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**Research and Development
Activities
Waste Fixation Program**

April through June 1975

September 1975

Prepared for the U.S. Energy
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under Contract E(45-1):1830

Battelle
Pacific Northwest Laboratories

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Waste Disposal
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QUARTERLY PROGRESS REPORT
RESEARCH AND DEVELOPMENT ACTIVITIES
WASTE FIXATION PROGRAM
APRIL THROUGH JUNE 1975

Compiled by
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Chemical Technology Department

September 1975

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QUARTERLY PROGRESS REPORT
RESEARCH AND DEVELOPMENT ACTIVITIES
WASTE FIXATION PROGRAM
APRIL THROUGH JUNE 1975

INTRODUCTION

This progress report is the eleventh 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, 1871, 1893, and 1908.

SUMMARY

Four engineering-scale in-canister melting tests were made. They established melting rates in 8-in. and 12-in.-diam canisters and investigated feed-rate limitations resulting from the use of in-canister fins.

The joule-heated ceramic melter has operated continuously for 165 days. The unit has been fed glass frit, calcine and frit powder, concentrated slurry, and liquid waste with powdered frits. Although the liquid feeding tests are preliminary only, they indicate that a system can be designed to directly convert liquid waste to glass in a joule-heated ceramic melter.

Work on the fluidized bed calciner concentrated on development of components of the unit. Improvements were made in feed and fuel nozzles, discharge valve, filters, and other areas.

A test of the spray calciner assessed the effect on the hot barrel of two side-mounted vibrators intended to remove calcine adhering to the walls. After a 100-hr test no measurable effect on the barrel could be found.

Four tests of the wiped film evaporator were conducted. In three runs the unit discharged to an in-canister melting system, and in one to the joule-heated ceramic melter.

Work is under way to reactivate the 324 Building B-cell for radioactive demonstrations of waste solidification processes.

Comparative leach tests demonstrated that the reference waste glass has higher leach resistance than many common minerals such as granite and marble.

A test program was completed which shows the pressurization potential of calcines stored in sealed canisters and subjected to high temperatures.

Tests were made of glass samples to measure the curium leach rate and assess the effect on leachability of alpha radiation damage. Leachability did not appear to be grossly affected by alpha dose.

Investigations were made of the long-term compatibility of certain refractory oxides in molten glass with the objective of selecting improved refractories for joule-heated melters. Of three chrome-oxide-based refractories tested two were extensively attacked while one showed only surface corrosion.

Glass samples doped with curium were examined to assess radiation damage and determine helium diffusion coefficients. Two helium release mechanisms were indicated, one related to radiation damage.

Vaporization behavior of glass and calcine samples at elevated temperature was investigated to evaluate storage and shipping accident conditions. Results show that the weight losses from glass and calcine are comparable at 1200°C, but that glass performs much better than calcine at lower temperatures.

In the development of alternative waste fixation processes several methods of coating calcine particles were tested. Also studied were plasma coating of glass marbles and formation of vitreous carbon-bonded pellets. Plasma sprayed refractories for corrosion protection of materials in contact with molten glass were tested.

At Pennsylvania State University investigations were continued aimed toward the retention of cesium and ruthenium in "supercalcines," with emphasis on use of aluminosilicates for cesium fixation. Nineteen supercalcine formulations were evaluated with promising results. Work continued to study the crystallization aspects of glass waste forms in support of programs at PNL.

The computer code system for providing ordered lists of the highest risk sequences from among the myriad failure sequences associated with large fault trees has been successfully demonstrated. Screening of fault trees with over 3,000,000 failure sequences was accomplished. The initial assessment of the liquid transfer, water basin storage, and transportation activities (fault trees) of the reference system was completed.

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

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

Four engineering-scale tests of in-can melting were made. A melting rate between 9 and 12 kg/hr was demonstrated for an 8-in. diam can containing five fins of equal radial length and fed wiped film evaporator (WFE) concentrate. A melting rate of 13 to 19 kg/hr was demonstrated for a 12-in. diam can containing eight fins of equal radial length and fed WFE concentrate. Several drop-in fin configurations were evaluated and were found to eliminate most fin distortion that had occurred with past designs.

In-can melting campaigns 8 through 11, completed during the reporting period, are summarized in Table 1. Campaigns 8 and 9 were both made using the same canister coupled to the WFE. The five fins were of an equal radial length of 3 1/4 in. and were tack welded to the internal wall of the canister. The melting rate was equal to the rate at which the WFE concentrate and frit were fed to the melter. Thus, from these results and those of campaign ICM-7,* we conclude that the melting capacity of an 8-in.-diam canister with internal fins, heated to 1075°C, is between 9 and 12 kg of solids per hour for a feed that is one part concentrate containing 35 wt% solids and three parts frit. This is about half the melting capacity demonstrated using a dry calcine feed.

* J. L. McElroy, Quarterly Progress Report, Research and Development Activities, Waste Fixation Program, BNWL-1908, Battelle, Pacific Northwest Laboratories, Richland, WA, July 1975.

TABLE 1. Summary of In-Can Melting Runs 8 Through 11

Run Number	ICM-8	ICM-9	ICM-10	ICM-11
Date of Run	4-2-75	4-9-75	6-26-75	5-14&15-75
Coupled To:	Wiped Film Evap.	Wiped Film Evap.	Screw Feeder	Wiped Film Evap.
Canister				
Diameter, inch	8 Sch 40	8 Sch 40	8 Sch 40	12 Sch 40
Length, inch	48	48	48	54
Wall Thickness, inch	0.32	0.32	0.32	0.375
Material	304L SS	304L SS	304L SS	304L SS
Fins	5	5	4	8
Batch				
Waste Type	Commercial	Commercial	Commercial	PW-7-2
Waste Form	WFE Concentrate (36.5 wt% solids)	WFE Concentrate (28.2 wt% solids)	Fluid Bed Calcine	WFE Concentrate (20.5 to 29.9 wt% solids)
Waste Oxide to Frit Ratio	1:3	1:2	1:2	1:2.6
Frit Type	73-1	73-1	--	73-1
Frit Form	-6/+20 mesh	-6/+20 mesh	--	-6/+20 mesh
Batch Preparation	None	None	--	None
Operating Parameters				
Total Time at Melt Temperature, hr	20.7	7	8	27.25
Surface Temperature Range, °C	1030-1075	1000-1075	1030-1065	925-1095
Nominal Melt Temperature, °C	1055	1025	1030-1065	1050
Feed Method	Continuous	Continuous	Continuous	Continuous
Feed Conditioning	Proportional	Proportional	--	Proportional
Max. Waste Oxide Feed Rate, kg/hr	8.4 as concentrate	6.2 as concentrate	--	5.9 as concentrate
Max. Frit Feed Rate, kg/hr	6.0	3.1	--	13.1
Max. Batch Feed Rate, kg/hr	9.1 solids	4.8 solids	8.3	19.0 solids
Melting Rate, kg/hr	9.1	>4.8	8.3	Between 13 and 19
Peak Power Consumption, kw	17.5	14.8	10	34
Cooling Rate, °C/hr				
1025 to 750°C	51	50	52	32
750 to 500°C	42	23	22	15
500 to 25°C	6	4	6	6
Product				
Type	Commercial (1:3)73-1	Commercial (1:2)73-1	Commercial (1:2)73-1	PW-7-2(1:2.6)73-1
Weight, kg	44.5	13.4	28.1	176.9
Volume, l	12.8	3.8	10.3	49.6
Bulk Density, g/cc	3.47	3.56	2.7	3.56
Apparent Density, g/cc				
Top	--	3.28	--	3.36
Center	3.42	--	3.09	3.49
Bottom	--	3.36	--	3.67
Leach Rate, wt% lost in 72 hr*	0.65	0.75	--	0.36

*Soxhlet Leach Test

After melting was completed and the canister temperatures were still at 1050°C, water was sprayed onto the inside wall above the melt level. This knocked the unfixed calcine off the walls into the melt but also generated large volumes of steam.

The length of the canister was measured before ICM-8 and following ICM-9. The nominal canister length of 48.6 in. increased 0.124 in. as a result of the two campaigns. Diameters of the canister were also measured before and after the two campaigns and were found to have increased below the melt level by 0.020 to 0.030 in. during ICM-8 and an additional 0.007 to 0.016 in. during ICM-9.

A drop-in fin design was used for ICM-10 comprising two rectangular plates with widths equal to the inside diameter of the can and crossed to divide the can into quadrants. Slots were cut into the outside edges of each fin to allow melt to flow between quadrants. The quadrants were equally filled even though much of the batch was fed into only two of them, and the fins were less distorted than those tack welded to the canister.

In-can melting Run 11 was made in a 12-in.-diam can with an 8-in.-diam neck. This contained a drop-in fin assembly consisting of eight equal length fins welded in a radial pattern around 2-in.-diam central rings. There was less than 1/8-in. clearance between the outside edges of the fins and the inside can wall. Slots were cut in the outer edges of the fins to permit melt flow from one section to another when sections were not uniformly filled. Viscosity of the melt at the center is too high to permit flow there.

ICM-11 was made to establish a melting rate for a 12-in.-diam, finned canister when it is fed batch of WFE concentrate and coarse frit. The PW-7-2 simulated nuclear waste concentrate was fed to the canister at rates varying between 9.8 kg/hr and 28.0 kg/hr and had total oxide contents ranging from 29.9 to 20.5 wt% respectively. The 73-1 frit was fed to the canister at a ratio of two parts to one part of oxide. Satisfactory melting

was sustained for 3 hr with a mean concentrate feed rate of 20.8 kg/hr and a mean frit feed rate of 8.2 kg/hr. This concentrate had a mean oxide content of 23.2 wt%; therefore the solids melting rate was 13 kg/hr, equivalent to 2.16 MTU/day at 378 liters/MTU.

Concentrate having an oxide content between 27.5 and 20.5 wt% was then fed at rates between 21.3 and 28.0 kg/hr respectively with a corresponding frit rate of 13.1 kg/hr. A bridge soon formed over the top of the fins and sealed off the neck of the canister. However, the bridge was not a direct result of the increased feed rate; two other factors contributed to its formation. When these two factors are controlled, the 12-in.-diam canister should be capable of sustaining a melting rate of 20 kg of solids per hour.

The first factor contributing to the formation of bridges is nonuniform filling of the sections between the fins. At the time the above-mentioned bridge formed, the concentrate was falling so that it was entering only three of the eight sections. One section soon filled with dry but unmelted material that began flowing over the top of the fins, thus starting the bridge. A method of uniformly distributing the feed among the eight sections must be devised before a maximum melting rate can be realized. Simply assuring that the concentrate is delivered at the center of the canister is not sufficient. When concentrate was dropped directly in the center, a dry, porous column accumulated there and mushroomed out over the top of the fins because the temperature at the center of the canister is too low to sustain a high melting rate there.

The second factor contributing to bridging is failure to maintain temperatures over 1000°C at the top of the can. Two of the three bridges that developed during run ICM-11 occurred when power to the single zone furnace was reduced because of overheating at the bottom of the canister where melting had been completed. These power reductions allowed the canister surface temperatures at the top of the fins to drop below 1000°C, and a bridge began to form. The solution to this problem is straightforward: a multizoned furnace should be used for in-can melting so that the lower sections of the canister can be cooled after melting in them is complete

while those sections where melting is still occurring can be maintained at maximum temperature. Heating the canister in this way should also limit the settling of CeO_2 in the melt.

Although frit was fed to the melter at a ratio of 2 to the oxide content of the concentrate, the ratio of frit to oxide in the glass was 2.6 to 1. This resulted from the large quantities of waste oxides that were deposited in the connecting section between the WFE and canister and in off-gas lines because of splashing and solids entrainment in the steam and NO_x released in the canister. The splashing can be minimized by proper design of a feed delivery and distributor spout. Effective methods of dealing with heavy solids loadings in the off-gas have been demonstrated with the spray and fluid bed calciners.

The product of the run is typical of those produced in earlier in-can melting runs except for the location of the shrinkage voids. The voids exist as pockets between the canister wall and the glass near the top rather than as an inverted cone in the top center.

The drop-in fin assembly was distorted very little. The 12-in.-diam section of the canister, nominally 42.65 in. long, increased in length by an average of 0.101 in. during the process.

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 glass.

The scale model ceramic melter described earlier* has been at operating temperature for 165 continuous days. Since last reporting, over 1800 kg of glass have been produced by the system. The unit has been fed glass frit, calcine and frit powder, concentrated slurry and the liquid waste. With a mixed batch of dry calcine and frit powder, the unit melted at a rate of 43 kg of

* C. C. Chapman, "Joule Heated Ceramic Melter," Quarterly Progress Report, Research and Development Activities Waste Fixation Program, October through December 1974, BNWL-1893.

glass/hr. While feeding liquid waste (concentration of 378 liters/MTU with the frit suspended in it), a capacity of 26 liters/hr was achieved. The results of the powder feeding and direct liquid feeding tests are given below.

Premixed Frit and Calcine Powder Feeding

Since the capacity of the present ceramic melter exceeds the available output from calcination equipment, a synthetic calcine was purchased for use in melting tests. The raw constituents used in the synthetic calcine to simulate PW-4b waste calcine were primarily the metal oxides. However, potassium, strontium and barium were present as nitrate compounds. This yielded a calcine high in nitrates (12.2 wt%). The synthetic batch of calcine and frit was a well mixed, -200 mesh powder which upon melting would yield a simulated waste glass with a frit to calcine ratio of 2.

During melting of the synthetic batch, feeding and draining were continuous. The length of the run was defined as the time from initial feeding to the time when the surface of the glass had again become molten after feeding had stopped. Using this definition, the total run time was 9.75 hr, in which 419 kg of glass were produced. Thus, the overall melting rate for the run was 43 kg of glass/hr. The power to the melter was controlled by maintaining the control thermocouple at 1170°C. The control thermocouple was located 3 in. below the surface of the molten glass, toward one end of the melting cavity.

From the beginning and throughout the entire test, the batch blanket never covered more than ~50% of the molten surface. It might be concluded that the feed rate was below capacity for this unit. However, the accumulation of a layer of molten molybdate salts on the surface of the glass may nullify the observed results since the salts may not be present under actual conditions. The influence of the molten salt may have been to enhance melting. Nonetheless, the melter operated smoothly throughout the test. Temperatures within the molten glass reached steady-state values in less than an hour.

The draining glass gave the first indication that molybdate salts were separating from the synthetic glass. After 6 hr of operation, fumes from the molten stream were noted, presumably from volatilization of the molybdate salts. Samples of the glass showed that droplets of the molybdate salt were dispersed throughout the glass. Although the molten molybdate salts may have obscured the results of this test, it appears that the present ceramic melter design has more than adequate capacity for melting the waste calcine from a 5 MTU/day reprocessing plant.

Laboratory melt tests using the synthetic calcine clearly showed that it yields much greater quantities of the molybdate salts than are produced from the calcined liquid waste. Thus, some intermediate reaction occurs during calcination which inhibits excessive molybdate phase separation.

Direct Liquid Feeding

Simulated liquid waste, type PW-7-2, was made up at a concentration of 378 liters/MT. Powdered frit was added to the liquid waste to yield, after evaporation and melting, a glass with a frit to waste oxide ratio of 2. This type of liquid waste was then fed to the ceramic melter. During the test, 99 liters of the liquid waste were fed in 3.4 hr. Twenty-five minutes after feeding had stopped, the surface of the glass was again molten. Thus the total run time was 3.8 hr, yielding an average feed rate of 26 liters/hr and a glass production rate of 8 kg/hr.

Because the melter system was not designed for liquid feeding, several features must be added to improve operation. The present system's major limitation is lack of adequate liquid feed rate control. In the test described here, the feed rate was controlled by manually adjusting a ball valve and monitoring drop-out rate from the feed tank. This crude control method can result in feeding at a rate higher than the melter's capacity before it is noted. When the feed rate is excessive, the entire melting cavity becomes covered by a crust of sintered material with boiling liquid waste on the top. While controlling the melter by temperature control, a flooded condition is readily identified because the power drops off rapidly. This flooded condition occurred during this test. Recovery from the flooded

condition requires that feeding be stopped for ~15 min. After a portion of the surface again becomes molten, feeding can be restarted. Though a flooded condition is easily recovered from, it does disrupt the smooth, efficient operation of the melter and should be avoided.

From previous tests with direct liquid feeding, it was observed that a portion of the surface remains molten unless feeding is excessive. The regions of molten glass shift to different areas of the surface. As liquid waste flows to the molten glass and evaporates, the oxide residue eventually covers the molten region. Simultaneously at some other location in the surface, the molten glass tears a hole in the crust and is exposed to the liquid waste. This phenomenon continues unless too much liquid is being fed. Because rapid liquid evaporation depends upon contact between molten glass and the liquid, a bubbler tube was immersed in the glass to assure that molten glass was exposed at the surface. In this test the flow rate through the bubbler was 10 scfh. Comparison between this test and previous ones without a bubbler indicates that capacity was improved.

The scouting tests with liquid feeding the melter have been brief. Not all limitations have yet been recognized, nor has the system been optimized. But test results are encouraging. A single-process system using a relatively small joule-heated ceramic melter now appears designable for converting the liquid waste from a reference 5 MTU/day reprocessing plant to a glass.

FLUIDIZED BED CALCINATION - W. J. Bjorklund and C. L. Timmerman

Fluidized bed calcination studies are intended to provide data for process and equipment development on the conversion of high-level commercial nuclear waste to a dry product. Development also encompasses direct and indirect coupling to melter systems for conversion of the calcine material to a glass form.

Equipment development has been the major effort this period under ERDA sponsorship. Significant items are as follows.

Propane Nozzle

A propane nozzle was formerly used to preheat the fluidized bed by directing the flame into the bed. This works satisfactorily for an initial startup; however, reuse of the nozzle is questionable due to potential plugging. The propane nozzle is now located in a special box just ahead of the plenum chamber. This location allows the bed to be preheated without risking the possibility of plugging the nozzle. The fluidizing air and combustion gas, at $> 700^{\circ}\text{C}$, are passed through the bed, and heat-up to the desired starting temperature for kerosene auto-ignition (375°C) is achieved in about 1 hr. Existing external heaters on the vessel are used to preheat the vessel $\sim 100^{\circ}\text{C}$, prior to propane burning, to avoid any condensation problems.

Quartz Viewing Window

The access door on the front of the calciner has been modified to incorporate a quartz viewing window. This allows inspection of the fuel combustion, fluidization characteristics and operating behavior.

Single Fluid Nozzle

Nozzle development has led to investigating use of a single fluid nozzle to replace existing air atomizing (two fluid) feed nozzles. Advantages would be: 1) significant reduction in off-gas flow, 2) more consistent spray pattern, 3) reduced control parameters, and 4) less equipment. Less attractive features of single fluid nozzles are: 1) required positive-pressure feed systems, 2) orifices are smaller for comparable flow rates than for two fluid nozzles, 3) cleanout needles are not available, and 4) they may run hotter than two fluid nozzles. Modifying commercial nozzle designs by incorporating a cleanout needle is being tried.

Rotary Valve

A 4-in. rotary valve has been installed on the product outlet from the calciner. This allows continuous product removal while maintaining a vacuum in the vessel. The questionable aspects are how well the valve will maintain a seal and whether it can survive in the high temperature ($300\text{--}500^{\circ}\text{C}$)

application. Limited testing has shown the valve to operate satisfactorily. Some air in-leakage has been noted, but it has not caused operating problems.

Bed Removal Device

A mechanism is being designed to remove material that will not flow freely from the bottom of the calciner during operation or shutdown. An auger device will transfer material from the calciner bed to the filter vessel discharge line. Special valve techniques will be tried to prevent air purging between vessels. This should be particularly useful in removing nozzle cakes or bed agglomerates.

Filter Vessel

A bank of sintered metal filters is being fabricated with about 70% more filtering area than the 15 ft² existing filters. The larger cluster will sit atop the existing vessel, thus leaving it essentially a collection chamber. This chamber will be modified to achieve a cyclone effect. A properly sized tangential gas inlet and a conical insert for gas outlet will be used. The existing filters have performed satisfactorily; however, it is believed that more filtering area will allow increased feed flow rate at lower filter pressure drop. The existing fluidized bed calciner (6.75-in. square bed) operates at 15 to 20 liters/hr with a 25 to 30 in. ΔP across the filters.

A composite of the above modifications is shown in Figure 1.

HEATED-WALL 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 heated-wall spray calciner barrel was maintained at 680 to 735°C for 100 hr while the two side-mounted vibrators were operated in cycles of 3 min off and 5.5 sec on. The cycles of the two vibrators were 180° out of time phase so that a vibrator was activated every 1 1/2 min. Therefore the vibrators acted for a total of 6 hr on the hot barrel wall.

FIGURE 1. Fluidized Bed Calciner

Measurements were made across the impact pads and across the barrel diameter 90° from the pads before and after the test, using a micrometer reading to 0.001 in. No measurable difference in barrel shape was found following the test. However, the action of the vibrators did cause the failure of all five thermocouples attached to the inside barrel wall.

WIPED FILM EVAPORATOR - R. D. Dierks

This study is intended to aid in developing design specifications for equipment to reduce nuclear fuel reprocessing, high-level waste slurries to a highly stable borosilicate glass product, suitable for long-term storage.

Four experiments were completed with the wiped film evaporator during the report period. In three experiments the evaporator discharged its slurry product directly into an in-can melting system to produce a borosilicate glass product. The fourth experiment was used to prepare a concentrated simulated waste material for use as feedstock for a ceramic melter system.

For those experiments in which the evaporator was directly coupled to the in-can melting system, the arrangement of the evaporator, frit feeder, and receiver furnace was essentially the same as described in the previous Quarterly Progress Report.* The feedstocks for the in-can melting demonstrations differed slightly in each case and ranged from a dilute formulation at 2000 liters/MTU to a concentrated slurry at 378 liters/MTU. Despite feedstock variations, a uniform evaporator product concentration ranging from 40 to 50 wt% solids was realized by appropriate adjustment of the evaporator steam jacket pressure. Coarse, dry frit was added to the receiving canister along with the evaporator concentrate in a 2:1 ratio of frit to the metal oxide content of the concentrate. The resultant mixture was then reduced to a glass material in the in-can melter system. Glass forming rates of 5 to 18 kg/hr were demonstrated with the direct coupled evaporator/in-can melting system.

* BNWL-1908

For the fourth experiment, frit ground to -325 mesh was added to the evaporator feedstock in a 2:1 ratio of frit to the metal oxide content of the feedstock. This mixture was then concentrated with the wiped film evaporator to a product containing about 35 wt% solids (oxide and frit). Approximately 60 liters of concentrate were subsequently used as feed for a joule-heated ceramic melter system. The frit was added to the feedstock before evaporation to provide a more intimate mixture of the frit and oxide in the subsequent melting operation and to avoid the need to maintain a separate feed control system synchronized with the waste feed rate for the external additions of the dry, solid frit. Operation of the evaporator with the frit-laden feed was without difficulty, although the product appeared to be somewhat gelatinous, restricting the flow out of the evaporator. Overall heat transfer characteristics were not significantly changed.

A visit to Artisan Industries in Waltham, Massachusetts, was made to participate in a series of tests with their thin film evaporator processing a simulated high-level liquid waste. For these tests a typical Purex-type waste slurry (PW-7) was supplied which contained about 150 g of metal oxides per liter and was made up to 378 liters/MTU. While the tests were not exhaustive and lacked precision, they did demonstrate that a thin slurry feedstock could be reduced to a dry, free-flowing solid in a single pass through a thin film evaporator without pre-concentration or tandem evaporator/dryer operation.

A similar series of demonstration tests is scheduled with the Luwa Corporation in Charlotte, North Carolina, to observe performance of their thin film evaporating equipment. Also, our pilot-sized wiped film evaporator will be modified to permit further study of the unit's capabilities to produce a dry powder product, particularly with feedstocks containing pulverized frit.

RADIOACTIVE DEMONSTRATIONS

The objectives of this program are to demonstrate fully radioactive, engineering-scale processes for converting commercial radioactive liquid waste to low-dispersible forms (Reference is glass). Expected results from these demonstrations will aid industry with design and licensing of fixation processes and provide needed product characterization data.

Solidification Cell (324 Building B-Cell) Reactivation - D. H. Siemens

Reactivation of B-Cell in preparation for radioactive demonstrations was resumed in February 1975. Scheduled startup is mid-FY 76. The first process to be operated will be a spray calciner coupled to an in-can melter to produce canisters of glass for evaluation. Synthetic feed, utilizing cesium to provide the decay heat, will be used for most demonstrations. This synthetic feed will be spiked with actual commercial high-level waste as required to study isotope behavior in the off-gas system.

Several major modifications are being made to the cell equipment. These include:

- Improved sampling systems (gas and liquid).
- Replacing the solidifier condenser with a packed tower quench scrubber.
- A more reliable, dual pump, solidifier feed system.
- Improved packing (mist eliminator) in the evaporator tower.
- Improved frit (glass former) addition system.
- Installation of additional cell viewing windows.

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.

MELT DEVELOPMENT - W. A. Ross

The objective of this work is to identify melt compositions which will contain high-level radioactive waste atoms in a stable glass network and which can be processed by in-can melting.

Incorporation of F^- , Cl^- , and I^- into 73-1 frit was tested. About 72% of the F^- and not more than 1 wt% of either the Cl^- or I^- was retained at 1000°C.

Leach testing of common minerals has demonstrated that the reference waste glass has higher Soxhlet leach resistance than many common minerals such as granite and marble.

Glasses Containing Halogens

Proposed reprocessing flow sheets have included F^- and I^- as part of the waste stream. A test to determine the solubility of these ions plus Cl^- was made by addition of 1 wt% of each of the ions as a sodium salt to -325 mesh 73-1 frit. The 40-g mixtures were heated to 1000°C and held 3 hr in a platinum crucible. Weight losses were determined and are shown for the samples and a standard in Table 2.

TABLE 2. Weight Loss of Halogens During Melting

<u>Glass Composition</u>	<u>Weight Loss, %</u>
73-1 Standard	0.16
73-1 + 1% F ⁻	0.44
73-1 + 1% Cl ⁻	1.15
73-1 + 1% I ⁻	1.15

The weight loss data indicates that about 72% of the F⁻ remained in the glass whereas about 99% of the Cl⁻ and I⁻ was vaporized. The vaporized fluoride in an engineering system could be recycled; however, other means will be required to contain I⁻, or major changes in the glass composition will be needed.

Leach Testing

To allow comparison of glass products to materials which have existed in nature for millions of years, a Soxhlet leach test was performed on a variety of common stable minerals. Most mineral samples were obtained from a collection prepared by Colorado Geological Industries, Inc. The basalt was obtained from the Atlantic Richfield Hanford Company and is typical of the Hanford area. The samples were crushed and subjected to a continuous 72-hr Soxhlet test. Table 3 shows the percent leached for each material. It should be noted that minerals can vary widely in composition and that this could significantly affect their leachability.

The 72-68 reference glass typically has a leachability value of about 0.7 wt%. This is among the lower values of the minerals and indicates that significant improvement in leachability as measured by the Soxhlet method cannot be expected for our complex system.

TABLE 3. Soxhlet Leachability of Common Minerals

<u>Minerals</u>	<u>Wt% Leached</u>
Quartz Crystals	0.41
Milky Quartz	0.50
Dolomite	0.55
Garnet	0.73
Corundum	0.77
Orthoclase	0.90
Granite	1.10
Quartzite	1.20
Felsite	2.10
Marble (Dolomite)	2.90
Clay Slate	4.10
Calcite	5.80
Basalt	6.10

THERMAL STABILITY OF CALCINES - W. A. Ross

The objective of this work is to determine the pressurization potential of calcines stored in sealed canisters and subjected to high temperatures.

The test program has been completed and results are being evaluated. The detailed results will be published as a separate document. Some major results can be summarized thus:

- 1) All calcines tested would produce more than 500 psi at $\sim 830^{\circ}\text{C}$ when loaded at 1.35 g calcine/cc of canister volume.
- 2) Amount of off-gas from a calcine at 1000°C was as high as 80 cc/g.
- 3) Calcining temperatures above 800°C would be required to eliminate pressurization of canisters.
- 4) The principal noncondensable gases from the calcines were O_2 , N_2 , NO_x , and CO_2 .

LEACH RATES OF MELT 72-68 CONTAINING ^{244}Cm - F. P. Roberts

The objective of this study is to determine the curium leach rate of melt 72-68 glass and to evaluate the effect of alpha radiation damage on the leachability of this glass.

Seven specimens containing 1 wt% $^{244}\text{Cm}_2\text{O}_3$ and one button containing no curium were subjected to the standard leach test.* The composition and preparation of the specimens were described in an earlier report of this series.** The curium-doped specimens were stored at room temperature for varying periods to allow the desired alpha dose to accumulate and then were leach-tested for 20 weeks. During the first eight weeks the leachant was renewed weekly and then every four weeks for the remainder of the period. The leachant was analyzed for potassium by flame photometry and for ^{244}Cm by total alpha counting. The incremental leach rates, R_n , for these two elements were calculated from:

$$R_n = \left(\frac{a_i}{A_0} \right) \cdot \frac{W}{ST_n}$$

where

a_i = amount of element leached during leachant renewal period

A_0 = amount of element initially present in the specimen

W = weight of specimen in grams

S = exposed surface in cm^2

T_n = leachant renewal period in days.

The accumulated alpha doses for the specimens are shown in Table 4. The doses were substantially larger at the end of the test than at the beginning.

* E. D. Hespe, "Leach Testing of Immobilized Radioactive Solids - A Proposal for a Standard Method," Atomic Energy Review, vol. 9, no. 1, pp. 195-207, 1971.

** J. L. McElroy, Quarterly Progress Report, Research and Development Activities - Waste Fixation Program - April-June 1974, BNWL-1841, 1974.

TABLE 4. Alpha Doses of Leach Test Specimens

<u>Specimen No.</u>	<u>Accumulated Dose at Beginning of Test, α/g</u>	<u>Accumulated Dose at End of Test, α/g</u>
B-71	0	0
A-4*	3.82×10^{17}	7.69×10^{17}
A-5*	2.43×10^{17}	5.30×10^{17}
A-6*	4.78×10^{16}	3.66×10^{17}
A-7	2.81×10^{17}	6.70×10^{17}
A-12	5.14×10^{17}	8.29×10^{17}
A-13	4.73×10^{17}	7.63×10^{17}
A-16	2.49×10^{17}	4.57×10^{17}

* Specimens were devitrified by holding at 750°C for seven days.

The measured leach rates are presented in Figures 2 and 3 for curium and potassium respectively. The leach rates for curium are one hundred fold lower than for potassium and do not show significant correlations with alpha dose. The potassium leach rates, likewise, showed no correlation with dose. However, the potassium leach rate of the nonradioactive specimen, B-71, was slightly but significantly lower than the curium-doped specimens. This may indicate that the radiation damage affecting leachability occurs at lower levels than covered by this set of measurements. In any case the leachability of the melt 72-68 formulation is not grossly affected by alpha doses up to $8 \times 10^{17} \alpha/g$, equivalent to waste storage up to 100 years (for a UO_2 fuel with 33,000 MWd/T exposure).

FIGURE 2. Curium Leach Rates

FIGURE 3. Potassium Leach Rates

CERAMIC-MOLTEN WASTE GLASS COMPATIBILITY - J. L. Bates

The goal of this study is to determine the rates of corrosion and corrosion mechanisms of refractory oxides in molten waste glasses. These data will be used to evaluate refractory lifetimes for use in nuclear waste fixation processes and to develop new refractories with improved properties. The immediate objective is to study refractory oxides for use in a ceramic-lined, joule-heated, waste glass melter.

The waste glass (72-68) was composed of 73.7 wt% 73-1 glass frit and 26.3 wt% PW-4b (DSS-16) simulated waste which includes 1.4 wt% UO_2 . The waste, frit, and UO_2 were melted prior to testing in a platinum crucible and held at 1250°C for 24 hr.

Refractory samples 1 cm² and 5 cm long, were suspended by a platinum wire in the molten waste glass contained in the platinum crucible. One-half of the sample was immersed in the glass, and the sample was rotated at 10 rpm.

The following chrome oxide base refractories have been tested:

- CC-100. An experimental fused case 80 wt% Cr_2O_3 containing small percentages of Al_2O_3 (3 wt%), SiO_2 (6 wt%), Fe_2O_3 (1 wt%), and MgO (9 wt%), with smaller amounts of TiO_2 and Ca . The structure is made up of a major high Cr_2O_3 phase containing small amounts of Al_2O_3 , SiO_2 , CaO , and TiO_2 surrounded by an apparent high Cr_2O_3 spinel phase containing larger amounts of Al_2O_3 , MgO , SiO_2 , CaO , and TiO_2 . Metallic iron inclusions are also present in the Cr_2O_3 phase (Figure 4). The grain size is large, between 0.04 and 0.13 cm.
- CA-100. An experimental fused case $\text{Cr}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ with significant amounts of Fe_2O_3 and smaller amounts of MgO , SiO_2 , CaO , and TiO_2 . (Composition to be determined.) The structure is two-phase, made up of an apparent major spinel structure containing principally Al_2O_3 and Cr_2O_3 surrounding a small unknown phase high in Cr_2O_3 (Figure 5). Grain size is large, ~0.06 cm.

Above Interface 50X

At Interface 100X

FIGURE 4. Microstructure of CC-100 High Cr₂O₃ Fused Refractory Showing Reaction of Waste Glass at and Above Liquid-Air Interface

At Interface

12X

Above Interface

100X

FIGURE 5. Microstructure of CA-100 Fused Cr_2O_3 - Al_2O_3 Refractory Showing Extensive Reaction of Waste Glass at and Above Liquid-Air Interface

- C-1215. A commercial dense-bonded, slip-cast 92.7 wt% Cr_2O_3 with 3.8 wt% TiO_2 , 0.4 wt% Fe_2O_3 , and small amounts of SiO_2 , CaO , B_2O_3 , and Al_2O_3 . This is a small-grained structure (0.004 cm diam) with the grains of Cr_2O_3 containing some titanium and very small amounts of iron. The grain boundaries contain nearly all the impurities of alkali metals, calcium, aluminum, and titanium (Figure 6).

The samples CC-100 and CA-100 oxides were tested at 1250°C in air 30 days (720 hr), and the C-1215 oxide was tested 7 days (168 hr).

After testing, the sample was withdrawn from the waste glass and cooled slowly. Each sample was sectioned and polished for metallographic examination. Measurements were made of sample width and compared with the pre-testing dimensions. (Measurements were accurate to ± 0.003 .) Table 5 reviews these results.

TABLE 5. Corrosion of Oxides

Oxide Type	Sample Dimensions								
	Below Glass-Air Interface, cm			At Glass-Air Interface, cm			Above Glass-Air Interface, cm		
	Before	After	Change	Before	After	Change	Before	After	Change
CC-100	1.0099	1.0099	0.0000	1.0190	1.0084	-0.0106	1.0140	1.0145	0.0005
	1.0099	1.0079	-0.0020	1.0119	1.0058	-0.0061	1.0157	1.0155	-0.0002
CA-100*	1.0140	0.9799	-0.0341	1.0077	0.9698	-0.0379	--	--	--
C-1215	1.0107	1.0000	0.0107	1.0133	1.0107	-0.0026	--	--	--

*Bottom tip of sample had corroded or broken off during testing.

The microstructural ceramographic examination was followed by scanning electron microscopy and electron microprobe evaluations to define more clearly the mechanisms of attack by the waste.

The characterization results are described below:

- CC-100. Corrosion was limited to sample surface, with the waste glass reacting with the high Cr_2O_3 spinel phase which surrounds the high major Cr_2O_3 phase (Figure 4). The zinc penetrated the spinel phase along cracks and grain boundaries. The Al_2O_3 , MgO , and SiO_2 were depleted somewhat from these areas, leaving a spinel phase metallographically indistinguishable from the original spinel phase. The iron concentration had not changed. However, the iron found initially as metal inclusions in the Cr_2O_3 phase (as-fabricated) had dissolved as the sample slowly reacted. The reaction did not penetrate into the bulk of the fused chrome beyond a 0.002 to 0.008-cm-thick corrosion layer on the surface. Some (Cr, Zn, Fe) oxide crystals ($\sim 0.008\text{-cm}^2$) were attached to the sample surface along with some residual waste glass.
- CA-100. This fused chromia-alumina refractory oxide experienced extensive attack by the molten waste glass (Figure 5). The sample width was reduced about 3.5%, and the bottom tip of the sample had corroded or broken off during the test. Extensive reaction occurred at the sample surface exposed to the glass, with large ($\sim 0.006 \times 0.050\text{-cm}$) crystals of reaction product forming in the residual glass. These crystals were the same as the reaction product, an oxide of Cr, Fe, and Zn. The waste glass had penetrated the entire sample along grain boundaries and cracks particularly, leaving only islands (0.005 to 0.015 cm diam) surrounded by the waste glass. These islands in the reacted areas were also oxides of Cr, Fe, and Zn oxide, but contained smaller amounts of Na, Si, Al, Ni, and Ti.

Except for these islands, all the aluminum had been removed from the refractory and was dissolved in the glass. No chromium was found in the waste glass, and titanium, present in the oxides originally, tended to remain with the chromium. Nickel and iron from the waste glass had also combined with the chromium and zinc.
- C-1215. This bonded, high-chrome refractory had been extensively attacked at the oxide surface by the molten waste glass (Figure 6). Some zinc from the waste had penetrated deeper into the oxide along the

Above Interface 100X

At Interface 100X

FIGURE 6. Microstructure of C-1215 High Cr₂O₃ Refractory Showing Reaction with Waste Glass at and Above Liquid-Air Interface

grain boundaries. The sample dimensions were reduced 0.25 to 1% with a reaction layer ~ 0.033 cm thick forming at the glass-oxide surface. The reaction layer and the crystals (0.003 to 0.005 cm diam) attached to the surface were composed of a Cr, Zn, and Fe oxide similar to that observed in the CC-100 and CA-100 samples. The attack occurred along the grain boundaries of the Cr_2O_3 , with the zinc reacting with the grain boundaries, which were high in Si and Ti with lesser amounts of Ca, Al, and Na. After the boundaries were reacted, the glass waste slowly reacted with the Cr_2O_3 grains.

Some general conclusions about the mechanism of corrosion are:

- Zinc in the molten waste glass readily attacks the spinel phase in the refractory oxides. Because the spinel phase contains the major portion of the non- Cr_2O_3 elements, it is difficult to assess whether the spinel phase is less resistant to attack by the waste glass or whether it is the presence of the Al_2O_3 or other oxides in the spinel which causes the corrosion.
- The molten waste glass slowly reacts with the impure Cr_2O_3 to form a Cr, Zn, and Fe oxide, with the iron being removed from the waste glass.
- No chromium is found in the waste glass.
- Attack occurs principally along cracks or grain boundaries which are also concentration areas of elements other than chromium, particularly Al, Mg, Ti, Si, and Ca.
- The fused chrome oxide has excellent corrosion resistance against the molten 72-68 waste glass at 1250°C.

The waste glass also contains boron, which cannot be detected by scanning electron microscopy and microprobe methods, and it may be a contributing factor in corrosion. However, borosilicate glasses are routinely melted in industry in high-alumina refractories without gross failure. This suggests that zinc is the principal agent in attacking the Al_2O_3 , MgO , and other oxides in the waste glass.

HELIUM IN GLASS - R. P. Turcotte

The objective of this study is the determination of helium diffusion coefficients in simulated waste glass.

To assess radiation damage effects and to provide relatively high helium inventories, samples doped with 1 wt% ^{244}Cm are being examined. The α decay proceeds as: $^{244}\text{Cm} \rightarrow ^{240}\text{Pu} + ^4\text{He} + 5.5 \text{ MeV}$. Helium release is being measured from thin discs as a function of time and temperature with a mass spectrometer system.

Results presented last quarter included establishment of a short-time diffusion coefficient at 350°C of $\sim 1 \times 10^{-8} \text{ cm}^2/\text{sec}$ and an activation energy of $\sim 15 \text{ kcal/mole}$ for two samples with low fractional helium inventories ($F_p \sim 0.05$). These preliminary results have been confirmed and extended to behavior at long times. Activation energies have been determined at a variety of helium inventories, and release from a powdered sample was examined during a programmed heating cycle. The diffusion coefficient in an undoped specimen was determined by prior equilibration with 1 atm helium and the Henry's Law solubility constant estimated.

In Figure 7, release data at 350°C are shown plotted as fractional release versus $(\text{time})^{1/2}$ for samples M_1 and M_2 . A distinct knee is observed for M_2 near midrange, clearly suggesting two release mechanisms are operative, shown in the figure as (A) and (B). The measured curve (M_2) is obtained by simple addition of fractional release ($M_2 = A+B$) for any given time. If the classical Fick's Law solution is applied, a D value of $1.25 \times 10^{-8} \text{ cm}^2/\text{sec}$ is obtained for the first $\sim 35\%$ of the release, with the second process (B), thereafter being rate controlling with an apparent $D = 1.0 \times 10^{-9} \text{ cm}^2/\text{sec}$. A probable cause for this behavior is discussed later.

In Figure 8, release rate data for four different samples and various fractional inventories are plotted as $\ln R$ (cc/sec) versus $1/T$ ($^\circ\text{K}$). The slopes give E_a/R and do not appear to vary greatly with either the helium inventory (F) or temperature. The curve labeled $F = 0.70$ (1) was obtained with a linear cooling-heating rate of 100°C/hr and is one of five

FIGURE 7. Fractional Helium Release Vs. $t^{1/2}$ at 350°C from Curium-Doped Discs, Showing Breakdown to Two Diffusion Paths (A and B)

FIGURE 8. Release Rate Data for Various Samples (1-4) and Different Fractional Inventories as Indicated. Plotted as $\ln(\text{rate})$ versus $1/T$, the slopes give the activation energy (E/R).

such runs all on the same sample, but with different helium inventories obtained by prior isothermal annealing, to give increasingly lower concentrations. The cooling and heating curves are separated by $\sim 10^\circ\text{C}$, a hysteresis likely due to the experimental method. In any case, the mean of the two curves gives excellent straight lines, as shown in Figure 9 at the fractional inventories indicated. The activation energies obtained from the slopes are given in Figure 10, where the trend is to lower values the higher the helium fraction. The data given in Figure 8 suggest that variation from sample to sample (e.g., compare 3 and 4) is of this order of magnitude so that the change with F is not significant. If we take $E = 15 \pm 1$ kcal/mole, virtually all data now in hand agree, and the diffusion coefficient can be expressed for process A as

$$D_A = 2.11 \times 10^{-3} \exp[-7500/T]$$

and for process B as

$$D_B = 1.69 \times 10^{-4} \exp[-7500/T].$$

The agreement between the expression for D_A (i.e., short time release) and coefficients obtained from isothermal runs [in brackets] at several temperatures is indicated:

$$200^\circ\text{C}, 2.74 \times 10^{-10} [2.7 \times 10^{-10}]$$

$$300^\circ\text{C}, 4.36 \times 10^{-9} [6.0 \times 10^{-9}]$$

$$350^\circ\text{C}, 1.25 \times 10^{-8} [1.3 \times 10^{-8}]$$

$$350^\circ\text{C}, 1.25 \times 10^{-8} [1.4 \times 10^{-8}]$$

Because helium solubilities in silicate glass systems are quite high by comparison to all other inorganic solids, it has been possible to homogeneously dissolve measurable quantities of helium in undoped 72-68 glass discs by simple equilibration with 1 atm He (4 days, 450°C). Several

FIGURE 9. Release Rate Data for a Single Sample at Various Fractional Inventories

FIGURE 10. Slopes of Lines in Figure 9 Plotted as E Vs. Fractional Helium Inventory

investigators have shown Henry's Law to be valid in helium-glass solubility studies ($C_s = K P_{He}$), so that the helium overpressure directly determines concentration in the solid (C_s). Based on the experiment indicated above, the constant is estimated to be 6.0×10^{-4} , in terms of $\text{cm}^3_{He}(\text{S.T.P.})/\text{cm}^3 \text{ glass}$.

The fractional release data at 350°C are given in Figure 11 and compared directly to results from the curium doped sample. The knee is clearly not present and can thus be attributed to radiation damage. The excellent agreement at low times between samples with and without radiation damage, strongly suggests that release path A, shown in Figure 7, arises from normal diffusion of untrapped helium. Release path B reflects the slow release of helium associated with radiation damage sites as they are annealed. By back-extrapolating the long-time data to short times (curium-doped), it appears that at 350°C, ~43% of the damage is annealed within a few minutes. The remaining damage requires more than 15 days for complete annealing at this temperature. Long-term data have been obtained at 250°C and 450°C on curium-doped discs, but have not yet been analyzed. Based on the interpretation given here, related information in the literature, and stored energy results obtained on the present glass (F. Roberts), we expect the damage fraction which is rapidly annealed to be ~25% to 250°C and ~75% at 450°C. This behavior is directly related to the broad range of energy levels expected for the variety of defect types possible in a glass system. Thus, some defects are unstable and anneal at low temperatures, while others are in deep (but metastable) energy wells and require high temperatures for annealing.

Several experiments were made to establish or disprove the existence of specific helium-defect traps in the radiation-damaged glass. To do this, portions of a diffusivity disc were ground to a 40- μm powder and heated in the mass spectrometer system at a rapid heating rate. The release, shown in Figure 12 as rate versus temperature, shows a single broad release peak with only minor indications of fine structure. The broad temperature range over which release occurs is compatible with the discussion above, suggesting that damage annealing occurs over a wide range of activation energies with no one defect type present in high concentration.

FIGURE 11. Fractional Helium Release at 350°C Compared for ^{244}Cm -doped ($\circ$) and Damage Free ($\bullet$) Samples

FIGURE 12. Release Rate from a <40 μM Powdered Sample Plotted Vs. Temperature, Showing a Single Broad Release Peak

The helium diffusion study in vitreous glass is essentially complete. The major effort during the next quarter will be directed toward applying the information generated to conditions now expected for actual waste storage. A formal report will be issued and direction for further study indicated.

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

In this task the stability of calcined nuclear waste products in a radiation environment is being investigated because of the potential pressure buildup of evolved gases in a waste container.

As part of this effort, we have determined the sorption of various gases on waste particles as a function of pressure and temperature. In the last quarterly report* we reported the results of sorption of several gases on PW-7 calcined waste particles. No measurable sorption of N_2 and O_2 was observed at room temperature. H_2 was not extensively investigated because preliminary tests showed that the sorption rate was very slow and that the sorption increased at increasing temperatures.

Sorption of CO_2 was again investigated. The increased uptake of CO_2 with increasing temperatures was confirmed. (Confirmatory tests used larger samples of waste to improve measurement accuracy. Thus it appears that a chemical sorption occurs rather than physical sorption. This may lead to the question of whether O_2 and perhaps N_2 would also show interaction with the waste materials at temperatures significantly above room temperature. This phenomenon is, however, not expected because the waste has already been calcined in air at high temperature.

These adsorption studies are important because the radiolytic data are more readily interpreted if we know how the product gases interact with the waste at various temperatures and pressures. We are currently not fully convinced that equilibrium conditions were achieved in the tests. But the times investigated are of the same magnitude as in the radiolytic studies so that the data is applicable to radiolysis data.

* BNWL-1908.

In previous reports we have discussed release of gas from irradiated calcined waste materials. In this quarter, we have further studied behavior of calcined waste (PW-7) under gamma irradiation.

Calcined waste was placed in a Pyrex tube to which stainless steel capillary tubing had been connected. This sample was exposed to radiation in the 3730 Building gamma facility. Pressure buildup was measured with an MKS differential capacitance manometer. Temperature was measured with thermocouples attached to the sample container. Generally, temperatures during the most intensive exposure remained at less than 20°C above ambient room temperature.

At a radiation level of about 1.9×10^5 rads/hr, the sample container pressure increased linearly at a rate of 0.9 torr/hr until an equilibrium value of 56 torr was reached. Gases present at equilibrium were analyzed and are shown in Table 6.

TABLE 6. Gas Product Composition from PW-7 Irradiation

<u>Gas</u>	<u>Percent</u>
O ₂	98.0
N ₂	1.27
CO ₂	0.45
H ₂	0.28
CO	<0.1
CH ₄	<0.01

The equilibrium pressure of 56 Torr was reproduced after numerous re-evacuations of the sample. The high percentage of oxygen is consistent with decomposition of the nitrate to nitrite where the net chemical reaction is probably

Significant radiation induced back reaction is also expected:

These experiments will be continued to determine the rate of gas release from exposure within a combined gamma and alpha radiation.

SS-9 CANISTER EVALUATION - METALLOGRAPHY - Y. B. Katayama

The objective of the evaluation is to determine the mechanism of containment penetration and to supply reference data for future canister material selection.

Trepanned samples from canister 36 of WSEP run SS-9 were polished for metallographic examination of the longitudinal cross sections. Five samples were taken from the canister as shown in Figure 13. These samples, 310 stainless steel, were electrolytically etched in 2 wt% chromic acid for 30 sec at 3 volts prior to viewing.

FIGURE 13. Sampling Locations, Canister 36

Canister 36 was highly sensitized during four years' storage in air at 400°C wall temperature. The canister failed after six months' storage in water. Analysis of the water showed high dissolved oxygen and chloride ions.

All the polished areas examined (Figures 14 through 18) were free of transgranular cracking, a stress corrosion cracking indicator. Gross intergranular cracking was observed on the internal surfaces of the sample taken near the fracture area. The weld area sample, Figure 17, had some micro-cracking extending through the weld and into the canister wall. Samples taken from areas free of macro-cracks, samples 2 and 5, were also free of micro-cracks.

Internal Surface Edge 75X

External Surface Edge 75X

Internal Surface Edge 225X

External Surface Edge 225X

FIGURE 14. Photomicrographs of Canister Wall Section from WSEP Canister 36--Sample Area #1 (Oxalic Acid Electrolytic Etch)

Internal Surface Edge 75X

External Surface Edge 75X

Internal Surface Edge 225X

External Surface Edge 225X

FIGURE 15. Photomicrographs of Canister Wall Section from WSEP Canister 36--Sample Area #2 (Oxalic Acid Electrolytic Etch)

Internal Surface Edge 75X

External Surface Edge 75X

Internal Surface Edge 225X

External Surface Edge 225X

FIGURE 16. Photomicrographs of Canister Wall Section
from WSEP Canister 36--Sample Area #3
(Oxalic Acid Electrolytic Etch)

Internal Surface Edge 75X

External Surface Edge 75X

Internal Surface Edge 225X

External Surface Edge 225X

FIGURE 17. Photomicrographs of Canister Wall Section from WSEP Canister 36--Sample Area #4 (Oxalic Acid Electrolytic Etch)

Internal Surface Edge 75X

External Surface Edge 75X

Internal Surface Edge 225X

External Surface Edge 225X

FIGURE 18. Photomicrographs of Canister Wall Section
from WSEP Canister 36--Sample Area #5
(Oxalic Acid Electrolytic Etch)

It can be concluded from this evaluation that 310 stainless steel becomes highly sensitized after prolonged air storage at elevated temperature and should not be subsequently stored in water. The high chloride concentration in the storage water accelerated the failure. To eliminate the sensitization problem, air stored canisters should be overpacked prior to water storage.

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.

Isothermal capsule-type compatibility tests were begun with calcine (PW-7 and PW-7 plus 100-fold increase in sodium content) and with glass prepared from these calcines (1 part) and 73-1 frit (2.8 parts). Capsule materials included 304L SS, Incoloy 800 and Inconel 600. A corrosion coupon was included in each capsule for corrosion rate determination via weight loss. Sixty-three capsules were prepared, 28 containing calcine and 35 containing glass. The capsules are being held at temperatures of 460, 1000 and 1300°F. Maximum exposure periods will range from one month for capsules at 1300°F to >2 years for capsules at 460°F. To date data are available only on specimens exposed at 1300°F for 1 month. Table 7 gives corrosion rates as determined by weight loss. Macroscopic examination of the capsules and corrosion coupons revealed no preferential attack. Sections of the capsules are being prepared for metallographic examination. This work has not been completed.

Exposures with glass prepared from PW-7 calcine and 73-1 frit will be started next month under nonisothermal conditions. In these tests the melt will be contained in a 304L cylinder fabricated from 3-in pipe, and heat will be supplied by an Incoloy-clad immersion heater located at the centerline of the cylinder. Thermocouples will be included to determine glass temperature at centerline, mid-radius, and near-wall positions. Coupons of materials including 304L, Incoloy 800, and Inconel 600 will be suspended in the glass at near-wall positions for weight loss determination and for metallographic examination.

TABLE 7. Capsule Compatibility Tests

Corrosion Rates at 1300°F after One Exposure Month

<u>Material</u>	<u>Waste Form</u>	<u>Waste Composition</u> ^(a)	<u>Corrosion Rate, mils/year</u>
304L	Calcine	A	1.3
Inc 800	"	A	1.1
Inc 600	"	A	0.3
304L	Glass	A	0.6
304L	"	B	0.4
Inc 800	"	A	1.0
Inc 800	"	B	0.3
Inc 600	"	A	0.2

a. A = flowsheet; B = flowsheet plus 100-fold increase in sodium content.

A Huey test (5 to 48 hr exposures to boiling 65 wt% nitric acid) was run on a specimen trepanned from a 310 SS canister which failed by stress corrosion cracking. The canister had a unique thermal history. It was stored for one year in water, followed by 3.5 years' storage in air (skin temp = 400°C), followed by 10 months' storage in water at 50°C, when failure occurred. A Huey rate of 173 mils/month was obtained, indicating the canister was severely sensitized and very susceptible to intergranular stress corrosion cracking. Similar results were obtained on a 304L SS canister with a similar thermal history. Huey tests on 304L specimens trepanned from 304L canisters shortly after melting was complete indicated little sensitization and excellent resistance to intergranular attack. These data indicate the severe sensitization of the failed canister resulted from prolonged storage in air at 400°C.

FULL-LEVEL RADIOACTIVE TESTS - Y. B. Katayama

Fully radioactive waste glass specimens will be prepared on a laboratory scale. Analysis of the off-gas will be made during melting of the radioactive

glass. Characteristics of fully radioactive glass specimens will be compared with nonradioactive glasses of similar chemical composition as a function of storage conditions.

The 2.6-kg batch of irradiated UO_2 power reactor fuel pellets (55,000 MWd/MTU, 1 3/4 years out-of-reactor) is being processed to separate the actinides from the fission product waste. This waste will be used for the full-level radioactive tests.

A 50-g sample of the irradiated UO_2 pellets was transferred to the 324 Building hot cells before reprocessing. This sample will be used to evaluate the leach properties in both distilled water and groundwater (0.01 M $CaCl_2$). These data will allow comparison of leachability of as-irradiated fuel pellets versus fully radioactive glass in storage conditions. Five grams of the irradiated UO_2 fuel pellets were leach-tested in room temperature distilled water for 14 days with a 0.5 wt% loss. Analytical results from leach solutions are not available at this time.

WASTE VAPORIZATION STUDIES - W. J. Gray

The purpose of this study is to investigate the vaporization behavior of wastes containing fission products during processing, shipment, and storage. Accident conditions involving high temperature and breach of the container during shipment and storage are of particular interest.

Data presented here briefly summarize and, where indicated, supersede those included in earlier reports.*

Figure 19 shows the weight loss from 73-167 glass samples of various depths after 4 hr in dry air at 1000°C. These data supersede earlier data (BNWL-1809), which were less complete and also plotted incorrectly. Although not shown, essentially the same behavior was found at 1200°C. The weight loss rates are affected by the fullness of the crucible as well as by depth

* Quarterly Progress Report, Research and Development Activities, Waste Fixation Program, BNWL-1799, p. 9, October 1973; BNWL-1809, p. 40, January 1974; BNWL-1826, p. 30, April 1974; BNWL-1841, p. 42, July 1974; BNWL-1871, p. 34, November 1974.

FIGURE 19. Weight Loss from Glass Samples of Various Depths after 4 hr in Dry Air at 1000°C

of the glass. Thus the amount of dead air space above the sample is obviously important. For all but the two thinnest samples efforts were made to leave the same amount of space above the sample. As this is difficult to do with accuracy, the result is considerable scatter in the data.

Since the two thinnest samples also had the most dead air space, a clear separation of the effects of sample depth and amount of dead air space has not been achieved. It is clear from these data, however, that there is little if any dependence on sample depth for free samples (i.e., no dead air space) thicker than about 10 mm. Furthermore, a thick free sample has about double the weight loss rate of the 3.2 mm samples from which most of the vaporization data to date have come.

Figure 20 is an Arrhenius plot of the weight loss of PW-4b calcine and of 73-167 glass. Sample weight in all cases was 2 g, but sample thickness

FIGURE 20. Weight Loss in Dry Air

was 6.4 and 3.2 mm, respectively, for the calcine and glass. The data fit a straight-line relationship surprisingly well for such a complex system; since the weight loss is so low at 800°C, these points are within experimental error of the lines drawn. Weight loss from the glass and calcine is comparable at 1200°C, but the glass performs much better than the calcine at lower temperatures.

An anomaly occurs in the weight loss data for the glass near 1150°C. The 1125 and 1175°C points fall on the lines but the 1150°C points, which are quite reproducible, fall below the lines and, in fact, below the 1125°C points. Apparently some stable compound forms over a very narrow temperature range, thereby lowering the vaporization rate. This phenomenon will be studied further.

Figures 21 and 22 show the vapor composition over glass samples heated in dry air and in air containing 7.1 wt% moisture. These data supersede

FIGURE 21. Vapor Composition

FIGURE 22. Vapor Composition

those reported earlier (BNWL-1871) because more reliable analytical procedures have been developed. Vapor composition over calcine heated in dry air is also shown for comparison. Note that vapor samples for the glass were taken after 4 and 12 hr, respectively, in Figures 21 and 22, whereas 6-hr calcine samples are shown in both figures. Elements not shown in these figures were found to exist in the vapor in very small amounts if at all.

The reader must be cautioned not to misinterpret these data, which show only vapor composition but indicate nothing about the total amount of vaporization. Thus the sum of all elements for a given temperature equals 100%.

To aid in correctly interpreting these data, consider the example of Te in dry air at 1200°C. Figure 21 shows 7.5% Te while Figure 20 shows a total weight loss of 44.5 mg/cm². Thus 3.34 mg/cm² of Te are lost in 4 hr. Figure 22 shows 4.5% Te while Figure 20 shows a total weight loss of 82 mg/cm². Thus (82-44.5) (0.045) = 1.69 mg/cm² of Te are lost during the 4 to 12-hr period. The total loss of Te in 12 hr is, thus, 5.03 mg/cm² or 9.96 mg since the sample area was 1.98 cm². However, the amount of Te originally present was (2 g) (0.384 wt%) = 7.68 mg. This discrepancy is due to the conservative assumption that none of the weight loss is due to oxygen. Nonetheless, most of the Te apparently is vaporized from thin samples at 1200°C in 12 hr. Furthermore, Figure 19 shows that a thick free sample would lose about twice as much per unit area as the 2 g (3.2 mm) sample, or about 10 mg/cm² of Te in 12 hr at 1200°C.

Two sets of glass samples run in dry air were analyzed to determine reproducibility. The results indicate that error bars of about ±10% apply to the values shown in Figures 21 and 22. An exception is B, where the detection limit is quite high. As the figures indicate, the amount of B present in some cases was assumed equal to the detection limit while in other cases a smaller amount was assumed based on data at other temperatures.

It is interesting that the 4-hr vapor composition for the glass is essentially independent of temperature, the only apparent exception being Te. This indicates that the heat of vaporization is about the same for all elements or that a single mechanism controls the vaporization of all elements.

Both seem unlikely, and it may simply be that the preponderance of Cs masks variations in other elements. The 12-hr vapor composition for the glass does show some temperature dependence although this may be primarily due to the fact that most of the Cs and Te has been lost after 12 hr at 1200°C.

It is also interesting that adding moisture to the air has no major effect on the vapor composition over the glass even though it was previously shown (BNWL-1871) that moisture substantially increases the vaporization rate. Moisture does seem to increase the relative amounts of B and Mo and to decrease the relative amounts of Cs and Ru but, again, the effect is not a major one.

In summary, for short times (up to at least 4 hr) one can take the vapor composition over the glass from Figure 21 and multiply this by the total weight loss from Figure 20 (the result should be about doubled for thick free samples) to obtain the loss for the different elements over the range 800 to 1200°C. One might even use an Arrhenius plot such as Figure 20 to extrapolate the data to lower temperatures although extrapolation outside the range of data should always be done with caution.

Finally, comparing the vapor compositions over the glass and over the calcine in Figures 21 and 22, note that the relative amount of Te is less and that the relative amount of Ru is substantially less over the glass.

THERMAL EFFECTS ON STORED GLASS - J. H. Westsik, Jr.

The purpose of this project is to determine changes in properties of high-level waste glass and of the glass-canister interface as functions of temperature and time.

The initial tests are being made with PW-4b-6(2.8)73-1 glass (composition shown in Table 8) stored in stainless steel or alumina crucibles for periods up to five years. Storage temperatures range from 300°C to 1000°C in 100°C increments. Table 9 shows the storage conditions. Devitrification, chemical segregation, and leachability will be studied as a function of the storage time and temperature.

TABLE 8. Composition of PW-4b-6 Waste and PW-4b-6(2.8)73-1 Glass

PW-4b-6 Molarity @ 378.5 g/MTU	PW-4b-6(2.8)73-1 Glass Weight Percent
0.010 Rb	0.22 Rb ₂ O
0.027 Sr	2.14 SrO
0.014 Y	0.38 Y ₂ O ₃
0.106 Zr	3.12 ZrO ₂
0.117 Mo	4.02 MoO ₃
0.059 Ru	1.88 RuO ₂
0.010 Rh	0.30 Rh ₂ O ₃
0.032 Pd	0.94 PdO
0.002 Ag	0.06 Ag ₂ O
0.002 Cd	0.06 CdO
0.012 Te	0.46 TeO ₂
0.054 Cs	1.82 Cs ₂ O
0.027 Ba	2.46 BaO
0.024 La	0.93 La ₂ O ₃
0.051 Ce	2.10 CeO ₂
0.023 Pr	0.94 Pr ₆ O ₁₁
0.0732 Nd	2.94 Nd ₂ O ₃
0.014 Sm	0.58 Sm ₂ O ₃
0.003 Eu	0.13 Eu ₂ O ₃
0.002 Gd	0.09 Gd ₂ O ₃
0.0196 U	1.26 UO ₂
0.05 Fe	0.95 Fe ₂ O ₃
0.012 Cr	0.22 Cr ₂ O ₃
0.037 Ni	0.66 NiO
0.025 PO ₄	0.42 P ₂ O ₅
0.010 Co	0.19 Co ₃ O ₄
	27.26 SiO ₂
	11.13 B ₂ O ₃
	4.05 Na ₂ O
	21.30 ZnO
	1.47 CaO
	1.47 MgO
	4.05 K ₂ O

TABLE 9. Storage Conditions for Thermal Effects on Stored Glass Study

Temperature	Time					
	2 Hours	1 Day	1 Week	2 Months	1 Year	5 Years
1000°C	A ^(a)					
900°C		A	A	A		
800°C		A	A	A		
750°C		A	A	A		
700°C			A	A	A	
600°C			A	A	A	
500°C				SS ^(b)	SS	SS
400°C				SS	SS	SS
300°C				SS	SS	SS

a. "A" indicates alumina crucible.
b. "SS" indicates stainless steel crucible.

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.

DEVELOPMENT OF COATED WASTE PARTICLES - W. J. Gray and M. F. Browning

The purpose of this study is to develop coating materials and processes which can be applied to waste particles to serve as a fission product barrier.

Coating of particles typical of those produced in a fluid-bed calciner (0.1 to 1 mm), as well as particles several millimeters in diameter, is being investigated. Although research on pyrocarbon (PyC) coatings has continued, primarily in the area of lower coating temperatures, the emphasis has changed to an investigation of other coating materials.

PyC can be deposited from acetylene at temperatures as low as 800°C, but coatings produced in this manner have not been satisfactory. By starting at 850°C with acetylene and then switching to MAPP gas* at 1150°C, however, Oak Ridge National Laboratory produced the coatings shown in Figure 23. The coatings exhibit good integrity, and the low initial coating temperature minimized loss of fission products via vaporization.

Other coating materials produced by chemical vapor deposition in a fluid bed (CVD/FB) have been investigated by Battelle's Columbus Laboratory (BCL). In selecting candidate coatings for the radioactive waste application these factors were considered:

* MAPP gas is marketed by ARCO, Inc., and consists primarily of methyl acetylene and propadiene with alkanes as stabilizers.

200 μm

80 μm

PYROLYTIC CARBON
WASTE

FIGURE 23. Waste Particles Coated with $\sim 40 \mu\text{m}$ of Pyrolytic Carbon

1. Resistance to air oxidation at $\approx 1000^{\circ}\text{C}$, the condition assumed to be associated with a fire.
2. Imperviousness to leaching in the environment in which the waste is stored. Typically this leaching media is anticipated to be slightly alkaline water at $\approx 100^{\circ}\text{C}$.
3. Resistance to attack by the leaching media referred to in No. 2.
4. Compatibility with waste material and encasement matrix materials at the temperature of storage (centerline temperature of one typical capsule design estimated to be $\approx 800^{\circ}\text{C}$).
5. Compatibility of coating process environment with waste material.
6. Adaptability of coating process to relatively large-volume production operated remotely in a hot cell.
7. Limitation imposed on coating process by volatility of waste above $\approx 800^{\circ}\text{C}$. Coatings requiring deposition at $> 800^{\circ}\text{C}$ might be used with barrier coatings applied at lower temperature.
8. Cost.

Table 10 identifies the coatings which have been successfully applied along with some process data.

TABLE 10. Successfully Applied Coatings

<u>Coating</u>	<u>Process</u> ^(a)	<u>Deposition Temperature, $^{\circ}\text{C}$</u>
Nickel ^(b)	Pyrolysis of Nickel Carbonyl	200 to 230
Mo/MoC ^(b)	Pyrolysis of Molybdenum Carbonyl	300 to 450
Cr_7C_3	Pyrolysis of Chromium Dicumene	500
Cr_2O_3	Hydrolysis of Chromyl Chloride	550 to 650
Silicon	Hydrogen Reduction of Trichlorosilane	800
SiO_2	Hydrolysis of Silicon Tetrachloride	800

a. All coating processes were carried out in hydrogen. Other fluidizing gases such as nitrogen could be used although some hydrogen would be required for hydrogen reduction and hydrolysis reactions.

b. These coatings were considered as only barrier coatings to be used in combination with one of the other coatings.

In attempting to coat waste, it was found that chromium dicumene and trichlorosilane vapor reacted with the waste. Thus a barrier coating of nickel was required before chromium carbide or silicon coatings could be applied. The remaining coatings evaluated could be deposited directly.

Of the coatings applied to date, the $\text{Ni/Cr}_7\text{C}_3$ and SiO_2 coatings shown in Figures 24 and 25 look best. They appear more adherent than the PyC coatings because only a few of the internals fell out during metallographic polishing, whereas most of the internals of the PyC coated particles fell out. In Figure 24 one can see much penetration of Ni into the porous calcine. Perhaps this partly causes the better adherence. For SiO_2 there may be some reaction with the calcine to produce a more adherent coating. The SiO_2 coatings are quite transparent and thus contain little if any porosity; also they were found nonpermeable in strong acid leach tests.

The $\text{Ni/Cr}_7\text{C}_3$ coated particles, subjected to several successive leach periods using the Soxhlet leach test, have shown these results:

<u>Time</u>	<u>Percent Wt Change</u>
1st 72 hr	-0.02
2nd 168 hr	0.00
3rd 168 hr	-0.02
<u>4th 168 hr</u>	<u>0.00</u>
total	-0.04

These results are at the limit of detectability and represent by far the most leach resistant waste form yet tested.

Although the $\text{Ni/Cr}_7\text{C}_3$ and SiO_2 coatings, in particular, look quite good, the coating uniformity, integrity, and overall structure in the batches prepared thus far in the program are not of as high a quality as is characteristically obtained by a CVD/FB process. This is thought to result from two factors: 1) the extremely angular shape of the particles to be coated and 2) the variation in calcined waste composition and density from area

FIGURE 24. Waste Particles Coated with $\sim 4 \mu\text{m}$ Cr_7C_3

FIGURE 25. Waste Particles Coated with $\sim 4 \mu\text{m}$ SiO_2

to area on individual particles. The angular shape interferes with fluidization, resulting in abnormally high nonuniformity of coating. It is also expected to affect uniformity of the calcined-waste coating on the alumina particles. The nonuniformity of waste coating contributed to a poor overcoating because the porous, high-reactive areas continue to outgas during coating. It is believed that these problems can be substantially reduced by using a spherical seed material for the calcining operation. But, if necessary, the shape and nonuniformity of waste materials used in this program can be accommodated by applying thicker protective coatings than considered needed if these factors were not present.

Most, if not all, of the CVD processes can also be conducted in a rotating drum, thereby permitting the coating of larger particles. Figure 26 is an example showing a $\sim 3/16$ in. diam glass bead coated with Cr_7C_3 .

FIGURE 26. Glass Bead Coated with $\sim 5 \mu\text{m}$ Cr_7C_3

WASTE FIXATION IN VITREOUS CARBON - L. R. Bunnell

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

As an advanced waste form, recent emphasis has focused on small pellets comprising mainly waste calcine. This concept has prompted some developmental effort in which carbon is used as the pellet binder. The purpose is to produce sound pellets at lower temperatures than could be obtained by sintering calcine and glass to produce glass-bonded pellets. Ideally, carbon

would fill all interstices and provide pellets which would not adhere to one another during processing at higher temperatures or during subsequent high-temperature coating.

Pellets 0.25 in. in diameter and about the same height were pressed at 20,000 psi using either vitreous carbon precursor resin* or a graphite cement** as binder in the amounts 5, 10, 15, 20, and 25 wt%. These were fired to 975°C in a vacuum of $<400 \mu$ at a linear rate of 6°C/hr. Shrinkage was small, $<5\%$, and the shrinkage of the binder ($\sim 20\%$ for polyfurfuryl alcohol) did not dominate as it did with objects made with 50 wt% polyfurfuryl alcohol resin. Metallography showed a rather large amount of reduced metal in the composites, and weight losses were correspondingly high.

A second set of pellets was made, again using the two binders in the amounts above. To determine the temperature at which reduction took place, a pellet of each binder fraction and type was withdrawn after cooling from 525, 580, 770, and 975°C after heating at 6°C/hr. The geometric density of each pellet was measured before and after firing. A fairly sharp density decrease occurred at temperatures above 600°C, but metallography showed metallic inclusions only in pellets heated to 975°C. In the past, these metallics have proven to be almost totally Mo with some indication of Fe.

The reduction reaction is noticeably more severe in these pellets than previously noted in glassy carbon bonded bodies cast as a plastic mass. The route for escape of gaseous reaction products such as CO and CO₂ is probably easier in the somewhat porous pellets than in the essentially nonporous bodies made previously. Reduction may also be somewhat calcine-dependent; PW-4b-4 was used for these experiments, while PW-4b-2 was used in the previous work.

Carbon-bonded pellets have fallen short of expectations. The reduction reaction precludes their use at high temperatures, and their porosity is greater than desired. Carbon-bonded bodies formed as a plastic mass (perhaps extruded) would seem to be a more desirable form. If sufficient carbon is

* Quaker Oats Resin RP100A

** Great Lakes Carbon Cement P-511

present that its shrinkage does not result in voids (this occurs at the 50 wt% calcine point), the gaseous reaction products should be contained to help suppress the reduction.

PLASMA SPRAY SYSTEM - J. J. Rasmussen

The purpose of this study is to evaluate coatings of ceramic refractories to reduce the rate of corrosion of materials in contact with the molten glass/waste product.

Previous corrosion studies showed that chromium oxide or zirconium oxide offered the best potential of the materials available for long-term protection. Thermal shock of the coatings appeared the most likely source of failure.

Test coupons were made from 304 stainless steel to evaluate the oxidation protection of the coatings and to determine if problems would arise from thermal shock. If the coupons were cleaned and roughened by grit blasting and a Ni/Cr alloy bond coat applied to the stainless steel, thermal shock was not a problem with the Cr_2O_3 or the ZrO_2 at 1100°C. The coatings are applied by blowing carefully sized powders into an argon plasma where they are melted and sprayed onto the target. The bond coat is nominally 0.002 to 0.004 in. thick, and the oxide spray coating is 0.005 to 0.008 in. thick. Oxide coatings up to 0.050 in. thick can be applied without problems from cracking during the spraying process.

Four sets of coated coupons were furnace-heated in air to 1100°C according to the following thermal schedule:

1. One set was in the furnace during heat-up, held at 1100°C for 1 hr, then removed and air-cooled on a refractory brick.
2. The second set was in the furnace during heat-up, held at 1100°C for 1 hr, then quenched in water.
3. The third set was inserted directly into the 1100°C furnace, held there for 1 hr, then furnace-cooled.
4. The fourth set was left in the furnace throughout the entire heating-cooling cycle and was at 1100°C for at least 2 hr.

The ZrO_2 showed no evidence of any thermal shock cracking. Metallography of the coating cross section showed that the ZrO_2 was firmly adherent to the stainless steel substrate and that the stainless steel had not oxidized. The Cr_2O_3 also showed no evidence of thermal shock, but the surface became somewhat powdery and material could be rubbed away from the substrate. The stainless steel showed no evidence of oxidation after 2 hr at 1100°C.

A ZrO_2 coating with the Ni/Cr base coat has been applied to a thermocouple well for use in a glass melting tank. The results of this test are not yet available.

Spray coatings have been made onto glass marbles to evaluate the potential for coating waste pellets. The marbles accepted the spray without any significant problems. The greatest difficulty was keeping them in the spray pattern. An angular component of the spray velocity was required to turn the marbles so that full surface coverage would be obtained. This nonvertical component, however, pushed the marbles out of the spray. To effectively spray spherical pellets of waste glass, a system will have to be designed which allows the pellets enough freedom of motion to rotate and yet restricts them so that they remain in the spray to be coated.

PELLET FORMING METHODS - A. A. Garrett

The objective of this task is to evaluate the disc pelletizer as a possible means of pelletizing calcined waste prior to coating with an inert material. The main purposes are to determine if a disc pelletizer can make high density, uniform spheres from a mixture of calcine and frit and to determine the feasibility of operating a disc pelletizer in a hot cell.

A 16-in. disc pelletizer and two feeders for calcine and frit have been installed in a dust hood. System debugging is currently underway. Initial plans include examining the effects of calcine and frit particle size, different binders, different disc speed/angles, and calcine/frit feed rates on the green and fired properties of the pellets.

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

The objective of this work is to develop a crystalline ceramic alternative to the glass nuclear waste form. If adequately consolidated, this waste form might stand alone; but it is also being considered as the innermost, or atomic level, barrier in a multiple layer optimum waste form which would also utilize glass, ceramic or metal matrices, impervious coatings, etc. Because this waste form utilizes the existing calcining processes with a compositionally modified waste liquid it has been termed "supercalcine". In theory, each nuclear waste species will be "fixed" in a thermodynamically stable crystalline compound or solid solution which will have suitable thermal stability and leaching resistance.

The following is a brief summary of progress during the last quarter. A detailed report of this work has been prepared*, and copies may be obtained from J. L. McElroy of PNL.

Phases for Cesium and Ruthenium Fixation - S. A. Gallagher, R. G. Johnston and G. J. McCarthy

Of a number of Ru-containing phases and solid solutions studied to date, one, SrRuO_3 , stands out as the best candidate for Ru fixation in supercalcine. Virtually no weight loss is recorded on firing SrRuO_3 in air at 1100°C for days, whereas RuO_2 (the Ru phase found in ordinary waste calcine) would be totally lost to vaporization in less than a day at that temperature. SrRuO_3 has the perovskite structure. Its solid solution behavior with the other perovskite structure phases formed in fired waste calcine and supercalcine and their effect on its thermal properties are being studied.

Cesium Aluminosilicates for Cs Fixation - G. J. McCarthy, D. E. Pfoertsch and C. A. Smith

It now appears that aluminosilicates are the best candidates for fixing Cs in stable, leach-resistant crystalline phases in supercalcine. There are

* G. J. McCarthy, Advanced Waste Forms Research and Development, Annual Report, COO-2510-5, June 11, 1975, 43 pp.

many ways in which the necessary alumina and silica may be added to the liquid waste. It is expected that some alumina-silica sources will react with cesium more readily than others.

Three classes of alumina-silica sources will be surveyed: phyllosilicates (clays, alkali-exchanged micas), tectosilicates (zeolites, alkali-exchanged feldspars and feldspathoids), and alumina-silica solutions-suspensions and dessicated gels. Clays and zeolites have long been used for Cs fixation in nuclear waste management. Reports of any relevant studies are being collected and solicited.

Several experiments have been performed with a selection of clay minerals obtained from campus sources and collections:

Kaolinite - Commercial Georgia Kaolin - $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$

Halloysite - Wagon West, Colorado - $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$

Pyrophyllite-1 - Commercial LAVITE used in high-pressure studies

Pyrophyllite-2 - Mineral specimen from Robbins, North Carolina

Montmorillonite - Belle Fourche, South Carolina - nominally

$(1/2\text{Ca},\text{Na})_{0.67}\text{Al}_{3.33}\text{Mg}_{0.67}\text{Si}_8\text{O}_{20}(\text{OH})_4$; the Ca, Na, Mg are variable, and it often contains small amount of Fe.

Montmorillonite-2 - Upton, Wyoming

Bentonite - "Volclay" Black Hills, South Dakota - clays with exceptionally high cation exchange capacity whose main constituent is montmorillonite.

Samples of these dried (but not dehydroxylated) powdered clays are suspended in water, mixed with various proportions of CsNO_3 solutions, dried, calcined and fired. The reaction containers are examined for signs of Cs volatilization, and the products are checked for " CsAlSiO_4 " and $\text{CsAlSi}_2\text{O}_6$ (pollucite) formation by X-ray diffraction. The following are highlights of the work completed during the last quarter.

- All of the clay - CsNO_3 samples gave a well-crystallized Cs aluminosilicate when fired at 1050°C for 2 hr and a moderately crystallized phase after 950°C for 2 hr. Some crystallization was noted when pyrophyllite - CsNO_3 samples were heated at 800°C for 2 hr.
- " CsAlSiO_4 " is not a stoichiometric phase and has at least two composition-dependent polymorphs. Near-stoichiometric CsAlSiO_4 has the hexagonal or orthorhombic symmetry ascribed to this phase in several previous studies, while Cs deficient " $\text{Cs}_{1-x}\text{AlSiO}_4$ " has the cubic or pseudocubic symmetry originally thought characteristic of this phase. The homogeneity range, thermal stabilities and crystallography of these phases are being studied.
- Some clays show a strong topotactic (structural) control over phase formation. For example, in spite of the fact that pyrophyllite has an $\text{Al/Si} = 1/2$ and should form pollucite ($\text{CsAlSi}_2\text{O}_6$) with an equimolar amount of Cs, it first forms the Cs-deficient (cubic) phase " CsAlSiO_4 " which slowly converts to $\text{CsAlSi}_2\text{O}_6$ on further heating.

Based on the clay samples studied to date, we conclude that there are no major differences in the ability of each of the clays to form aluminosilicates for Cs fixation at a typical supercalcine processing temperature (1050°C). But montmorillonite and bentonite would be our first choices for forming $\text{CsAlSi}_2\text{O}_6$ (pollucite) and halloysite for forming CsAlSiO_4 , based on the degree of crystallinity obtained and on the formation of the stoichiometric stable phase. These clays will be tested in compatibility studies and supercalcine formulations.

Compatibility Studies - G. J. McCarthy and M. T. Davidson

To rationally design supercalcine formulations it is necessary to know which are the most stable phases formed in the complex oxide systems made up of waste and proposed additive cations.

Twenty-four reactions have been studied to date. From these, two illustrative examples will be discussed below.

Zirconia is one of the major components of PW-4b calcine. In many of the supercalcine formulations studied to date, SrZrO_3 has been identified in the products when Sr had been used as a MoO_3 -fixation additive. Which oxide has a greater SrO affinity, MoO_3 or ZrO_2 ?

Run CS-5 exhibits the simple behavior described by the above reaction. SrO reacts preferentially with MoO_3 , leaving ZrO_2 unreacted. This means that in supercalcine formulations only the Sr necessary for MoO_3 fixation must be added without the need for concern that it will react with ZrO_2 rather than MoO_3 .

As described below, a successful preliminary supercalcine formulation recently developed uses Sr+Al+Si as the only additives, with the objective of forming pollucite for Cs fixation and SrMoO_4 for MoO_3 fixation. It was essential to know first whether a mixture of the appropriate components would actually react to form $(\text{CsAlSi}_2\text{O}_6 + \text{SrMoO}_4)$ and whether these two phases are compatible over the 1050 to 1200°C firing range.

After the solutions containing the appropriate cations are dried and calcined, pellets pressed from the powders are heated in Pt foil cups contained in high silica refractory bricks. When Cs is a component in any run, we use a fresh brick and carefully note its appearance. A white "stain" in the vicinity of the pellet indicates Cs volatilization from the pellet and reaction with the brick.

The diffractograms of CS-19 showed well crystallized pollucite ($\text{CsAlSi}_2\text{O}_6$) plus SrMoO_4 at both temperatures, confirming the proposed reaction and demonstrating the compatibility of the two phases. There was no stain observed on the brick, implying that Cs was adequately "fixed" by this alumina-silica source in a sufficiently refractory phase. The results of this run and of several promising supercalcine runs based on it led to the preparation of supercalcine formulation 75-1.

Supercalcine Formulations - G. J. McCarthy and D. E. Pfoertsch

Nineteen possible supercalcine formulations have been evaluated since the last report and several of the most recent look very promising.

The major problem to date in supercalcine development has been finding the right group of additives to react with Cs preferentially to form a sufficiently refractory phase so that no Cs is volatilized during firing at 1050 to 1200°C. At present a run is considered successful if it shows no volatilization on firing of any waste species during the silica tube test (described in the last quarterly progress report). By this criterion several successful formulations have been developed using strontium nitrate, aluminum nitrate and a silica sol (LUDOX) to modify the liquid waste composition. The waste formulation used is a simplified version of PW-4b containing only RE^{3+} , Zr, Mo, Ce, Cs, Fe, Sr, Ba, PO_4 , Cr, K (for Rb) and Ni. Based on these successful runs, a preliminary supercalcine formulation, 75-1, has been prepared for submission to PNL. Briefly, it calls for 2.5 times the $[Al \text{ (as } Al(NO_3)_3) + 2Si \text{ (as LUDOX-AS)}]$ necessary for pollucite formation with Cs to be added to the waste liquid. The Sr added is about 1.5 times that necessary for $SrMoO_4$ formation. This formulation has about 70% waste loading.

The phase assemblage after firing of this formulation includes a phase not proposed when the formulation was specified and not previously observed in our studies. By considering the positions and intensities of the reflections, it was identified as having the apatite structure type similar to that of a samarium silicate we studied some years ago.* After further study, the best match of the data was found to be with a group of alkaline earth-rare earth silicates.** The stoichiometric analogy of this phase to apatite is not obvious and requires defects ($\square$) on two of the crystallographic sites:

M = Sr, Ba

RE = La, Ce (?), Pr, Nd

* G. J. McCarthy et al., J. Inorg. Nucl. Chem., vol. 29, p. 253, 1967.

** D. A. Grisafe and F. A. Hummel, Am. Mineralog., vol. 55, p. 1131, 1970.

It is likely that when this type of phase is prepared from a complex waste formulation other substitutions take place and some or all defect sites are filled. Since there are coupled defects on both cation and anion sites, the latter is especially likely. For this reason we have introduced another phase shorthand notation, A_{ss} = apatite structure solid solution, rather than reporting a unique composition and stoichiometry.

This A_{ss} phase is apparently very stable, since it occurred in almost every supercalcine run in which SiO_2 was used as an additive (see below). Nothing is known of its compatibility with Cs aluminosilicates and little is known about the cations (especially Cs) which may be substituted in solid solution with it. For these reasons some of our time in coming months will be spent on crystal chemical and compatibility studies involving this solid solution phase.

Crystalline Phase Formation in Heat-Treated Waste Glasses and Waste-Glass Composites - G. J. McCarthy and C. A. Smith

Part of our effort continues in support of crystallization aspects of the glass waste form programs at PNL. This work has a direct link to our purely crystalline waste form because many of the phases found to be exceptionally stable in silicate-containing supercalcine formulations could be the same as those observed to crystallize from waste-containing silicate glasses.

A heat-treated zinc borosilicate - PW-4b glass waste form studied some time ago by X-ray diffraction showed beginning crystallization at $\sim 650^\circ C$ with the appearance of a scheelite structure phase, S_{ss} (probably $(Sr, Ba, Ca, RE, Na)MoO_4$). At higher temperatures a fluorite structure phase, F_{ss} (probably $(Ce, RE, Zr)O_{2-x}$), also appears. Willemite (Zn_2SiO_4) is added to these phases after heat treatment above $\sim 800^\circ C$. A small amount of undissolved (?) RuO_2 is noted in each heat-treated glass sample. Zn_2SiO_4 is the only phase not also observed in our fired waste calcine and supercalcine studies; Zn has never been used as an additive.

A sample of the "glass-sintered" waste form under study at PNL* has been analyzed for crystalline phase formation. It was prepared from a mixture of 75-10 frit and PW-4b-2 calcine pressed and fired at 875°C for 2 hr.* The product showed relatively good crystallization despite the rather low firing temperature and short time. This could be due largely to the familiar "mineralizing" effect of the alkalis Na and K in the frit and calcine. There was also a broad maximum in the diffractograms characteristic of the presence of noncrystalline phases (glass and amorphous oxides).

All of the major crystalline phases were identified. The probable compositions of the four major phases were:

1. F_{ss} (5.35) $(Ce, RE, Zr)O_2$
2. S_{ss} $a_o = 5.26\text{\AA}$ $(Sr, Ca, Ba, RE, Na)MoO_4$
 $c_o = 11.94\text{\AA}$ scheelite structure
3. S_{pss} $a_o = 8.36\text{\AA}$ $(Ni, Zn, Mg, Co)(Fe, Cr)_2O_4$ - spinel structure
4. $REBSiO_5$. This phase occurs in nature as the mineral stillwellite $(La, Ce)BSiO_5$.

These four phases account for ~90 wt% of the crystalline phase assemblage. A number of weak unindexed reflections are also observed. Zircon ($ZrSiO_4$) could account for some of them, but we cannot identify this phase unambiguously. Phases which might have been expected but were not present include wellemite (Zn_2SiO_4), Na_2MoO_4 , $P_{ss}(Sr, Ca)ZrO_3$, $P_{ss}(NdFeO_3)$ and the silicate apatite structure phases such as $(Sr, Ca)_3RE_6Si_6O_{24}$.

The presence of phases made up of components from the glass frit and the waste calcine (S_{ss} and stillwellite) confirms the SEM observations and the conclusion of Ross that there is considerable reaction between these two constituents of the sintered waste form.

Again we note that F_{ss} , S_{ss} and S_{pss} have also been observed in our other crystalline phase formation studies. Stillwellite has not been noted previously, but then boron has never been a component in any formulation.

* W. A. Ross, in Quarterly Progress Report Research and Development Activities Waste Fixation Program, J. L. McElroy, Compiler, BNWL-1871, p. 39, November 1974.

SYSTEMS SAFETY EVALUATION

*The purpose of the Systems Safety 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 and cost implications of these systems. Currently, the likelihood and consequences (risk) of potential release incidents are being estimated for a reference system for the management of high-level waste that includes liquid storage through retrievable surface storage operations.**

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

The objective of this effort is to develop a suitable automated methodology for evaluating large fault trees representative of complex waste management facilities and operations. The approach is to develop a computer code system capable of importance-screening very large numbers of failure sequences (cut sets). The screening is to be based on a crude measure of risk rather than on probability or consequences individually. Cut sets so identified as constituting relatively high risk will be retained for more detailed analysis.

Computer Code System

A computer code system for screening and then ordering the myriad failure sequences (cut sets) associated with large fault trees has been developed. (See Figure 27.) Code FAULT, for identifying cut sets, is a Pacific Northwest Laboratories (PNL) improved version of TREEL-MOCUS.**,[†] The capacity has been greatly increased, and an improved routine for counting the cut sets in a tree prior to analysis has been added. Also, PNL-derived equations,

* The reference system is described in previous WFP Quarterly Progress Reports, BNWL-1761, BNWL-1809, and BNWL-1826.

** P. Chatterjee, Fault Tree Analysis: Min Cut Set Algorithms, ORC 74-2, University of California, Berkeley, CA, January 1974.

[†] J. B. Fussel et al., MOCUS-A Computer Program to Obtain Minimal Sets from Fault Trees, ANCR-1156, Aerojet Nuclear Co., Idaho Falls, ID, August 1974.

FIGURE 27. Schematic of Screening Process

based largely on those in the Reactor Safety Study Draft,^{*} have been added to calculate cut set probabilities. As indicated in the previous report,^{**} on-line and standby components and detection, repair, maintenance and testing, and allowed outage times can be accommodated as well as nonrepairable components (events).

Another code, FAULTG, has been written which, with the use of a new cut set identification algorithm, much more efficiently performs the same functions as FAULT. Output from FAULT or FAULTG includes the cut sets identified

* USAEC, An Assessment of Accident Risks in U.S. Commercial Nuclear Power Plants, WASH-1400, Draft, Appendix II, vol. 1, "Fault Tree Methodology," August 1974.

** Quarterly Progress Report Research and Development Activities Waste Fixation Program, January-March, BNWL-1908, 1975.

and associated probabilities. Provisions are included to screen cut sets using probability and event chain length cutoffs. This screening is accomplished by considering the consequences aspect of risk and, specifically, the maximum inventory of material available for release.

Output from FAULT (FAULTG) is fed into the PNL-developed code RAFT along with release fractions for the basic events comprising the cut sets. The release fractions may have distributed values, each with a conditional probability. These fractions, when coupled with the maximum inventory value, provide the index of consequences. RAFT is then used to combine probabilities and consequences, i.e., provide a risk measure for each cut set and finally rank (order) cut sets in terms of risk.

Figure 28 is a sample fault tree illustrating the use of these codes. The logic description of this tree shown in Table 11 and the input data shown in Table 12 are input into FAULT. In the input data (Table 12) P is the probability of an initiating event, Q the "component" unavailability and M an index of repairability (M=0 for repairable component or event and M=1 if nonrepairable). The output from FAULT for the sample tree is shown in Table 13. The output indicates there are 17 cut sets* with the number of basic events associated with individual cut sets ranging from one to ten. As shown in Table 13, the highest probability, 3×10^{-4} , is associated with a one-term cut set. Since the fault tree is being evaluated on the basis of risk, the reduction to minimal cut sets is not performed.

The output from FAULT plus basic event release fractions and associated conditional probabilities (Table 14) and the total inventory available (e.g., in terms of grams) are input into RAFT. Table 15 gives the RAFT output for the eight highest risk cut sets. Cut set $X_{10}X_{26}$, which has a probability of 6.9×10^{-6} , has the highest risk measure, 1.37 g/year. This latter value represents 57% of the total risk for the sample case. Review of Table 15 shows that the four highest risk cut sets ($X_{10}X_{26}$, X_{10} , $X_{29}X_{30}$, and $X_{11}X_{12}X_{13}$) represent 99% of the total.

* There are actually 18 cut sets, but one redundant cut set is eliminated by the computational algorithm.

FIGURE 28. Sample Fault Tree

TABLE 11. Logic Input for Sample Fault Tree

Gate Name	AND/OR GATE	Gate Inputs (A = Gate, X = Basic Event)						
		A1	A2	A3	A4	A5	A6	X10
A23	OR	A1	A2	A3	A4	A5	A6	X10
A1	AND	A7	X11					
A2	OR	A8	A17	A12	A18			
A3	AND	X1	X2	X3				
A4	AND	X4	X5	X6				
A5	AND	X7	X8	X9				
A6	AND	A13	X14					
A7	AND	X12	X13					
A8	AND	X10	X26					
A9	AND	A14	X17					
A10	AND	A15	X18					
A11	AND	A16	X22	X23				
A12	AND	X11	X25					
A13	AND	X15	X16					
A14	AND	X21	X27					
A15	AND	X19	X20					
A16	AND	X24	X28					
A17	AND	A9	A10	A11				
A18	AND	A19	A20	A21				
A19	AND	X29	X30					
A20	OR	X29	X31	X32				
A21	OR	A22	X30	X32				
A22	AND	X29	X31					

TABLE 12. Probability Data for Sample Tree

Basic Event Name	M*	Probability ($P = \lambda T$)	Component Unavailability
X29	1	.020000000	.020000000
X31	1	.007000000	.007000000
X32	1	.070000000	.070000000
X30	0	.030000000	.008000000
X24	1	.009000000	.009000000
X28	0	0.000000000	.070000000
X19	1	.020000000	.020000000
X20	1	0.000000000	.008000000
X21	0	.010000000	.002000000
X27	0	0.000000000	.200000000
X15	0	.009000000	.003000000
X16	0	0.000000000	.003000000
X11	1	.009000000	.009000000
X25	0	0.000000000	0.000000000
X10	1	.000300000	.000300000
X26	0	.030000000	.008000000
X12	0	.060000000	.008000000
X13	0	0.000000000	.009000000
X7	1	.070000000	.070000000
X8	0	.010000000	.002000000
X9	1	.007000000	.007000000
X4	0	.025900000	.003330000
X5	0	.030000000	.008000000
X6	0	.090000000	.020000000
X1	1	.020000000	.020000000
X2	1	.030000000	.030000000
X3	1	.050000000	.050000000
X22	1	.008000000	.008000000
X23	0	0.000000000	1.000000000
X18	1	.001000000	.001000000
X17	0	.040000000	.007000000
X14	0	.020000000	.007000000

* M = 0, Repairable event
M = 1, Nonrepairable event

TABLE 13. Fault Output (Indicated Cut Sets and Probabilities) for Sample Fault Tree

No.	Probability	Cut Set Components									
1	3.000E-04	X10									
2	6.900E-06	X10	X26								
3	0.	X11	X25								
4	4.600E-04	X29	X30								
5	3.078E-06	X11	X12	X13							
6	3.000E-05	X1	X2	X3							
7	8.540E-06	X4	X5	X6							
8	2.613E-06	X7	X8	X9							
9	3.690E-07	X14	X15	X16							
10	2.520E-06	X29	X30	X31							
11	2.520E-05	X29	X30	X32							
12	2.520E-06	X29	X30	X31							
13	2.520E-05	X29	X30	X32							
14	2.520E-06	X29	X30	X31							
15	1.519E-07	X29	X30	X31	X32						
16	1.519E-07	X29	X30	X31	X32						
17	5.838E-18	X17	X18	X19	X20	X21	X22	X23	X24	X27	X28

TABLE 14. Release Fractions (RF) and Conditional Probabilities (CP) for
Sample Tree, Total Inventory = 1×10^6 grams (Raft Input)

EVENT	RF(1,EVENT)	CP(1,EVENT)	RF(2,EVENT)	CP(2,EVENT)	RF(3,EVENT)	CP(3,EVENT)	RF(4,EVENT)	CP(4,EVENT)
1	1.000000E-03	9.000000E-01	2.000000E-02	1.000000E-01				
2	1.000000E-02	8.000000E-01	1.000000E-01	2.000000E-01				
3	1.000000E+00	1.000000E+00						
4	2.000000E-03	1.000000E+00						
5	1.000000E+00	1.000000E+00						
6	1.000000E+00	1.000000E+00						
7	1.000000E-01	9.000000E-01	2.000000E-01	1.000000E-01				
8	1.000000E+00	1.000000E+00						
9	1.000000E-04	9.000000E-01	1.000000E-03	9.000000E-02	1.000000E-02	1.000000E-02		
10	1.000000E-03	9.900000E-01	1.000000E-01	1.000000E-02				
11	2.000000E-02	1.000000E+00						
12	1.000000E+00	1.000000E+00						
13	1.000000E+00	1.000000E+00						
14	1.000000E-03	1.000000E+00						
15	1.000000E+00	1.000000E+00						
16	1.000000E+00	1.000000E+00						
17	1.000000E+00	1.000000E+00						
18	1.000000E-03	9.000000E-01	1.000000E-02	1.000000E-01				
19	1.000000E+00	1.000000E+00						
20	1.000000E+00	1.000000E+00						
21	1.000000E-03	9.500000E-01	2.000000E-02	5.000000E-02				
22	1.000000E-04	8.000000E-01	1.000000E-03	1.000000E-01	1.000000E-02	1.000000E-01		
23	1.000000E+00	1.000000E+00						
24	1.000000E-03	8.000000E-01	5.000000E-03	1.000000E-01	1.000000E-02	7.000000E-02	1.000000E-01	3.000000E-02
25	1.000000E+00	1.000000E+00						
26	1.000000E+02	1.000000E+00						
27	1.000000E+00	1.000000E+00						
28	1.000000E+00	1.000000E+00						
29	5.000000E-04	9.000000E-01	3.000000E-03	1.000000E-01				
30	1.000000E+00	1.000000E+00						
31	1.000000E+00	1.000000E+00						
32	1.000000E-03	9.000000E-01	7.000000E-03	9.000000E-02	3.000000E-02	1.000000E-02		

TABLE 15. Raft Output (Ordered Risk Values) for Sample Tree (Values Shown for Only Eight Cut Sets)

CUTSET PROBABILITY = UNAVAILABILITY TERM = FAILURE SEQUENCE ; LARGEST 2 RISK(S) 6.900E-01 6.831E-01	6.900000E-06 0. 10 26 CONTRIBUTING RELEASE FRACTION(S) 1.000E-01 1.000E+02 1.000E-03 1.000E+02	Accumulative Risk Fraction = TOTAL RISK FOR FAILURE SEQUENCE= 5.724710E-01 1.373100E+00	} Risk for two member cut set $X_{10}X_{26}$ is 1.37 (Prob. = 6.9×10^{-6}); highest risk cut set 57 percent of total risk.
CUTSET PROBABILITY = UNAVAILABILITY TERM = FAILURE SEQUENCE ; LARGEST 2 RISK(S) 3.000E-01 2.970E-01	3.000000E-04 0. 10 CONTRIBUTING RELEASE FRACTION(S) 1.000E-01 1.000E-03	Accumulative Risk Fraction = TOTAL RISK FOR FAILURE SEQUENCE= 8.213714E-01 5.970000E-01	
CUTSET PROBABILITY = UNAVAILABILITY TERM = FAILURE SEQUENCE ; LARGEST 2 RISK(S) 2.070E-01 1.380E-01	4.600000E-04 0. 29 30 CONTRIBUTING RELEASE FRACTION(S) 5.000E-04 1.000E+00 3.000E-03 1.000E+00	Accumulative Risk Fraction = TOTAL RISK FOR FAILURE SEQUENCE= 9.652084E-01 3.450000E-01	
CUTSET PROBABILITY = UNAVAILABILITY TERM = FAILURE SEQUENCE ; LARGEST 1 RISK(S) 6.156E-02	3.078000E-06 0. 11 12 13 CONTRIBUTING RELEASE FRACTION(S) 2.000E-02 1.000E+00 1.000E+00	Accumulative Risk Fraction = TOTAL RISK FOR FAILURE SEQUENCE= 9.908739E-01 6.156000E-02	
CUTSET PROBABILITY = UNAVAILABILITY TERM = FAILURE SEQUENCE ; LARGEST 1 RISK(S) 1.708E-02	8.539600E-06 0. 4 5 6 CONTRIBUTING RELEASE FRACTION(S) 2.000E-03 1.000E+00 1.000E+00	Accumulative Risk Fraction = TOTAL RISK FOR FAILURE SEQUENCE= 9.979945E-01 1.707920E-02	
CUTSET PROBABILITY = UNAVAILABILITY TERM = FAILURE SEQUENCE ; LARGEST 4 RISK(S) 1.200E-03 5.400E-04 4.800E-04 2.160E-04	3.000000E-05 0. 1 2 3 CONTRIBUTING RELEASE FRACTION(S) 2.000E-02 1.000E-01 1.000E+00 1.000E-03 1.000E-01 1.000E+00 2.000E-02 1.000E-02 1.000E+00 1.000E-03 1.000E-02 1.000E+00	Accumulative Risk Fraction = TOTAL RISK FOR FAILURE SEQUENCE= 9.990101E-01 2.436000E-03	
CUTSET PROBABILITY = UNAVAILABILITY TERM = FAILURE SEQUENCE ; LARGEST 2 RISK(S) 1.134E-03 7.560E-04	2.520000E-06 0. 29 30 31 CONTRIBUTING RELEASE FRACTION(S) 5.000E-04 1.000E+00 1.000E+00 3.000E-03 1.000E+00 1.000E+00	Accumulative Risk Fraction = TOTAL RISK FOR FAILURE SEQUENCE= 9.997981E-01 1.890000E-03	
CUTSET PROBABILITY = UNAVAILABILITY TERM = FAILURE SEQUENCE ; LARGEST 1 RISK(S) 3.690E-04	3.690000E-07 0. 14 15 16 CONTRIBUTING RELEASE FRACTION(S) 1.000E-03 1.000E+00 1.000E+00	Accumulative Risk Fraction = TOTAL RISK FOR FAILURE SEQUENCE= 9.999519E-01 3.690000E-04	

Fault trees of over 3,000,000 cut sets have been successfully screened to less than 100 key sequences using the above code system. The surviving sequences must then undergo a more detailed analysis to improve upon the crude calculations used in the screening process.

Common Mode Failure Analysis

A brief review was completed of current techniques for treating common mode failures (CMFs). Points were reviewed in the PNL risk analysis at which CMF oversights could arise. The present approach for drawing fault trees automatically handles certain types of CMFs. Procedures were scoped out for defending against the remaining types of CMF. Some methodology effort would be required, including development of a computer code to facilitate the automated sorting of factors common to various cut sets, e.g., component location or manufacturer. Flagging of those cut sets which are logical CMF candidates would allow detailed analysis of this much smaller set of failure sequences.

RISK ASSESSMENT - P. J. Pelto, E. S. Murphy, L. V. Kimmel and J. M. Taylor

The objective of this effort is to assess the risk associated with the liquid storage, liquid transfer, solidification, water basin storage, transportation, "offsite" retrievable surface storage, and solids handling activities of the reference system. Fault trees are being used to identify potential failure events, i.e., events that could conceivably result in the release of radionuclides from containment/confinement barriers.

High-Level Liquid Storage and Transfer

Top events of the high-level liquid storage (HLLS) and transfer (HLLT) fault trees were presented in the last quarterly report.* These trees have now been completed. The HLLS tree has yet to be formally reviewed. When the review has been completed, probability and release data will be assigned to the basic events of the tree. The tree will then be analyzed using the computer codes FAULT and RAFT.

* Quarterly Progress Report Research and Development Activities Waste Fixation Program, January-March, BNWL-1908, 1975.

The complete fault tree for the high-level liquid transfer system, based on pipe runs contained by a stainless steel-lined concrete trench, is shown in Figure 29. Because of the different source forms (liquid and gas) for the radioactive material involved, the determination of risk (AXB) required separate analysis to be made for different branches of the tree. The tree located three types of release of radioactive material: release of radioactive material to the air, to ground surface, and to ground water. The initial evaluation of the tree, using computer codes FAULT and RAFT, is given in Tables 16, 17 and 18.

The release sequence or events are ranked in order of severity, the top events in the table being the sequence that releases the most radioactive material.

Solidification

During the last quarter, the fault tree for the solidification (calcination-glass conversion) process has evolved into a final form. Figure 30 presents the top levels of this tree. The tree in its entire form is very complex and quite large, containing 212 separate input events and 215 individual gates, many of which receive multiple use within the tree via transfers. The tree was reviewed by members of the Safety Analysis Staff as well as the Process Demonstration Staff. The input data base has been established, and the FAULT-RAFT analysis process has been initiated.

Water Basin Storage

The water basin storage fault tree was processed through FAULT and RAFT. Loss of cooling and resulting meltdown of canisters seemed to dominate in this initial assessment. The result is tentative until a more detailed treatment of severe external environments is made.

Transportation

For a release of radioactive material to occur during rail transportation of solidified high-level waste from a reprocessing plant to an interim surface storage facility, both the waste canister and the shipping cask must be

TABLE 16. Liquid Transfer - Release of Radioactive
Material to the Atmosphere

RELEASE SEQUENCE

1. Human error (excavation) fails concrete vault, liner and piping.
2. Excavation occurs with deteriorated concrete.
3. Severe environment (earthquake) fails concrete vault, liner, and vapor pipe.
4. Excavation occurs with radioactive material present from leaking concrete expansion joint.
5. Excavation fails concrete vault and liner, with contamination present in trench.
6. Severe environment fails vault and liner, with contamination present in trench.
7. Excavation fails concrete vault, liner and liquid piping with a fraction becoming airborne.
8. Primary failure of liner associated with defective concrete releases contaminated gas to atmosphere.

TABLE 17. Liquid Transfer - Release of Radioactive
Material to Groundwater

RELEASE SEQUENCE

1. Human error (excavation) fails concrete vault, liner and liquid and vapor pipes.
2. Severe environment (earthquake) fails concrete vault, liner, and piping.
3. Human error fails trench liner and vapor piping, with a fraction of vapor entering the ground.
4. Severe environment fails concrete vault and liner, with a failed pipe from corrosion existing.
5. Severe environment fails concrete vault and liner, with failed liquid pipe from manufacturing defect.
6. Defective concrete, primary failure of liner and corrosion failed pipe.
7. Concrete expansion joint failure, primary failure of liner and corrosion failed pipe.
8. Severe environment fails concrete vault and liner with liquid pipe failed from primary failure.

TABLE 18. Liquid Transfer - Release of Radioactive
Material to Ground Surface

RELEASE SEQUENCE

1. Severe environment fails trench, liner, piping and carries radioactive material to surface.
2. Human error (excavation) fails trench, liner and piping and carries radioactive material to surface.
3. Severe environment fails concrete trench, liner with failed liquid pipe from corrosion.
4. Primary failure of liquid pipe. Severe environment fails concrete and liner and carries material to surface.
5. Installation error causes failure of liquid pipe; severe environment causes trench and liner to fail and carries material to surface.
6. Liquid pipe rupture due to blockage and severe environment fails liner and concrete and carries material to surface.

breached. The risk study assumes the following possibilities relative to the condition of these containment barriers during shipment:

- Transportation with good (nondegraded) containment barriers
- Transportation with a good shipping cask and a bad (degraded or breached) canister
- Transportation with a bad (degraded or breached) shipping cask and a good canister
- Transportation with a bad shipping cask and a bad canister.

Initiating events capable of producing containment failure can be grouped in four categories. These categories include:

- Train accidents
- Natural disasters and falling aircraft
- Physical or chemical reactions induced by the radioactive waste
- Monitoring and package closure errors.

A spectrum of radioactive releases from the containment system can be associated with each potential failure sequence identified by the transportation fault tree. The amount of radioactive material released depends on the prior condition of the containment system, on the severity of the initiating event, and on the nature of the interaction of the initiating event

FIGURE 30. Top Levels of Waste Solidification Fault Tree

with the containment system. Failure events which lead to spectrum-type releases are handled in the transportation fault tree by use of inhibit gates. Computer codes used for evaluation of the tree permit assignment of as many as four conditional probabilities and associated release fractions to each logic modifier of an inhibit gate.

A preliminary analysis of the rail transportation fault tree has been performed with the aid of computer codes FAULT and RAFT, and the dominant failure sequences have been identified. Detailed evaluation of the dominant failure sequences is proceeding.

CONSEQUENCES OF RESUSPENSION OF AN AIRBORNE RELEASE - T. W. Horst

Materials accidentally released to the environment can present an airborne hazard in two ways. First, the original release may result in an airborne plume. Further, since the material in this original plume may deposit on the ground, there is an additional potential airborne hazard due to the resuspension and atmospheric transport of the deposited material. The objective of this study is to investigate the relative hazard of the resuspended material compared with that of the original plume.

To assess the relative importance of resuspension to the evaluation of an airborne hazard, resuspension calculations are proceeding which integrate over the same climatological variation in wind speed, wind direction and atmospheric stability used to calculate the original airborne contamination pattern. The average resuspended air concentration may then be properly compared with the original pattern. Activity this quarter has concentrated on creating the computer programs required to facilitate the orderly handling of the various data arrays needed. Programs were developed to calculate and output to magnetic tape the airborne distributions of resuspended material for all wind directions and atmospheric stabilities; to calculate the climatological frequency distribution of wind speed, wind direction, and stability, using Hanford Meteorological Tower data; and to combine the above two codes to obtain climatologically averaged resuspensions. This task is almost completed and results will begin to be available early in the following quarter.

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