HW-72324	61-4
	<u>1962</u>		
First		HW-73412	62-1
Second		HW-74375	62-2
Third		HW-75220	62-3
Fourth		HW-76262	62-4
	<u>1963</u>		
First		HW-77299	63-1
Second		HW-78188	63-2
Third		HW-70140	63-3
Fourth		HW-80526	63-4
	<u>1964</u>		
First		HW-81862	64-1
Second		HW-83320	64-2
Third		HW-84467	64-3
Fourth		HW-84603	64-4
	<u>1965</u>		
First		BNWL-76	65-1
Second		BNWL-139	65-2
Third		BNWL-170	65-3
Fourth		BNWL-213	65-4
	<u>1966</u>		
First		BNWL-267	66-1
Second		BNWL-306	66-2
Third		BNWL-365	66-3
Fourth		BNWL-410	66-4

* Reference notation used in this report.

<u>Quarter</u>	<u>Year</u>	<u>Report Number</u>	<u>Reference*</u>
	<u>1967</u>		
First		BNWL-434	67-1
Second		BNWL-507	67-2
Third**		BNWL-677	67-3
Fourth		BNWL-771	67-4
	<u>1968</u>		
First		BNWL-824	68-1
Second		BNWL-889	68-2
Third		BNWL-923	68-3
Fourth		BNWL-1003	68-4
	<u>1969</u>		
First		BNWL-1074	69-1
Second		BNWL-1186	69-2
Third		BNWL-1263	69-3
Fourth		BNWL-1311	69-4
	<u>1970</u>		
First		BNWL-1401	70-1
Second		BNWL-1494	70-2
Third		BNWL-1533	70-3
Fourth		BNWL-1557	70-4

* Reference notation used in this report.

** Reports for the period July through October, 1967.
Reporting periods are now February-April, May-July,
August-October, and November-January.

CONTENTS

INTRODUCTION.	1
SUMMARY	1
WSEP CELL-EQUIPMENT DECONTAMINATION - J. L. McElroy	2
EVALUATION OF SOLIDIFIED WASTE PRODUCTS	2
Nonradioactive Laboratory Studies	2
Leach Rates of Borosilicate Glasses - F. P. Roberts	2
Radioactive Laboratory Studies-Status - F. P. Roberts and C. Hampton, Jr.	5
Product Measurement, Testing, and Storage	7
Solids Storage Engineering Test Facility (SSETF) - J. L. McElroy	7
Water Breeching of the PG-6 Pot - J. L. McElroy, J. E. Mendel, and F. P. Roberts	9

FIGURES

1	PG-6 Pot, Showing Upper and Middle Core Drill	11
2	Upper Core Drill Hole on PG-6 Pot	12
3	PG-6 Pot in Environmental Storage	14
4	PG-6 Pot Temperature History	15

TABLES

1	Composition of Simulated Rising Level Glass	3
2	Composition of Frit 111-15	4
3	Sodium and Strontium Leach Rates with Borosilicate Solids	4
4	Accelerated Leach Tests with Borosilicate Solids	5
5	Progress of Product Evaluation Tests in the Radioactive Laboratory	6
6	SSETF Test Summary	8
7	Laboratory Analysis of PG-6 Core Hole and Core Drill Samples	17

QUARTERLY PROGRESS REPORT
RESEARCH AND DEVELOPMENT ACTIVITIES
FIXATION OF RADIOACTIVE RESIDUES
February, March, and April 1971

INTRODUCTION

This progress report is the forty-ninth in a series presenting research and development activities in the field of radioactive wastes.

Experimental work charged to programs other than those of the Division of Reactor Development and Technology is sometimes included for general interest and completeness; such work is identified in the headings.

SUMMARY

Decontamination of B-Cell and the associated WSEP equipment for standby is approximately 70% complete.

Nonradioactive laboratory measurements on borosilicate solids indicates insignificant effects on leach rates in water storage at 100°C versus storage of 600°C. Sodium leach rates are 4 to 15 times greater than strontium leach rates. The solid from rising level glass is approximately 10 times more leachable than that from the in-pot melting process.

A total of seven pots containing solidified radioactive waste from WSEP have been core-drilled, and the samples are undergoing testing.

Core-drilling a WSEP pot containing 3-year-old, devitrified phosphate glass revealed that a recent leak had developed in a thermowell which had permitted approximately 2 liters of water

to enter the pot. The water had penetrated or dissolved approximately 20 kilograms of the original 174 kilograms of solid present.

WSEP CELL-EQUIPMENT DECONTAMINATION

J. L. McElroy

The radioactive demonstration of the WSEP solidification processes was terminated in October 1970. Since that time the major operating objective has been toward putting the WSEP processing cell (B-Cell) in standby. The cell is being partially decontaminated and decommissioned to assure that during standby the cell will be safe, that minimum surveillance will be required, and that a complete decontamination can be performed at a later date with minimum difficulty and cost.

Major activities have included the flushing of the cell and equipment with water and/or alkaline permanganate and dilute nitric acid solutions, the concentration and disposal of radioactive waste and flush solutions, and the transfer of the WSEP waste pots to the Solids Storage Engineering Test Facility (SSETF) for storage. Decontamination is approximately 70% complete.

EVALUATION OF SOLIDIFIED WASTE PRODUCTS

NONRADIOACTIVE LABORATORY STUDIES

Leach Rates of Borosilicate Glasses - F. P. Roberts

The sodium and strontium leach rates of simulated products from the pot rising-level glass and the spray in-pot melting processes have been measured using the standard (slow) leach test. Total leachability of these solids, using the accelerated leach test have also been determined.

The simulated rising-level glass, as shown in Table 1, was prepared by mixing the glass-formers (SiO_2 , B_2O_3 , and Na_2O) with a calcine corresponding to PW-4m waste. The mixture was heated in platinum for 24 hours at 900°C . It was then poured into two stainless steel beakers which were cooled at 30°C/hr . One was stored at 600°C and the other at 100°C for a period of 8 weeks.

TABLE 1. Composition of Simulated Rising Level Glass

<u>Constituent</u>	<u>Wt%</u>
Waste oxides	40
SiO_2	21
B_2O_3	27
Na_2O	12

The simulated in-pot melting solid was prepared by mixing 30 wt% calcine corresponding to PW-4m waste with 70 wt% of special frit 111-15 in Table 2. The mixture was heated to 850°C and held at that temperature for 24 hours. The melt was poured into two stainless steel beakers and cooled at 30°C/hr . One was stored at 600°C and the other at 100°C for a period of 8 weeks. Both the rising-level glass and the in-pot melting specimens are nonhomogeneous. In both cases, the bulk of the product appears to be a dispersion of a grey phase in a dark-green phase. In addition, a small amount of a yellow third phase appears on the surface. Care was taken to avoid inclusion of the yellow phase in the leach test specimens.

TABLE 2. Composition of Frit 111-15

<u>Constituent</u>	<u>Wt%</u>
B ₂ O ₃	36
SiO ₂	32
ZnO	15
CaO	1.5
MgO	1.75
SrO	1.75
BaO	1.75
Na ₂ O	4.0
K ₂ O	6.0

The sodium and strontium leach rates obtained by the standard leach test are given in Table 3. The rising-level glass is more leachable by a factor of 10 than the solid from in-pot melting. The effect of storage temperatures on the leachability does not appear to be significant. Sodium is more leachable than strontium by factors ranging from 4 to 15.

TABLE 3. Sodium and Strontium Leach Rates with Borosilicate Solids

<u>Duration of Test, Weeks</u>	<u>Sodium Leach Rate,</u> <u>g/cm²/d × 10⁵</u>		<u>Strontium Leach Rate,</u> <u>g/cm²/d × 10⁵</u>	
	<u>100°C</u>	<u>600°C</u>	<u>100°C</u>	<u>600°C</u>
	<u>Storage</u> <u>Temperature</u>	<u>Storage</u> <u>Temperature</u>	<u>Storage</u> <u>Temperature</u>	<u>Storage</u> <u>Temperature</u>
<u>In-Pot-Melting</u>				
2	2.0	2.0	0.40	0.38
4	1.3	1.3	0.29	0.29
6	1.2	1.3	0.28	0.28
8	1.3	1.3	0.26	0.27
<u>Rising-Level Glass</u>				
2	19	22	4.2	1.8
4	15	16	2.6	1.1
6	13	21	2.0	1.4
8	11	14	1.7	0.27

The results from the accelerated leach test are given in Table 4. As with the standard leach test, the rising-level glass is shown to be much more leachable than the in-pot melting solid.

TABLE 4. Accelerated Leach Tests
with Borosilicate Solids

	Weight Loss, % of Original	
	100°C Storage Temperature	600°C Storage Temperature
<u>In-Pot Melting</u>		
First 24 hours	2.7	2.7
Second 24 hours	2.9	2.5
Third 24 hours	<u>2.9</u>	<u>2.5</u>
TOTAL (a)	8.3	7.4
<u>Rising-Level Glass</u>		
First 24 hours	46	45
Second 24 hours	6.0	7.0
Third 24 hours	<u>2.4</u>	<u>1.9</u>
TOTAL (a)	51	50

a. The total weight loss is taken from the measurement after the final leach test period.

RADIOACTIVE LABORATORY STUDIES-STATUS - F. P. Roberts
and C. Hampton, Jr.

Seven of the WSEP pots have been core-drilled and satisfactory samples have been obtained for radioactive testing. Table 5 shows the status of the various radioactive laboratory tests. Satisfactory samples could not be obtained for the dispersion test for the two borosilicate products in Runs SS-12 and PC-9. The core-drilling technique did provide minimum samples for direct gamma counting and leach testing,

TABLE 5. Progress of Product Evaluation Tests
in the Radioactive Laboratory

<u>Run Number</u>	<u>Sample Number</u>	<u>Leach Test</u>	<u>Dispersion Test</u>	<u>Direct Gamma Scan</u>
PG-6 ↓	29A	o		x
	29B		x	x
	29C			x
	30A			x
	30B			x
	32A			x
	32B			x
	32C			x
	32D	o		x
PG-7 ↓	2A	x		
	2B		x	x
	21A	x		x
	21B	x		x
	21C		x	x
	22A	x		x
	22B		x	x
	22C	x		x
PG-10 ↓	16A	o		x
	16B			x
	16C		x	x
	17A			x
	17B	o		x
SS-6 ↓	19A	o		
	19B		x	x
	20A	o		x
	20B			x
	20C			x
SS-10 ↓	7A	x		x
	7C			x
	23A			x
	23B			x
	23C			x
SS-12	34A	o		x
PC-9	13	z		o
	14			o
	37			o
	38			o
	39	z		o

o in progress
x completed
z to be started

and these tests are in progress. It is planned to extend the leach tests to longer periods of time than the originally scheduled 12 weeks.

The high-temperature volatility studies using radioactive samples of the WSEP pots are now underway. In these studies, radioactive samples of solidified waste will be heated to 800°C to 1100°C, and volatilization of cesium and cerium will be measured as a function of time.

PRODUCT MEASUREMENT, TESTING, AND STORAGE

Solids Storage Engineering Test Facility (SSETF) - J. L. McElroy

Six pots are presently in test in environmental tests pods in SSETF. Two additional pots are in standby condition as a result of pot core drilling operations, and will be returned to test after their thermocouples are replaced. The original pot thermocouples are subject to failure at the connector because the thermocouple connector is located in a high temperature environment within the environmental pod when the pot is in test. Replacement thermocouples have the connector above the pod. The test summary for SSETF pots is given in Table 6.

The PG-6 pot was not placed back into environmental testing after it was found that water had entered and attacked the product through failed pot thermocouple wells (see "Water Breaching of the PG-6 Pot" later in this section). A pot containing borosilicate glass solids from pot calcination Run PC-9 (rising-level glass) was selected as an environmental test replacement for the PG-6 pot. The PC-9 (RLG) pot will be maintained in an air environment at an average solids temperature of approximately 600°C to study the effect of prolonged elevated temperature on the solids.

As shown in Table 6, seven WSEP pots have been core-drilled to obtain solids samples for evaluation in the

TABLE 6. SSETF Test Summary

Run Number Pot Number Cubicle Number	Waste Type	Testing Started	Pod Environment	Maximum Temperature, °C			Core Drill Sampled
				Pod	Pot Wall	℄	
Environmental Test Pots							
SS-4 40 A-21-3	PW-2	9/11/69	Water	85	85	103	
PG-6 ^(a) 39	PW-1	10/01/69		(out of test)			1/15/71
PC-6 ^(b) 30 A-21-4	PW-2	11/17/69	Air	490	---	---	
SS-8 43 A-21-2	PW-1	1/05/70	Air	480	---	520	
SS-10 54 A-32-4	PW-4m	2/09/70	Standby ^(c)	190	220	---	11/19/70
PG-7 37 A-32-3	PW-2	5/15/70 ^(d)	Air	435	---	555	8/18/70
SS-9 36 A-31-1	PW-4m	6/12/70	Air	480	480	525	
PG-8 46 A-31-2	PW-4m	6/29/70	Standby ^(c)	250	---	---	
PC-9(RLG) 58 A-21-1	PW-4m (borosilicate)	4/21/71	Air	450	530	760	12/29/70 3/11/71
Nonenvironmental Test Pots ^(e)							
SS-12(IPM) 48	PW-4m (borosilicate)	---	---	---	---	---	12/1/70 3/2/71
PG-10 53	PW-4m	---	---	---	---	---	12/9/70
SS-6 42	PW-1	---	---	---	---	---	12/22/70

a. Removed from test 1/13/71 for core sampling. Replaced with PC-9 pot on 4/21/71.

b. All centerline thermocouples are inoperative

c. Minimum monitoring - air environment and no auxiliary electrical heat. These pots will be put back in test after their thermocouples are replaced.

d. Auxiliary electrical heat first applied on 4/26/71.

e. These pots are stored in the open, ambient air.

radioactive laboratory. The solids in five of these pots were successfully sampled using a low-speed (250 to 500 rpm) motor with an air-cooled bit. These pots all contained either spray-solidified ceramic or devitrified phosphate glass. The remaining two pots (SS-12 and PC-9) contained brittle borosilicate solids, and required the use of a high-speed (3450 rpm) motor with a water-cooled bit to obtain partially acceptable samples. With the low-speed, air-cooled bit, the borosilicate glass samples shattered and were ground into pieces too small to use. Although the samples still shattered with the high-speed drill, some of the pieces were large enough for evaluation and the surface area could be estimated so that leach tests could be performed. Further core drilling of pots is unlikely for the rest of the current fiscal year.

Water Breeching of the PG-6 Pot - J. L. McElroy, J. E. Mendel, and F. P. Roberts

The PG-6 phosphate glass pot (an 8-inch-diameter stainless steel pot) was successfully filled with phosphate glass PW-1 solids in May 1968. The pot was placed in interim water storage in B-Cell immediately after the run, and in October 1969 the pot was transferred from B-Cell where the solidification test was performed, to A-Cell where it was placed in a controlled water environment in SSETF. The pot was removed from the water environment in January 1969 for core drilling to obtain samples of the 32-month-old product. When the pot was core-drilled, a thick semi-fluid material ran out of the top core drill hole and down the side of the pot.

Core drill samples from the top, middle, and bottom of the pot showed the product to be devitrified and to have a reasonably uniform fission product distribution. A semi-fluid region at the top core drill hole had a water content of 15 wt% while scrapings from the middle hole were only 4 wt% water. The product in the bottom hole appeared chalky and crumbly, and

although it appeared dry (<0.1 wt% water), it also appeared to have been wet at some time. Inspection of the top surface of the pot solids revealed them to be crumbly and cracked like a dried-up bed of clay. A rod was pushed down 8 inches into the surface, indicating that the product had deteriorated to at least this depth. Figure 1 is a photograph which shows the top and middle core holes in the pot, and Figure 2 shows a closeup of the top hole.

Water entered the PG-6 pot through failed pot thermocouple wells while the pot was in water in the environmental test pod. Thermowell failures were detected by the inability to pull a substantial vacuum on either of the thermowells, and by pressure increases in the pot when applying air to the end of the thermowells. The intermediate thermowell (located halfway between the pot centerline and the pot wall) indicated a more substantial leak than the centerline thermowell. The thermowells were sound at the start of the environmental test as indicated by a vacuum leak test result of 8.3×10^{-8} atm-cm³/sec for the pot and pot-to-pod piping at the start of the test. This leak check indicated that the pot did not have leaks and that the pot did not contain volatile material or off-gassing would have prevented the successful leak check.

With the failed thermowells it was possible for water in the environmental pod to enter the pot and attack the hot, devitrified product and cause degradation and severe leaching. The water level in the pod was nominally nine inches below the thermowell opening but the pod was overfilled to above the openings on one known occasion. The approximate net volume inside the thermowells was 0.5 liter with thermocouples installed. This volume of water is less than that estimated to be in the product (approximately 2 liters). It is believed that the additional water entered the pot from condensation that occurs in the upper region of the environmental pod. The pod

Neg 710217-6

FIGURE 1. PG-6 Pot, Showing Upper and Middle Core Drill

Neg 710217-12

FIGURE 2. Upper Core Drill Hole on PG-6 Pot

water was maintained at 75 to 95°C and vapors were condensed by the upper pod cooling coil and the top pod flange. The condensed moisture dripped onto the thermowell opening and entered the pot. This situation is depicted in Figure 3.

During the filling of the waste receiver in May 1968, the wall temperature was maintained at 575°C to promote slumping of the glass in the pot to assure uniform filling. The maximum centerline temperature encountered during the run was approximately 900°C. The steady-state pot centerline temperature was 780°C with a 400°C wall temperature while the pot was setting in the furnace with cooling air on. The temperature history of the pot is presented in Figure 4. From this plot it is seen that after the run in May 1968, the pot centerline temperature has been below approximately 400°C, and the average temperature was approximately 200°C. During the time the pot was in an environmental test pod (where the thermowell is known to have failed), the centerline temperature decreased from 190 to 125°C.

A review of existing corrosion data indicate that corrosion of 304L stainless steel at temperatures of 825°C or less in phosphate glass melts is less than 0.012 inches/yr. The PG-6 pot thermowells are made of 310 stainless steel which, for this type of service, is a better material. The thermowells are made of 1/2 and 3/4 inch schedule 80 pipe (about 0.15-inch wall thickness). The estimated actual corrosion rate for the thermowells, averaged over the entire life from pot filling to core drilling, is 0.06 inches/yr. Based on the pot temperature history (below about 400°C as shown in Figure 4 and the existing corrosion data), the thermowells should not have failed.

Possible explanations for the corrosive failure of the thermowells are being evaluated. A sticky substance found on the surface of devitrified phosphate glass samples in the

Neg 711566-1

FIGURE 3. PG-6 Pot in Environmental Storage

FIGURE 4. PG-6-Pot Temperature History

laboratory may exude from the product and cause corrosion. It may also be possible that activation corrosion is being initiated during the period when the pot is at high temperature (i.e., while filling the pot), and that corrosion continues because deactivation does not occur during pot cool-down. Corrosion data indicate that activation may occur at about 875°C.

A scan was made of the pot wall thickness using an ultrasonic device. Measurements were taken from 12 inches above the product to the bottom of the pot at intervals of 4 to 6 inches and in 10 locations around the pot at each level measured. The thicknesses were fairly uniform (varying from 0.313 to 0.352 inches), and indicate no pot wall corrosion occurred. (The standard wall thickness for 8-inch schedule 40 pipe is 0.322 inches.)

Samples of the solidified waste were obtained from the PG-6 pot and the results of the analysis of these samples are given in Table 7. In addition to the core samples, samples were taken of the semi-fluid material in the pot in Zone 1, 26 inches down from the top of the pot. (This material solidified rapidly when the temperature decreased from the 100°C pot centerline temperatures to the cell ambient temperature of about 40°C.) Samples were also taken from the solidified material that had oozed down the pot wall and from the crumbs in the Zone 3 hole, 51 inches down from the top of the pot. Data from these samples show that the semi-fluid material had a water content of about 15 wt%, that it was very soluble in water, and that it was acidic.

The data indicate that the water probably entered the pot in the vicinity of the upper portion of the solidified waste as shown in Figure 3. From analyses of water in the fluid samples, the average water content was 10 wt% and the estimated net volume of aqueous phase was equivalent to a 4-inch diameter

TABLE 7. Laboratory Analysis of PG-6 Core Hole and Core Drill Samples

Sample Number and Location	Gamma Energy Analysis, Counts/min-g ^(a)				Water Content, wt%	Solubility on ^(c) Dry Basis, wt%	Na Content on Dry Basis, wt%	P Content on Dry Basis, wt%	Na/P ^(e) Ratio	pH
	¹³⁴ Cs	¹³⁷ Cs	¹⁴⁴ Ce	¹⁰⁶ Ru						
W-1095, Semi-fluid from Top Hole No. 29	8	201	14	6	15	89	11.1	33	0.34	3 ^(f)
W-1098, Solid Scrapings from Top Hole, No. 29	12	354	41	20	15	75	10.6	25	0.42	----
W-1097, Solid Scraping from Side of Pot	11	266	28 ^(d)	9	11	73	10.5	24	0.44	----
W-1096, Solid Tear Scraping from Side of Pot	17	400	32	19	13	92	11.9	30	0.40	----
W-1099, Solids from Middle Hole, No. 30	22	542	685	23	4	17	5.7	16	0.36	----
Core Drill Samples										
29-A (Top Core. 26 inches from top of pot)		31	167							
29-B (Top Core. 26 inches from top of pot)		36	168							
29-C (Top Core. 26 inches from top of pot)		32	171							
30-A (Middle Core. 51 inches from top of pot)		32	196							
30-B (Middle Core. 51 inches from top of pot)		32	196							
32-C (Bottom Core. 89 inches from top of pot)		32	154							
32-D (Bottom Core. 89 inches from top of pot)		32	158		<0.1					
32 (Bottom Core. 89 inches from top of pot) Random Pieces		---	---							

a. Precision of $\pm 4\%$ on core samples and $\pm 20\%$ on others.

b. Based on weight loss on heating to slightly over 100°C.

c. Based on approximately one gram dry solid placed on 10 ml water.

d. Average of 2 counts.

e. Feed Na/P = 0.3 (51.75 g/l Na/198.80 g/l P)

f. 2 g sample in 10 ml water.

by 3-foot high cylindrical section in the top of the pot. From these bases, the amount of water present was estimated at about 2 liters and the amount of solid which was penetrated or dissolved was estimated at about 20 kilograms of the 174 kilograms originally present.

The Na/P ratio in the semi-fluid material was slightly higher than that theoretically in the solid. The normal sequence of water attack on phosphate solids is to leach out low-valent cations leaving a skeleton of high-valent phosphate material. It appears that the leaching continued until the skeleton became weakened and a considerable volume of it collapsed. The collapsed skeleton should contain most of the rare earths and remain relatively insoluble.* Because the leaching had advanced so far, only about 23% of the phosphate remained with the skeletal remnants. (This was calculated assuming a Na/P ratio of 0.39 in the dissolved material, and assuming that all sodium was dissolved.)

The liquid rising to the top of the dissolved material would be expected to have the highest Cs/Ce ratio because the cerium phosphate residue, having a higher molecular weight, will tend to settle. The liquid rising to the top should also contain the most water and be the least viscous. Therefore, the liquid first out of the top hole and the sample from inside the hole (which is in effect a supernate sample of the remaining material) would be expected to have the highest Cs/Ce ratio, which they do.

* It is known that the Ce-144 leach rate is usually about 10^{-7} g/cm²/day and relatively independent of the Cs-137 leach rate; thus the cerium leach rate is often a factor of 100 lower than that of cesium. A factor of about 70 is required to explain the analytical results in Table 7.

The material which drained from the top hole is more concentrated than the material remaining inside. More rapid evaporation based on the higher surface to volume ratio explains this. The solids material from the middle hole has a much lower Cs/Ce ratio, nearer to that of the solid. Less water reached this point in the pot, thus leaching had not advanced very far.

The gamma energy analysis of the core drill samples indicates a nearly uniform distribution of fission products from the top to the bottom of the pot. The slight increase in Ce-144 in the middle (mid-plane) core is believed to be insignificant. The core samples are of the solid product within 1-1/2 inches of the pot wall.

Accelerated leach rate data with devitrified PW-1 phosphate glass product indicate that as high as 20 to 50 wt% of the product is leached away during three days in boiling water.⁽¹⁾ From this information, it is not surprising to find the dissolved material in the pot because boiling and refluxing were probably occurring within the pot for at least several days. Additional efforts to duplicate the reaction of water with the product of PG-6 were carried out in the laboratory using non-radioactive phosphate glasses prepared from PW-1 type waste. Both good quality glass and devitrified glass were tested in order to evaluate the effect of devitrification which occurs on storage at elevated temperatures.

Two specimens of the devitrified solid were placed in a flask fitted with a reflux condenser. One was immersed in the water and the other was suspended in the vapor phase. The

1. R. J. Thompson, J. E. Mendel, J. H. Kleinpeter. Waste Solidification Demonstration Program: Characterization of Nonradioactive Samples of Solidified High-Level Waste Table 6.1, BNWL-1393. pp. 6.2 (June 1970).

flask was heated to the boiling point of the water and maintained at that temperature for 33 days. A specimen of the vitreous solid was immersed in boiling water in a second flask for 32 days. Visual observations were made periodically, and at the end of the test period the specimens were removed, dried at 200°C, weighed, and sectioned.

The devitrified specimen immersed in boiling water began reacting almost immediately. After 90 minutes the initially dark-grey color of the solid had changed to light tan. One day later the specimen had deteriorated markedly and the aqueous phase had become saturated with soluble salts. Recrystallization of these salts was evident, and at the end of the test it was difficult to distinguish the original specimen from the material which had dissolved and reprecipitated. After drying the mass for 16 hours at 200°C, the surface was coated with a sticky substance which was exuding from the solid. The weight loss measurement was meaningless because of the recrystallization. A cross-section of the mass revealed that the reaction had completely penetrated the specimen and that the solid was visually homogeneous.

The devitrified specimen suspended in the vapor phase reacted somewhat more slowly than that in the liquid phase. Six days elapsed before the sample color completely faded, and at the end of the test the sample was still intact; however, the specimen lost 48% of its original weight during the 33-day test. The cross-section again showed that the reaction had completely penetrated the sample.

The vitreous sample immersed in boiling water gave evidence of only slight reaction. A thin layer of salt covered the sample surface by the end of the second day, but otherwise no visual evidence of reaction was noted. The weight loss was 16.5% over the 32-day period.

The behavior of the devitrified specimens resulted in reaction products very similar to those observed in the PG-6 pot. This test substantiated the conclusion that the PG-6 product had undergone severe leaching by the water that penetrated the pot.

An attempt was made to determine the amount of radioactivity that entered the pod water from the pot (the water was transferred out before the pot was core-drilled). Radiation readings of the external cell piping through which the pod water was transferred indicated that an excessive amount of radioactivity did not pass through the piping, as the readings were near normal. Since the pot thermowell openings were normally above the surface of the pod storage water, the main mechanism for activity transfer from the pot to storage water would have been by distillation.

Continuous monitoring of the PG-6 pot pressure during environmental storage indicated no pressurization during the breeching by water. This can partially be attributed to condensation of vapors (refluxing) in the top of the pot.

It is believed that production pots may eventually not require thermocouples and hence thermowells may not be in the pots; however, if thermowells are required and if this type failure is only appropriate to thermowells, then a revised method will be required for locating thermocouples in the pots when this type of waste product is made.

A summary was made of the leak testing of the phosphate glass pots. Phosphate glass pot PG-7 was known to have developed a similar leaky thermowell during a 10-month time span between leak checks. The summary revealed that PG-1, PG-2, and PG-3 were leak checked within a month after filling and have not been rechecked. However, these pots contained

relatively little fission product heat. As such, they may not have a corrosion problem because the product was maintained at lower temperatures and probably had not oozed liquid if they were not devitrified. Pot PG-5 has not been checked but will be soon. The PG-5 pot emitted nearly 9 kilowatts of heat at filling. However, because it is a 12-inch diameter pot, the maximum centerline temperature during air storage was only 650°C.

DISTRIBUTION

No. of
Copies
OFFSITE

1	<u>AEC Chicago Patent Group</u> G. H. Lee
1	<u>AEC Dayton Area Office</u> P. O. Box 66 Miamisburg, Ohio, 45342 E. A. Walker, Chief Operations Branch
180	<u>AEC Division of Technical Information Extension</u>
2	<u>AEC Division of Materials Licensing</u> 4915 St. Elmo Avenue Bethesda, Maryland 20014 John A. McBride R. B. Chitwood
1	<u>AEC Division of Naval Reactors</u> M. E. Miles
1	<u>AEC Division of Production</u> W. L. Lennemann
5	<u>AEC Division of Reactor Development and Technology</u> Asst. Dir. for Reactor Technology E. E. Sinclair Chief, Fuel Recycle Br., W. H. McVey W. H. Regan
6	<u>AEC Division of Waste and Scrap Management</u> C. B. Bartlett G. Daly H. A. Nowak Alex F. Perge H. R. Soule R. D. Walton
4	<u>AEC Idaho Operations Office</u> P. O. Box 2108 Idaho Falls, Idaho 83401 K. K. Kennedy

No. of
Copies

- 3 Allied-Gulf Nuclear Services
 P. O. Box 35
 Florham Park, New Jersey 07932
 R. L. Newman
 A. Schneider
 J. J. Shefcik
- 3 Argonne National Laboratory
 S. Lawroski
 J. Loeding
 R. C. Vogel
- 1 Argonne National Laboratory
 P. O. Box 2528
 Idaho Falls, Idaho 83401.
 P. Fineman
- 4 Atomic Energy of Canada Limited
 Chalk River Nuclear Laboratories
 Scientific Document Distribution Office
 Chalk River, Ontario, Canada
- 2 Atomic Energy Research Establishment
 Harwell, Didcot, Berks, England
 K. D. B. Johnson
 Dr. J. B. Lewis
- 2 AAEC Research Establishment
 The Director
 Private Mail Bag
 Sutherland, NSW 2232
 Australia
 L. H. Keher
 P. A. Bonhote
- 1 Bhabha Atomic Research Centre
 Head, Waste Treatment Division
 Apollo Pier Road, Bombay - 1
 K. T. Thomas
- 1 Bhabha Atomic Research Centre
 Organic Waste Laboratory
 Plutonium Plant Site
 Trombay, Bombay,
 India
 Keshava Chandra

No. of
Copies

- 1 Bhabha Atomic Research Centre
Scientific Officer (C),
Waste Treatment Division,
Engineering Hall No. 5,
Trombay, Bombay - 85
N. S. Sunder Rajan
- 1 Burns and Roe, Inc.
700 Kinderamack Road
Oradell, New Jersey 07649
P. P. DeRienzo
Chief Nuclear & Process Engineer
- 1 CEA-CHC Boite
Postale No. 510
Paris 15, France
F. Dumahel
- 4 Centre de Marcoule
B. P. 106
30 - Bagnols S/Ceze
France
Mrs. R. Bonniaud
C. J. Jouannaud
F. Laude
C. Sombret
- 2 Centre d'Etudes Nucleaires
de Fontenay-aux-Roses
Boite Postale 6
92 - Fontenay-aux-Roses, France
M. J. Pomerola
P. J. Regnaut
- 1 Centre d'Etudes Nucleaires de Saclay
Service des Produits de Fission
Boite Postale No. 2
91 Gif/Yvette, France
Andre J. Roggenbass
- 1 CNEN
Health Protection Division
Viale Regina Margherita 125
Roma, Italy
Ferruccio Gera

No. of
Copies

- 1 Commission of the European Communities
General Directorate XV
200 rue de la Loi
1040 Brussels
Belgium
Dr. P. Kruys
- 1 Dow Chemical Company (AEC)
D. L. Ziegler
- 6 duPont Company, Aiken (AEC)
R. M. Girdler
C. H. Ice
L. H. Meyer
C. M. Patterson
E. B. Sheldon
D. S. Webster
- 1 duPont Company, Wilmington (AEC)
J. R. Thayer
- 1 EURATOM
Health Physics Div.
29, Rue Aldringer
Luxembourg, Belgium
Rene Amavis
- 3 European Institute for Transuranium
Elements
P. O. Box 2266
75 Karlsruhe/W. Germany
Birgit Seufert
- 1 European Nuclear Energy Agency
38 Boulevard Suchet
Paris 16, France
Dr. E. Wallauschek
- 1 French Atomic Energy Commission
Cadarache
Boite Postale No. 1
13 - Saint-Paul-Lez-Durance (France)
P. E. Pottier
- 1 General Electric Company
175 Curtner Ave.
(M/C 160)
San Jose, California 95125
R. G. Barnes

No. of
Copies

- 1 General Electric Co.
Midwest Fuel Recovery Plant
Route 1, Box 219-B
Morris, Illinois 60450
S. G. Smolen
- 2 General Electric Company
Vallecitos Nuclear Center
Vallecitos Road
Pleasanton, California 94566
Dr. W. H. Reas
- 2 Gesellschaft fur Strahlenforschung
mbH München
3392 Clausthal-Zellerfeld
Bornhardstasse 22
Germany
Prof. Dr. H. Borchert
Dr. I. K. Kühn
- 1 Harvard School of Public Health
665 Huntington Ave.
Boston, Massachusetts 02115
Dade W. Moeller
- 1 Hitachi Works, Hitachi Ltd.
Nuclear Power Plant Dept.
1-1 Saiwai-cho
3-chome
Hitachi-shi, Ibaraki
Ken 317
Japan
A. Shimozato
- 3 Idaho Nuclear Corporation
P. O. Box 1845
Idaho Falls, Idaho 83401
G. O. Bright
J. A. Buckham
B. R. Wheeler

No. of
Copies

- 1 Illinois State Geological Survey Division
Urbana, Illinois 61801
J. C. Frye, Chief
- 1 India Atomic Energy Establishment
Waste Treatment Plant and Decontamination
Center
Bombay 85, India
Mr. Victor Amalraj, Plant Superintendent
- 1 The Johns Hopkins University
209 Ames Hall
Baltimore, Md. 21218
A. Wolman
- 1 Junta de Energia Nuclear
Division de Materiales
Ciudad Universitaria
Madrid-3
Spain
Dr. Leandros Ramos
- 1 Kansas State Dept. of Health
Environmental Health Division
Topeka, Kansas 66612
Robert C. Will
- 1 KFA - Julich
Abteilung Dekontamination
517 Julich 1
P. O. Box 365
Fed. Rep. of Germany
Dr. K. H. Rattay
- 1 Lawrence Radiation Laboratory, Berkeley (AEC)
Technical Information Division Library
- 1 Lawrence Radiation Laboratory, Livermore (AEC)
Technical Information Division Library
- 1 Los Alamos Scientific Laboratory (AEC)
C. W. Christenson
- 3 Ministry of Education & Research
53 Bonn
Heussalle 2-10
Germany (Fed. Rep)
Dr. J. Mehl

No. of
Copies

- 2 Mound Laboratory (AEC)
 S. Freeman
 J. J. Goldin
- 1 MPR Associates, Inc.
 1140 Connecticut Ave. N.W.
 Washington, D.C. 20036
 Librarian
- 1 National Lead Company
 111 Broadway
 New York, New York 10006
 Stephen Brown
- 1 National Academy of Sciences
 Committee of Radioactive Waste Management
 National Research Council
 2101 Constitution Avenue
 Washington, D.C. 20418
 Dr. Cyrus Klingsberg,
 Tech. Secretary
- 1 NYS Atomic & Space Development Authority
 230 Park Ave., Rm 2425
 New York, N. Y. 10017
 J. G. Cline, General Manager
- 2 N Nuclear Fuel Services, Inc.
 P. O. Box 124
 West Valley, N. Y. 14171
 J. P. Duckworth, Plant Manager

 6000 Executive Blvd, Suite 600
 Rockville, Maryland 20852
 Dr. E. D. North, Director of
 Technical Administration
- 1 Nuclear Research Center
 Waste Management Dept.
 D 75 Karlsruhe
 Weberstr. 5
 Germany
 Dr. H. Krouse
- 1 Nuclear Safety Associates
 1055-R Rockville Pike
 Rockville, Maryland 20852
 W. A. Rodger

No. of
Copies

- 2 Numec
 Apollo, Penn. 15613
 R. F. Duda
 L. L. Zahn
- 4 Oak Ridge National Laboratory (AEC)
 Central Research Library,
 Document Reference Sect.
 Central Research Library,
 ORNL
 Laboratory Records Dept.,
 ORNL
 Laboratory Records Dept.,
 ORNL-RC
- 2 Radiation Protection Dept.
 Luisenstrasse 46,
 Bad Godesberg, West Germany
 H. M. Holtzem
 G. Straimer
- 1 Dr. H. F. Ramdohr
 c/o Friedrich Uhde
 GmbH
 10-12, Deggingstrasse
 46 Dortmund
 Germany
- 3 Studiecentrum voor Kernenergie,
 SCK, CEN
 Boeretang, 200,
 2400 Mol. Belgium
 Dr. L. Baetsle
 Dr. P. Dejonghe
 Library
- 2 Tokai Works
 Power Reactor and Nuclear Fuel Development
 Corp.
 Tokai-Mura,
 Ibaraki-Ken, Japan
 M. Ichikawa
 Library

No. of
Copies

- 7 Union Carbide Corporation (ORNL)
 P. S. Baker
 R. E. Blanco
 J. O. Blomeke
 W. C. Clark
 F. M. Empson
 H. B. Godbee
 M. E. Whatley
- 1 United Kingdom Atomic Energy Authority
 Risley, England
 D. W. Clelland
- 1 University of Arizona
 Tucson, Arizona 85721
 E. S. Simpson, Professor of Hydrology
- 1 University of Minnesota
 Environmental Health Research
 and Training Center
 Room 1108, Mayo Memorial Hospital
 Minneapolis, Minnesota 55455
 Dr. C. P. Straub
- 1 The University of Texas at Austin
 Engineering Laboratories Bldg. 307
 Austin, Texas 78712
 Dr. E. F. Gloyna
- 2 U. S. Bureau of Mines
 Washington, D.C. 20240
 J. W. Watkins Dir., Petroleum Research
- 1 U. S. Geological Survey
 Washington, D.C.
 R. L. Nace
- 1 USDA National Agricultural Library
 Current Serial Record
 Beltsville, Maryland 20705
- 1 Vanderbilt University
 Box 1670, Stn B
 Nashville, Tennessee
 P. A. Krenkel

ONSITE-HANFORD

- 1 AEC Chicago Patent Group
 R. M. Poteat (Richland)

No. of
Copies

6	<u>AEC Richland Operations Office</u> J. T. Christy O. J. Elgert (2) J. E. Goodwin C. L. Robinson W. E. Lotz
1	<u>Atlantic Richfield Company</u> P. O. Box 370 Richland, Washington 99352 H. C. Rathvon
14	<u>Atlantic Richfield Hanford Company</u> S. J. Beard M. H. Campbell J. B. Fecht W. M. Harty R. E. Isaacson L. M. Knights J. D. Moore G. C. Oberg H. P. Shaw P. W. Smith R. E. Smith R. E. Tomlinson J. H. Warren File Copy
2	<u>Douglas United Nuclear, Inc.</u>
4	<u>RDT Assistant Director for Pacific Northwest Programs</u> P. G. Holsted (1) A. D. Toth (1)
3	<u>WADCO Corp.</u> J. M. Atwood A. G. Blasewitz (2)

No. of
Copies

25

Battelle-Northwest

R. E. Burns
G. M. Dalen
V. L. Hammond
J. N. Hartley
M. M. Hendrickson
R. K. Hilliard
G. Jansen
J. D. Kaser
J. L. McElroy (2)
J. E. Mendel
F. L. Mourich
R. E. Nightingale
L. D. Perrigo
F. P. Roberts
K. J. Schneider
C. J. Touhill
N. G. Wittenbrock
Technical Information Files (5)
Technical Publications (2)