QUARTERLY PROGRESS REPORT
RESEARCH AND DEVELOPMENT ACTIVITIES
WASTE FIXATION PROGRAM
OCTOBER THROUGH DECEMBER 1974

Battelle

Pacific Northwest Laboratories
Richland, Washington 99352

FEBRUARY 1975

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Compiled by
J. L. McElroy
Nuclear Waste Technology Department

February 1974

On January 19, 1975, research and development programs of the U.S. Atomic Energy Commission (AEC) became part of the newly formed Energy Research and Development Administration (ERDA). In this report, since it refers to work done in 1974, most references are to AEC programs.

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INTRODUCTION

This progress report is the ninth in a series that presents research and development activities in radioactive waste fixation. Previous progress reports were BNWL-1699, 1741, 1761, 1788, 1809, 1826, 1841 and 1871.

SUMMARY

Three engineering-scale tests and six laboratory tests of in-can melting were made during the last reporting period. The engineering-scale tests were made in 8 in.-diam 304 stainless steel canisters with PW-4b-2 (3:1) 73-1 premixed feed. One of the canisters had eight internal fins for improved heat transfer. Melting rates of 23 lb of feed per hr were achieved in the canisters without fins while melting rates greater than 45 lb/hr were obtained in the finned canister.

Experience from previous test melters and information from experts in the glass industry have been used to design a scale model ceramic melter.

Exploratory agglomeration tests were performed by Ferro-Tech Inc. using a simulated PW-4b spray calcined waste and -325 mesh 73-1 frit blend. The blend pelletized readily in a disc pelletizer, and sodium hydroxide solution was identified as a promising binder. The disc pelletizer was also used to mix calcine and frit. Briquetting was explored, but was not satisfactory for hot cell applications.

Shakedown runs of the newly installed fluidized bed calciner were successfully completed, including testing of the combustion, feed and off-gas systems.

Experiments with the wiped film evaporator have established the feasibility of directly coupling the evaporator to a metallic-type melter to produce a borosilicate type glass. These experiments have also demonstrated that the glass former (frit) can be added to the feed material and processed through the evaporator, and that a low-head gravity system is adequate for feeding the evaporator. Problems with the transfer of concentrate from the evaporator to the melter and with solids entrainment in the melter off-gas remain unresolved.

The developmental spray calciner was operated for 39 hr to convert 711 liters of type PW-7a-2 simulated high-level waste to 135 liters of calcine. A feed rate of 23.6 liter/hr was achieved. During the run a spray nozzle air cap having a ceramic insert, a modified nozzle cleanout needle assembly, and a vibrator acting on the side of the calciner barrel were evaluated. All modifications performed better than the equipment they replaced. No problems with the spray calciner were experienced during the run.

A series of laboratory scale experiments have been completed showing the buildup of stored energy due to alpha particle emission in synthetic high-level waste incorporated in borosilicate glass. At an alpha dose equivalent to 140 years storage time the stored energy reached 21 cal/g of glass in specimens stored at room temperature (22-25°C).

Using an electronic manometer system, helium diffusivity in simulated waste glass is being examined. Curium-244-doped glass discs have been fabricated and helium release measured as a function of time and temperature for two samples after 62 days storage at room temperature. Release behavior could not be directly fitted to simple diffusion theory, with strong evidence for trapping at radiation-induced (or other) defect sites.

A 310 stainless steel canister was cycled to canwall penetration by storage water. The rapid penetration suggests the need to prevent the sensitization of stainless steel when it is to be used as containment material for high-level waste fixation products.

Two methods were originally considered for utilizing the sinterability of calcine-frit mixtures. The first was to form pellets which would then

be incorporated in another matrix such as a metal. The second method was to prepare large sintered shapes within the canister. The second approach has received the major attention during the quarter. Additional characterization of the sintered product has also been completed.

At Pennsylvania State University a study was completed of the phases formed during firing of a simplified system containing the ten most abundant elements in PW-4b. Ten distinct phases were identified. A final report on silica matrix isolation of wastes by hot pressing is in preparation. Some final runs with PW-7 are under way for inclusion in the report. Development of super calcine formulations is proceeding, with cesium appearing to be the major problem in super calcine design.

A fault tree for risk analysis of waste shipment was constructed. Preliminary dose calculations were performed to ascertain the relative impact on man of radionuclides released from waste to river water. Comparison of physical properties showed that for three frequently cited release mechanisms, relatively massive glass/ceramic products are inherently less dispersible than leachable, high surface-to-volume ratio calcines.

COMMERCIAL WASTE FIXATION

The purpose of this task is to develop processes and equipment for converting liquid high-level radioactive waste to a stable, relatively nondispersible form for storage and ultimately, disposal. This objective is generally being accomplished by development of a two-step approach, calcination or concentration, followed by melting to form a silicate glass.

IN-CAN MELTING - H. T. Blair and R. B. Dakan

The purpose of this study is to further develop a method of melting a mixture of nuclear waste calcine and glass former using the storage canister as the melting crucible.

Three engineering scale tests and six laboratory tests of in-can melting were made during the last reporting period. The engineering scale tests were made in 8-in. diam 304L stainless steel canisters with PW-4b-2 (3:1) 73-1 premixed feed. One canister had eight internal fins for improved heat transfer. Melting rates of 23 lb of feed per hr were achieved in the canisters without fins while melting rates greater than 45 lbs/hr were obtained in the finned canister. The six laboratory tests evaluated in-can melting of spray calcined PW-4b-2, PW-7a-2, and PW-7b-2 (compositions shown in BNWL-1841 and 1871) blended with 73-1 frit in ratios of 1:3 and 1:2. All tests produced vitreous, multiphase products.

The objective of the three engineering-scale in-can melting tests was to establish a maximum melting rate. All three tests were made in canisters fabricated from 4 to 5-ft lengths of 8-in. diam 304L stainless steel Sch 40 pipe. The batch for all three tests was mechanically blended PW-4b-2 spray calcined, simulated waste and -325 mesh, 73-1 frit combined in a 1:3 ratio and fed to the canister with a volumetric screw feeder.

For the first test, designated ICM-7, the empty canister was heated to 1000°C before feed was introduced at a rate of 60 lb/hr for 30 min followed by a 1.5 hr hold at temperature to completely melt the 30 lb of

batch. The batch was then fed at a rate of 20 to 25 lb/hr for 2 hr and 25 to 30 lb/hr for 1 hr. Exterior canister temperatures were maintained at between 950°C and 1000°C during the batch feeding. The feeding was followed by a 1 hr hold at an exterior temperature of 1000°C followed by cooling at an approximate rate of 33°C/hr. Center temperatures averaged 950°C to 975°C during melting.

Introducing the batch into the hot canister produced rapid generation of volatiles that carried solids into the off-gas line. Inspection of this line after the run showed only a slight accumulation of sintered product at the port in the canister cap. No accumulation of batch had occurred in the feed port.

This run produced a vitreous, multiphase material having three distinct zones. The bottom zone is a glassy, void free, gray material. The middle zone is greener and has some voids. The top zone is almost a foam. There is a large doughnut shaped void between the bottom and middle zones. The voids and foam areas in this first run were believed due to an inadequate post run heat treatment for degassing.

The second engineering-scale run, designated ICM-8, was made to test the hypothesis that melting rate could be maximized by using more of the available surface area of the canister to transfer heat to the melt. The canister filled with 3 ft (72 lb) of batch was lowered into a preheated 1000°C furnace. The melt level in the canister was maintained at 3 ft by feeding batch as necessary while the exterior temperature was held between 1000°C and 1070°C. A total of 192 lb of batch was added to the canister during the 9 hr run giving an average melting rate of 23 lb/hr. This is not significant improvement over the ICM-7 rate. Following batch feeding, the melt was held at 1000°C for 4 hr before cooling. The cool down was similar to that of ICM-7.

The product of ICM-8 is better than that of ICM-7, as shown in Figure 1. It is still multiphase but is more vitreous, has few pores, and is more uniform from top to bottom.

Neg 747315-1

FIGURE 1. Interior of Product Produced by ICM-8

There was some spalling on the outer surface of the canister, particularly below the 3-ft level. The integrity of the canister was not threatened, but the higher temperature and longer time at temperature seem to be responsible.

The diameter of the canister below the melt level was about 0.02 in. greater after the run than it was before. The diameter of the canister above the 3-ft level had not changed. This increase in diameter is believed caused by the difference in thermal expansion of the melt product and the 304L stainless steel. Because the contraction of the steel is greater than that of the glass, as the canister is cooled, that metal around the glass is constrained from contracting to its original diameter. Therefore, it is placed in tension. There is concern that this tensile stress could be a driving force for corrosion of the canister. Also, the ideal cooling cycle for producing a stress-free glass may result in some sensitization of the 300 series stainless steels.

The third engineering-scale in-can melting test, designated ICM-11, was made in a canister containing eight internal fins, as shown in Figure 2. These fins were tack welded to the canister wall at the top and bottom. The purpose of the fins was to improve heat transfer into the melt, and thus more closely approximate the melting of self-heating, high-level, nuclear waste and obtain a higher melting rate.

FIGURE 2. Eight-Inch Diameter Finned Canister

The empty canister was heated to 1050°C, and 100 lb of batch was then fed at 90 lb/hr. This 100 lb was completely melted within 1-1/2 hr, giving a melting rate of 65 lb/hr. Fifty pounds of batch were then fed at 45 lb/hr, and the melting rate equalled the feed rate. Therefore, the melting rate is assumed greater than 45 lb/hr, perhaps as high as 65 lb/hr for the finned canister. This could not be confirmed because bridging at the top of the fins and plugging of the feed and off-gas lines required an interruption in the feed addition. The cap assembly for feeding and venting the in-can melting process is being redesigned to resemble the concept shown in Figure 3.

Exterior temperatures were maintained at 1050°C during the melting. Following melting the exterior temperature was held at 1000°C for 2 hr. The melt center temperature was also at 1000°C during this time. The canister of product was cooled as the two earlier canisters were.

FIGURE 3. In-Can Melting Concept

The product of ICM-11 is shown in Figure 4. There is a 5 to 6 in. layer of devitrified material at the top. In this zone are bright yellow agglomerations assumed to be sodium molybdate. Well developed crystals of sodium molybdate are on the surface. The rest is a highly vitrified, multi-phase material. Toward the center and bottom the crystalline phase occurs as larger, more widely spaced clusters while near the outside the crystals are smaller and more uniformly distributed in the black glass matrix. The crystals are typical of CeO_2 seen in many previous melts. The product did not adhere to the canister walls as in the two previous runs and was not fractured.

Neg 747918-2

FIGURE 4. In-Can Melted Glass with Internal Fins

The canister showed considerable spalling from the outer surface below the melt level, and the diameter in this region had increased by about 0.020 in. as a result of the process. The fins had been bowed during the melting cycle.

Six laboratory tests were conducted in 2-in. diam 304L stainless steel crucibles. The melting behavior of various calcines and calcine-frit ratios are evaluated on this scale. The most significant result of these tests is that batches containing the PW-7a type calcine foam during melting while the batches containing PW-4b calcine do not. The foaming is believed caused by the 18% nitrate content of the calcine. It was learned that rapid heating of the melt through the 600 to 800°C temperature range can minimize foaming.

Two-to-one frit-to-calcine ratio blends were successfully vitrified at 1050°C in the stainless steel crucibles. The multiphase product does not differ much in appearance or density from those produced with 3:1 blends. Leach rates are now being determined for comparison.

JOULE-HEATED CERAMIC MELTER - C. C. Chapman

The objective of this work is to develop a reliable ceramic melter design which can be used for converting radioactive waste to a glass.

The potentially long, reliable service life of a ceramic melter is a major feature in its favor. From operating characteristics of past test melters and information from experts in the glass industry, a scale model ceramic melter has been designed and is being assembled. (See Figure 5 for a top view of the melter with the container lid removed.) The melting cavity is 14 in. wide, 12 in. deep and 30 in. long.

A fused cast chrome-spinel material (80% Cr_2O_3) is used as the glass contact refractory, while backup refractories are of zircon. The refractory brick assembly is maintained in position by spring loaded, water cooled, sidewall plates. In addition to maintaining tight refractory joints, the plates cool the refractories to decrease the rate of corrosion

1. Cooling/Constraining Plate	6. Glass Contact Refractory
2. Drain Electrode/Batch Skimmer	7. Backup Refractory
3. Overflow Drain	8. Compression Spring
4. Overflow Drain Electrode	9. Bottom Drain
5. Main Electrode	10. Container Flange

FIGURE 5. Scale Model Ceramic Melter
Schematic, Top View

and insure containment of the molten glass by freezing any glass that might seep through the refractory joints.

The main electrodes are 2 in. thick, 12 in. wide Inconel[®] 690 plates suspended from the top of the refractories at both ends of the melting cavity. The overflow draining cavity, 6 in. wide, 10 in. long, 14 in. deep, is centered on the melting cavity sidewall. The overflow cavity electrode serves both as a power source for the drain cavity and a batch powder skimmer.

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The unit is equipped with two drains. A freeze valve is located in the bottom of the melting cavity for complete draining of the melter. In the overflow cavity a 6-in. standpipe with a reciprocating plunger can be used to control draining. The plunger may be used as a simple mechanical plug or as a freeze plug by internally cooling the tip of the plunger.

The entire melter has been designed to operate under a partial vacuum by placing the melter within a flanged, stainless steel box. Temperatures at 47 different positions within the melter system will be monitored and recorded to characterize melter operation. During future operational testing, emphasis will be on determining:

- Melting capacity of the unit for
 1. dry powder batch feeding
 2. concentrated waste slurry feeding
 3. direct waste liquor feeding
- Design features which limit melter life
- Identification of any characteristic which would influence use of this type melter.

SOLIDS PROCESSING - H. T. Blair

The purpose of this study is to evaluate and develop methods of blending nuclear waste calcines and glass-forming frits and of conveying and metering such blends to a melter.

Two days of agglomeration tests were performed by Ferro-Tech Inc. personnel and observed by Battelle-Northwest representatives at Ferro-Tech's research facilities at Grosse Ile, Michigan. The tests were made with simulated PW-4b-2 spray calcined waste and -325 mesh 73-1 frit. The calcine had an initial bulk density of 70.6 lb/ft³ and the frit a bulk density of 63.2 lb/ft³. The blends of these solids pelletized readily but require a binder.

Mixtures were prepared by blending 12 lb of frit and 4 lb of calcine in a Hobart mixer. Separate streams of frit and calcine were also

proportionally fed in a 3 to 1 ratio from two separate feeders directly into the pelletizing disc. The pellets produced from the latter type of feed were nearly a homogeneous blend.

The pellets produced using a sodium hydroxide solution as the binder were the most satisfactory. They had the lowest moisture content and attrition loss and the highest dry bulk density.

Water was used both to prewet the blend for dust control and to agglomerate the blend in the pelletizing disc. Thus the pelletizing of nuclear waste calcine in a hot cell will be a challenge if temperatures are above 100°C. Another wetting agent will have to be identified.

Briquetting was determined unsatisfactory for hot cell operation because the machine is complicated and the process generates many fines that must be recycled.

Using a disc pelletizer in place of a mechanical blender to prepare batch for a melter has several advantages. The disc pelletizer is not as complicated as a mechanical blender. No plows, beaters, or ribbons are forced through the blend causing wear by abrasion. No rotating shafts pass through seals into the batch. The product is not only blended, but is densified, is dustless, is free flowing, and will not separate when conveyed.

A 16-in. diam disc pelletizer and two screw feeders were ordered for further developmental work.

FLUIDIZED BED CALCINER - W. J. Bjorklund

Fluidized bed calcination studies are designed to provide a system to convert high-level radioactive liquid waste to a dry solid product. The product will subsequently be converted to a glass form believed to be the most stable means of storing the waste.

During this period the initial operation of the newly installed equipment was begun. Shakedown runs of the combustion, feed and off-gas systems have been successfully completed. Modifications made to date have included:

1. Drilling out the holes in the fluidizing air distributor plate to improve fluidizing. Initial tests showed too high a pressure drop across the 6.75-in. square plate. The 100 holes were enlarged to 0.046 in. in diameter.
2. A stainless steel steam jet was installed directly in the off-gas line to provide increased vacuum availability. The new system, capable of drawing over 50 in. of water vacuum, greatly increases the capacity of the off-gas filters.

In general, operation at this early date has been very satisfactory. Performance of the sintered metal filters has been encouraging.

Plans for the next quarter include coupling the fluidized bed calciner to a melter. Various solids handling equipment needed to feed the melter is being considered. The in-can melter will be the first tried, followed by the ceramic melter.

WIPED FILM EVAPORATOR - R. Dierks

The information being obtained in this study is intended to aid in developing design specifications for equipment to reduce high-level waste slurries to a solid borosilicate glass.

Several experiments have been performed with the wiped film evaporator discharging its concentrated product by gravity directly into a metallic melter operating at 1200°C immediately below the evaporator. Adding the glass former directly to the simulated high-level waste slurry as a <325 mesh powder avoids the problems of metering the solid frit into the melter in the appropriate ratio with the concentrate discharge. In addition a more homogeneous mixture of the glass former and the metal oxides of the waste is obtained. The problems of pumping the abrasive frit-laden waste slurry are avoided by using a gravity feed system to the evaporator since the evaporator does not require a pressurized feed system. With an appropriate nitric acid balance in the waste/frit slurry the settling rate and viscosity of the mixture can be reasonably well controlled. Abrasion of the evaporator has not yet been observed.

The major problem encountered with the directly coupled evaporator/melter system has been in transferring the concentrate from the evaporator to the melter. The several approaches investigated include use of boiling water cooled nozzles which keep the concentrate above its freezing point and below its calcination point. But no approach has yet proved totally satisfactory.

Another problem is excessive carryover of solids with the gases from the melter. This may be caused by transferring the concentrate to the melter at too low a solids content, resulting in excessive boiling in the melter. If so, improved design of the transfer section and fuller use of the evaporator's capability may reduce the problem. However, several melter off-gas recycle systems have been investigated which will not only recycle to the evaporator any solids mechanically carried out of the melter, but may possibly recycle materials with a tendency to volatilize from the melter.

DEVELOPMENTAL SPRAY CALCINER - H. T. Blair

The objective of this work is to provide for commercial nuclear fuel reprocessors a reliable system for conversion of high-level radioactive, liquid waste to dry, stable calcine.

The operating parameters and results of the developmental spray calciner run designated DSS-18 are given in Table 1, and the composition of the feed designated PW-7a-2 used for this run is shown in Table 2. This is the third type of feed successfully calcined with the developmental spray calciner. This feed composition is based on the PW-7 composition; however, the sodium content of PW-7a is greater because of Allied-General Nuclear Service's decision to blend the ILW and HLW. Rare earth mix was added to the simulated waste batch in sufficient quantity to provide a cerium content by weight equal to the total cerium and uranium content of the as-defined PW-7a. This was done because recent indications are that uranium will behave in the glass structure much as cerium does. Didymium (rare earth mix without cerium) was added to the batch to provide sufficient

**TABLE 1. Operating Parameters and Results of Development
Spray Solidification Run DSS-18**

Date	Day				
October 1974	4	5	6	7	8
<u>Feed</u>					
Type(a)			PW-7a-2		
Specific Gravity			1.28		
Temperature, °C(b)	24-39	25-39	25-42	25-47	25-47
Nozzle pressure, psig	28	25	25	26	27
Feed rate, liter/hr	14.8	16.7	16.7	19.4	23.6
Total feeding time, hr	5.5	5	11	12	5.5
Total feed consumed, liter	81.5	83.4	183.9	233.0	129.6
Number of unplanned interruptions	0	0	0	0	0
Total down time, min.	0	0	0	0	0
<u>Atomizing Feed Nozzle(c)</u>					
Atomizing air flow, scfm	7.3	6.6	6.6	6.5	6.5
Atomizing air pressure, psig	45	40	40	40	40
Atomizing air temperature, °C	16	16	15	16	15
<u>Calciner</u>					
Furnace temperature, °C - Zone 1	780	810	800	820	800
- Zone 2	710	725	720	720	715
Internal wall temperature, °C					
35 cm below feed nozzle	745	770	760	770	750
71 cm below feed nozzle(d)	700	700	700	700	700
107 cm below feed nozzle	685	680	680	675	670
137 cm below feed nozzle(e)	700	700	700	700	700
160 cm below feed nozzle(f)	680	695	675	na	na
Power consumption, kW - Zone 1	100	88	209	246	122
- Zone 2	82	62	161	194	102
Vacuum, in. of water					
Normal	9.2	9.2	9.2	8.0	7.6
During filter blowback	4.4	5.2	3.2	1.6	0.8
Air inleakage, scfm	0	0	0	0	0
<u>Calciner Vibrator(g)</u>					
Cycle time, min.	2	2	2	2	2
Pulse time, sec.	3	3	3	3	3
Air supply pressure, psig	44	44	44	40	44
<u>Calciner Off-Gas Filter</u>					
Blowback air temperature, °C	270	265	260	265	265
Blowback air pressure, psig	60-70	75	80	80	80
Blowback cycle, min	3-2	2	2	2	2
Blowback pulse, sec	0.25	0.25	0.25	0.25	0.25
Filter pressure drop, in. of water	9.0	10.5	12.5	14.0	15.5
	11.0		13.8	15.8	

TABLE 1. (contd)

	Day				
	4	5	6	7	8
<u>Calcliner Off-Gas Filter (contd)</u>					
Total noncondensible flow to filters, scfm	7.3	6.6	6.6	6.5	6.5
Total gas flow to filters, acfm	37.6	39.2	39.9	44.7	50.6
Filter chamber temperature, °C	290	290	300	310	300
Filter face velocity, ft/min	2.4	2.5	2.6	2.9	3.3
Permeability, ft/min-in. of water	0.22-0.27	0.24	0.19-0.21	0.18-0.20	0.21
Solids deentrainment factor(h)	20 to >190				
<u>Product</u>					
Type	Calcine				
Weight, kg	121.5				
Volume, liter	135.3				
Feed-to-product volume ratio	5.2				
Equivalent waste, tonne	1.9				
Aerated bulk density, g/cc	0.69				
Working bulk density, g/cc	0.87				
Packed bulk density, g/cc	1.15				
Compressibility, %	39.6				
Angle of repose, degrees	43				
Sodium content, wt %	8.0-8.1				
Chromium content, wt %	1.2				
Iron content, wt %	4.4-4.5				
Nickel content, wt %	0.34-0.35				
Lanthanum content, wt %	7.8-8.0				
Cerium content, wt %	11.1-12.3				
Neodymium content, wt %	6.0-6.1				
NO3 content, wt %	18.2				
Moisture content, wt %	0.31-0.36				

- See Table 2 for composition of Type PW-7a-2 feed.
- Feed temperature rose steadily from minimum to maximum values each day due to pump friction.
- Spraying Systems Co. air atomizing nozzle setup No. 42 with B₄C insert in air cap. See Figure 6.
- Zone 1 furnace control temperature.
- Zone 2 furnace control temperature.
- The thermocouple at the 160-cm level failed 10-6-74 at 11:35 am.
- Cleveland Vibrator Company modified 1300 AC Vibra-Might vibrator acting on the side of the calciner barrel by a shaft extending through the furnace wall.
- Based on analyses of condensate and scrubber solution for Cr, Ni, and Fe. Values are low due to accidental filter bypassing problems.

TABLE 2. Composition of PW-7a-2 Simulated Waste
Used for Spray Calcliner Run DSS-18

As-Defined PW-7a		PW-7a-2 Composition	
Constituents	Concentration M at 378 liter/MTU	Concentration M at 378 liter/MTU	Chemical Substitutes Used
H	1.00	1.00	
Fe	0.10	0.159	
Na	0.59	0.59	
Cr	0.012	0.012	
Ni	0.005	0.035	
PO ₄	0.10	0.10	
Mo	0.095	0.117	
Tc	0.022	None	Mo
Sr	0.027	0.027	
Ba	0.027	0.027	
Cs	0.054	None	K
Rb	0.010	None	K
Y	0.014	0.137	(a,b)
La	0.024	0.146	(a,b)
Ce	0.051	0.239	(a)
Pr	0.023	0.030	(a,b)
Nd	0.071	0.104	(a,b)
Pm	0.0019	None	(a,b)
Sm	0.014	0.0171	(a,b)
Eu	0.003	None	(a,b)
Gd	0.153	0.0114	(a,b)
Zr	0.106	0.106	
Ru	0.059	None	Fe
Rh	0.010	None	Co
Pd	0.030	None	Ni
Te	0.012	0.012	
Ag	0.002	0.002	
Cd	0.002	0.002	
U	0.110	None	(a)
Np	0.0085	None	(b)
Pu	0.001	None	(b)
Am	0.0018	None	(b)
Cm	0.0004	None	(b)
		0.064	K
		0.01	Co
		0.0009	Dy(a)

- a. A commercial rare earth mixture nominally containing 0.2% Y₂O₃, 24% La₂O₃, 48% CeO₂, 5% Pr₆O₁₁, 17% Nd₂O₃, 3% Sm₂O₃, 2% Gd₂O₃, and 0.8% other rare earth oxides was used to obtain a Ce content by weight equal to the sum of the Ce and U contents of the as-defined PW-7a type waste.
- b. Didymium nominally containing 4% Y₂O₃, 39% La₂O₃, 2% CeO₂, 10% Pr₆O₁₁, 34% Nd₂O₃, 5% Sm₂O₃, 4% Gd₂O₃, 2% Dy₂O₃, 0.2% Ho₂O₃, 0.4% Er₂O₃, and <0.1% of each of the others was used to obtain a rare earth element content by weight equal to the sum of Np, Pu, Am, Cm and the rare earths except Ce contents of the as-defined PW-7a type waste.

lanthanum, praseodymium, and neodymium as substitutes for gadolinium, neptunium, plutonium, americium, and curium.

The spray calciner was operated for periods of 5 to 12 hr a day for 5 days. When the feed was not being pumped to the calciner, the barrel wall temperatures were reduced to 500°C, air was passed through the nozzle at a rate of 6.5 scfm, the filter blowback cycle was increased to 15 min, and the vibrator was turned off. No problems were experienced while running the calciner in this intermittent manner, and use of the nozzle clean-out needle was never required to restart feed flow.

The feed rate was increased from the usual 15 liter/hr to a maximum sustained rate of 23.6 liter/hr. The limiting factor was the filters' pressure drop. In contrast to some previous experience, the pressure drop across the filters became constant within a few hours of the start of operation each day and remained constant as long as the feed rate remained unchanged. The reason for this stability of the pressure drop across the filters is not yet known, but this stability permitted trouble-free operation of the spray calciner at feed flowrates which are considered high for the capacity of the off-gas filters. Examination of the filters following the run showed that they were uniformly coated with approximately 1 mm of soft, fine powder penetrated by pin holes.

The solids deentrainment factor reported may be too low because during operation at high flowrates, the seal pot was blown several times. When this occurs, calcine is introduced directly into the condenser. This increases the Cr, Ni, and Fe content of the condensate and scrubber solution.

The calcine produced during run DSS-18 appears similar to that produced from type PW-4b simulated waste, which does not contain ruthenium. Its density falls between those of PW-4b and PW-6 type calcines produced in the spray calciner. This calcine will be used for solids processing equipment and melter developmental work.

Several modifications to the spray calciner system were evaluated during run DSS-18. One modification was use of an air cap on the atomizing spray nozzle which was made of 304 stainless steel and fitted with a

B_4C insert in the critical wear area as shown in Figure 6. Measurements made before and after the run using a machinist's microscope having a precision of 0.0003 in. show that the spray orifice diameter had increased 0.0018 in. at the exit and an average of 0.0117 in. at the internal mixing end. This wear data and that of the previously used 303 stainless steel air caps cannot be compared because no measurement data has been collected on the latter caps. However, the performance of the carbide insert is considered an improvement because no deterioration of the feed flow characteristics were noted during the 39 hr run. Indications of 303 stainless air cap wear were noted within 29 to 31 hr of run time at elevated feed rates during a previous run, DSS-15.

FIGURE 6. Spray Calciner Feed Nozzle Assembly with B_4C Insert in Air Cap

The B_4C insert was not affected by at least seven thermal shocks of 200°C temperature change in a few seconds when feed or water flow through the nozzle was turned on or off.

An air cap made of 96% alumina has been evaluated in the nozzle test station at feed rates of 15 to 30 liter/hr for 45 hr. No measurable change has occurred in the critical orifice diameter. However, results from the test station cannot be directly compared to performance in the spray calciner because the test station operates at ambient temperature while the nozzle in the spray calciner operates at temperatures between 100°C and

500°C. An alumina air cap was not used in the DSS-18 run because it breaks at the weak area shown in Figure 7. Figure 7 also shows a proposed design change to eliminate this weak area.

FIGURE 7. Proposed Modification to Strengthen Alumina Air Cap

Another modification to the nozzle assembly was the use of a bellows to effect a seal with the cleanout needle instead of the use of packing around the needle shaft. The cleanout needle worked well when tested at the start of the run. Use of the needle was never required during the run, but it still moved freely when inspected during disassembly, and there were no leaks. Bellows were previously used successfully during the WSEP program.

A third modification evaluated was the side-mounted vibrators described in an earlier report.* Only one of the vibrators was used during DSS-18. Wall scaling was anticipated because of the sodium in the feed, but the interior of the barrel following the run showed less scale than usually occurred during runs using PW-4b type feed. Following the run the spray calciner barrel showed no measurable distortion of the barrel wall or impact pad in the area acted on by the vibrator. There was some spalling at the point of impact on the pad.

* Quarterly Progress Report July through September 1974, BNWL-1871,
December 1974.

WASTE FORM CHARACTERIZATION

The purpose of waste form characterization is to measure the properties of candidate solidified products (solidified waste and canister) as a function of composition, processing parameters, and storage conditions. The measurements are used 1) to assure operability of the manufacturing processes, and 2) to provide data for safety analyses of high-level waste management. The ultimate goal is to characterize the physical and chemical properties of the waste forms so thoroughly that when they are placed in retrievable storage, and later in ultimate disposal, full confidence can exist that their behavior is known and that any changes or any interactions with their environment which may occur are wholly predictable.

STORED ENERGY MEASUREMENTS - F. P. Roberts

The objectives of the task are to experimentally determine the buildup of radiation-induced stored energy in solidified high-level wastes as a function of the storage time and storage temperatures, and to characterize the thermal behavior of the solidified waste when the stored energy is released. The results of the study are to be used to establish whether or not stored energy constitutes a hazard in waste storage.

A series of tests was performed to determine buildup of stored energy resulting from alpha decay in synthetic solidified high-level wastes. The tests were carried out using 10-g buttons of borosilicate glass stored at an ambient temperature of 22 to 24°C. (See the Quarterly Progress Report, April, May, June 1974, BNWL-1841, of this series for a description of the composition and preparation of the specimens.) The specimens contained known amounts of ^{244}Cm with specific alpha activities ranging between 1.72×10^{15} and 3.20×10^{15} $\alpha/\text{day/g}$.

The stored energy buildup was determined by periodically measuring the energy release on 50-mg samples of the crushed buttons. The energy release measurement was accomplished using the differential scanning calorimeter previously described.

The cumulative alpha emission at the time of the measurement was calculated from the known specific alpha activity and the time period elapsed since annealing of the button.

Twenty-eight measurements on seven different buttons have been carried out. The results (see Figure 8) show the stored energy buildup as a function of the alpha dose. The relatively rapid buildup at low alpha doses followed by a gradual decrease in the rate of buildup indicates that self-annealing is occurring.

The equivalent age of the test specimens corresponding to stored solidified high-level waste can be obtained from Figure 9, which gives the cumulative alpha dose as a function of the age of the waste. The data in

FIGURE 8. Stored Energy Buildup in Borosilicate Glass

FIGURE 9. Alpha Dose in Stored High-Level Waste

Figure 9 is based on a light-water reactor - 3.3% enriched UO_2 fuel with a burnup of 33,000 MWd/T, assuming 99.5% separation of uranium and plutonium 150 d after discharge. The high-level waste is assumed solidified at this time in a form resulting in 163 kg of solids per metric ton of heavy metal.

From Figures 8 and 9 it can be seen that the stored energy buildup reaches 21 cal/g at an equivalent age of 140 years.

HELIUM IN GLASS - R. P. Turcotte

The objective of this study is the determination of helium diffusivity in simulated waste glass in order to assess effects of radiation damage. Samples doped with ^{244}Cm are being examined. For these, relatively large helium inventories are generated with simultaneous extensive radiation damage from the 5.5 MeV alpha particle and recoil daughter ($^{244}\text{Cm} \rightarrow ^{240}\text{Pu} + ^4\text{He}$). Helium release is being measured from thin discs as a

function of time and temperature. Some X-ray diffraction work is also being undertaken to determine the extent of radiation-induced devitrification.

Work during the quarter included attempted release measurements on undoped specimens and measurement of release from two curium-doped samples by both constant rate of heating and isothermal methods. The helium solubility in undoped samples is too low for quantitative study on the manometer system and will be delayed until a mass spectrometer is operational next quarter. There was no significant change in the X-ray diffraction pattern of curium-doped samples after 1 month of self-damage.

The helium release behavior for two of the curium-doped glass samples (72-68) has been examined after allowing ingrowth for 62 days. For the slab geometry employed, and assuming a homogeneous distribution of ingrown helium, the Fick's law solution for fractional gas release (F) as a function of the diffusion coefficient (D) takes the form

$$F = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp[-D(2m+1)^2 \pi^2 t / \ell^2] \quad (1)$$

where D has the units cm^2/sec , t is time (sec) and ℓ is the slab thickness (cm). It has been shown* that the diffusion coefficient can be accurately estimated from a knowledge of the time required for release of one-half of the gas present as given by

$$D = 0.04939 / (t/\ell^2)_{1/2} \quad (2)$$

This estimate can then be used as a starting point toward fitting Equation (1) to the experimental data. Although the release fraction is given as an infinite series, convergence is rapid and calculated curves agree to better than 0.1% for 5 and 20 terms. A small Fortran program was written

* J. Crank and G. S. Park, Trans. Far. Soc., vol. 45, p. 240, 1949.

to generate the theoretical release curves given in Figure 10. These cover the range of potential D (1×10^{-5} to 1×10^{-9} cm^2/sec), based on literature reports of diffusion in more conventional glasses. Plotted as fractional release versus time, a very strong dependence is evident (Figure 10) over times well suited to the experimental method employed.

Results for sample A-26-1 are given in Figure 11, plotted as pressure versus temperature. Two heating rates were used, showing little effect. Two isothermal runs of 5 hr each increased the total gas measured to near 5×10^{-2} torr, nearly twice that expected. There is no clear explanation for the excess, and until a mass spectrometer system is operational (next quarter), the gas composition is unknown but assumed to be only helium. The experiments on undoped samples lend some validity to this assumption in that comparable isothermal runs give no pressure rise above background.

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FIGURE 10. Theoretical Gas Release Curves Plotted as Fraction Release Versus Time for Various Values of the Diffusion Coefficient

Neg 747913-5

FIGURE 11. Helium Release from Curium-Doped Disc Plotted as Pressure Versus Temperature

The experiments shown in Figure 12 for sample A-26-2 do appear to yield a total gas release near that expected. It is likely, of course, that other gases will be released at high temperatures through oxide decomposition, bubble migration, etc. The release is clearly nonclassical. Each isothermal step taken as a separate experiment gives an initial rapid release with a sharp drop in release rate at longer times. In Figure 13, the first isotherm at 312°C is considered in more detail. If the total helium inventory is ignored and the long time data are instead taken as approaching a limiting unit-fraction release for that temperature, a good fit of the theoretical curve (Equation 1) is obtained with $D = 1.15 \times 10^{-6} \text{ cm}^2/\text{sec}$. If the true helium inventory is considered, however, it is not possible to obtain a reasonable fit, with much smaller coefficients required to match the long time data and very poor overall agreement, particularly considering extrapolations to $t > 100 \text{ min}$.

Although the isotherms were conducted consecutively, with increasingly lower inventories with increasing temperature, the situation is well approximated by the curves as redrawn in Figure 14, with a shift along the time

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FIGURE 12. Isothermal Release Curves Plotted as Pressure Versus Time

Neg 747913-1

FIGURE 13. Isotherm at 312°C
Plotted as Fractional Release Versus
Time. Theoretical curves based on
the true Helium inventory (D_T) are
compared to the step fractional
release

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FIGURE 14. Isotherms Replotted as
Pressure Versus Time

axis, starting each isotherm at $t = 0$. Clearly, each curve considered independently and compared to the theoretical curves given in Figure 11 can be fit only to diffusion constants in the range 1×10^{-5} to 1×10^{-6} cm^2/sec . It is also clear, however, in considering true helium inventories, that there can be no direct match to the simple diffusion theory covering the full temperature range. In Figure 15, the true fractional release after 60 min heating appears to correlate linearly with temperature. Close agreement with the data given in Figure 12 for sample A-26-1 is obtained if the true helium inventory for the latter is taken as the calculated value.

Neg 747913-7

FIGURE 15. Release Fractions After 60 Min (Sample 2) and from the Dynamic Run (Sample 1) Plotted Versus Temperature

Although these are considered preliminary data, the lack of agreement between true fractional release and simple diffusion theory is not entirely unexpected. Trapping by radiation-induced (or other) defects is considered the only plausible explanation for the observed behavior. It is suggested that ingrown helium is trapped in defect sites over a wide range of stabilization energies. Thus escape from traps is highly dependent on temperature, 300°C exceeding the required activation energy for only ~15% of the entire inventory and 500°C exceeding ~80% of the inventory, as suggested by Figure 15. Once free, diffusion is approximately classical, as shown by the good fit given in Figure 13, based on this assumption.

The model suggested here is not more than an extension of similar observations and interpretations reported for crystalline solids. Several related studies involving diffusion in radiation-damaged crystals (usually by high-energy ion implantation) show clearly the large reduction in net

release at a given time and temperature (effective diffusion coefficient) as observed here. The details are different, as might be expected, and several types of theoretical analysis have been suggested as applicable to radiation-damaged systems. As experiments continue, these models will be examined for relevance to this work. From an engineering viewpoint, it would now appear that total helium release will occur at temperatures exceeding 500°C. Significant fractional release will occur at temperatures above 250°C in all cases with an apparent high diffusivity ($D > 1 \times 10^{-6} \text{ cm}^2/\text{sec}$) but to a temperature-dependent limit in terms of the fraction released.

RADIOLYTIC GAS GENERATION - G. L. Tingey and W. D. Felix

In this task we are investigating the stability of calcined nuclear waste products in a radiation environment. Previously we reported the results of radiolytic decomposition of water and nitrate compounds contained in the waste product. This decomposition has the potential for causing pressure buildup in the container. Thus the extent of the decomposition is of interest in evaluating the stability of the system.

Evaluating results of earlier studies of radiolytic decomposition of the calcined waste showed that more information on interaction of the solid waste with gases was required both to interpret the decomposition data and to permit prediction of pressure generation in the waste system. Thus, we are determining surface properties of specific materials and measuring their sorption properties.

During the quarter we have obtained samples of two types of calcined waste (PW-4b and PW-7) both prepared by fluidized bed techniques. Each sample was sieved to determine the particle size distribution and to obtain a sample with a relatively narrow particle size range. The particle size distribution is given in Table 3.

Optical microscopy was then performed on each waste material using the size range which made up the largest fraction of the material.

TABLE 3. Particle Size Distribution for Calcined Waste

PW-4b-4 ICPP-Final Bed		PW-7-2 ICPP Run #54	
Particle Size (μM)	Fraction of Total	Particle Size (μM)	Fraction of Total
>500	0.093	>350	0.088
350-500	0.035	250-350	0.202
250-350	0.710	175-250	0.332
175-250	0.135	125-175	0.356
125-175	0.026	90-125	0.017
<125	0.001	60-90	0.003
		<60	0.002

Figures 16 and 17 are micrographs of the PW-4b and PW-7 waste materials, respectively. The micrographs show the layered structure formed during the fluidized bed calcining. Some particles still contain the Al_2O_3 seed material which was added at the start of the run. Of major importance to this program is the large volume of internal porosity and thus large surface area for gas adsorption. These pores seem to be connected with cracks so that most of the porosity is open to the surface.

To quantitatively determine the surface area, a sample of the PW-7-2 was outgassed thoroughly at temperatures up to 900°C and nitrogen absorption measured at -195°C . During outgassing about 1.3 m moles of gas at STP was released per gram of waste. This gas release produced a fractional weight loss of about 6%, assuming all the gas to be NO_2 .

Using the BET equation and the nitrogen absorption data, a surface area of $1.5\text{M}^2/\text{g}$ was determined.

During the next quarter the sorption isotherms for N_2 , O_2 , NO_2 , NO , CO_2 and H_2O will be measured at temperatures up to 700°C .

a - 85X (4J1406B)

b - 212.5X (4J1406C)

c - 212.5X (4J14060)

FIGURE 16. Optical Micrographs of Calcined Waste - PW-4b-4 Final Bed.
Particle size = 250-350 μM

a - 85X (4J1570D)

b - 85X (4J1570G)

c - 212.5X (4J1570E)

d - 212.5X (4J1570H)

FIGURE 17. Optical Micrographs of Calcined Waste - PW-7-2 ICCP Run #54.
Particle size = 125-175 μM

FULL-LEVEL RADIOACTIVE TESTS - Y. B. Katayama

Fully radioactive waste glass specimens will be prepared on a laboratory scale. Analyses of the off-gas will be made during melting of the radioactive glasses. Characteristics of the fully radioactive glass specimens will be compared with nonradioactive glasses of similar chemical composition as a function of storage conditions.

An approximately 2000-g supply of irradiated UO_2 power reactor fuel (55,000 MWD/MTU, 1 1/2 years out-of-reactor) has been arranged for. The fuel is scheduled to arrive at PNL in early February. The in-cell glass-making equipment has been designed. Radioisotope volatility will be studied by condensing the volatilized material on a water-cooled plate. This plate is readily removable, and its composition can be chosen to facilitate radioisotopic analysis and/or removal of condensate.

THERMAL FRACTURE BEHAVIOR OF GLASS IN SIMULATED GLASS CANISTERS - W. A. Ross

This study is to provide data on the fracture behavior of glass in canisters when exposed to various thermal shocks.

Glass, due to its low thermal conductivity and brittle nature, is subject to thermal shock. Canisters of glass require slow cooling rates if monolithic forms are to be maintained. For example, a 12-in. diam casting must be cooled at less than 2°C/hr below the annealing point to avoid cracking. These low cooling rates do not appear practical when compared 1) to the adiabatic heating rates of waste canisters, 2) process times and control requirements, and 3) normal atmospheric temperature cycles.

A series of tests at widely varying cooling rates has been conducted to provide data on the severity of cracking obtained by various cooling rates.

Two canisters were formed from 6-in. diam Sch. 10 stainless steel pipe. The pipes were split lengthwise before filling. To reduce glass-canister bonding and glass leakage, the canisters were lined with a 1/8-in. Fiberfrax[®]

[®] Carborundum Company Trademark.

paper. The canisters were held inside a furnace at 550°C, and approximately 35 lbs of 72-68 (PW-4b-2: [3.0] 73-1) glass at 1150°C was poured into the canisters. One canister was removed shortly after filling and was hung in air. A thermocouple was located at the canister-glass interface to record the cooling rate. The second canister was held in the furnace and cooled slowly. A 6-liter stainless steel beaker was used for a third canister and was surrounded by water during its filling and cooling period.

Surface cooling rates were determined at the annealing point (~510°C) for the canisters. The sample in air cooled at ~475°C/hr, the canister in the furnace cooled at ~35°C/hr, and the canister in the water was estimated to have a cooling rate in the range of 2000 to 20,000°C/hr.

The glass after cooling showed that the degree of fracture was highly dependent on the radial location, with the outside highly fractured. The outer materials provided a thermal barrier and allowed the inner material to cool more slowly and, therefore, remain in larger pieces. While the castings were fractured, the pieces were interlocked and could not be removed until the canisters were opened or split. The handling operations resulted in some minor breakage, but the particle size distribution should not be grossly affected. The glass after being removed was screened into various size fractions. The resulting particle size data are shown in Figure 18. The distributions are nearly linear on the log-log plot. The distribution lines are also nearly equidistant. It should be noted that the particle size tends to be quite large, with even the most highly fractured specimen having ~99% of material at sizes greater than 0.050 in., which is well above the size easily dispersed in the air.

Since surface area and particle size are directly related, a calculation of surface area was made from the particle size distributions. The fragments were not spherical but appeared to be plate-like, and the calculation was based on a plate of dimension $1/2a \times a \times 2a$ with the a dimension taken as the midrange particle size from the sieve data. The calculated surface areas for the fractured specimens have been divided by the surface area of a 6-in. diam monolith ($0.102 \text{ cm}^2/\text{g}$). Such a monolith was previously prepared by cooling at 0.5°C/hr in the annealing range. The

FIGURE 18. Particle Size Distribution for 6-in. diam Canister Cooled in Different Modes

relative surface area for the various cooling rates is shown in Figure 19. This shows that the maximum increase in surface area from rapid cooling (water quench) is of the order of a factor of 20 to 25 over that of a fully annealed sample. It is anticipated that cooling rates for normal processing would be in the range of 20 to 500°C/hr and will increase the surface area up to a factor of about 15.

FIGURE 19. Effect of Cooling Rate on the Surface Area of 6-in. diam Glass Castings

STRESS CORROSION CRACKING OF A WSEP 310 STAINLESS STEEL CANISTER -

Y. B. Katayama and J. E. Mendel

The storage of Waste Solidification Engineering Prototype (WSEP) Canisters in the Solid Storage Engineering Test Facility (SSETF) enables the evaluation of canister material corrosion behavior and corroboration of nonradioactive corrosion data.

Canister No. 36 from WSEP run SS-11 with an air-stored history of 4 years with a wall temperature of about 400°C was transferred to a water-filled environmental test pod in the Solid Storage Engineering Test

Facility (SSETF). The 310 stainless steel canister wall was penetrated after 6 months' exposure to the water at 50°C. Preliminary evaluation of the data indicates the penetration was by intergranular corrosion of a highly sensitized and stressed canister wall. A significant, 13 ppm, chloride concentration conducive to stress corrosion was found in the environmental test pod water. The SSETF air storage temperature was ideal for carbide precipitation in the grain boundaries of the nonannealed 310 stainless steel canister. This impoverishment of chromium in the thin envelope surrounding each grain is called sensitization. The sensitization and associated corrosion cracking will be studied during radiometallurgical examination of trepanned samples representing the crack area, weld area, and macrocrack-free area. Figure 20 is a drawing illustrating the magnitude and location of the cracking. Figure 21 is a photograph (reduced to about 0.8X) of the major crack area.

FIGURE 20. Magnitude and Location of Cracking

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FIGURE 21. Large Crack on Canister 36, Approximately 0.8X

Corrosion testing Huey equipment has been installed in C cell of the 324 Building radiochemical engineering cells. This boiling 65% nitric acid test is being done on a 310 stainless steel sample from canister 36 and a 304L stainless steel sample from the WSEP run SS-12 canister.

The 310 stainless steel canister, pot No. 36, was fabricated by W. G. Rovang and Associates in Portland, Oregon, and received by Battelle in March 1968. No Certification of Materials, Certificate of Tests or weld heat treatments were required by the purchase order. Canister 36 was filled in run 21 of the Waste Solidification Engineering Prototypes (WSEP) conducted March 24 to 28, 1969. Twelve batch dumps were required to fill the canister with 68 liters of ceramic product weighing 194 kg. This product had a self-generating heat rate density of 106 W/liter. The average steady-state canister centerline temperature in the air-cooled furnace was 594°C, with an average centerline-to-wall temperature difference of 242°C. The difference in bulk density of 2.87 kg/liter compared to the analytically-measured density of 3.32 kg/liter indicated the possibility that approximately 14% voids were present in the solidified waste.

THERMAL CONDUCTIVITY OF WASTE CALCINE - W. A. Ross

The thermal conductivity of calcine is one of the limiting parameters in equipment design. This work has been undertaken to provide data on materials which should closely represent actual waste calcine.

The method chosen to determine thermal conductivities is the line source method described by several authors.*,**

The equipment was set up and operated with several different samples. All tests are conducted in air, and the effects of density and temperature are being determined.

* W. Woodside and J. H. Messmer, "Thermal Conductivity of Porous Media. I. Unconsolidated Sands," Jour. of App. Phy., vol. 32, no. 1, pp. 1688-1699, September 1961.

** W. M. Underwood and R. B. McTaggart, "The Thermal Conductivity of Several Plastics, Measured by an Unsteady State Method."

The current results indicate that the data are reproducible and within ~5% of values obtained in similar systems. The system is based on a theoretical model, and errors should be minor.

A sample of PW-4b fluid bed calcine has been studied in the system. The temperature and density dependence of thermal conductivity have been determined and are shown in Figures 22 and 23, respectively. The linear fit of the data over the ranges tested appears justified with current experimental accuracy. The largest deviation from the linear line in Figure 23 is less than 2.5% relative. To allow maximum use of the data, the temperature and density dependence of thermal conductivity have been combined, and

FIGURE 22. Thermal Conductivity of PW-4b Fluid Bed Calcine Versus Temperature

FIGURE 23. Thermal Conductivity of PW-4b Fluid Bed Calcine Versus Bulk Density

Equation (1) is suggested for use up to 700°C and densities between 2.1 and 2.3 g/cm³.

$$k = [0.177 + 0.1 (\rho - 2.1)] [1 + 0.00148T] \quad (1)$$

where

k is in watts/m°C,
 ρ is in g/cm³, and
 T is in °C.

Further tests will be required to verify the high density-high temperature applicability of the equation.

It should be noted that the increase in conductivity with density is such that the temperature difference between centerline and surface for a self-heating canister is independent of density.

CANISTER CORROSION STUDIES - R. F. Maness

Canister corrosion studies are an integral part of the Waste Fixation Program, including investigations of corrosion under processing conditions and during long-term storage of candidate solidified waste forms.

Compatibility studies were started to determine the suitability of 304L as a canister material to contain calcine. Data obtained to date indicate very light corrosion of the interior walls of a 304L canister will occur under storage or transport conditions. A more comprehensive compatibility study will begin early in CY75.

A few corrosion tests were made pertinent to in-can melting. The data obtained indicated 304L would be a satisfactory can material at temperatures up to 1000°C. Tests were also made to determine the corrosiveness of melts prepared from PW-7 calcine under agitation conditions. Inconel 690 at a lineal velocity of 236 in./min exhibited no preferential attack in melt at 1150°C.

One compatibility study was made with PW-4c-1 (Table 7, BNWL-1841) fluidized bed calcine using two levels of nitrate (0.50 and 2.50%), three levels of water (0.20, 0.50 and 2.00%) and three temperatures (60, 90, and 300°C). Two of the above compositions were formulated with and without 1.0% fluoride. One composition included 0.018% Br, 0.032% I, and 0.061% Se added as KBrO_3 , KIO_3 and Na_2SeO_4 . The calcine was contained in closed (by welding) capsules fabricated from 1-in. diam 304L tubing. Each capsule contained a 304L coupon and a 304L-mild steel (309 filler metal) weldment, the latter simulating the presence of mild steel cooling lines welded to the ID of the proposed canisters. Corrosion rates of the coupons and weldments after 9 months' exposure to a given system are given in Table 4. Attack of

TABLE 4. Calcine--304L Stainless Steel Compatibility
9 Month Exposure

Capsule	Weight %			Temp. °C	Corrosion Rate, mils/year	
	<u>NO₃</u>	<u>H₂O</u>	<u>F</u>		<u>304L</u>	<u>304L-mild Steel Weldment</u>
1	0.50	0.20	-	60	0.003	
2	0.50	0.20	-	90	0.005	0.01
3	0.50	0.20	-	300	0.003	0.04
4	2.50	0.50	-	60	0.008	0.01
5	2.50	0.50	-	90	0.005	0.03
6	2.50	0.50	-	300	0.003	0.05
7	0.50	2.00	-	60	0.004	
8	0.50	2.00	-	90	0.004	0.04
9	0.50	2.00	-	300	0.006	0.04
10	2.50	2.00	-	60	0.005	0.05
11	2.50	2.00	-	90	0.004	0.04
12	2.50	2.00	-	300	0.006	0.05
13	0.50	0.20	1.0	60	0.002	0.06
14	0.50	0.20	1.0	300	0.003	0.14
15 ^(a)	2.50	2.00	1.0	90	0.004	0.03

a. Also 0.018 Br, 0.032 I, 0.061 Se

the 304L coupons was nil in all cases, as evidenced by visual examination and 0.002 to 0.008 mils/year as determined by weight loss. Corrosion rates of the weldments as determined by weight loss after cleaning in alkaline permanganate followed by citric acid varied from 0.01 to 0.14 mils/year. Attack was uniform and was limited to the mild steel portion of the weldment. Mild steel comprised about one-half of the surface area of the weldments. Inspection of sectioned capsules revealed no attack. The ID of the capsules was electropolished prior to use to facilitate inspection for corrosion. This study was terminated after 9 months' exposure because the calcine form used had become obsolete and because the fluidized bed calcine used contained no cesium.

A short-term (2-month) compatibility study was made with 304L stainless steel exposed to PW-7 calcine (laboratory produced) at 1000°F. The containers were closed (by welding) capsules fabricated from 1-in. diam 304L tubing; each capsule contained a sensitized (1 hr at 1250°F, water quenched) 304L corrosion coupon. Variables were water, halogen and sodium content. The systems evaluated and the 304L corrosion rates obtained are given in Table 5.

TABLE 5. PW-7 Calcine--304L Stainless Steel Compatibility
Conditions: 2-Month Exposure at 1000°F

Capsule	Weight %				304L Corrosion Rate, mils/year
	<u>NO₃⁻</u>	<u>H₂O</u>	<u>Halogen(a)</u>	<u>Other(a)</u>	
1	3.2	0.42	nil	-	0.6
2	3.2	2.00	nil	-	0.4
3	3.2	2.00	0.18 Br - 0.032 I	0.061 Se	1.3
4	3.2	2.00	0.10 Cl (as NaCl)	-	1.2
5	3.2	0.42	0.18 Br - 0.032 I	0.061 Se	1.9
6	3.2	0.42	0.10 Cl (as CsCl)	-	1.2
7	3.2	2.00	0.10 Cl (as CsCl)	-	1.0
8	3.2	2.00	1.0 Cl (as NaCl)	-	1.5

a. Br, I, and Se added as KBrO₃, KIO₃ and Na₂SeO₄

Corrosion rates of the 304L coupons were determined by weight loss after descaling in alkaline permanganate followed by nitric acid. These data were collected to permit an estimate of canister corrosion which would occur during transport of calcine. The weight loss data obtained indicate negligible corrosion. No preferential attack of the capsules was observed; however, a metallographic examination of capsules and contained corrosion coupons is in progress to determine any subsurface attack. Data are not yet available.

A comprehensive compatibility study of solidified waste now in the planning stage will begin early in CY 75. Variables to be evaluated

include waste form (calcine and glass), material (304L and Incoloy 800), condition of capsules (as-fabricated and stress relieved), calcine composition (NO_3^- , H_2O , Na and halogen content, temperature (125, 460, 1000, and 1300°F), and time (0.25, 1, 2, and X years).

A few tests pertinent to in-can melting were made. Corrosion specimens prepared from a number of alloys were exposed to a melt prepared from PW-4b calcine (1 part) and frit 73-1 (2.8 parts). Exposures were made in the melt and in the vapor phase for 100 hr at 950, 1000 and 1050°C. The results, given in Table 6, indicate corrosion occurring at 100°C on a 304L canister during the filling operation (about 100 hr) will be slight.

TABLE 6. Corrosion Rates Pertinent to In-Can Melting

Conditions: Corrosion specimens exposed to liquid and vapor phase of melt prepared from PW-4b calcine (1 part) and frit 73-1 (2.8 parts) for 100 hr at indicated temperature.

<u>Material</u>	<u>Melt Temp. °C</u>	<u>Corrosion Rate, mils/month</u>	
		<u>Melt</u>	<u>Vapor</u>
304L	950	3.2	4.5
310	950	1.7	1.0 pitting
304L	1000	15 pitting ^(a)	8.8
310	1000	1.8	5.1
410	1025	dissolved	disintegrated
Inc 600	1050	7.6	4.6
Inc 601	1050	4.0	3.8
Inc 690	1050	2.5	2.5
18-18-2	1050	38	2.0
Incoloy 804	1050	2.7	3.1
Multimet	1050	2.0	disintegrated

a. About 5 mils deep

Tests were also made to determine the corrosiveness of melts prepared from PW-7 calcine and frit 73-1 under agitation conditions. These tests were prompted by heavy corrosion which occurred on the pilot-scale Inconel 690 melter and stirrer when severe agitation (500 rpm) was used. It was later determined that a lineal velocity of 236 in./min was adequate to produce a homogeneous melt. Laboratory tests were therefore made at this velocity. The corrosion specimens (1 in. x 1 in.) in the form of a paddle were rotated at 75 rpm. Exposures were for 200 to 250 hr at 1150°C. The results obtained are given in Table 7.

TABLE 7. Corrosion in Stirred Melts
 Conditions: Melt temperature = 1150°C,
 lineal velocity of corrosion
 Specimen = 236 in./min

<u>Material</u>	<u>Corrosion Rate, mils/month</u>
Inconel 690	1.3
Inconel 690 with weld overlay	4.8
Incoloy 804	5.9
Haynes 25	72
Haynes 188	83

Metallographic examination of the Inconel 690 specimen showed no preferential attack.

ALTERNATIVE WASTE FIXATION PROCESSES

The goal of this task is to develop alternative waste fixation processes and evaluate their waste form products to assure that viable processes will be available for containment of high-level wastes. The alternative processes and products are to be compared for cost and safety to the current reference process and product, silicate glass castings in large metal canisters. Alternative processes are now being developed on the laboratory scale. After the most promising concept(s) are selected, further engineering-scale development will be undertaken.

ENGINEERING EVALUATION OF ALTERNATIVE WASTE FIXATION PROCESSES -

J. E. Mendel, L. L. Ames and A. A. Garrett

Alternative waste form concepts are being evaluated for their engineering/technical feasibility, product desirability, and cost. The overall project objective is the selection and engineering-scale process development of an alternative waste form process which will provide improved economy or safety over glass castings in stainless steel canisters, the reference waste form.

As the first step in this task a document is being prepared which will describe potential alternative waste forms processes and assemble the information available on the processes. This information will serve as the basis for selecting one or more processes for engineering-scale development. The first draft of the document is scheduled to be completed by the end of March.

GLASS SINTERING - W. A. Ross

This study is to determine the feasibility of glass sintering as a waste fixation process.

In-Canister Forming Methods

A low-pressure (~ 12 psi) hot pressing method was tested on 0.66-in. diam canisters and found to be limited by side wall friction to lengths of

approximately 1.5 in. Additional tests have been performed with increases in pressure, increases in canister diameter (to 1.9 in.), and with wall coatings of boron nitride, to determine their effect on the length of sintered column in contact with the wall. It was found that doubling the pressure increased length about 40%, that nearly tripling the diameter increased length only 15% and wall coating increased length about 25%. It therefore appeared that a simple pressing would not be sufficient to fill long canisters with sintered product.

Two alternative schemes were also tested. The first involved presintering the mixture in the canister, allowing it to shrink away from the wall and gain strength. Then a weight was applied at the top of the column with the intent that the bottom would densify first and flow due to the combined hydrostatic and applied pressures. Efforts were also made to cool the upper regions to reduce its sintering and creep rates. Several tests, however, were not successful. The second alternative was the use of impact forming. For this method the canisters were filled with the mixture and heated to near the sintering temperature, and then the canister was lifted about 1/4 in. and dropped, about 5 times per min. This method was also unsuccessful.

In-can methods have an additional problem in that it may be difficult to avoid at least some bloating. This is because nearly isothermal conditions should exist within the sample during sintering. For nonheating materials in large diameters this must be controlled by very low heating rates, but with self-heating material the heating rate must be near the adiabatic heating rate (heating rate for fully insulated material). It was calculated to require about 1 hr for the center of a 12-in. diam mass to begin cooling after the surface is cooled. And since sintering temperatures of 675°C are required for sintering and samples begin to bloat at ~705°C, the adiabatic heating rate should not be more than 25°C/hr. For 5-year-old waste this would not be a problem since the adiabatic heating rate is low, ~25°C/hr (depending on the calcine type and loading). However, with new waste (150 days old) the adiabatic heating rate would be about 250°C/hr. This would not allow sufficient time to sinter and begin cooling before bloating temperatures would be exceeded.

Bloating of sintered products was tested to determine the potential pressurization effect on a containment canister. A loading of 1.1 g/cm^3 sintered product/canister volume was tested. The canister was sealed at 500°C and then the temperature was increased to 900°C . The sample volume expanded to about 70% of the canister volume, but gas pressure increased within the canister less than 10 psi. This behavior indicates that although some residual off-gases are still present after the 675°C sintering, their quantity is small and bloating of the sintered product due to accidental high temperature exposure would probably not result in canister failure due to pressure generation. Additional tests at higher product loadings will be required to confirm this.

Characterization of Sintered Glass

A pellet formed from 30% PW-4b-2 calcine and 70% 73-1 frit by sintering at 675°C for 2 hr was examined by SEM (scanning electron microscope). Figure 24 is a typical area at 100X. The central area in Figure 24 was magnified for Figure 25 and was used for X-ray analysis of specific areas. The large dark area was analyzed in section "A" and determined to be SiO_2 , probably a residual grain from frit formation. Section "B" was a calcine particle, but showed some Zn, Ca, and Si which have diffused from the frit. Section "C" is basically a frit area with small amounts of Ce, Ni and Fe present, elements that are present only in the calcine. These results indicate that the frit is matrix encapsulating the calcine and is also reacting to some degree with the calcine.

Leach testing of sintered products has been extended to include fluidized bed calcines. Both PW-7 and PW-4b products when sintered with 60 to 65% 73-1 frit have moderately high leach rates (i.e., 1.9 to 2.4 wt.% in the first 24 hr of soxhlet leaching). In view of the results of the SEM examination, it is likely that sintered materials will have higher leach rates than melted glass since reactions between the frit and calcine will be less extensive.

FIGURE 24. 100X SEM Micrograph of Sintered Pellet Containing 30% PW-4b-2 Calcine and 70% 73-1 Frit

FIGURE 25. 1000X SEM Micrograph of Central Area of Figure 24

Future Development

While sintering in can does not appear to be practical, the use of sintering to form shapes for incorporation into another matrix such as a metal is still attractive. The combination of a disk pelletizer to form shapes and then sintering may provide a simple combination and will be tested during the next quarter. This combination would be much simpler than standard glass forming methods and offers the potential for making a form which would not be as thermal shock sensitive as large-diameter castings.

VITREOUS CARBON WASTE FIXATION - L. R. Bunnell

This study is directed toward developing applications for vitreous carbon in the encapsulation of radioactive waste calcine.

Work has continued on the production of samples of vitreous carbon containing calcined waste, generally PW-4b-2. Some work has been done on leach resistance of these samples. These are described separately below.

A. Leach Testing

The resistance of any containment material to leaching in water is a crucial consideration in its evaluation. Since there is no known mechanism for dissolving carbon in water, the carbon itself should be essentially immune to attack by water. When the material is fractured, calcine particles are directly exposed to the water. It is assumed that only the calcine on the surface is available for leaching if the concentration of calcine is low enough that particles do not impinge on each other.

Evaluation was done by means of the standard PNL accelerated leach test.* The procedure was modified to allow for the molecular sieve nature of vitreous carbon, which did not permit weighing to a constant weight at room temperature. Initial samples exhibited a definite weight gain after leach testing. After this was discovered as the cause for the problem,

* J. E. Mendel, A Review of Leaching Test Methods and the Leachability of Various Solid Media Containing Radioactive Wastes, BNWL-1765, July 1973.

weighings before and after leaching were done on a thermobalance at 110°C after an initial drying at 200°C. During drying and weighing, dry breathing air at 3 scfh was flowed past the sample in its stainless steel mesh bag. Some loss in precision occurred, but weighings were generally reproducible to ± 0.3 mg or less. Leach test results for three samples containing different percentages of PW-4b-2 calcine are shown below in Table 8.

Leach rate decreases as a function of waste loading as expected. Some long-term leach tests with these samples may be desirable to examine surface access effects. Samples of leach solution will be submitted for analysis in order to identify the most leachable species in this case.

TABLE 8. Accelerated Leach Test Results for Calcine Containing Vitreous Carbon

<u>Sample</u>	<u>Wt.% Loss First 24 hr</u>	<u>Cumulative Wt.% Loss Second 24 hr</u>	<u>Cumulative Wt.% Loss Third 24 hr</u>
Vitreous Carbon No Calcine	0.09%	0.13%	Not Leached
82 wt/% Vitreous Carbon 18 wt/% Calcine	0.44%	0.47%	0.52%
47 wt/% Vitreous Carbon 53 wt/% Calcine	0.27%	0.29%	0.42%
33 wt/% Vitreous Carbon 67 wt/% Calcine	1.72%	1.86%	Not Leached Because >1% Limit

B. Large Vitreous Carbon Bodies

Until recently our experiments have proceeded under the assumption that no cracks were permissible in waste-containing vitreous carbon. This introduced a thickness limitation of $\sim 1/8$ in., a fairly severe restriction. If one assumes that some cracking is permitted, larger bodies become feasible.

An experiment was conducted in which a larger piece was fabricated containing 50 wt/% PW-4b-2 calcine, 50 wt/% polyfurfuryl alcohol resin.*

* Quaker Oats RP100A.

The piece was originally 1 in. OD x 1-1/2 in. in height. Another sample was fabricated containing 40 wt% calcine, 50 wt% resin, and 10 wt% 10- μ m polyethylene spheres. Again, a 1 in. OD x 1-1/2 in. in height solid cylinder was cast and cured as usual. Some previous experiments have shown that polyethylene spheres can provide gas removal without cracking, even though they are isolated. The mechanism for this is not understood at present. The pieces were carbonized to 1000°C in a vacuum at a heating rate of 6°C/hr. Micrographs are shown in Figures 26 and 27. It is seen that the sample containing no polyethylene exhibited only fairly coarse cracking but is quite dense, and the sample containing polyethylene is not very dense but is crack free. Since a smaller polyethylene addition may produce a similar effect, the idea is being pursued further. At present, two samples of 2 in. OD, batched as above, are being carbonized.

C. Vitreous Carbon-Calcine Microspheres

Vitreous carbon may be able to function as waste containment at a much smaller size level in a manner similar to the fluidized bed process being examined at PNL.* If polyfurfuryl alcohol is catalyzed and then injected dropwise into agitated vegetable oil at 100°C, the material breaks into rather perfect spheres and hardens within seconds. The same process will work with waste-loaded resin, except the spheres may not be as perfect because of the greater apparent viscosity of the mixture. Carbonization of the spheres could also be done in a few hours, because the diffusion distance for gas elimination is much smaller. The process may thus be made continuous.

The results of an initial effort are shown in Figure 28 as 30 wt% of PW-4b-2 calcine added to catalyzed resin and spheroidized in 100°C vegetable oil in a blender. This batch was then to be recoated by filtering the oil and cleaning in acetone, then mixing with resin and respheroidizing. Processing to 1000°C in vacuum was done in only 9 hr. It can be seen that the recoating was not successful, and that some spheres resulting from the

* Quarterly Progress Report Research and Development Activities Waste Fixation Program, July-September 1974, BNWL-1871.

FIGURE 26. (a) 8X Macrograph of Bulk Sample Containing No Polyethylene, Showing Few Large Cracks, Low Porosity
(b) 50X View of (a) Above

FIGURE 27. (a) 8X Macrograph of Bulk Sample Containing Polyethylene, Showing Lack of Cracking. Large pores resulted from incomplete degassing during casting
(b) 50X View of (a), Showing Porosity Created by Polyethylene

FIGURE 28. 100X Micrograph of Spheres Made as Described in the Text

FIGURE 29. 1200X Micrograph of Sphere Containing Calcine, Showing the Continuous Surface Carbon Membrane

unloaded resin are present. Also, some pores are present inside the particles. The origin of these pores is not understood. As shown in Figure 29, the surface of the sphere is covered by a thin but continuous carbon fiber. These early results are regarded as encouraging. Some more samples will be generated, ultimately producing samples for leach testing.

ADVANCED PRODUCT FORMS RESEARCH AND DEVELOPMENT (PENNSYLVANIA STATE UNIVERSITY) - G. J. McCarthy

The Materials Research Laboratory at Pennsylvania State University, University Park, PA, is operating under a subcontract to investigate advanced solidified waste forms, e.g., forms other than melt-formed glasses or glass-ceramics. Overall objectives of the program are to develop fundamental understanding of the crystal chemistry of calcined high-level waste and to use this understanding to develop solidified waste forms with enhanced chemical and thermal stability. Near-term objectives are 1) to complete a laboratory-scale study on the use of hot-pressing techniques for high-level waste fixation and 2) to develop a "super calcine" formulation, prepared by chemically mixing specially chosen additives to the waste solution so that all of the individual radioactive atoms will be isolated in inert phases when the waste is calcined.

Phases Formed on Firing a Simplified PW-4b Calcine - G. J. McCarthy and M. T. Davidson

It has been noted previously that to identify the phases formed on firing PW-4b calcine and to secure background information necessary for designing more suitable crystalline hosts for waste cations, selected subsystems of the full PW-4b would be studied. This work has now been completed.

Oxides of the ten most abundant cation species in PW-4b* were selected since they would most likely be responsible for phase formation. The general system was Ce-Nd-Fe-Mo-Zr-Cs-Ni-U-Ba-Sr-O with each cation present in the PW-4b ratio. The use of Nd as a stand-in for all of the trivalent

* Included Stand-ins: Fe for Ru, Mo for Tc, and Ni for Pd.

rare earths has been explained previously (BNWL-1826). By carefully selecting only those sub-systems which would give new crystal chemical and phase formation information it was possible to complete this study with 32 out of the thousands of possible subsystems.

Phase Formation

The X-ray diffractograms of each of the 32 batches fired at 750°C for 2 hr closely resembled that of PW-4b given the same treatment. There were very broad, weak reflections which could be assigned to one or more Fss phases. However, when samples of each batch given the 750°C treatment were pelletized and fired again at 1050°C for 6 and 48 hr, the diffractograms showed relatively sharp reflections which were essentially identical for both firing times. This indicated that the 6-hr firing was sufficient to give a steady-state phase assemblage at that temperature. Table 10 lists the phases observed by X-ray diffraction after this 6-hr firing. Additional samples of 750°C fired batches from each sub-system were fired at 1350°C for 6 hr. The phases formed during this heat treatment are given in Table 11.

Surprisingly, in this 10-component oxide system, only 10 distinct types of phases were observed. Five of these, NiO , Fe_2O_3 , Nd_2NiO_4 , SrNd_4O_7 and SrZrO_3 , occurred in only a few subsystems and will not be discussed further.

Five others occurred more frequently:

Fss: At least one fluorite structure solid solution was present in every subsystem. The approximate cell parameter was calculated for each phase, usually from the (311) reflection, and is reported in parentheses in Tables 10 and 11. The values ranged from 5.28 to 5.52 Å, and the relative intensities corresponded closely to those reported for CeO_2 .

TABLE 10. Phase Formation after Firing at 1050°C for 6 Hr

Composition (subsystem)	Phase Assemblage *	Wt. loss (%)
Ce-Nd (1)	S - Fss(11.03) **	3.1
Ce-Nd-Zr (3)	M - Fss(5.42) + M - Fss(5.34)	2.0
Ce-Nd-Mo (2)	M - Fss(5.42) + M - Nd ₂ Mo ₃ O ₁₂	3.1
Ce-Nd-Fe (5)	S - NdFeO ₃ + M - Fss(5.46)	1.7
Ce-Nd-Sr (16)	S - Fss(5.51)	5.0
Ce-Nd-Ni (9)	S - Fss(5.52) + W - Nd ₂ NiO ₄ + VW - NiO	1.5
Ce-Nd-U (23)	S - Fss(B - 5.51)	1.4
Ce-Nd-Cs (26)	S - Fss(11.02)	21.2
Ce-Nd-Zr-Mo (4)	M - Fss(5.38) + MW - Fss(5.28) + S - Nd ₂ Mo ₃ O ₁₂	4.0
Ce-Nd-Zr-Fe (6)	S - Fss(5.29) + M - NdFeO ₃	2.8
Ce-Nd-Fe-Mo (7)	S - Nd ₂ Mo ₃ O ₁₂ + M - Fss(5.43) + W - NdFeO ₃ + W - Fe ₂ O ₃	0.4
Ce-Nd-Fe-Mo-Zr (8)	M - Nd ₂ Mo ₃ O ₁₂ + M - Fss(5.39) + M - Fss(5.28) + W - Fe ₂ O ₃	0.6
Ce-Nd-Mo-Sr (17)	S - Fss(5.50) + M - SrMoO ₄	1.5
Ce-Nd-Fe-Sr (18)	S - Fss(5.46) + S - Pss(3.90)	1.5
Ce-Nd-Zr-Sr (20)	S - Fss(5.46) + M - SrZrO ₃	1.3
Ce-Nd-Fe-Mo-Sr (19)	S - Fss(5.42) + S - NdFeO ₃ + M - SrMoO ₄	1.8
Ce-Nd-Fe-Mo-Zr-Sr (21)	M - Fss(5.30) + M - SrMoO ₄ + W - NdFeO ₃	1.5
Ce-Nd-Fe-Ni (10)	S - NdFeO ₃ + M - Fss(5.46) + W - NiFe ₂ O ₄	1.5
Ce-Nd-Mo-Ni (11)	S - Fss(5.47) + M - Nd ₂ Mo ₃ O ₁₂ + VW - NiO	1.8
Ce-Nd-Zr-Ni (13)	S - Fss(5.48) + M - Fss(5.36) + VW - NiO	1.8
Ce-Nd-Fe-Mo-Ni (12)	M - Fss(5.45) + M - Nd ₂ Mo ₃ O ₁₂ + W - NiFe ₂ O ₄ + W - NdFeO ₃	1.5
Ce-Nd-Fe-Zr-Ni (14)	M - Fss(B - 5.35) + M - NdFeO ₃ + W - NiFe ₂ O ₄	2.4
Ce-Nd-Fe-Mo-Zr-Ni (15)	S - Nd ₂ Mo ₃ O ₁₂ + M - Fss(5.33) + W - NiFe ₂ O ₄	1.8
Ce-Nd-Fe-Mo-Zr-Ni-Sr (22)	S - Fss(5.32) + M - SrMoO ₄ + M - NdFeO ₃ + W - NiFe ₂ O ₄	1.3
Ce-Nd-Fe-Mo-Zr-U (24)	M - Fss(5.37) + M - Fss(5.33) + M - Nd ₂ Mo ₃ O ₁₂ + W - Fe ₂ O ₃	1.6
Ce-Nd-Fe-Mo-Zr-Ni-Sr-U (25)	S - Fss(B - 5.35) + M - NdFeO ₃ + M - SrMoO ₄ + W - NiFe ₂ O ₄	1.3
Ce-Nd-Fe-Cs (30)	S - NdFeO ₃ + S - Fss(5.45)	15.2
Ce-Nd-Mo-Cs (28)	S - Fss(5.48) + M - Nd ₂ Mo ₃ O ₁₂	23.0
Ce-Nd-Zr-Cs (29)	M - Fss(5.40) + M - Fss(5.37)	17.8
Ce-Nd-Fe-Mo-Zr-Cs (31)	S - Fss(5.30) + M - NdFeO ₃ + W - Nd ₂ Mo ₃ O ₁₂	8.5
Ce-Nd-Fe-Mo-Zr-Sr-Ni-U-Cs (32)	M - Fss(5.38) + S - Fss(5.34) + M - SrMoO ₄ + M - Pss(3.91) + W - NiFe ₂ O ₄	3.2
Ce-Nd-Fe-Mo-Zr-Ni-U-Cs-Sr-Ba (27)	S - Fss(5.40) + S - Fss(5.35) + M - Pss(3.92) + M - Sss + W - NiFe ₂ O ₄	2.3

* Intensity of phase in diffractograms: S = Strong, M = Medium, W = Weak, VW = Very Weak.
B = broad reflections. Fss = Fluorite structure solid solution, Pss = perovskite structure solid solution
Sss = Scheelite structure solid solution

** Number in parentheses is the cubic or pseudocubic unit cell parameter of this phase.

TABLE 11. Phase Formation after Firing at 1350°C for 6 Hr

Composition (subsystem)	Phase Assemblage*	Wt. loss (t)
Ce-Nd (1)	VS - Fss(11.0)	3.2
Ce-Nd-Zr (3)	M - Fss(5.39) + M - Fss(5.34)	2.4
Ce-Nd-Mo (2)	M - Fss(5.45) + M - Nd ₂ Mo ₃ O ₁₂	4.0
Ce-Nd-Fe (5)	M - NdFeO ₃ + M - Fss(5.43)	2.1
Ce-Nd-Sr (16)	S - Fss(5.50) + M - SrNd ₄ O ₇	5.0
Ce-Nd-Ni (9)	S - Fss(5.50) + W - NiO	2.0
Ce-Nd-U (23)	S - Fss(5.50)	2.0
Ce-Nd-Cs (26)	S - Fss(11.02)	21.3
Ce-Nd-Zr-Mo (4)	M - Fss(5.30) + M - Nd ₂ Mo ₃ O ₁₂	5.9
Ce-Nd-Zr-Fe (6)	M - Fss(5.37) + M - Fss(5.27) + W - NdFeO ₃	2.8
Ce-Nd-Fe-Mo (7)	S - Fss(5.41) + M - Nd ₂ Mo ₃ O ₁₂ + W - NdFeO ₃ + W - Fe ₂ O ₃	7.0
Ce-Nd-Fe-Mo-Zr (8)	S - Fss(5.31) + M - Nd ₂ Mo ₃ O ₁₂ + W - NdFeO ₃ + W - Fe ₂ O ₃	16.4
Ce-Nd-Mo-Sr (17)	S - Fss(5.50) + M - SrMoO ₄	1.7
Ce-Nd-Fe-Sr (18)	S - Fss(5.48) + S - Pss(3.90)	2.0
Ce-Nd-Zr-Sr (20)	S - Fss(5.46) + SrZrO ₃	3.8
Ce-Nd-Fe-Mo-Sr (19)	S - Fss(5.42) + S - SrMoO ₄ + S - NdFeO ₃	2.4
Ce-Nd-Fe-Mo-Zr-Sr (21)	S - Fss(5.32) + M - NdFeO ₃ + M - SrMoO ₄	4.5
Ce-Nd-Fe-Ni (10)	S - NdFeO ₃ + M - Fss(5.47) + VW - NiFe ₂ O ₄	3.5
Ce-Nd-Mo-Ni (11)	S - Nd ₂ Mo ₃ O ₁₂ + M - Fss(5.46) + W - NiO	4.9
Ce-Nd-Zr-Ni (13)	S - Fss(5.43) + M - Fss(5.35) + VW - NiO	4.9
Ce-Nd-Fe-Mo-Ni (12)	S - Nd ₂ Mo ₃ O ₁₂ + M - NdFeO ₃ + M - Fss(5.46) + W - NiFe ₂ O ₄	11.2
Ce-Nd-Fe-Zr-Ni (14)	M - Fss(5.33) + M - NdFeO ₃ + W - NiFe ₂ O ₄	4.7
Ce-Nd-Fe-Mo-Zr-Ni (15)	S - Nd ₂ Mo ₃ O ₁₂ + M - Fss(5.33) + W - NiFe ₂ O ₄ + W - NdFeO ₃	12
Ce-Nd-Fe-Mo-Zr-Ni-Sr (22)	S - Fss(5.32) + M - SrMoO ₄ + M - NdFeO ₃ + W - NiFe ₂ O ₄	2.0
Ce-Nd-Fe-Mo-Zr-U (24)	S - Fss(5.32) + M - Nd ₂ Mo ₃ O ₁₂ + W - Fe ₂ O ₃	4.4
Ce-Nd-Fe-Mo-Zr-Ni-Sr-U (25)	S - Fss(5.37) + M - Fss(5.33) + M - SrMoO ₄ + M - NdFeO ₃ + W - NiFe ₂ O ₄	2.3
Ce-Nd-Fe-Cs (30)	S - NdFeO ₃ + S - Fss(5.44)	15.5
Ce-Nd-Mo-Cs (28)	S - Fss(5.50) + W - Nd ₂ Mo ₃ O ₁₂	25.0
Ce-Nd-Zr-Cs (29)	M - Fss(5.40) + M - Fss(5.37)	18.8
Ce-Nd-Fe-Mo-Zr-Cs (31)	S - Fss(5.31) + M - NdFeO ₃ + W - Nd ₂ Mo ₃ O ₁₂	22.1
Ce-Nd-Fe-Mo-Zr-Sr-Ni-U-Cs (32)	M - Fss(5.38) + S - Fss(5.34) + M - SrMoO ₄ + M - Pss(3.91) + W - NiFe ₂ O ₄	12.7
Ce-Nd-Fe-Mo-Zr-Ni-U-Cs-Sr-Ba(27)	S - Fss(5.38) + S - Fss(5.35) + S - Sss + M - Pss(3.91) + W - NiFe ₂ O ₄ + VW - Pss(3.96)	10.5

* Intensity of phase in diffractograms: S = Strong, M = Medium, W = Weak, VW = Very Weak.
 Fss = Fluorite structure solid solution, Pss = Perovskite structure solid solution, Sss = Scheelite structure solid solution.

- Nd₂Mo₃O₁₂: This phase was identified from the powder pattern reported by Nassau et al.* Slight shifts in reflections of the pure phase in subsystem 2 and others imply small amounts of Ce⁴⁺ substitution. Ustinov et al.** have reported the existence of Ce₂Mo₃O₁₃, and a small amount of this may substitute in Nd₂Mo₃O₁₂.
- NdFeO₃: Readily identified as having the distorted perovskite GdFeO₃-type structure. Reflections coincide in many subsystems with those of a sample of pure NdFeO₃ prepared for comparison. Its pseudocubic perovskite cell parameter is 3.88 Å. In some of the more complex subsystems, shifted reflections indicated solid solutions. In this case the phase is reported as Pss and the cubic or pseudocubic cell parameter accompanies it. Pss occurs in fired PW-4b.
- SrMoO₄: The X-ray reflections of this scheelite structure phase correspond closely to those of pure SrMoO₄. It is also one of the phases observed in fired PW-4b, but larger interplanar spacings imply the partial substitution of Ba and perhaps Cs or RE³⁺ for Sr.
- NiFe₂O₄: Again, the powder pattern of this spinel structure phase corresponds to a pure phase NiFe₂O₄ in the simplified waste formulation subsystems. It is observed in fired PW-4b but with slightly shifted reflections, implying partial substitution of Co²⁺ or Fe²⁺ for Ni and Cr³⁺ for Fe³⁺.

Weight Losses on Firing

Weight losses were recorded for each of the two firings reported in Tables 10 and 11. Since no special precautions were taken to handle the samples only in dry, inert atmospheres or to insure that the 750°C pre-firing had thoroughly denitrated and dehydrated them, the numerical values

* K. Nassau et al., J. Phys. Chem. Solids, vol. 30, p. 1225, 1969.

** O. A. Ustinov et al., Russ. J. Inorg. Chem., vol. 15, p. 1318, 1970.

should be taken as semiquantitative only. Weight losses could be due to absorbed or chemically combined gases like NO_x and H_2O or to the loss of oxides to volatilization and in a minor way to a reduction in valence state by certain cations with accompanying loss of oxygen. The first factor does contribute since systems with even the most refractory oxides (1, 2, 5, 9, etc.), typically show a weight loss of several percent. Of the 10 oxide components in this study, two, Cs_2O and MoO_3 , are good candidates for volatilization at high temperatures unless they are stabilized by forming sufficiently refractory complex phases. The case of cesium oxide is obvious since all of the subsystems containing Cs show high weight losses. It may also carry off some of the other, normally more refractory, constituents of the subsystems in the form of complex vapor species. For example, in subsystem 29, Cs_2O constitutes only ~12 wt% of the component oxides, but a weight loss of ~18% was recorded. Even allowing for several percent loss due to NO_x and H_2O , the result suggests that several wt% of other oxides were lost also.

Subsystems containing Mo but no Sr also show higher weight losses, especially after the 1350°C firing (3, 4, 7, 8, 12, 15, 24, 28, 31). The $\text{Nd}_2\text{Mo}_3\text{O}_{12}$ phase melts at ~1100°C and thus could have a relatively high vapor pressure at 1350°C. In most cases the 1350°C fired pellets showed signs of partial melting and materials losses when this phase was present. Comparison of identical subsystems except for the presence of Sr (2 and 17, 7 and 19, 8 and 21, 15 and 22) shows a significant reduction in weight losses when much of the Mo is stabilized as the more refractory SrMoO_4 .

It is apparent that a very useful continuation of the research presented here would be the study of weight loss due to volatilization in many of the subsystems as well as the full waste. The work would best be carried out by in situ thermogravimetric analysis with arrangement for quantitatively collecting vaporized species for subsequent analysis.

Silica Matrix Isolation by Hot Pressing - G. J. McCarthy and M.T. Davidson

This part of our project is nearly complete, and a final report will be issued soon. It has been shown that a hard, dense composite waste form can be produced by hot pressing an intimate mixture of 20 to 30 wt%

of PW-4b spray calcine with about 65% crystalline quartz and about 10% of a low-melting, low-viscosity lead borosilicate glass. The best results have been obtained at a hot pressing temperature of 1200°C for low glass content mixtures and as low as 900°C for high glass content mixtures. Leachability tests by the soxhlet method have shown that some of the better hot pressed waste forms have leaching resistance comparable to the best glass waste forms at the same level of waste loading.

Microstructural and microchemical characterization of the products, now in progress, indicates that the dispersion of the waste calcine in the matrix is quite uniform and that average particle sizes are close to 10 μm .

Several final runs are under way using the new PW-7 series of waste compositions.

Supercalcine Formulations Based on PW-4b - G. J. McCarthy,
D. E. Pfoertsch and C. A. Smith

The process of designing supercalcine formulations based on a series of crystal chemical hypotheses was described in the last quarterly report (BNWL-1871). Seven more formulations have been prepared and fired and the products characterized for phase formation. It is beyond the scope of this report to describe each set of phases proposed, additives used and phases observed. However, one example will serve to illustrate the work in progress.

SW-6:

Hypotheses: Ce + Zr to form $(\text{Ce}_{0.75}\text{Zr}_{0.25})\text{O}_2$
 Nd + Zr to form $\text{Nd}_2\text{Zr}_2\text{O}_7$
 Mo + Cs + Zr to form " $\text{Cs}(\text{Mo},\text{Zr})\text{O}_3$ "*
 Mo + Sr + Ni to form $\text{Sr}(\text{Ni},\text{Mo})\text{O}_3$
 Sr + Ca + Mo to form $\text{Sr}(\text{Ca},\text{Mo})\text{O}_3$
 Cr + Nd to form NdCrO_3
 Ba + Sr + Fe to form $(\text{Ba},\text{Sr})\text{FeO}_{3-x}$

* Phases in quotes are not known to exist.

Formulation: The 9-component, simplified PW-4b liquid* + $\text{Sr}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$ and $\text{ZrO}(\text{NO}_3)_2$ as required by phases proposed plus sufficient $\text{Sr}(\text{NO}_3)_2$ and $\text{ZrO}(\text{NO}_3)_2$ to form one-half molar excess SrZrO_3 in the fired mixture.

Results (1050°C, 6 hr): Phases observed by X-ray diffraction were two perovskite structure-solid solutions (Pss) with $a_0 = 4.07\text{\AA}$ and $3.92\text{\AA}$, a fluorite structure solid solution (Fss) with $a_0 = 5.37\text{\AA}$ and a small amount of scheelite structure solid solution.

The major Pss phase is almost pure SrZrO_3 ($a_0 \approx 4.10\text{\AA}$) with some substitution, perhaps of $\text{Nd}(\text{Fe,Cr})\text{O}_3$ and $(\text{Ba,Sr})\text{FeO}_{3-x}$, responsible for the small reduction in cell size. The Fss phase is the familiar CeO_2 -rich solid solution with ZrO_2 among other components responsible for the reduction in cell size from the $5.41\text{\AA}$ value of pure CeO_2 . The second minor Pss phase is probably rich in $\text{Nd}(\text{Fe,Cr})\text{O}_3$ and/or SrFeO_{3-x} since both of these have cell parameters near $3.90\text{\AA}$. Finally, the very weak Sss phase appears to be mostly SrMoO_4 .

Several conclusions can be drawn from these results. SrZrO_3 is not a good host solid solution for other perovskite structure phases since another Pss phase apparently immiscible in SrZrO_3 , was formed. Weight loss on firing this formulation indicated significant losses of oxides, very likely those of Cs and of some Mo. Cell parameter shifts indicative of Cs solid solution were not noted. Results from other runs where zirconates were to be the major phases formed also imply that Cs cannot be bound in sufficiently refractory form by forming zirconates.

The results of the phase formation studies with selected additives can be combined with the results from pure PW-4b discussed above to derive even more useful information on the crystal chemical roles of waste cations:

* Ce, Nd (for trivalent rare earths), Fe (for Ru), Mo, Zr, Cs, Ni (for Pd), U and Sr in PW-4b atomic ratios.

- Zr First preference in phase formation is with alkaline earths to form $AZrO_3$ ($A = Ca, Sr, Ba$) phases. Next, it will form Fss with either CeO_2 $[(Ce,Zr)O_2]$ or $RE_2O_3(RE_2Ar_2O_7)$. Preference among the last two possibilities not yet determined.
- Ba,Sr First preference is with Mo to form $(Ba,Sr)MoO_4$. Next with Zr to form $(Ba,Sr)ZrO_3$.
- Fe With RE^{3+} to form $REFeO_3$. When present in excess of that stoichiometric amount, with Ni to form $NiFe_2O_4$.
- Mo With Ba, Sr to form $(Ba,Sr)MoO_4$. Possible role in Pss but not yet certain.
- RE^{3+} (Nd as stand-in) With Fe to form $REFeO_3$. Next with Ce and/or Zr to form $(Ce,RE)O_{2-x}$ and/or $RE_2Zr_2O_7$.

No conclusions have been reached yet on Cs, Ni and Cr. Cs appears to be the major problem in supercalcine design. However, by knowing the crystal chemical preferences of most of the other cations we can now focus on finding formulations which form satisfactory phases to contain Cs.

Oxide Crystal Chemistry of Cs and Ru - S. A. Gallagher,
G. J. McCarthy and R. G. Johnston

As just described, of the major components of PW-4b, Cs appears to be the greatest problem in designing a ceramic waste form. Thus a separate study is examining the complex oxide crystal chemistry of Cs. Several possible Cs containing phases and solid solution systems were examined during the quarter:

All four were meant to be perovskite structure phases and, if they could have been formed, might have been sufficiently refractory and leach-resistant. In all cases the Cs volatilized during firing and did not form the proposed phases. The observations support the conclusion that Cs does not readily form zirconates which are sufficiently stable at high temperatures (1050-1200°C).

The oxide crystal chemistry of Ru is also being studied separately. This element forms a perovskite structure phase with Sr, SrRuO_3 . To see if this phase would form solid solutions with the abundant perovskite phases in zirconate supercalcine formulations, the systems SrRuO_3 - BaZrO_3 and SrRuO_3 - SrZrO_3 were studied. Surprisingly, no evidence for even a small amount of solid solution in either end member was noted. Thus, when Ru is added to the simulated wastes used in supercalcine formulation, SrRuO_3 should not be expected to be soluble in the $(\text{Ba,Sr})\text{ZrO}_3$ phase.

There is another class of Ru phases which may form in supercalcine. Pyrochlore structure phases of $\text{Re}^{3+} + \text{Ru}$, $\text{RE}_2\text{Ru}_2\text{O}_7$, are known, and solid solution behavior of these is currently under investigation.

SAFETY AND SYSTEMS EVALUATION

*The purpose of the Systems Evaluation Task is to define and investigate waste management systems in relation to the containment, immobilization, and isolation of the wastes and to evaluate the risk implications of these systems. Specifically, both the likelihood and consequences of potential release incidents are being estimated for a reference system that includes liquid storage through retrievable surface storage operations.**

FAULT TREE EVALUATION METHODOLOGY - T. H. Smith, P. J. Pelto and G. D. Seybold

The objective of this work segment is to develop a suitable automated methodology for evaluating fault trees. The approach is to develop a computer code system capable of importance-screening the thousands of failure sequences arising in the analysis of complex fault trees. The screening is to be based on a crude measure of risk rather than on probability or consequences individually. High-risk cut sets so identified would be retained for more detailed analysis.

Existing codes considered potentially useful for various segments of this screening were reviewed. Many were found to be inappropriate. A code this screening were reviewed. Many were found to be inappropriate. A code developed by the Atlantic Richland Hanford Company was found to be suitable, when considerably modified, for a portion of the analysis. The remainder of the analysis is to be performed by means of a code now being written at Battelle, Pacific Northwest Laboratories. When the code system is in place, it will be checked out on the fault tree representing water basin solid storage.

TRANSPORTATION OF SOLIDIFIED HIGH-LEVEL WASTE - E. S. Murphy, W. S. Kelly and R. J. Hall

The purpose of this activity is to estimate the risk in shipment of high-level solidified waste by rail transportation from a reprocessing plant

* The reference system is described in previous reports of the series of quarterly progress reports, BNWL-1761, BNWL-1809, and BNWL-1826.

to an interim storage facility (RSSF). Work during the report period centered on characterization of the waste containment system and on development of a fault tree for identification of failure modes and failure sequences which could cause a breach of containment during transportation.

It is assumed that two containment barriers--a waste canister and a shipping cask--must be breached in order to have loss of containment. The canister has been described in a previous report.* The waste shipment cask description is based on a conceptual design by Oak Ridge National Laboratory.** The cask is approximately 10 ft in diam by 15 ft long and weighs about 100 tons. It has the capability for transporting nine waste canisters in a solid steel matrix surrounded by lead shielding. For the present analysis, it is assumed that the cask would be designed to meet 10 CFR 71, with an appropriate safety factor. Tie-downs would hold the cask to the rail car in any accident at speeds below 10 mph. The energy to cause tie-down failure is equivalent to the KE of the cask at 10 mph.

A fault tree for risk analysis of the waste shipment, with the top event being "Loss of Containment Occurs During Transportation," has been constructed. Branches considered in the tree include: 1) transportation with good (nondegraded) containment barriers which are both breached during transportation, 2) transportation with degraded containment barriers which are both breached during transportation, and 3) breach of one containment barrier before transportation begins, with the second barrier breached during transportation. Initiating events capable of causing stresses leading to containment failure include: 1) transportation accidents, 2) natural disasters, 3) physical or chemical reactions induced by the radioactive waste, and 4) acts of war or sabotage.

* Quarterly Progress Report, BNWL-1809, p. 73, January 1974.

** J. O. Blomeke, C. W. Kee and R. Salmon, Projected Shipments of Special Nuclear Material and Wastes by the Nuclear Power Industry, ORNL-TM-4631, Oak Ridge National Laboratory, Oak Ridge, TN, p. 26, August 1974.

For initial evaluation of the tree the following simplifying assumptions have been made:

1. Any event which results in failure of a good (i.e., nondegraded) cask will also result in failure of the canister.
2. Crushing will not cause containment failure. Mechanical stresses which will cause containment failure are impact and puncture.
3. Immersion by itself will not produce containment failure. Immersion must act on a defective cask or must be accompanied by mechanical damage to the cask.
4. Stresses imposed by the radioactive waste (i.e., corrosion, high temperature, high pressure, radiation damage) can cause canister failure but not cask failure.

Work is currently under way to assign failure probabilities and release fractions and to evaluate the failure modes (cut sets) described by the fault tree.

Dose to Man from Liquid Pathways - D. B. Shipler

Preliminary dose calculations were performed to ascertain the relative impact on man of radionuclides released from shipped and stored waste materials to river water. A variety of liquid pathways were used, and doses to the total body and several organs were calculated.

The results were evaluated 1) to predict potential critical radiation exposure pathways from radioactive waste materials through river water to man and 2) to determine those radionuclides which contribute most of the dose to the total body and other critical organs.

The parameters, dose factors, pathway analyses, and computer codes used in these calculations are used routinely in the preparation of environmental statements for commercial LWRs for the USAEC. In addition, they have been modified and adapted for use in preparing environmental impact statements and performing other environmental assessments for a variety of governmental and industrial nuclear facilities, such as uranium fuel plants,

mixed oxide plants, light water and liquid metal breeder reactors, gas cooled reactors, several waste management studies, and a variety of research and development studies.

Pathway and dose factor parameters for these codes were selected after considerable field experience, literature searching, and discussions with recognized experts in the various fields of study involved. They have all been reviewed, discussed and approved by persons in several branches of the USAEC. In general, they have been documented and accepted as the best available data.

Source terms were calculated using computer code ORIGEN* and normalized to 1 g of waste material. This inventory was modified 1) to represent the radionuclides present in 10-year old LWR waste materials being shipped to storage and 2) to represent weighted average waste material 10 years old and older accumulated in storage through 1989.

The releases during shipment and storage were assumed to happen at Hanford. State-of-the-Art computer codes--ARRRG** and FOOD[†]--were used to calculate doses to man from liquid pathways. These codes also calculate the percent contribution of each radionuclide to the dose of each organ through each pathway.

The source term from computer code ORIGEN was matched to computer files containing dose factors used in computer codes ARRRG and FOOD. These files contain dose factors for 182 of the principal radionuclides associated with LWRs and resultant waste products. Eighty-seven of these principal radionuclides matched and were used for preliminary analysis of the impact of releasing waste materials into liquid pathways.

* M. J. Bell, ORIGEN--The ORNL Isotope Generation and Depletion Code, ORNL-4628, Oak Ridge National Laboratory, Oak Ridge, TN, May 1973.

** J. K. Soldat, N. M. Robinson and D. A. Baker, Models and Computer Codes for Evaluating Environmental Radiation Doses, BNWL-1754, Battelle Pacific Northwest Laboratory, Richland, WA, February 1974.

† USAEC, Draft Environmental Statement, Waste Management Operations, Hanford Reservation, WASH-1538, prepared by the U.S. Atomic Energy Commission, Richland, WA, September 1974.

One gram of each form of waste material was assumed to be completely soluble and released continuously during 1 year into a river having an annual average flow rate of 10^4 cfs. All pathways and parameters for each release were identical, making it possible to directly compare impacts and radionuclide contributions to each organ dose calculated. The dose to each organ from each pathway is summarized in Table 12.

TABLE 12. Summary of Radiation Doses to Individual from Liquid Pathways (mrem/year)

Pathway	Stored Materials					
	Skin	Total Body	GI-LLI	Thyroid	Bone	Liver
Fish		9.6E-2 (a)	8.3E-3	5.1E-7	1.1E-1	1.6E-1
Crustacea		4.8E-3	3.2E-2	1.3E-7	1.2E-2	4.6E-3
Molluscs		4.8E-3	3.2E-2	1.3E-7	1.2E-2	4.6E-3
Drinking Water		3.8E-3	7.1E-3	4.2E-8	9.3E-3	3.2E-3
Shoreline	1.4E-2	1.2E-2	1.2E-2	1.2E-2	1.2E-2	1.2E-2
Swimming	1.4E-5	6.2E-6	6.2E-6	6.2E-6	6.2E-6	6.2E-6
Boating	<u>7.1E-6</u>	<u>3.1E-6</u>	<u>3.1E-6</u>	<u>3.1E-6</u>	<u>3.1E-6</u>	<u>3.1E-6</u>
Subtotals	1.4E-2	1.2E-1	9.1E-2	1.2E-2	1.6E-1	1.8E-1
Produce		9.2E-3	1.6E-2	1.6E-7	2.6E-2	5.7E-3
Eggs		3.0E-5	2.4E-5	4.2E-9	5.8E-5	3.4E-5
Milk		6.8E-3	2.5E-3	2.0E-8	9.8E-3	9.7E-3
Meat		<u>9.5E-4</u>	<u>2.9E-4</u>	<u>1.5E-7</u>	<u>1.3E-3</u>	<u>1.4E-3</u>
Subtotals		<u>1.7E-2</u>	<u>1.9E-2</u>	<u>3.4E-7</u>	<u>3.7E-2</u>	<u>1.7E-2</u>
TOTALS	<u>1.4E-2</u>	<u>1.4E-1</u>	<u>1.1E-1</u>	<u>1.2E-2</u>	<u>2.0E-1</u>	<u>2.0E-1</u>
← Shipped Materials →						
Fish		5.5E-1	4.7E-2	4.1E-6	6.1E-1	8.4E-1
Crustacea		2.7E-2	1.7E-1	3.9E-7	6.6E-2	2.2E-2
Molluscs		2.7E-2	1.7E-1	3.9E-7	6.6E-2	2.2E-2
Drinking Water		2.2E-2	4.0E-2	4.1E-7	5.3E-2	1.7E-2
Shoreline	7.0E-2	6.0E-2	6.0E-2	6.0E-2	6.0E-2	6.0E-2
Swimming	7.8E-5	3.3E-5	3.3E-5	3.3E-5	3.3E-5	3.3E-5
Boating	<u>3.9E-5</u>	<u>1.6E-5</u>	<u>1.6E-5</u>	<u>1.6E-5</u>	<u>1.6E-5</u>	<u>1.6E-5</u>
Subtotals	7.0E-2	6.9E-1	4.9E-1	6.0E-2	8.6E-1	9.6E-1
Produce		5.3E-2	9.1E-2	1.3E-6	1.5E-1	3.0E-2
Eggs		1.7E-4	1.4E-4	2.1E-9	3.3E-4	1.9E-4
Milk		3.9E-2	1.5E-2	9.2E-8	5.5E-2	5.2E-2
Meat		<u>5.5E-3</u>	<u>1.6E-3</u>	<u>3.9E-8</u>	<u>7.3E-3</u>	<u>7.7E-3</u>
Subtotals		<u>9.8E-2</u>	<u>1.1E-1</u>	<u>1.5E-6</u>	<u>2.1E-1</u>	<u>9.1E-2</u>
TOTALS	<u>7.0E-2</u>	<u>7.9E-1</u>	<u>6.0E-1</u>	<u>6.0E-2</u>	<u>1.1</u>	<u>1.1</u>

a. $9.6E-2 = 9.6 \times 10^{-2}$ (typical)

Preliminary Comparison of Calcine and Glass/Ceramic Waste Forms -

W. K. Winegardner

Information collected during the course of the risk analysis of the reference system permits a variety of preliminary but valuable comparisons. For example, a method of contrasting potential differences in safety that could result from management of high-level waste in the form of calcine rather than glass/ceramic is to compare the amount of material that could be released to man's environment, accidentally or otherwise, as the result of postulated driving forces.* Available information permits at least a preliminary comparison for three well known and frequently cited potential mechanisms for accidental release of radionuclides during the processing, handling, transportation, and storage activities in the management of solids: 1) release upon contact with water; 2) volatilization upon exposure to high temperature; and 3) impact, followed by airborne dispersion of particulates. This information shows that for all three mechanisms, relatively massive glass/ceramic products are less dispersible and, therefore, superior for isolation or safety to the leachable, high surface-to-volume ratio calcines.

Results of the overall comparison are summarized in Figure 30 as the ranges of the ratio of calcine to glass/ceramic release expected for each of the three release mechanisms. Except for extremely high temperatures (above 1200°C), the potential for calcine release is 100 to 100,000 times greater than that for glass/ceramics. Given two release incidents of equal intensity, of relatively short but equal duration, and involving equal amounts of calcine and glass/ceramic, significantly more material, including radionuclides, would be released from calcine if containment and/or confinement barriers failed.

The degree of isolation (safety) of waste management systems can be discussed as the product of the likelihood (events/unit time) and magnitude

* Calcines are considered to be the leachable solids having a high surface-to-volume ratio while the glass/ceramics are the relatively nonleachable solids having a low surface-to-volume ratio (cast or pressed into shapes).

FIGURE 30. Potential Differences in Release of Calcine and Glass/Ceramics

of the consequences (consequences/event) of potential release situations, i.e., in terms of risk (consequences/unit time) to man. Assuming comparable radionuclide inventories, specific radioactivities (Ci/g), and relatively straightforward pathways to man for the material released in the above two incidents, analysis of radiological consequences will indicate higher doses for the calcine release simply because more material is released. Differences in radiological consequences between the two incidents will essentially be proportional to the differences in the quantity of material released. Furthermore, since in most instances the likelihood of release will be independent of waste form, differences in risk will also be proportional to differences in quantities released. Thus, the results of

Figure 30 can be used to predict differences in the risk to the public between management of solid waste in the calcine or glass/ceramic form.

Although the techniques used in the evaluation are useful as an early indication of comparative risk, no judgment can be made on the acceptability of the risk associated with the management of either waste form. It is reemphasized that the information used in the development of Figure 30 is, in certain instances, preliminary. For example, the particle size distribution of candidate calcine products is not well defined, and efforts are currently under way to obtain information on impact and volatility relative to more massive glass/ceramic products. Physical properties used in the development of release ratios are summarized in Figure 30.

IMPACT TESTING OF GLASS IN SIMULATED CANISTERS* - T. H. Smith and
S. L. Sutter

The objective of this work segment is to investigate and formulate procedures for predicting the amount of waste glass breakup in simulated canisters. Both glassy and purposely devitrified specimens are being investigated.

Fines screening for both small and large specimens has been completed. The results are being analyzed and correlated between the two series of tests. Writeup of a final report is under way.

* Also see BNWL-1826, BNWL-1841, and BNWL-1871 of this report series.

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