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QUARTERLY PROGRESS REPORT
RESEARCH AND DEVELOPMENT ACTIVITIES
WASTE FIXATION PROGRAM
DECEMBER 1972 THROUGH MARCH 1973

Battelle

Pacific Northwest Laboratories
Richland, Washington 99352

APRIL 1973

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December 1972 through March 1973

Compiled by
A. M. Platt
Nuclear Waste Technology Department

April 1973

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QUARTERLY PROGRESS REPORT
RESEARCH AND DEVELOPMENT ACTIVITIES
WASTE FIXATION PROGRAM

December 1972 through March 1973

INTRODUCTION

This progress report is the second in a series that presents research and development activities in the field of radioactive waste fixation. The first progress report, BNWL-1699, presented a description of the proposed activities within the current Waste Fixation Program.

SUMMARY

A number of different borosilicate enamel-type formulations were investigated in which the major cations were lead, copper, or zinc. From these, a zinc borosilicate glass was selected for intensive study as a high-level waste fixation media. This glass forms fluid melts at 1150 °C and can incorporate up to about 40 wt % waste calcine. With this type glass, the PW-6 (high sodium waste) product leachability is intermediate between Pyrex and bottle glass, where the PW-4b ("clean" waste) product leachability is comparable to that of Pyrex glass.

Inconel[®] 690 has been chosen as the material of construction for the first developmental continuous melter. Inconel 690 corroded at a rate of only 2.1-3.5 mils/month at 1150 °C, and 4.3 to 5.4 mils/month at 1200 °C in a PW-6 melt formulation. In a zinc bearing PW-4b enamel melt the corrosion rate at 1150 °C

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was 1.4-1.9 mils/month. The creep strength of Inconel 690 is not known but at the melter operating conditions it is estimated to exceed 200 psi for 10,000 hours to rupture.

Preliminary scoping studies conducted with PW-4b wastes in a fluidized bed at ICPP show promise of a workable flowsheet. Calcination of PW-6 waste presents an entirely different problem due to the presence of sodium nitrate. A PW-6 run conducted at 800 °C, with aluminum nitrate added to form NaAlO_2 , was successful. However, mechanical problems are anticipated at an 800 °C bed temperature and a lower temperature flowsheet is being sought.

Core drill samples obtained from a canister of borosilicate glass (WSEP Spray In-Pot Melting Run SS-12) after 2.8 years of interim storage in air reveal no significant deterioration of the glass. Although there are many cracks and fractures within the glass, the thermal conductivity and leach rate of the glass have not changed and it does not appear to have devitrified.

A correlation between the anticipated alpha radiation doses in solidified waste glasses, and literature reports of radiation damage to glasses, indicates significant alpha radiation damage could occur to the waste glasses within 100 years, the time period designated for retrievable storage. Analysis of the spatial distribution of thermal neutron flux in a typical water-stored waste canister indicates the maximum neutron flux (from spontaneous fission and α, n reactions) will exist at the glass-canister interface. Neutron damage in this area, in a glass containing 11.1 wt % B_2O_3 , is expected to be a factor of 10^4 less than that due to alpha decay of actinides.

COMMERCIAL WASTE SOLIDIFICATIONLABORATORY STUDIESMelt Development - J. E. Mendel and I. M. Warner

A number of borosilicate enamel-type formulations were investigated, in which the major cations were lead, copper, or zinc. From these, a zinc borosilicate glass, designated Frit 73-1, was selected for intensive study as a high-level waste fixation media. The lead glasses appeared too corrosive for use with the chrome-nickel alloy continuous melter, and the copper glass melts were too viscous at 1150 °C, the proposed melter operating temperature.

Properties of Melts Prepared with Glass Frit 73-1. The composition of Frit 73-1 is (wt %):

SiO ₂	37.0	CaO	2.0
B ₂ O ₃	15.1	MgO	2.0
Na ₂ O	5.5	SrO	2.0
K ₂ O	5.5	BaO	2.0
ZnO	28.9		

Frit 73-1 forms a fluid melt at 1150 °C and, when combined with PW-4b waste calcine ("clean" waste), forms fluid melts at 1150 °C which can incorporate up to at least 40 wt % waste calcine (Table 1). This ability to operate over a wide range of frit:calcine ratios is a necessary property for the waste fixation process, where separate streams of frit and waste calcine will be added to the melter continuously at controlled rates. Considerable variation from nominal flowrates for the two streams should be tolerable without greatly affecting process operation or product quality.

TABLE 1. Waste Glasses Prepared with Frit 73-1

Waste Type	Frit:Calcine Wt Ratio	% Fission Product Oxide	Product Form	Est. Viscosity at 1150 °C	% Wt Loss, After 3, 24-Hour Leach Periods	
					Standard Accelerated Leach Test (a)	Soxhlet Leach Test (b)
-	0 0	0	Homogeneous Glass	<500 poises	0.17	1.43
PW-4b	14.1:1	5			0.09	0.74
	6.5:1	10			0.31	1.06
	4.1:1	15			0.08	0.43
	2.8:1	20			0.18	0.57
	2.0:1	25			0.13	0.44
	1.5:1	30			0.27	0.83
PW-6	3.0:1	9.2			0.19	2.09

		Bottle Glass			1.30	4.21
		Pyrex Glass			0.18	0.55

a. Procedure described in USAEC Report BNWL-1425.

b. See Figure 1.

The preliminary data shown in Table 1 indicates that, if a nominal frit:calcine processing ratio of 2.8:1 is chosen, sufficient leeway is available for normal processing variations with PW-4b waste. Actually, the minimum usable frit:calcine ratio has not been determined; a ratio of 1.5:1 yielded an apparently satisfactory glass.

Frit 73-1 is also adaptable to the processing of PW-6 calcine (high sodium waste), with some sacrifice in product leachability (Table 1). At a frit:calcine ratio of 3:1 the PW-6 product leachability was intermediate between that of Pyrex and bottle glass, whereas the PW-4b product leachability is comparable to that of Pyrex glass. The effect of varying frit:PW-6 calcine ratio has not been determined.

Plans are now to investigate Frit 73-1:waste glass properties thoroughly. Initial emphasis will be on melter corrosion and thermal devitrification behavior. If satisfactory performance is demonstrated in these studies, an experimental program to

evaluate long-term radiation stability of these glasses, using laboratory-scale samples spiked with ^{244}Cm , will be started.

Preparation of Glass from Frit 73-1 and Fluidized Bed Calcined Waste. Development of techniques for fluidized bed calcination of the prototypical power reactor high-level wastes PW-4b and PW-6 is being done by Allied Chemical at the Idaho Chemical Processing Plant. Fluidized bed calcine from the last 10 hours of a 52-hour run with PW-4b waste in a 4-inch development calciner (Run PW-4b-3) was obtained from Allied Chemical and melted with -20 mesh Frit 73-1 to make glasses in the laboratory. A frit:calcine weight ratio of 2.78:1 was used. Glasses which flowed readily at 1150 °C were made with (1) the as-received calcine, and (2) various size fractions, including 500-841 microns (these coarser particles contained remnants of the Al_2O_3 seed bed material), 149-250 microns (essentially Al_2O_3 -free), and the fines (extremely small particles collected from the off-gas). The glasses resembled others prepared with Frit 73-1 and PW-4b waste, except for the presence of some light-gray inclusions of, as yet, unknown composition. The presence of the inclusions did not affect leachability adversely. They are not thought to represent a problem, but further investigations must be made.

Waste Glass Leaching Measurements - J. E. Mendel and I. M. Warner

Difficulties with the standard accelerated leach test, which has been in use for scouting evaluations of waste glasses at the Pacific Northwest Laboratory, were described in the last quarterly progress report.* The measured leach rate of a borosilicate waste glass was found to vary significantly with sample size. Larger sample sizes yielded lower leach rates.

* Quarterly Progress Report, Research and Development Activities, Waste Fixation Program, BNWL-1699, Compiled by A. M. Platt, Battelle-Northwest, December 1972.

Examination of the literature on the chemical durability of commercial silicate glasses revealed that similar behavior has been observed previously, i.e., leaching rates have been inhibited by ions previously leached from the glasses.* To avoid the same problem, certain minimum flowrates have been specified for leach test procedures in which the leachant contacts the sample in a single pass.**

Soxhlet Leach Test. A Soxhlet leaching apparatus (Figure 1) is being evaluated as a replacement for the presently-used accelerated leach test. The advantage of the technique is that the sample is contacted with continually replenished distilled water, thus "poisoning" of the leaching mechanism by ions in solution is minimized. It is interesting that, in the first meeting on waste solidification held in the U.S., Thomas proposed a standard leach test utilizing a Soxhlet extractor.†

Generally the Soxhlet leach test yields results which are a factor of 3-4 higher than those obtained by the standard accelerated leach test (Table 1). In some instances the difference is even greater. As an example, the leach rate of the "base" glass, described in the last quarterly report, was 18.8% weight loss in 72 hours with the Soxhlet apparatus versus 1.4% by the standard accelerated leach test.

Leach Rate Units. Results of the accelerated leach tests discussed above are expressed as percent weight loss after a

* W. A. Weyl and E. C. Marboe, The Constitution of Glasses, A Dynamic Interpretation Volume II: Part One, Intersciences Publishers, New York, 1964. See pp 1118-1119.

** W. Heimerl, H. Heine, L. Kahl, H. W. Levi, W. Latze, G. Malow, E. Schiener, and P. Schubert, Research on Glasses for Fission Product Fixation, Summary Report, January 1968 - June 1971, HMI-B109. Hahn-Meitner Institut, Berlin, September 1971.

† H. C. Thomas, "Proposed Standard Leach Test", pp 87-89, Report of Working Meeting on Fixation of Radioactivity in Stable, Solid Media at the John Hopkins University, June 19-21, 1957, TID-7550, March 1958.

FIGURE 1. Soxhlet Extractor Leach Test

given time at a given temperature and are obtained by actually weighing samples, prepared in a standard fashion, before and after leaching. The accelerated tests, which are made at elevated temperatures on powdered samples, are valuable for making rapid comparisons.

Slow leach tests, usually conducted with larger samples at lower temperatures, are required to predict long-term leaching behavior. Weight loss measurements are not practical, at least during the early stages of these tests. The results must be based on analyses of certain ions in the leach liquid, yet for the most practical application the results are reported as a bulk corrosion rate, usually $\text{g/cm}^2\text{-day}$ or cm/week . Since different ions leach at different rates, different "bulk" leach rates result. To avoid the confusion that this causes, we are adopting the suggestion of H. W. Godbee,* and will start reporting long-term leaching results as,

$$\text{fraction of A leached } (\text{cm}^2/\text{g})^{-1} \text{ day}^{-1}$$

where A is the specific ion analyzed, i.e., cesium cerium, etc. It should be noted that the numerical value of the leach rate and method of calculation is the same as that used previously. The advantage is that the basis for the data is now explicitly stated as part of the leach unit.

Melter Corrosion Studies - R. F. Maness

Corrosion tests were made with PW-6 calcine incorporated into a glass prepared from SiO_2 , H_3BO_3 , $\text{Al}(\text{NO}_3)_3$ and CaCO_3 . The melts were contained in alumina crucibles at 1150 and 1200 °C

* H. W. Godbee, C. W. Clark and C. L. Fitzgerald, "Physical Properties of Solids Incorporating Simulated Radioactive Wastes", pp 566-584, Proceedings of the Symposium on the Solidification and Long-Term Storage of Highly Radioactive Wastes, February 14-18, Richland, Washington, CONF-660208, November 1966.

with one specimen exposed to the melt phase and another to both melt and vapor. Data obtained are given in Table 2. Corrosion rates at 1150 °C ranged from 2 to 7 mils/month for seven different alloys. Corrosion in the melt phase increased by factors ranging from 1.2 to 4.4 as a result of increasing the test temperature from 1150 to 1200 °C with the smaller values being attributed to Corronel 230 and Inconel 690. No preferential attack at the melt-vapor interface was noted in any case.

Physical property data obtained by the International Nickel Company with Inconel 690 at elevated temperatures are given in Table 3. A pull test is planned on an Inconel 690 tensile specimen after long term (approximately 1000 hour) exposure to melt at 1150 °C to determine any gross change in strength or ductility.

Corrosion data obtained with a melt prepared from PW-6 calcine which contained 1 wt % ruthenium are given in Table 4. Corrosion of 20-45-5 alloy and Corronel 230 appeared to be increased by factors of about 4 and 2, respectively as a result of the ruthenium addition. Little or no effect on Inconel 690 corrosion was noted. No preferential attack was noted in any case.

Corrosion rates obtained in a lead-bearing waste melt are given in Table 5. Corrosion rates of Inconel 690, Corronel 230, and 50 Cr-50 Ni alloy in the melt phase ranged from 7 to 12 mils/month, whereas corrosion of Inconel 601 and 20-45-5 alloy was catastrophic. Corrosion at the melt-vapor interface was severe in all cases. The penetration rate at the interface area of the Inconel 690 specimen was estimated to be about 90 mils/month.

A zinc-bearing melt composition prepared with PW-4b calcine has desirable physical properties and a low leach rate (melt 72-68). Corrosion tests were made with this melt at 1150 °C with the results given in Table 6. In contrast to the

TABLE 2. Corrosiveness of Waste Melt as a Function of Temperature

Melt Composition: 100 g PW-6 calcine, 64 g SiO_2 , 42 g H_3BO_3 , 100 g $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 40 g CaCO_3 165 hour exposure in alumina crucibles

Alloy	Corrosion Rate at 1150 °C, mils/mo		Corrosion Rate at 1200 °C, mils/mo	
	Melt	Interface	Melt	Interface
Hastelloy X	5.4	6.0	24	28
Corronel 230	2.1	2.3	4.9	6.1
Inconel 617	6.3	5.3	21	32
Inconel 601	6.5	5.6	17	18
Inconel 690	3.5	2.1	4.3	5.4
Inconel 600	7.2	8.5	-	-
50 Cr - 50 Ni	5.1	3.5	-	-

TABLE 3. Physical Properties of Inconel 690^(a)

Temp. °F	Yield Strength 0.2%, ksi (b)	Ultimate Tensile Strength, ksi	Elongation Before Rupture, %	Reduction in Area Before Rupture, %
Room Temperature	40	101	49	73
600	28.5	84.5	48	68
1000	30	81.5	51	65
1400	25.8	45	68	57
1600	19	27	90	88
1800	8.5	14	84	93

a. Unreported data from International Nickel Company

b. ksi = thousands of lb/in²

TABLE 4. Corrosiveness of Ruthenium-Bearing Waste Melt

Melt Composition: 100 g PW-6 calcine, 64 g SiO_2 , 42 g H_3BO_3 ,
100 g $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 40 g CaCO_3 and one
wt. percent Ruthenium added as $\text{Ru}(\text{OH})_3$.

Exposure in alumina crucibles for 165 hr
at 1150 °C.

<u>Alloy</u>	<u>Corrosion Rate, mils/mo</u>	
	<u>Melt^(a)</u>	<u>Interface^(a)</u>
20-45-5	10 (2.7)	9.6 (2.9)
Corronel 230	4.8 (2.1)	3.3 (2.3)
Inconel 690	2.9 (3.5)	1.9 (2.1)

a. Parenthetical numbers are values determined in similar tests in the absence of ruthenium.

TABLE 5. Corrosiveness of Lead-Bearing Waste Melt

Melt Composition: 100 g PW-4b calcine, 266 g PbSiO_3 , 58 g KNO_3 ,
96 g SiO_2 .

Exposure in alumina crucibles at 1150 °C
for 150 hours.

<u>Alloy</u>	<u>Corrosion Rate, mils/mo</u>	
	<u>Melt</u>	<u>Interface</u>
Inconel 690	12	26 ^(a)
50 Cr - 50 Ni	6.7	41 ^(a)
20-45-5	83	dissolved
Corronel 230	7.0	24 ^(a)
Inconel 601	dissolved	dissolved

a. Severe attack at melt-vapor interface area.

TABLE 6. Corrosiveness of Zinc-Bearing Waste Melt

Melt Composition: 6.85 g PW-4b calcine, 6.70 g H_3BO_3 , 6.80 g SiO_2 , 2.77 g $NaNO_3$, 2.17 g KNO_3 , 15.72 g $Zn(NO_3)_2 \cdot 6H_2O$, 0.66 g $CaCO_3$, 2.34 g $Mg(NO_3)_2 \cdot 6H_2O$, 0.75 g $Sn(NO_3)_2$, 0.63 g $Ba(NO_3)_2$.

Exposure in alumina crucibles for 283 hours at 1150 °F.

<u>Alloy</u>	<u>Corrosion Rate, mils/month</u>	
	<u>Melt</u>	<u>Interface</u>
Inconel 690	1.4 (a)	1.9 (a)
Inconel 600	7.5 (a)	13.2 (b)
20-45-5	7.8 (a)	3.5 (a)

a. Broad, shallow pit formation

b. Intergranular attack

results obtained with a lead-bearing melt, none of the test materials were preferentially attacked at the melt-vapor interface. In addition, the general corrosiveness of the melt was light, Inconel 690 corroding at a rate of less than 2 mils/month. Some broad, shallow pit formation was noted on the test coupons after 283 exposure hours. However, this attack (unless much more severe after long exposure) was not sufficiently severe to prevent usage of the melt composition.

ENGINEERING STUDIES

Developmental Spray Calciner - W. F. Bonner and H. H. Irby

Design of the integrated spray calciner-continuous melter for nonradioactive solidification was finalized and construction work is about 75% complete. Operations are expected to begin in June of 1973.

Melter Development - J. D. Kaser, J. L. Bates and D. H. Siemens

Inconel[®] 690 has been chosen as the material of construction for the first developmental continuous melter made of a material other than platinum. Inconel 690 is a new alloy manufactured by Huntington Alloys Inc. of Huntington, West Virginia. This alloy was chosen from the many tested, based on corrosion resistance and availability. For example, Inconel 690 corroded at a rate of only 2.1 to 3.5 mils/month at 1150 °C and 4.3 to 5.4 mils/month at 1200 °C in a PW-6 melt formulation.* The creep strength is not known but is estimated to exceed 200 psi for 10,000 hours to rupture. This should be sufficient to withstand expected maximum stresses. It has been decided that it is more timely to build and test a melter for creep resistance during nonradioactive operation than to conduct lengthy laboratory creep tests.

The general configuration of the melter and melter furnace is shown in Figure 2. The melt will be discharged through the bottom spout which will be operated as a freeze valve. The melter is entirely supported by its upper flange. A wall thickness of 0.5 inches was chosen because this was the only thickness of material immediately available.

A ceramic melter development program has also been initiated so that an alternative is available in case metallic melters prove to be unserviceable or in case operation at temperatures exceeding the limits for base metal melters (~ 1200 - 1300 °C) results in a significantly better final product. To date, several samples of candidate materials have been accumulated. These include (1) fused cast $ZrO_2-Al_2O_3$, (2) fused cast $Cr_2O_3-MgO-Al_2O_3$ and (3) fused cast $Al_2O_3-Cr_2O_3$. When a

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* Table 2 - Corrosion Studies, this report.

FIGURE 2. Calcine Melter for Radioactive Wastes

promising high-temperature melt composition is formulated these samples will be tested for corrosion resistance. Investigation of the possibility of using a small melter-furnace from the commercial glass industry is also being pursued.

Melter Solids Feeder - D. H. Siemens and W. F. Bonner

Conversion of radioactive waste into nonleachable glass requires addition of selected glass-forming chemicals to the calcined waste prior to melting. Experience in the WSEP program has shown that these chemicals are best added as a solid frit during the melting phase of the process.

To add the frit, a positive displacement solids feeder has been developed and fabricated and is presently being tested for use with the WFP melter system. Data indicate that the feeder is capable of the following:

1. Frit can be fed in small, semi-continuous, amounts to promote homogeneity in the melt.
2. Feed rate is proportional to cycle time and is reproducible to within 5% of the feed rate.
3. After 70 hours of trouble-free operation there is no evidence of wear.

As can be seen from Figure 3, the operation of the solids feeder is very simple. The only moving part is an air-operated reciprocating piston containing a hole (slide valve) for metering the solids. With the piston in the load position, the slide valve is open to the hopper, thus permitting frit to fill the cavity. The piston then moves to the dump position and, in so doing, moves from under the hopper and away from the plate forming the bottom of the cavity, thus dumping the measured amount of frit into the chamber leading to the melter.

FIGURE 3. Slide Valve Solids Feeder

Nonradioactive Fluidized Bed Calciner - L. L. Taylor (Allied Chemical Corp.), W. F. Bonner and J. D. Kaser (PNL)

A fluidized bed calciner to be coupled with a continuous melter is presently being developed by Allied Chemical Corporation, Idaho Chemical Programs. This equipment will be used to determine flowsheets, calciner operating conditions, and off-gas cleanup requirements by processing simulated nonradioactive commercial wastes. The design information submitted by Allied Chemical Company will be used in fabrication of an integrated fluidized bed calciner-continuous melter system for demonstration of solidification of radioactive wastes at PNL.

Preliminary scoping studies conducted with PW-4b wastes show promise of a workable flowsheet. The initial scoping studies examined the calcination of the straight waste concentrated by

about 25%, and a 4:1 volume ratio blend of the PW-4b waste with 2.1M aluminum nitrate.

A 4-inch calciner scoping study conducted with the PW-4b waste concentrate was successful for 12.5 hours of operation at 500 °C. The duration of the run was too short to exhibit particle size control. The final bed was uniform in size and void of particle agglomerates. X-ray diffraction analysis of the product indicated an amorphous structure which was assumed to be a mixed oxide matrix.

A second run with aluminum nitrate addition was less successful as bed agglomerates, probably formed on the feed nozzle, resulted in erratic calciner operation. Based on the previous successful run with the PW-4b waste concentrate without additives, further studies with feed additives were dropped, and emphasis was placed on the concentrated waste.

An extended run of 52 hours with the PW-4b waste concentrate demonstrated that consistent long-term operation is feasible. Although particle size control of the fluidized bed remains in question, control may not prove critical with a recently proposed method of operation. This would involve operating with an inert bed for seed material and allowing all of the calcine to elutriate out of the bed to the filters where it would then fall directly into the melter.

Calcination of the PW-6 waste presents an entirely different problem due to the presence of sodium nitrate. The wide range of temperatures encompassing sodium nitrate decomposition, as well as a tendency toward agglomeration in this range, makes a sodium nitrate product unacceptable.

The first of four scoping runs conducted with PW-6 waste examined the addition of aluminum nitrate and calcination at 800 °C in an attempt to form NaAlO_2 . After 10.5 hours of operation, the final bed was in good condition; x-ray

diffraction indicated a generally amorphous structure. Although this appears to be a reasonable approach, anticipated mechanical problems at 800 °C may require lower operating temperatures before this flowsheet can be considered workable.

Oxalic acid was added to the PW-6 waste, in an unsuccessful attempt to form sodium carbonate during calcination. Erratic calciner operation resulted in a forced shutdown less than 4 hours into the run. A large clinker composed of sodium nitrate was formed in the calciner.

The addition of sulfuric acid to form a sodium sulfate product was examined in a 5.5 hour run at 450 °C. Due to a buildup of small agglomerates on the distributor plate this run was only a limited success.

Aluminum fluoride will form cryolite (Na_3AlF_6) during calcination when mixed with a sodium bearing waste. An 8-hour run at 450 °C indicated that this flowsheet appears to be adaptable to long-term calciner operation with high sodium wastes. However, additives such as sulfate and fluoride will not be used since they may either impair the quality of the final product (glass) or cause corrosion problems in the solidification system.

Additional scoping studies with various feed additives and operating conditions are needed in conjunction with the PW-6 wastes.

AEC WASTE SOLIDIFICATIONSOLIDIFICATION EQUIPMENT - J. D. Kaser

As a result of the plutonium production operations at Hanford, large volumes of high-level radioactive waste have been accumulated. Most of this waste will consist of roughly 4×10^7 gallons of alkaline salt cake and liquor after volume reduction by the Hanford "In-Tank Solidification (ITS) Program." This waste will be made up mainly of sodium carbonate, nitrite, nitrate, aluminate, and hydroxide, with a varying amount of free water. The principal isotopes will be ^{137}Cs and ^{90}Sr .

The volume, chemical composition, radiochemical composition, and physical form make these wastes unique compared to nuclear power reprocessing wastes, so that separate development of suitable solidification processes is appropriate. The Atlantic Richfield Hanford Company (ARHCO) has identified three major processes specifically for solidification of ITS waste, and has carried out scouting experiments and laboratory experiments that showed these processes warrant further development and evaluation. These processes can be broadly placed into three categories: (1) melting with exothermic reactions between a metal or semimetal such as aluminum or silicon and an oxidizing compound such as Fe_2O_3 or NaNO_3 ; (2) endothermic melting a mixture of dried ITS waste, borates and sand or basalt; and (3) a hydrothermal reaction process to form an insoluble structure.

Therefore this task is being undertaken to define product composition, to develop engineering-scale, remotable equipment, and to demonstrate the most promising process(es) on radioactive wastes in order to provide a technical basis for a final process selection and implementation.

The main effort to date has involved assembling available process information and planning the experimental program. It has been decided to first develop equipment for the endothermic melting process and second develop equipment for the hydrothermal process. Any equipment development to be done on the exothermic process will be deferred toward the end of the program. This order of process development was chosen based on processing cost estimates, present degree of development, and engineering difficulty.

The endothermic melting process is the most developed of the three processes and is similar to other demonstrated waste melting processes such as the melting step which forms borosilicate glass in the spray solidification process. The endothermic melter involves melting 10 parts by weight of sand or basalt together with 10 parts of ITS salt cake and 1 part B_2O_3 to form a glassy solid. Further, it has been estimated that both the capital and operating costs for the endothermic melting process are considerably less than for the exothermic process.* Although no detailed engineering or cost study has yet been made for the hydrothermal process, its cost will probably be intermediate between the cost of the endothermic process and the cost of the exothermic process based on the chemicals and equipment requirements.

ITS waste compositions have been defined by Kupfer and Schulz** and are given in Table 7. Process flow diagrams have been defined by Haddad for the endothermic and exothermic processes.*

* T. R. Haddad, "Engineering Study - Salt Cake Immobilization - Basalt Melt and Thermite Process," ARH-2652, December 15, 1972.

** M. J. Kupfer and W. W. Schulz, "Application of the Hanford Thermite Process to Increase Immobilization of In-Tank Solidified Waste," ARH-2458, September 1972.

TABLE 7. Composition of Simulated ITS Waste^(a)

<u>Component</u>	<u>Composition, wt %</u>	
	<u>ITS-1(b)</u>	<u>ITS-2(c)</u>
NaNO_3	34.0	38.0
Na_2CO_3	22.0	13.8
NaNO_2	18.6	19.9
NaOH	12.4	1.8
CsNO_3	4.1	3.6
NaAlO_2	3.4	14.6
$\text{Sr}(\text{NO}_3)_2$	2.1	1.8
SrCO_3	2.1	1.8
NaH_2PO_4	0.7	1.3
Na_2SO_4	0.3	1.6
NaCl	0.3	0.9

a. T. R. Haddad, ARH-2652, December 15, 1972.

b. In-Tank Solidified Waste Type #1.

c. In-Tank Solidified Waste Type #2.

The hydrothermal process has been designed for the solidification of ITS bottom liquor. A typical bottom liquor composition is given in Table 8.

TABLE 8. ITS Waste Bottom Liquor Composition^(a)

NaOH	5 M
NaNO_3	2.5 M
NaAlO_2	1 M

a. From personal communication with G. S. Barney of Atlantic Richfield Hanford Company.

RADIOACTIVE DEMONSTRATIONSSOLIDIFICATION CELL (B-CELL) REACTIVATION - B. O. Kahle and
W. F. Bonner

Reactivation of B-cell in preparation for radioactive demonstrations is continuing with the major present effort on overhauling the in-cell cranes. Piping and instrument checkout is also continuing and improvements in the liquid and gas sampling systems have been designed to provide more representative samples with greater efficiency.

Since November 1972, approximately 550 ft³ of unusable radioactive equipment has been removed from the hot cells in shielded boxes for burial at the ARHCO Hanford site. The Maximum radiation level at 1 foot from the 1-1/2 inch-thick steel wall box was 40 R/hr.

SOLIDIFICATION EQUIPMENTMist-Elimination Element - W. F. Bonner

The glass fiber Brink mist eliminator used during the WSEP program to decontaminate radioactive evaporator vapors was recently determined to be less efficient than originally specified. The eliminator was purchased in 1965 at which time it was quoted as removing essentially 100% of all mist particles <3 μ at our processing conditions. However, this element is now specified as being capable of removing up to 75% of the <3 μ particles. This undoubtedly contributed to the evaporator decontamination performance being less than anticipated during the WSEP runs.

The mist eliminator was recently removed from the evaporator tower for inspection. After 4 years of service the unit was basically intact with no apparent holes in the fiber, but the individual fibers had become short and fluffy, almost powder,

instead of the original long, spindly fibers. Although there is no obvious explanation for the change, it is postulated that the large surface area exhibited by the fine glass fibers coupled with a flow of 100 °C dilute nitric acid through the element could result in leaching of the glass, thus bringing about the observed fiber breakdown. The effect of the fiber breakdown on the mist eliminator performance is unknown.

During processing the mist eliminator fibers apparently retained a significant amount of radionuclides. With 2-1/2 years passed since radioactive material was processed, an ionization chamber placed in contact with the mist eliminator read the gamma radiation to be 140 R/hr above cell background.

PRODUCT CHARACTERIZATIONMEASUREMENTS ON CORE-DRILLED SAMPLES - J. E. Mendel

The canister of borosilicate glass prepared in WSEP Run SS-12 was core drilled in three locations after 2.8 years of interim storage (Core No. 64, 18.5 inches from bottom, Core No. 65, 34.5 inches from bottom, and Core No. 66, 56.5 inches from bottom). All evidence indicates that the glass in the canister, prepared by the Spray Solidifier In-Pot Melting process, contains many cracks and fractures. By using the combination of a new thin-walled unnotched drill bit and a 10,000 RPM drill motor, better samples were obtained than previously, yet the longest dimension of any of the sample fragments was approximately 1 inch. Measurements made on the canister and the core samples indicate that no significant deterioration of the SS-12 product has occurred after exposure to more than 10^{11} R self-induced radiation over a 2.8 year period.

WSEP Run SS-12 was completed April 7, 1970, and was core sampled once before, after 11 months interim storage, 7 months in water and 4 months in air. A photograph of a core sample taken at that time appears on page 5.6 of BNWL-1666* and shows the definite glassiness of the product at that time. Since the first core drilling SS-12 has been stored in air in a pot storage rack in A-cell.

SS-12 Thermal Conductivity

A few of the thermocouples on SS-12 are still operative, sufficient to indicate the ΔT between wall and centerline is about 25 °C. Based on a calculated heat content of 400 watts in SS-12 after 2.8 years, the effective thermal conductivity

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

of the borosilicate product is now $0.74 \text{ W/(m}^2\text{)} (^\circ\text{C/m)}$. This corresponds very closely to the value shown in Figure 5.10, BNWL-1666, for IPM borosilicate glass at less than 100°C . It may be concluded that the thermal conductivity has not changed.

SS-12 Wall Thickness Measurements

Wall thickness measurements made by ultrasonic scanning ranged from 0.326 to 0.340 inches. Nominal initial wall thickness for the canister was 0.333 inches (Table 5.8, BNWL-1666) and these measurements are representative of the normal scatter that is found in the in-cell ultrasonic scans. It is concluded that no significant corrosion has occurred during the 2.8 years of interim storage. But it should also be noted that this 304L stainless steel canister is coated in most areas with what appears to be rust. The "rust" is particularly noticeable on the top 2 feet of the canister.

The thermowells in several WSEP waste canisters, including SS-12, have leaks. Tests made at the completion of the core drilling indicated both the centerline and the intermediate thermowells in SS-12 leak.

SS-12 Product Appearance and Homogeneity

Visual examination of the core samples from SS-12 canister with the C-cell periscope showed clearly that the bulk of this IPM borosilicate glass remains vitreous after 2.8 years storage. The innermost portions of the samples (3 inches from the wall) appeared to have some crystallization within the glassy matrix. A sample of surface slag or rubble was also obtained. Core drill No. 66 penetrated either a pocket or a small central pipe of material that had not completely fused at the end of the run. This material, designated Sample 66D, was enriched in cesium and had an abnormally high leach rate.

Except for the surface slag, the SS-12 glass is very homogeneous as indicated by the gamma spectrometry results shown in

Table 9. The $^{137}\text{Cs}/^{144}\text{Ce}$ ratio, which is being used as an index of homogeneity, varied less than $\pm 2\%$ both longitudinally and axially. The sample of surface slag from the back of hole 66 was enriched in ^{137}Cs to make the $^{137}\text{Cs}/^{144}\text{Ce}$ ratio about 30% higher than in the bulk glass.

TABLE 9. SS-12 Borosilicate Glass Homogeneity
After 2.8 Years Storage

<u>Sample No.</u>	<u>Longitudinal Location (a)</u>	<u>Axial Location (b)</u>	<u>Sample Weight, gram</u>	<u>$^{137}\text{Cs}/^{144}\text{Ce}$ Ratio</u>
64A	18.5 in.	Wall	5.81	2.10
64C	18.5 in.	Center	19.73	2.07
65A	34.5 in.	Wall	5.50	2.06
65C	34.5 in.	Center	0.915	2.02
66A	56.5 in.	Wall	2.74	2.08
66C	56.5 in.	Center	6.18	2.05
66D ^(c)	56.5 in.	Center	0.150	2.67

-
- a. Distance from bottom of canister.
- b. All core drill holes were approximately 3 inches deep. Center samples are from bottom of hole.
- c. Sample is a small piece of lava-like product from the surface slag described in the text.

SS-12 Leach Rate

Preliminary leach data obtained on Samples 64A, 64C, and 66D are shown in Table 10. The leach rates are the same as those obtained previously, within the precision of the measurements. Little, or no decrease in product durability has occurred after 2.8 years interim storage and exposure to over 10^{11} R beta and gamma radiation. The initial leach rate of the surface slag was a factor of 100 higher than that of the bulk glass, but decreased rapidly.

TABLE 10. Leach Rate of WSEP IPM Borosilicate Glass
After 2.8 Years Interim Storage

Cumulative Time Leached	Leach Rate @ 25 °C, Fraction Cesium Leached (cm ² /g) ⁻¹ day ⁻¹		
	Wall	Centerline	Surface Slag
1 day	9.6×10^{-5}	7.9×10^{-5}	9.3×10^{-3}
1 week	5.3×10^{-5}	2.4×10^{-5}	1.9×10^{-4}
2 weeks	5.3×10^{-5}	1.9×10^{-5}	4.5×10^{-5}

WASTE CONTAINER INTEGRITY DURING INTERIM STORAGE - J. E. Mendel,
W. K. Winegardner, J. L. Brimhall, and W. D. Felix

A preliminary analysis of the stability of waste canisters during interim (100 year) storage in an Engineered Storage Facility was conducted. Emphasis was placed on potential mechanisms for the loss of integrity of stainless steel canisters containing calcined high-level waste while stored in nonboiling water-filled basins. Failure mechanisms investigated by literature survey included canister corrosion; canister pressurization as the result of the gases formed by either radiolytic decay or radiolysis of residual water and nitrate; and loss of ductility as a result of the helium embrittlement of stainless steel.

A program to investigate both corrosion at the solid waste-canister interface and the probability for pressurization as a result of radiolysis is to be carried out at PNL.

Corrosion

The search indicated that with proper material selection, design, and coolant quality, corrosion phenomena associated with the water-canister interface should be of little consequence to canister integrity. The preceding statement is an extrapolation of information since corrosion data for the lifetimes expected are nonexistent. Reported steady-state uniform corrosion rates for austenitic stainless steel in water, less than 0.0001 inches

per year, would be of little consequence to the integrity of the relatively massive waste containers. There are several forms of local corrosion, arising from relatively specific exposure conditions, that can result in severe attack of stainless steels. However, such exposure conditions can be controlled. More specifically, alloy composition and physical metallurgy can be specified and controlled while deleterious species and ions and corrosion products can be removed by ion exchange or evaporation. Perhaps the most insidious phenomenon that could occur would be a potential loss of corrosion resistance by microstructural changes resulting from long times-at-temperature (in a radiation environment). Physical metallurgy can, of course, be monitored by using coupon samples.

Nondestructive examination has revealed no obvious interaction between solidified waste and the walls of canisters from the former Waste Solidification Engineering Prototypes Program. However, there is insufficient data to extrapolate with confidence out to 100 years. (Corrosive failure of internal thermowells appears to have been observed in the WSEP canisters. Thermowell failure may not be a problem since reprocessors may not have thermowells in their canisters and if they do, they can be seal-welded shut.) It is postulated that low temperature (nonboiling) exposure where moisture is present in the solid waste could be as significant as high temperature exposure where there is no moisture.

Pressurization

Present information indicates that high-level waste calcine may contain as much as 0.5 wt % each of water and nitrate at the time the calcine is sealed in the storage canister. Decomposition of either could result in the pressurization of the canister. Maintaining the temperature below the processing temperature (400 to 900 °C, depending on the process) can prevent thermal decomposition or vaporization during subsequent storage and

transportation. On the other hand, decomposition due to radiolysis, yielding gaseous products, is unavoidable.

A brief examination of the potential for pressurization in the waste canisters containing calcine leads to the following tentative conclusions:

1. Complete radiolysis of the water and nitrate in the canisters must be assumed since almost no data has been found for the radiolytic decomposition of either chemisorbed water or highly dispersed nitrate. The principal radiolytic products will be gaseous H_2 and O_2 . The surfaces of the hot oxide calcine should catalyze recombination of these gases to form water, thereby lowering the probability for appreciable pressures of H_2 or O_2 during the first few years of canister storage. However, as the canisters age and become cooler, the recombination rate will be slower, and there may be a potential for mixtures of H_2 and O_2 to exist in older canisters.
2. During the initial storage period, when rapid recombination of H_2 and O_2 is postulated, the overall effect of radiolysis will be to change the water from its initial tight chemically bound form to an unbound form which is free to vaporize at 100 °C. Calculations reveal the potential for steam pressures well above 100 psig when canisters are removed from water basin cooling, even after 10 years aging.
3. Several reactions can occur in the canisters to reduce the quantity of gaseous radiolysis products. Hydrogen diffusion, loss of oxygen by oxidation of mild steel canister parts, and strong adsorption of H_2O on some oxides are all examples of potential removal mechanisms. However, the quantitative significance of these reactions in reducing the hazards potential remains undefined.
4. Pressurization due to helium produced from alpha particles will be negligible.

5. Much of the concern with radiolytic gas production could probably be avoided by subjecting the calcine to a temperature soak at about 900 °C, i.e., purposely promoting thermal decomposition and venting under controlled conditions.

Helium Embrittlement

Under the proper conditions, the presence of helium can lead to the embrittlement of stainless steel. The embrittlement is due to the formation and/or introduction of helium gas bubbles in the grain boundaries of the stainless steel. The metal will fracture intergranularly with low ductility when the gas bubbles are present. It is generally understood that the bubbles result from the migration and coalescence of helium atoms at elevated temperature. However, helium embrittlement of the walls of high-level waste canisters is not expected to be a problem because of the following:

1. As long as the temperature is below 700 °C, helium atoms cannot coalesce into bubbles and cause embrittlement.
2. The amount of helium produced by n, α reactions from neutrons is orders of magnitude less than required to produce embrittling effects.
3. The helium produced by α particle bombardment forms only in a very small interior surface layer of the canister wall. It is inconceivable that this thin layer could affect the total ductility.

RADIATION DAMAGE IN BOROSILICATE GLASS - D. F. Newman

A major mechanism for radiation damage in waste glasses is the deposition of the entire kinetic energy of an alpha particle as thermal energy producing a "thermal spike." A thermodynamic description on a microscopic scale is needed to describe this effect, since the range of an alpha particle in glass is about 2×10^{-3} cm. Furthermore, the glass surrounding a thermal spike is at a much lower temperature and provides

the heat sink necessary to rapidly quench the small volume of heated glass. The possible duration of a high temperature region, rising several thousand degrees and involving several thousand atoms or molecules, might be 10^{-10} to 10^{-11} second. Micro-regions of precipitated silica, which could be leached more easily than from ordinary glass, would probably form.

The breakdown of the structure of glass was reported by Lind* where scaling and cracks appeared in a pyrex vessel used to store a radium chloride solution. Similar vessels containing radium and polonium compounds have been known to be so weakened by irradiation as to explode when the internal gas pressure was increased.** Pyrex glass samples bombarded with integral doses of approximately 4×10^{16} α 's/cm² from ²¹⁰Po showed a series of very fine cracks on the surface.† Such doses correspond to the deposition of about 10^{19} alpha particles per cm³ which must give rise to a considerable internal pressure. The resulting strain alone may account for the cracking and surface breakdown observed.

Sources of Alpha Particles in Waste Glasses

Alpha particles are produced in waste glasses by two principal sources: (1) high-level waste generated in the reprocessing of irradiated fuels contains substantial quantities of actinide nuclides which decay naturally by alpha particle emission; (2) neutrons produced by both the (α ,n) and spontaneous fission processes can escape from a solidified waste canister stored in a water basin and slow down to thermal or near-thermal energies in water before being reabsorbed by ¹⁰B in the waste glass and producing alpha particles by the (n, α) reaction.

* S. C. Lind, Science, 68, 643 (1928).

** K. W. Bagnall, Quart. Rev. Chem. Soc., 11, 30 (1957).

† D. G. Tuck, "Radiation Damage to Glass Surfaces by α -Particle Bombardment," International Journal of Applied Radiation and Isotopes, Vol. 15, p. 53 (1964).

The compositions of typical fuels discharged from light water reactors were obtained from ORIGEN calculations.* This fuel was operated at 30 megawatts per metric ton of heavy metal initially charged to the reactor (30 MW/MTHM) and had an exposure of 33,000 MWd/MTHM. The fuel was reprocessed 150 days after discharge from the reactor and 0.5% of both uranium and plutonium in the fuel was assumed to report to waste. Waste compositions were calculated after reprocessing for decay times of 0, 1, 2, 5, 10, 50 and 100 years.

The alpha particle emission rates were calculated from actinide concentrations in the waste using half-life and decay scheme branching ratio data listed by Wapstra** and Lederer.† Results of the calculations for the cumulative alpha emission from natural decay are shown as a function of decay time after reprocessing in Figure 4. During the first 100 years after reprocessing approximately 1.2×10^{23} and 3.0×10^{24} α 's/MTHM would be emitted from the natural decay of actinides in the waste from LWR UO_2 fuel and LWR Pu recycle fuel, respectively.

The volumes of solidified reprocessing waste per metric ton of LWR fuel are currently estimated at 1.5 to 3 ft³. Since the lower volume would have a higher alpha particle emission per unit volume, the solidified high-level waste was assumed to be 2 ft³/MTHM of fuel processed. The alpha particle emission density in the waste (2 ft³/MTHM) during the first 100 years after reprocessing would be 2.1×10^{18} and 5.3×10^{19} α 's/cm³ for UO_2 and Pu recycle, respectively. If radiation damage to waste glasses is

* J. P. Nichols, et al., "Projections of Fuel Reprocessing Requirements and High Level Solidified Wastes from the U.S. Nuclear Power Industry," ORNL-TM-3965 (Draft), Oak Ridge National Laboratory, (September 1972).

** A. H. Wapstra, "Actinide Fingerprints," Actinides Review, Vol. 1, pp. 44-50 (1967).

† C. M. Lederer, J. M. Hollander, and I. Perlman, Table of Isotopes, 6th Edition, John Wiley and Sons, New York (1967).

FIGURE 4. Cumulative Alpha Emission in Wastes

a problem at this specific volume, some of the basic assumptions currently used for planning and design studies in the waste fixation program may be affected.

Neutron Emission Due to (α ,n) Reactions

Nearly all the actinide nuclides with half-lives longer than 100 days decay primarily by emission of alpha particles. Waste solidified in borosilicate glass contains mostly light elements mixed with small amounts of alpha emitting actinides. Determination of the neutron yield from the glass requires a knowledge of: (1) neutron yield as a function of alpha particle energy for each of the important light elements, and (2) the composition of the glass. The neutron yields from alpha particles incident on thick targets of boron, sodium, magnesium, silicon, oxygen,

iron, potassium and calcium were evaluated by Van Tuyl.* In applying these values to mixtures of alpha emitter and light elements, allowance must be made for the mole fractions of the light elements present, the mole fraction of the alpha emitter, and the shielding factors for all elements in the mixture.

The borosilicate glass composition used in this study (type 72-68)** had a B_2O_3 content of 11.1 wt %, which is near the lower end of the usual range of boron content in borosilicate waste glasses. In spite of this fact, approximately 85% of the neutrons emitted due to (α, n) reactions were from boron. Thus, the neutron emission rate due to (α, n) reactions in borosilicate glass is expected to be nearly proportional to the boron content.

Neutron Emission Due to Spontaneous Fission

Most of the transuranium nuclides undergo spontaneous fission and emit 2 or 3 neutrons, on the average, in the process.† The spontaneous fission process is enhanced for those nuclei with both an even number of protons and an even number of neutrons in the nucleus (such as ^{246}Cm , ^{244}Cm , ^{242}Cm , ^{242}Pu , ^{240}Pu , and ^{238}Pu). The spontaneous fission rates were calculated for each of the transuranium nuclides which undergo this process, using the actinide concentrations in the waste (obtained as described previously) and the neutron emission rates due to spontaneous fission listed by Vaane.††

* H. H. Van Tuyl, "Estimation of Neutron and Photon Yields from Alpha Reactions," (Private communication) Battelle, Pacific Northwest Laboratories.

** See Laboratory Studies, this report.

† Reactor Physics Constants ANL-5800, p. 22, Argonne National Laboratory (1963).

†† J. P. Vaane, "Hazards Connected with the Handling of Transuranium Elements and Methods used for the Protection of Personnel," Actinides Review, Vol. 1, p. 339 (1969).

These neutron emission rates are dependent only on the transuranium nuclide composition of the waste, unlike the neutron emission rates due to (α, n) reactions which are highly dependent on the boron content of the glass.

For the waste from UO_2 fuel in type 72-68 borosilicate glass 60% of the total number of neutrons emitted during the first 100 years after reprocessing result from spontaneous fission, as shown in Table 11. For the case of Pu recycle fuel waste, about 75% of the neutrons are emitted by the spontaneous fission process, during the first 100 years after reprocessing. The total number of neutrons emitted by the Pu recycle waste is about 40 times larger than that of waste from UO_2 fuel.

TABLE 11. Total Neutron Emission from Waste in Borosilicate Glass During the First 100 Years After Reprocessing

	<u>LWR UO_2 Fuel Equilibrium Cycle Waste</u>	
Neutron Emission Due to (α, n) Reaction	2.08×10^{17}	$\frac{\text{neutrons}}{\text{MTHM}}$
Neutron Emission Due to Spontaneous Fission	2.97×10^{17}	$\frac{\text{neutrons}}{\text{MTHM}}$
Total Neutron Emission	5.05×10^{17}	$\frac{\text{neutrons}}{\text{MTHM}}$
	<u>LWR Pu Recycle Fuel Waste</u>	
Neutron Emission Due to (α, n) Reaction	0.53×10^{19}	$\frac{\text{neutrons}}{\text{MTHM}}$
Neutron Emission Due to Spontaneous Fission	1.67×10^{19}	$\frac{\text{neutrons}}{\text{MTHM}}$
Total Neutron Emission	2.20×10^{19}	$\frac{\text{neutrons}}{\text{MTHM}}$

Analysis of Neutron Induced Alpha Emission in Borosilicate Glass

Radiation damage in boron-containing glasses due to alpha particle emission has been widely investigated by exposing glass samples to neutron fluences in reactors. Thermal and near-thermal energy neutrons are absorbed in boron and produce alpha particles by the reaction

Due to conservation of energy and momentum the alpha particle is emitted with a kinetic energy of about 1.8 MeV while the lithium nucleus recoils with a kinetic energy of about 1 MeV. This reaction is not expected to produce as much damage in glass as the typical 6 MeV alpha particle emitted from natural decay of an actinide nuclide because of the more limited extent of local melting in a thermal spike. Thus, the correlation of the density of alpha particles emitted in borosilicate glass with neutron fluence and damage for the ^{10}B (n,α) reaction, if applied to the density of alpha particles emitted by actinide decay, will underestimate the damage produced in waste glasses. A weighting factor equivalent to the ratio of kinetic energies released in an α-decay and a ^{10}B (n,α) reaction should probably be applied to the damage equivalence correlation.

During the first 100 years after reprocessing the total neutron emission would be 5.05×10^{17} and 2.20×10^{19} neutrons/MTHM from the waste of LWR UO_2 fuel and LWR Pu recycle fuel, respectively, as shown in Table 11. The neutron slowing down code HRG-3* and the transport-theory thermalization code BRT-1**

* J. L. Carter, Jr., "HRG-3: A Code for Calculating the Slowing-Down Spectrum in the P_1 or B_1 Approximation," BNWL-1432, Battelle Pacific Northwest Laboratories (June 1970).

** C. L. Bennett and W. L. Purcell, "BRT-I: Battelle-Revised-THERMOS," BNWL-1434, Battelle Pacific Northwest Laboratories (June 1970).

were used to calculate neutron fluences in a typical borosilicate glass waste canister, 12-inches in diameter with a 0.25 inch thick stainless steel clad on an 18-inch square pitch, in a water basin. The neutron flux in the waste glass is highest at the outer surface of the glass. The intensity of the neutron flux diminishes rapidly from the value at the surface, with increasing distance from the surface, due to self-shielding effects. The maximum total neutron fluence in the glass (at the outer surface) assuming a specific waste volume of 2 ft³/MTHM of fuel reprocessed would be 3.68×10^{14} neutrons/cm² for LWR UO₂ waste and 1.60×10^{16} neutrons/cm² for LWR Pu recycle waste, during the first 100 years after reprocessing. The density of alpha particles emitted from ¹⁰B (n,α) reactions in the glass due to these neutron fluences would be 2.84×10^{14} α's/cm³ and 1.23×10^{16} α's/cm³, respectively for UO₂ and Pu recycle waste. Using the damage equivalence correlation discussed above, the total neutron fluence which would produce damage in the borosilicate glass (11.1 wt % B₂O₃) equivalent to the emission of 2.1×10^{18} α's/cm³ and 5.3×10^{19} α's/cm³ from actinide decay in UO₂ and Pu recycle waste, respectively, would be 5.7×10^{18} neutrons/cm² and 1.4×10^{20} neutrons/cm². Exposure of pyrex glass (12 wt % B₂O₃) to 3×10^{19} neutrons/cm² produced chipping at the surface,* and at exposures of 2×10^{20} neutrons/cm² the thermal conductivity decreased by almost 45 percent.**

Conclusions

These results would indicate that significant radiation damage could be predicted in waste glasses due to natural decay

* C. Bopp, O. Sisman, and R. Towas, "Radiation Stability of Ceramics," Solid State Division Semiannual Progress Report, ORNL-1945, August 30, 1955.

** D. S. Billington, "Solid State Division Semiannual Progress Report," Oak Ridge National Laboratory, Oak Ridge, Tennessee, ORNL-1945, W-7405-eng-26, January 30, 1956.

of actinide nuclides. This damage is distributed uniformly in the volume of waste glass due to the extremely short range of alpha particles (about 2×10^{-3} cm) and the uniform distribution of high-level waste (including the alpha emitting actinides) in the glass. Unlike the damage due to neutron emission, the damage produced by the alpha particles emitted from the decay of actinides should be nearly independent of the boron content in the waste glasses. The damage predicted in waste glasses due to neutron emission is about a factor of 10^{-4} smaller at the glass surface than that from alpha particles emitted during actinide decay, decreasing to a factor of 10^{-6} one centimeter from the surface. Thus, the glass damage due to neutron emission is negligible in comparison to that due to alpha particles emitted from the decay of actinide nuclides.

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