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**Quarterly Progress Report
Research and Development Activities
Waste Fixation Program
July through September 1975**

Compiled by
J. L. McElroy
Chemical Technology Department

January 1976

**Prepared for the U.S. Energy
Research and Development Administration
under Contract E(45-1):1830**

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Under Contract E(45-1)-1830

Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151

Price: Printed Copy \$6.00; Microfiche \$2.25

QUARTERLY PROGRESS REPORT
RESEARCH AND DEVELOPMENT ACTIVITIES
WASTE FIXATION PROGRAM
JULY THROUGH SEPTEMBER 1975

Compiled by
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QUARTERLY PROGRESS REPORT
RESEARCH AND DEVELOPMENT ACTIVITIES
WASTE FIXATION PROGRAM
JULY THROUGH SEPTEMBER 1975

INTRODUCTION

This progress report is the twelfth 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, 1908 and 1932.

SUMMARY

Engineering-scale in-canister melting tests were made to evaluate the use of silicon to prevent formation of water-soluble molybdate phases in melts. The tests demonstrated that silicon metal powder added to the feed stock effectively prevents formation of such phases. A test also showed that coatings of ZrO_2 or chromium carbide on stainless steel canisters prevent oxidation during the in-can melting process.

The joule-heated ceramic melter has been at operating temperature for more than 250 days. Difficulties were encountered while melting a batch containing a reducing agent, excessive quantities of which resulted in metal oxide reduction and deposition of molten metal in the melting cavity.

Tests of the spray calciner demonstrated very effective removal of scale by the barrel vibrators. In one run using a larger feed nozzle, a processing capacity exceeding 75 ℓ /hr was achieved.

Thermal analysis of canister design concepts examined effects of type of storage, use of fins, emissivity, canister size and cracks in glass.

Pressurization tests show that all types of calcine can produce very high pressures within the canister unless the calcine is post-treated at temperatures greater than 850°C.

Electrical conductivity measurements of glass frit with and without simulated waste additions were performed. The waste-containing glass has an electrical conductivity a factor of 2 to 3 lower than pure frit. It appears that zinc and/or sodium, potassium, and cesium are the major conducting ions.

Initial studies on the effects of alpha and recoil bombardment (from ^{244}Cm doping) on devitrification of waste-containing glass were completed. The effect of curium is to inhibit the formation of some of the crystalline phases normally observed in as-prepared and devitrified glass without the curium dopant.

The devitrification behavior of a waste-bearing zinc orthosilicate glass is being studied using optical microscopy, electron microprobe, and x-ray diffraction examination. Major phases precipitating during annealing are Zn_2SiO_4 and SnMoO_4 with crystalline CeO_2 and palladium being present in the as-prepared glass.

Fine calcine particles have been agglomerated into larger particles suitable for coating via chemical vapor deposition. Thermal stability tests of nickel and Cr_7C_3 coatings on waste calcine have been conducted, and deterioration has occurred at temperatures as low as 500°C .

Waste-containing pellets have been successfully coated by plasma spraying Al_2O_3 powder. Calculations indicate that plasma spraying of large pellets is feasible on a production scale.

Seven scoping runs made with a disc pelletizer indicate that it can provide a simple, inexpensive process for making high-quality pellets from calcine-frit powders.

Development of an extrusion process for forming waste pellets has started. The problem of nitrate salt mobility was solved by denitration, but the problem of cracking due to the high drying rate and sintering shrinkage remains to be solved.

Risk assessment has been used to systematically identify dominant sequences for the accidental release of radionuclides during the

solidification, basin storage, and rail transport activities of high-level waste management. Release of routine hot cell contamination via failed ventilation system filters is included in all of the dominant operations-related sequences tentatively identified for the solidification activity. Loss of cooling and resulting meltdown of waste canisters dominated the top sequences initially identified for basin storage. A derailment accident where containment barriers are breached by mechanical forces was the top sequence identified for the rail transport.

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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, W. A. Ross

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.

In-can melting test 10 (ICM-10), a summary of which was presented in the last quarterly report, was made to test on an engineering-scale the effects of adding 3 wt%, -325 mesh, silicon metal to the batch to inhibit the formation of the water-soluble molybdate phase that rises to the surface of the melt. The addition resulted in an exothermic reaction seen as bright blue flames on the surface of the melt, and white sparks in the thick smoke above the melt. This burning put a heavy loading of solids into the off-gas. Analysis of these solids showed the major constituents to be cadmium, lanthanum, molybdenum, nickel, tellurium, elemental silicon, and zinc oxide. The exothermic reaction also significantly reduced the power consumption during the melting. No yellow molybdate phase was present on the surface of the melt following the run.

Table 1 summarizes in-can melting run 12. This run was made to further evaluate methods for prevention of the formation of soluble molybdate phases in the product and to evaluate effects of these methods on the in-can melting process. These methods included the use of 75-75 frit in place of 73-1 and the addition of only 1.5 wt%, -325 mesh, silicon metal to the batch. The simulated waste calcine, the frit, and the silicon were blended in a mixer. The canister was charged with 19.7 kg of batch and lowered into the furnace, which was preheated to 1060°C. About 3 1/2 hr were required to melt this batch, giving a melting rate of 5.5 kg/hr. Twenty-three kg of

TABLE 1. Summary of In-Can Melting Run 12

<u>Run Number</u>	<u>ICM-12</u>
Date of Run	8-19-75
Coupled to	Vibra Screw Feeder
Off-gas Treatment	Spray Calciner Filters
<u>Canister</u>	
Diameter, inch	8 Sch. 40
Length, inch	48
Wall Thickness, inch	0.32
Material	304L SS
Fins	None
<u>Batch</u>	
Waste Type	PW-7a-2
Waste Form	Spray Dried Calcine
Waste Oxide-to-Frit Ratio	1:2
Frit Type	75-75
Frit Form, mesh	-6/+20 and -325
Additives	1.5 wt% Silicon (-325 mesh)
Batch Preparation	Mechanically Blended
<u>Operating Parameters</u>	
Time at Melt Temperature, Hr	8
Surface Temperature Range, °C	1000-1085
Nominal Melt Temperature, °C	1050-1065
Batch Feed Method	Batch and Continuous
Batch Conditioning	Preblended
Max. Batch Feed Rate, kg/hr	17.6
Melting Rate, kg/hr	7.7 Batch and 14 Continuous
Max. Power Consumption, kW	13.4
Cooling Rate, °C/hr	
1025 to 750°C	48
750 to 500°C	20
500 to 100°C	7
<u>Product</u>	
Type	PW-7a-2(1:2) 75-75 + 1.5% Si
Weight, kg	49.9
Volume, L	19.2
Bulk Density, g/cc	2.60
Apparent Density, g/cc	
Top	2.54
Middle	3.19
Bottom	3.26
Leach Rate,* Wt% lost in 72 hr	
Top	0.33
Middle	0.41
Bottom	0.51

* Soxhlet Leach Test

batch were then rapidly fed to the canister and melted in 3 hr, giving a melting rate of 7.7 kg/hr. Batch was then fed at rates between 13 and 17.6 kg/hr and melting kept up with the feed rate until it approached 17.6 kg/hr. The canister surface temperatures were maintained at 1065°C while these rates were being determined.

Although foaming of the initial batch was anticipated because of the NaNO_3 content of PW-7a-2 calcine, it did not occur, nor did the rapid exothermic reaction experienced during ICM-10 occur. The atmosphere above the melt was not filled with entrained solids, and only traces of Si and Zn in excess of that present in calcine were found in the deposits on the filters. Bubbles less than 1/2 in. in diameter did burst at the melt surface during the melting. Some of the bubbles left a dark pocket in the melt, while others burst with a blue-white flame which heated the pocket to a brighter orange than the color of the surrounding melt. An exothermic reaction was evidenced also by the relatively low power requirements of the furnace during melting. Fourteen to sixteen kW are usually required, but only 10 to 13 kW were used during melting of ICM-12. The melt was held at 1055°C for 2 hr after the last of the batch was fed to the canister and before the programmed cooling was started.

The product of ICM-12, shown in Figure 1, contains no visible molybdate phase separation, and no cerium oxide clusters are visible in the glass or settled at the bottom of the melt. However, crystals, which are being identified, can be seen throughout the glass. The product has good leach resistance, but the density is lower than those of earlier runs, which are as high as 3.7 g/cc. The upper third of the glass contains many small

FIGURE 1. Product of ICM-12, Opened for Inspection

bubbles, which occur more frequently as the top of the melt is approached. These bubbles indicate that a longer fining period is required for this composition.

A protective coating of zirconia was plasma sprayed onto the exterior of the ICM-12 canister as a 4 in.-wide band around the canister 14 in. above the bottom. The area within the band was prepared by grit blasting; then a nickel-chromium base coat was sprayed onto the surface followed by sprayed ZrO_2 . The coating maintained its integrity throughout the melting process while heavy spalling was observed above and below the band. A section of the coated canister was removed for metallographic examination, and results are shown in Figures 2 and 3. Figure 2 shows the glass-canister interface. Corrosion appears to be occurring on the stainless canister, but it is limited to the surface only. Figure 3 shows the ZrO_2 -canister interface. The ZrO_2 is well bonded to the canister, and the crack observed has occurred in the ZrO_2 rather than through the interface proper. Oxidation of the canister is evident, but this is probably from a previous heat treatment when the canister was unprotected. The test results to date indicate that a ZrO_2 or a chromium carbide coating on the stainless steel in-can melter canisters can eliminate the external spalling problem.

Requirements for a seven-zone, resistance-heated furnace for engineering-scale development of the in-can melting process were prepared and a procurement specification was sent to ten major suppliers with an invitation for quotations. The furnace working chamber will accommodate a canister 8 ft tall by 24 in. in diameter and have controlled cooling for canister quenching and glass annealing studies. Five proposals were received which represent a variety of different heating, cooling and insulating concepts. The proposals are being evaluated.

a. 100X

b. 250X

FIGURE 2. Glass-canister Interface from In-Can Melting Canister

a. 250X

b. 250X

c. 500X

FIGURE 3. Zirconia-canister Interface from In-Can
Melting Canister, Coated after First Heating Cycle

JOULE-HEATED CERAMIC MELTER - G. C. Chapman

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

The ceramic melter presently undergoing testing has been at operating temperature for over 250 days. Difficulties were encountered while melting a batch containing a reducing agent. Excessive quantities of the reducing agent resulted in metal oxide reduction and deposition of molten metal in the melting cavity.

Operation

Since last reporting, five separate melting tests were completed. Additional testing was delayed due to problems with oxide reduction in one of the melting tests. The most significant tests are summarized below.

Addition of Reducing Agent to Batch

Separation of molybdate salts during melting has been a problem with some waste glass compositions. In laboratory tests a reducing agent was found to be a successful additive for eliminating molybdate phase separation. Thus, this approach was attempted in an engineering-scale test in which more than 200 kg of batch with the reducing additive were melted.

Two hours after feeding was started, sudden changes were observed in load resistance through the glass. Load resistance became more and more erratic until the test was ultimately terminated. The load resistance varied between normal and a very low resistance, indicating periodic shorting between the electrodes. The condition worsened until the power level was too low to sustain production melting. When batch feeding was stopped and the cold cap had partially melted, flames at the surface of the molten glass could be observed. This phenomenon continued for over two weeks, but gradually subsided. Analysis of the off-gas and samples of the oxidized residues indicated that zinc, tellurium and cadmium were the primary species which had oxidized at the surface.

In retrospect it appears that an excessive amount of the reducing agent had been added to the batch. Although the reducing agent had successfully

precluded the formation of molybdate salts, the excess had reduced zinc, tellurium, cadmium and other oxides to their elemental state. Since tellurium, zinc and cadmium boil at glass melting temperatures, they boiled to the glass surface and rapidly oxidized. Since this test a molten nickel zinc alloy has been found in pockets in the floor of the melter. After nearly 90 days at temperature, the molten metals on the floor have apparently corroded 1 to 2 in. into the chrome oxide refractory.

Four tests have been completed during the 90 days following the test with the reducing agent, and continued testing is planned. Although the reduction of metal oxides is not expected in the projected solidification process, it provides an opportunity to evaluate the system operation under a severe condition. Because the molten metal is corroding the refractory, it may be possible to evaluate the capability of the wall cooling plates for containing the molten materials.

During the test with the additive the thermowells were completely corroded off at the glass-air interface. This was attributed to dissolution of the metallic thermowells by the molten zinc and tellurium during the experiment. The severely corrosive nature of these molten metals may have also caused significant corrosion to the main electrodes; however, probing of the electrodes under the glass surface does not indicate catastrophic corrosion.

Current Control

Since the difficulties with the reducing agent, the melter has produced over 800 kg of glass in four separate tests. In all of these tests the melter was operated under constant current control. In this control mode, the controller does not require direct measurement within the molten glass as does a temperature control system. Current control has the advantage of controlling the melter completely outside the hot cell without in-cell instrumentation. Although initial temperature monitoring equipment would be required for calibration of a given melter with heat dissipating waste, control could soon be based on the load resistance of the glass monitored outside the hot cell.

Broad variations in sodium content in the waste glass might cause some difficulties. However, if the resistivities of glasses are similar at the desired melting viscosity, current control should be satisfactory. Glasses with sodium oxide content ranging from 3 to 6 wt% have been melted with constant current control without problems.

HEATED-WALL SPRAY CALCINER - L. S. Romero

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 spray calciner was operated 48 hr to convert 960 liters of simulated waste of various feed composition (PW-7a, PW-4b, and Super Calcine) to 510 lb of calcine. The super calcine is a new feed composition* successfully calcined with the developmental spray calciner. Super calcine** is a modified PW-4b feed composition with the addition of "Ludox," an ammonia stabilized silica. The spray calciner demonstrated that super calcine can be produced on an engineering scale without any problems. In a preliminary run employing a larger feed nozzle, the calciner demonstrated a capacity exceeding 75 L/hr using a high-sodium composition feed (PW-7a).

The vibrators were evaluated under scaling conditions using simulated waste composition PW-7a (high sodium content). Scaling conditions were introduced by lowering the atomizing pressure from 36 to 20 psig, thus producing inadequate atomization of the feed. Inadequate atomization produces coarse spray droplets that are not sufficiently dried prior to striking the hot walls. Scale was sighted through a glass view port installed on the top flange of the barrel and detected by the thermocouple located at the nozzle. Even after scaling periods of 4 to 7 hr, the vibrators removed scale that ranged up to 1/2 in. thick, using one 3-sec vibrating pulse. The vibrators are presently located at the center of the barrel.

* G. J. McCarthy, First Quarterly Report, C00-2510-6, p. 29, August 5, 1975.

** G. J. McCarthy, Waste Fixation Program Quarterly Progress Report, January-March 1975, BNWL-1908, p. 61, June 1975.

One of the five air caps of the improved design* made of 96% alumina has accumulated 44 1/2 hr in the spray calciner and 275 1/2 hr in the nozzle test station at feed rates of 15 to 20 liters/hr. No measurable wear has occurred in any critical area of the air cap. The new design has proven successful in eliminating breakage problems.

WIPE 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.

Two series of tests were completed during the report period in the pilot plant facilities of two commercial manufacturers of wiped film evaporators. The purpose was to determine if a simulated high-level waste slurry could be evaporated to a free flowing solid product in a single pass through a wiped film evaporator incorporating the latest commercial evaporator technology.

While both series of tests lacked precision and encountered considerable difficulty in coping with the nitric acid solvent of the feedstock, they did demonstrate that a simulated high-level waste slurry can be evaporated, in a single pass, to a free flowing solid containing from 10 to 20 wt% liquid. Processing rates were estimated to be in the range of 2 to 20 liters/hr ft² of evaporator heat transfer surface.

One series of tests was performed in the Artisan Industries pilot plant in Waltham, Massachusetts, and the other in the LUWA pilot facility in Charlotte, North Carolina. At Artisan Industries, a small horizontal evaporator, a powder Rototherm, was used. The evaporator had 0.88 ft² of heat transfer surface, and the rotor, equipped with a standard ribbon blade, was driven through a Graham variable speed drive with a 10-hp motor. While this unit was equipped with a hot oil heating system, for these tests the heat transfer medium was limited to 120 psig steam (177°C). At the LUWA

* H. T. Blair, Waste Fixation Program Quarterly Progress Report, October-December 1974, BNWL-1893, p. 22, February 1975.

pilot plant two machines were tested, one a 10.8-ft² D-210 Horizontal Dryer, with a rotor containing a standard array of "pusher," "mixing," and "spring" paddles, driven at 350 to 500 rpm with a 7.5-hp Veridrive motor. This unit was heated with 120 psig steam initially, and later with hot oil up to 290°C. The second LUWA machine tested was a 3.0-ft², CP-150 Vertical Dryer, with a rotor fitted with standard, type P, swinging pendulum blades and driven at 1575 rpm with a 5-hp motor. This unit was heated with oil at 290°C. A simulated high-level waste slurry (PW-7-2) was supplied as a feedstock for all the tests at both locations.

A free flowing "dry" powder product was produced by both the Artisan Rototherm unit and the LUWA D-210 Horizontal Dryer when they were operated with 120 psig (177°C) steam in the heating jackets. Operating characteristics of both units were quite similar: their capacity was an order of magnitude less than that anticipated, and much rotor power was required to scrape the dried product from the heat transfer surface.

Generally the product formed was a coarse, granular or flaky material like freeze-dried coffee, but under certain operating conditions a coarse, rolled crumb was produced. The product was a free flowing solid that appeared dry, but actually contained from 10 to 20 wt% of about 17 M nitric acid. The product was highly deliquescent and became soft and sticky quickly on exposure to moist air. Little, if any, denitration of the nitrate salts was achieved in the evaporators, and the products ranged from 55 to 58 wt% oxide, with 100% oxide defined as the material remaining after holding a sample at 900°C for 24 hr.

In both pilot plants, feedstock flow control was inadequate, and sustained or steady-state operating conditions were never achieved. No correlation was realized between the product composition and the estimated feedstock flow rates at the time the product samples were taken. But it is estimated that the maximum capacities achieved were about 20 lb/hr (7 liters/hr)/ft² of heat transfer surface for the Rototherm unit, and about 6 lb/hr (2 liters/hr) for the D-210 Horizontal Dryer. Both units operated with loud scraping noises when producing a dry powder. On

disassembly after the tests, some of the rotor blades of the D-210 Dryer required readjustment. No damage was observed in the Rototherm unit.

While the Rototherm unit was equipped for hot oil heating, the tests with this unit were limited to the use of 120 psig heating steam. The D-120 Dryer, however, was tested with hot oil up to 290°C with a resultant increase in its maximum capacity to about 14 lb/hr (5 liters/hr)/ft². Of most interest was the fact that at the higher temperatures, the input power to the rotor decreased to nearly the same power required to turn the rotor with no feedstock flow to the evaporator. While product composition was essentially unchanged, its appearance changed to a smaller and more uniform size, ranging from a flour-like material to a coarse (1/16-in.) prill. A rough correlation of the capacity of the unit versus the heating oil temperature suggests that a higher capacity for the unit could be realized with temperatures above 290°C. However, the electrical power input to the hot oil system was limited, and higher oil temperatures could not be sustained.

A second LUWA machine was tested, a CP-150 Vertical Dryer. The rotor of this machine was fitted with hinged paddles, somewhat like a swing hammer mill and was driven at 1575 rpm by a 5-hp motor. This unit was tested only with a hot oil heating medium at 290°C. It produced a material that averaged about 11 wt% liquid (17 M HNO_3) and had the very uniform consistency of flour, or balls perhaps 5 to 10 mils in diameter. The capacity reached 32 lb/hr (11 liters/hr)/ft². Again, the electrical power input capacity to the hot oil heating system limited the evaporator's performance. Very little scraping or rotor power increase was noted in the operation of this machine, and no damage to the rotor was observed on disassembly following the brief tests. However, more buildup of solids on the paddles and on the rotor shaft was noted with this machine than with either of the two horizontal machines tested.

In general, the tests were successful in demonstrating that a solid, free flowing product could be realized from a simulated high-level waste slurry in a single pass through a commercially available wiped film evaporator. However, the precision and depth of the tests were so inadequate that capacities and the problems of sustained operations could only be estimated.

RADIOACTIVE DEMONSTRATIONS - D. H. Siemens

The objective of this program is 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

Reactivation of B-Cell in preparation for radioactive demonstration of the spray calciner/in-can melter HLW fixation process continued. Fabrication and installation of the required equipment pieces is about 70% complete.

Negotiations are in progress for radioactive cesium and spent reactor fuel for use as feedstock in the demonstration runs.

CANISTER THERMAL ANALYSIS - J. B. Duffy

The purpose of this work is to predict the thermal performance of various canister design concepts so that an optimum design can be selected.

Thermal modeling of proposed canister designs has been accomplished with the HEAT4 computer program.* This program solves finite difference equations which approximate the partial differential equations for steady-state and transient heat transfer. Variable thermal properties are allowed in the program, such as thermal conductivity, density, specific heat, and internal heat generation as functions of position, temperature, and time. Table 2 lists the values for several thermal properties used in the model. Unless otherwise specified, these values are common to all canister designs studied.

A parametric analysis of canister design was conducted to better understand the variables involved and thus provide a firmer basis for reference

* W. D. Turner and M. Siman-Tov, HEATING3 - An IBM 360 Heat Conduction Program, ORNL-TM-3208, Union Carbide Corporation, Nuclear Division, Oak Ridge, TN, February 1971.

TABLE 2. Canister Modeling Data

GLASS PROPERTIES

Thermal Conductivity (Btu/hr·in.·°F)	0.04466 at 212°F
	0.07974 at 1600°F
	0.07994 at 1742°F
	0.1640 at 1832°F
	0.4800 at 2012°F

(linear interpolation between points)

Heat Generation (W/l)	150 at 1 yr
	77 at 2 yrs
	48 at 3 yrs
	26 at 5 yrs
	15 at 10 yrs

Specific Heat (Btu/lb·°F)	0.28 (constant)
------------------------------	-----------------

Density (lb/in. ³)	0.07225 (constant)
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BOUNDARY CONDITIONS

Ambient Air Temperature	70°F
Radiation Coefficient	$0.833 \times 10^{-11} \text{ Btu/hr} \cdot \text{in}^2 \cdot \text{°F}^4$
Convection Coefficient	$1.319 \times 10^{-3} (\Delta T)^{1/3} \text{ Btu/hr} \cdot \text{in}^2 \cdot \text{°F}$

design selection using 1-year-old waste and 800°C maximum centerline temperature as guidelines.

To provide information on canister diameter selection, two parameters were considered: centerline temperature and usable volume. Previous work has not yielded detailed information on the size and number of fins required for a given canister size. The actual usable area within the canister has thus been unknown. Modeling with the HEAT4 program has sufficiently analyzed fin design to permit prediction of the usable area within the canister. Canister diameters from 4 to 12 in. have been studied. Canisters with a diameter greater than 10 in. require internal fins when their contents have a heat generation density greater than 150 W/liter (1-year waste). Figure 4 shows the increase in usable area as larger canister diameters are used. For canister diameters of 10 in. or less, no fins are required. Hence the usable area (solid line) is 100% of the total canister area (dotted line). As the diameter exceeds 10 in., more fins are required. Thus the usable area becomes a decreasing fraction of the total area. An acceptable

FIGURE 4. Canister Volume Versus Diameter
for Canister with Internal Fins

fin design has been found for the 12-in. canister. This design calls for 4.5-in. x 1/4-in. suspended fins at a 45° spacing, a total of 8.94 in.². This leaves a usable area of 103 in.². The usable area for canister diameters greater than 12 in. has not yet been calculated, but it is expected that a 14-in. diam finned canister will have about 122 in.² of usable area and that the percent of usable area will rapidly decrease with increasing canister diameter.

Figure 5 shows the glass centerline temperatures for nonfinned canisters in both ambient air and water storage modes. The 12-in. finned canister is also shown for both storage modes. To keep the glass temperatures below the recommended 800°C, fins are needed for any canister diameter greater than 10 in. during air storage (12 in. during water storage).

Obviously, the storage mode selected as the design condition influences the canister diameter to be selected. Although the principal storage mode for the canisters is a water bath, process requirements and credible accidents will cause the canisters to be stored for some time in ambient air.

FIGURE 5. Glass Centerline Temperatures Versus Canister Diameter (1 Year Waste)

Following the "worst-case" design philosophy, it is recommended that air storage be used as the design condition. Other parameters to be considered include the thermal safety factor desired and the canister volume desired. (Note that a 12-in. finned canister provides twice the usable volume as the nonfinned 8-in. canister with about the same glass temperature.) A 12-in. diam canister with internal fins is currently considered the reference design.

The storage performance of the 12-in. reference canister is shown in Figure 6. Both ambient air (21°C) and water (54°C canister wall temperature) storage modes are shown. It is seen that air storage increases the glass centerline temperature to a value only about 50% higher than the water storage. Since the reference canister was designed from an air storage basis, removal of the canister from liquid storage (or loss of coolant) does not create an unacceptable temperature rise in the glass. If the canister were to be designed strictly for water storage, the fin configuration would undoubtedly be changed and it would not perform well when removed from water. The temperature distribution for the reference canister submerged in water is shown in Figure 7. From this curve it appears that an optimum water storage design would probably allow the fins greater spacing.

FIGURE 6. Thermal Performance of 12-in. Diam Reference Canister

FIGURE 7. Temperature Distribution, 12-in. Diam Reference Canister in Water

During air storage, axial convection effects at the canister outer surface could produce significantly hotter ambient air temperatures at the upper portions of the canister. Figure 8 shows the effect of an increased ambient air temperature on the centerline and surface temperatures of the reference canister. These canister temperatures are not affected much by higher air temperatures. Axial effects due to convection are thus not expected to be a problem during air storage periods.

Surface emissivity of the canisters is a property which could pose problems. An emissivity of 0.7 was assumed for the reference canister because of a lack of measured values. An earlier report on the Waste Solidification Program (BNWL-1583) indicates that an emissivity of 0.6 may be appropriate. As seen in Figure 9, the canister temperatures are not increased much by such a small change. However, several factors could conceivably cause the surface emissivity to drop significantly (especially spalling, oxidizing and other phenomena which occur during the thermal processing of the canister.) If these phenomena caused the surface emissivity to drop as low as 0.2, some modifications would be required on the reference design (closer fin spacing). Surface emissivity of the canisters is thus a property to be investigated, but one which can be compensated for fairly easily. During water storage, of course, a low emissivity would not affect the canister performance.

Fracturing has been observed in the solidified glass matrix. The possible thermal effects of such cracks were investigated analytically by modeling a complete (360°) fracture in the glass across which only radiation heat transfer can occur (a vacuum gap). Figure 10 shows the effect of such a crack in an 8-in. nonfinned canister. A 120°C temperature drop is seen at the crack (located at a radius of 2.00 in.), which causes a nearly equal rise in the centerline temperature. Figure 11 shows a similar crack for the 12-in. reference canister. The 12-in. canister, which is finned, shows only a 12°C temperature drop at the crack and a 6°C rise in centerline temperature. This low temperature change is due to the fins, which provide continuity through the crack. Although glass fractures have been found, thermal effects such as those illustrated in Figures 10 and 11 have not been observed. It must be assumed that either the fracture surfaces remained in intimate contact or that the canister instrumentation has not detected such phenomena.

FIGURE 8. Effects of Ambient Air Temperature, 12-in. Reference Canister

FIGURE 9. Effects of Surface Emissivity, 12-in. Reference Canister

FIGURE 10. Thermal Effects of Glass Cracking, 8-in. Nonfinned Canister

FIGURE 11. Thermal Effects of Glass Cracking, 12-in. Reference Canister

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.

PRESSURIZATION POTENTIAL OF CALCINE - W. A. Ross

The potential pressurization of canisters by the thermal decomposition of residual anions in a calcine waste form has been investigated.

Calcined waste oxides contain three major types of volatiles. The major problem is residual nitrates, most likely NaNO_3 and CsNO_3 , which are not decomposed at the current calcining temperatures. They do not appear to decompose until temperatures are sufficient to allow a compound such as Na_2MoO_4 to form. Water is also present in the calcine to a degree which varies with humidity and temperature. The third source of gas is a carbonate. It is not known which element(s) forms the carbonate; however, it is likely that the carbonates may be forming in fluidized beds with in-bed combustion since carbonates have been shown to form at calcining temperatures in gas absorption studies.*

To determine the pressurization potential of various calcines, an apparatus was built which contained calcine in small-diameter thick-walled vessels connected by small-diameter tubing to a pressure transducer. The vessels were inserted into a programmed furnace. The program increased the

* G. L. Tingey and W. D. Felix, "Radiolytic Gas Generation," Waste Fixation Program Quarterly Progress Report, January-March 1975, BNWL-1908, pp. 46-47, June 1975.

temperature in steps of about 100°C and remained at each temperature until pressure equilibrium was obtained or approached. At temperatures below 600°C, equilibrium could be obtained in one hour or less; however, at higher temperatures, equilibrium was only approached since time at temperature was limited to 7 hr. Figure 12 shows the increase in pressure with time at 830°C for a PW-7-2 fluid bed calcine. The results of runs with various types of calcine are shown in Figure 13. The values shown have been corrected for the effect of having a volume external to the furnace (the transducer). This is only 7% at 200°C but amounts to 31% at 820°C. There was some potential of water vapor condensing outside of the furnace system and reducing pressure, but no values for this effect were determined. There were also indications that some of the gases may have been reacting with the steel, lowering the effective pressure. Because of these and other effects the data could be lower than would result in larger diameter canisters. Each type of calcine seems to have its own behavior pattern. The fluidized bed calcines and laboratory prepared calcines have lower pressures below 500°C due to their longer

FIGURE 12. Pressure Increase with Time for PW-7-2 (Fluid Bed) Calcine at 830°C

FIGURE 13. Decomposition Pressure in Sealed Calcine Canisters

exposure at calcining temperatures than the spray calcines. The maximum pressures can be correlated to sodium content. PW-4b has the lowest sodium, PW-7 next, and PW-7a has the highest sodium content. During the run with PW-7a the test had to be terminated due to the very high pressure being generated at 820°C. Pressures at higher temperatures were not measured because of the reduced strength of the vessels.

Total gas volumes for the calcines were determined at 1000°C by collection of the gases over oil and are compared to NO_3^- and H_2O content in Table 3. The gas release as a function of temperature is shown in Figure 14. Again, equilibrium in the 650 to 850°C interval was not obtained even though samples were allowed to remain at temperatures for periods up to 3 days. The amount of gas generated is expected to be a function of the time-temperature history for the material. Increased times and temperatures

TABLE 3. Calcine Gas Generation Potential at 1000°C

Calcine Type	NO ₃ ⁻ Content, Wt%	H ₂ O Content, Wt%	Gas Volume at STP cc/g
PW-7a-2 (Spray Calcine)	15.7	0.67	81.0
PW-4b-3 (Spray Calcine)	2.53	0.51	7.9
PW-7-1 (Laboratory Calcine)	0.79	0.35	7.0
PW-7-2 (Fluid Bed Calcine)	5.14	0.34	13.1

FIGURE 14. Offgas from PW-7-2 Fluid Bed Calcine

favor the decomposition of the NO_x gases into N₂ and O₂, which increase the number of moles of gas and, of course, the volume and/or pressure. The values reported should, therefore, be used as guides only and not as absolute values.

One possible method to stabilize the calcine is to heat it high enough to decompose the gases just before sealing. Tests of this concept were

made by heating the vessel to a desired temperature and leaving it open to the atmosphere. After 2 hr at the increased calcining temperature the vessel was sealed, the transducer connected, and the temperature increased to 830°C. The resulting pressures are shown in Figure 15. From these results it can be concluded that temperatures of about 850 to 900°C would be required to form a "stable" calcine.

FIGURE 15. Effect of Higher Calcining Temperature on PW-7-2 Fluid Bed Calcine

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

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

Elevated temperature, long-term storage of PW-4b-6(2.8)73-1 glass has been started, and the first samples have been removed for characterization. The specimens were sectioned into TOP, MIDDLE, and BOTTOM layers. Each

layer is currently undergoing tests to determine its physical and chemical properties. X-ray diffraction and electron microprobe are being used to determine the extent of chemical segregation and devitrification. Density, porosity, and Soxhlet leach rate are being measured for each zone. Long-term leach tests will be started next quarter.

PHASE BEHAVIOR - R. P. Turcotte and J. A. Campbell

The phase behavior task is directed toward general understanding of the glass making and devitrification processes. The effort will be aimed primarily toward determination of phase separation by microscopy, microchemical analysis (i.e., microprobe-x-ray fluorescence), and x-ray diffraction methods.

Microstructural Analyses

A major effort will be the study of devitrification in glass 72-68, prepared initially at 1000°C, with portions subsequently annealed at temperatures 400 to 1000°C and examined as a function of time. The samples prepared were sectioned into top, middle, and bottom fractions (of the original crucible melt). The top fractions have been examined during the past month.

In Figure 16, bright field micrographs at 200X show contrast differences for at least six phase types, depending on treatment. The as-prepared glass (1000°C) contains a great deal of very fine undissolved material of light and dark contrast (cerium-rich and ruthenium-rich); large chunks of a rhodium-rich phase; small, frequently spherical Pd metal deposits; and occasional pieces of stainless steel which probably come from the walls of the crucible. The relative microprobe analyses are given later. At lower temperatures, there is little apparent change in any of the separate phases already present in the as-made glass. A dendritic molybdenum rich phase and/or a zinc rich phase, however, become dominant features. It is particularly clear in the 900°C, 1-day micrograph that the Zn_2SiO_4 phase does cause extensive cracking and can provide a bubble trapping interface. In other devitrified samples obtained at temperatures under 800°C, the Zn_2SiO_4 occurs in a much finer dispersion and crack development is significantly less.

1000°C, 4 hours

900°C, 1 week

250 μm

900°C, 1 day

800°C, 1 day

FIGURE 16. Devitrification Micrographs (200X), Glass 72-68

We have so far completed detailed microprobe analyses on only two samples, one being the glass as-prepared, the other devitrified one day at 800°C. X-ray maps of all cationic elements present were obtained except for boron (which cannot be done by fluorescence methods). Table 4 lists elements for which evidence of significant phase separation was obtained. Except for the rare earths, which have interferences from preceding elements in the series (palladium and silver also have contributions from rhodium), the analysis is fairly straightforward. In addition to mapping of regions for a given element, direct counting of all major species in a given particle (phase) was used to obtain a more quantitative analysis.

TABLE 4. Glass 72-68 Phase Separation

Elements in Glass Solution			Elements with Major Concentration as Separate Phases
Na	P	Y	I. Ru
K	Te	La	II. Ce
Rb	Si	Pr	III. Rh, Zn, [Fe], [Cr], [Ni]
Cs	Ag	Nd	IV. Pd
Mg	Cd	Sm	V. Zn, Si
Ca	Zr	Gd	VI. Mo, Sr
Ba	Ni	U	
Fe	Cr		

Examples of x-ray maps showing phase separation are given in Figure 17 for the 800°C devitrified sample. All optically discernible features correlate well to the various elemental concentrations, most easily seen by comparison to a light microscope (optical image) similar to those given in Figure 16. The major new phases other than those present in the as-made glass are the molybdenum-rich and zinc-rich regions.

The analytical results for all phases observed (corrected in some cases for matrix contributions) are given in Table 5 and for the glass matrix in Table 6. Although not entirely satisfactory, the numerical results are generally reasonable. The measured mass ratios for the SrMoO_4 and Zn_2SiO_4 devitrification products agree well with chemical formulae (verified by the

FIGURE 17. Microprobe X-ray Maps, Glass 72-68 (Devitrified)

x-ray diffraction patterns) for the molybdate, but not so well for the silicate phase. The absolute values (Table 5) are often low due to contributions from the glass matrix which can only be approximately subtracted. As a second iteration, we will select samples with physically large examples of a given phase type to eliminate matrix contributions and where possible, provide phases observed in pure form to serve as standards.

TABLE 5. Glass 72-68 Phase Analyses

Phase/Main Element	Major Elements in wt%	Sample Type	Maximum Mole % Possible	Probable Compounds (wt% M)
I/Ru	Ru(79)	1000°C 4 hr	0.7	RuO ₂ (76)
II/Ce	Ce(70+)	800°C 1 day	1.4	CeO ₂ (81)
III/Rh	Rh(56), Zn(17), Fe(2)	800°C 1 day	0.1	--
	Rh(61), Zn(17), Fe(2), Cr(2)	1000°C 4 hr		
IV/Pd	Pd(94), Zn(2?)	1000°C 4 hr	0.5	Pd (100)
V/Mo	Mo(27), Sr(23), Ca(2?)	800°C 1 day	0.9	SrMoO ₄ (35)(39)
VI/Zn	Zn(45), Si(13)	800°C 1 day	14.6	Zn ₂ SiO ₄ (59)(13)

The results given in Table 6 suggest that ~ one-half the cerium is in glass solution, essentially no ruthenium is dissolved, two-thirds of the palladium precipitates as metal (dissociation pressure for $\text{PdO} \rightarrow \text{Pd} + 1/2\text{O}_2$ reaches 1 atm O_2 at 875°C) and while a rhodium-rich phase (III) is observed, the significance of the matrix analyses for concentrations ~0.5 wt% is clearly questionable. The changes with devitrification (comparing 1000°C to 800°C) suggest that one-third of the zinc crystallizes as Zn_2SiO_4 , and that 25% of the strontium, and 37% of the molybdenum precipitate. (Note that the stoichiometry of SrMoO_4 requires $\text{Sr}/\text{Mo} = 1$.) Except for the analysis of cerium, which should be good, the rare earth values do not appear meaningful, nor do several other low concentration species.

X-ray Diffraction Analyses

The objective of this subtask is to obtain a direct correlation between structural (diffraction) behavior and the microstructural studies above.

Figure 18 compares a vitreous sample held at 1000°C for 2 hr (A) and the devitrified sample of glass at 800°C for 1 day (B). The patterns are

TABLE 6. 72-68 Glass Matrix Compositions, wt%

Element	Concentration As Weighed	1000°C, 4 hr ^(b)	800°C, 1 day ^(b)
Na	3.06	3.8	3.7
Mg	0.90	1.0	0.9
Rb	0.21	-	-
Si	13.0	16.9	17.9
Sr ^(a)	1.86	2.0	1.5
Y ^(a)	0.06	0.2	0.3
P	0.19	0.2	0.2
Zr	2.43	1.6	1.8
Mo	2.86	1.9	1.2
Ru	1.50	0.1	0.1
Rh	0.26	0.2	0.2
Pd	0.85	0.3	0.2
Ag	0.06	0.2	0.2
Cd	0.05	0.3	0.2
K	3.42	3.6	3.7
Ca	1.07	1.0	1.0
Te ^(a)	0.38	0.3	0.3
Cs ^(a)	1.80	2.6	2.3
Ba	2.27	1.8	1.7
La	1.65	1.1	0.6
Ce	3.13	1.1	1.6
Pr ^(a)	0.33	0.2	0.9
Nd ^(a)	1.15	2.1	3.5
Sm	0.20	0.7	0.7
Gd	0.14	0.5	0.3
Fe	0.70	0.6	0.7
Ni	0.07	0.3	0.2
Cr	0.16	0.2	0.1
Zn	17.4	16.9	11.6
U	1.31	1.3	1.1

a. 1000°C glass (72-68) as standard

b. Mean of 3 determinations

averaged from slow scan diffractometer traces (G.E., Cu) and Debye Scherrer films (114 mm), relying on the diffractometer for intensity estimates. If one looks for similarities in the two diffraction patterns, it is apparent that both samples contain a fluorite type phase with a lattice parameter close to that for CeO₂ (a). The 1000°C, 2-hr vitreous sample (A) also has palladium metal present (b). The 800°C, 1-hr sample has SrMoO₄ (d) and

FIGURE 18. Diffraction Patterns for Vitreous and Devitrified Glass 72-68. A--1000°C, 2 hr, vitreous; B--800°C, 1 day, devitrified. Dashed lines indicate unidentified reflections. a--CeO₂; b--Pd; c--Zn₂SiO₄; d--SrMoO₄

Zn₂SiO₄ (c) present, but neither of these phases is found in the vitreous sample. The dashed lines have not yet been indexed. The intensities of the diffraction patterns are not normalized to a common scale. For example, the peak intensities for the vitreous samples on an absolute basis are much lower than patterns for devitrified samples.

The results obtained from the x-ray powder diffraction patterns can be correlated with those obtained by the use of microscopy. Of the phases listed in Table 5, we are able to identify II (CeO₂), III (Pd), V (Zn₂SiO₄), and VI (SrMoO₄) as being present. The rhodium-rich phase (III) is in such low absolute concentration that identification by diffraction methods is unlikely.

RADIATION DAMAGE - R. P. Turcotte and J. A. Campbell

The objectives of the investigation of radiation damage to simulated waste glass include structural damage studies (^{244}Cm doping, alpha bombardment), helium diffusion work and determination of actinide location.

We determined last quarter that diffraction patterns from 1 wt% Cm and undoped samples were markedly different. A thorough analysis is given this quarter. The curium-doped samples were obtained by vitrification in air at 1200°C, the undoped at 1000°C, both being held at temperature ~4 hr. No compositional differences should exist. The discussion given in the Phase Behavior section of this report should generally apply to the results given in this section.

The vitreous samples, with and without curium present, are compared in Figure 19. For the sample with 1 wt% $^{244}\text{CmO}_2$ (A), neither the fluorite-type structure nor palladium is present as in the vitreous sample containing no curium (B). It is observed that several unidentified reflections (dashed lines) are common to both samples. Comparing the two patterns shows that more than one phase is involved. Microprobe analysis was started on curium doped samples to resolve such differences.

The diffraction patterns and phases identified in devitrified samples C (700°C, 7 days, 1 wt% curium) and D (750°C, 9 days, no curium) are given in Figure 20. Zn_2SiO_4 (c), SrMoO_4 (d) and a fluorite-type structure (a) were all found in sample D. The Zn_2SiO_4 (c) phase was not found in sample C. Although there is good reason to expect eventual amorphization of any silicate related crystalline structure, it will be surprising if Zn_2SiO_4 is not formed since it is the major devitrification product in undoped glass. The thermal treatment (700°C) should be a strong enough driving force to eliminate most structural damage, and the x-ray pattern (C) was taken within a few hours of removal from the annealing furnace. We will repeat the experiment, but with a very short interval between removal from the furnace to taking the diffractometer scan. Also, a devitrified undoped sample will be α -bombarded using our $^{238}\text{PuO}_2$ source to obtain a time dependence for any structural changes.

FIGURE 19. Diffraction Patterns for Vitrified Samples with and without Curium. A--Vitreous, 1 wt% Cm; B--Vitreous, no Cm. Dashed lines indicate unidentified reflections. a-- CeO_2 ; b--Pd; c-- Zn_2SiO_4 ; d-- SrMoO_4

FIGURE 20. Diffraction Patterns for Devitrified Samples with and without Curium. C--Devitrified 700°C , 1 week, 1% Cm; D--Devitrified 750°C , 9 days, no Cm. Dashed lines indicate unidentified reflections. a-- CeO_2 ; b--Pd; c-- Zn_2SiO_4 ; d-- SrMoO_4

The present devitrified sample (Cm-doped) was reexamined one month after preparation. No major differences in the diffraction pattern were observed.

ELECTRICAL CONDUCTIVITY OF MOLTEN NUCLEAR WASTE GLASSES - J. L. Bates

The electrical conductivity of molten waste glass is important in the design and operation of Joule-heated, electric, waste glass melters; in the production of quality-controlled nuclear waste glasses; and in understanding the properties of the solid and molten waste glasses.

The purpose of this study is to determine the electrical conductivity of some simulated nuclear waste glass compositions including the basic waste-free frit. The compositions and sources of the waste glasses tested are summarized in Table 7.

Measurement Technique

The electrical conductivity was measured in air using two parallel platinum plates immersed to a known depth into the molten glass.

The resistance between the two electrodes was measured using two different techniques.

- A direct measurement of resistance was obtained using a milliohm meter. The current leads were attached to the voltage probes. The measurements were made at 40 Hz. Resistance was read directly to $\pm 3\%$ and no external reference resistor or oscillator was inserted into the measurement circuit. Resistance values were limited to 1000 ohms or less.
- A direct measurement of resistance was obtained using an impedance bridge at 1000 Hz. Resistance values were accurate to $\pm 1\%$, and measurements could be made from 10^{-3} to 10^{-6} ohms. DC measurements were obtained with the resistance being measured after the dc current had been applied for one minute. The dc resistance changes with time resulting from polarization effects if the glass is wholly or partially ionic.

TABLE 7. Composition of Waste Glasses

Waste Glass	Oxide																															
	SiO ₂	ZnO	B ₂ O ₃	Na ₂ O	K ₂ O	CaO	MgO	SrO	BaO	MoO ₃	La ₂ O ₃	ZrO ₂	CeO ₂	Fe ₂ O ₃	Nd ₂ O ₃	NiO	TeO ₂	Pr ₆ O ₁₁	P ₂ O ₅	Cr ₂ O ₃	CoO	Al ₂ O ₃	CdO	Sm ₂ O ₃	Gd ₂ O ₃	Eu ₂ O ₃	MnO ₂	Cs ₂ O	Ag ₂ O	Y ₂ O ₃		
73-1 ^(a) Frit	37.0	28.9	15.1	5.5	5.5	2.0	2.0	2.0	2.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ICM-0 ^(b)	25.4	19.3	10.1	3.7	4.9	1.5	1.3	2.3	2.8	5.7	5.4	4.6	4.2	2.9	2.1	0.9	0.7	0.7	0.4	0.3	0.3	0.1	0.1	-	0.2	-	-	-	-	-	-	-
ICM-3 ^(c)	27.8	21.7	11.3	4.1	4.1	1.5	1.5	1.5	2.6	4.6	2.3	3.6	4.5	2.4	1.6	0.8	0.5	0.5	0.5	0.3	0.2	-	0.1	-	0.2	0.1	-	0.8	-	-	-	-
ICM-6 ^(d)	26.7	20.9	10.9	4.2	4.1	1.4	1.4	2.2	2.5	3.7	2.7	3.5	5.4	2.4	1.9	0.7	0.4	0.6	0.5	0.3	0.3	-	0.1	0.3	0.2	0.1	0.4	2.2	-	-	-	-
ICM-7 ^(e)	24.7	19.3	10.1	3.7	4.4	1.3	1.3	2.0	2.3	3.9	5.6	3.0	6.3	2.9	4.2	0.6	0.4	0.3	1.6	0.2	0.2	-	0.1	0.7	0.5	-	-	-	-	0.1	0.3	

a. Waste-free glass frit.

b. Synthetic waste glass with frit to PW-4b waste ratio of 2:1.

c. In-can waste glass melt #3 with frit to PW-4b waste ratio of 3:1.

d. In-can waste glass melt #6 with frit to commercial waste ratio of 2.6:1.

e. In-can waste glass melt #7 with frit to PW-7-2 waste ratio of 2:1.

Results

The electrical conductivity results for the glass frit 73-1 without waste are shown in Figure 21. The conductivity varies as a function of frequency, especially at the higher temperatures, with the dc measurements demonstrating the lowest conductivity values and the highest being measurements at 1000 Hz. This is consistent with the assumption that the conduction is highly ionic. The effect of frequency is larger above 800 to 900°C, with the values at 40 and 1000 Hz identical below 800°C. The dc conductivity is lower by a factor of about 10 and shows hysteresis effects at the lower temperatures.

The dc electrical conductivity is very time dependent, decreasing with time. The values in Figure 21 represent resistances one minute after the voltage was applied.

FIGURE 21. Electrical Conductivity of Molten 73-1 Glass Frit without Waste as a Function of Frequency

The electrical conductivities for the in-can melted waste glasses, ICM-3, ICM-6, and ICM-7 were the same within experimental error at all temperatures (Figures 22 and 23). These molten waste glasses also exhibit a frequency dependence similar to the waste-free frit, 73-1, but the magnitude was not as great as that for the waste-free glass. The electrical conductivity of these waste glasses is less than that of the waste-free frit and greater than that of the laboratory-prepared PW-4b waste glass (ICM-0). The electrical conductivity at 40 Hz for the 73-1 frit is less at high temperatures than the other waste-containing glasses; however, at 1000 Hz the conductivity is higher at all temperatures. The cause of these unusual frequency effects is not understood but presumably relates to the degree and type of ionic conductivity in the melts.

FIGURE 22. Electrical Conductivity of Molten Waste Glasses, ICM-0, ICM-3, ICM-6, and ICM-7 at 1000 Hz

FIGURE 23. Electrical Conductivity of Molten Waste Glasses, ICM-0, ICM-3, ICM-6, and ICM-7 at 40 Hz

The addition of simulated nuclear waste to the glass frit decreases the electrical conductivity by only a factor of two to three. This relatively small decrease is undoubtedly related to the presence of some one or more metal conducting ions present in the waste-free glass frit which make it highly conducting even before the waste is added. The fact that the electrical conductivity decreases suggests that a dilution of this metal occurs when waste is added or that the waste inhibits the carrier movement.

Most silicates, both solid and liquid, conduct electrically by the diffusion of metal ions, in particular the alkali metals. Other metals which often can contribute to conduction in silicates are iron and zinc. The waste free frit (73-1) contains significant amounts of zinc, potassium, and sodium which can conduct independently or collectively. As a comparison, the compositions of these glasses for these elements are summarized in Table 8. The combined combination of alkali metals (sodium, potassium, cesium) is nearly identical for all the waste and frit glasses. Only when zinc alone or zinc plus alkali metals are compared is the concentration of potential carriers higher in the 73-1 frit, thereby resulting in a higher conductivity. Iron appears to have no major effect. Thus it might be concluded that zinc, alone or combined with sodium, potassium, and cesium, is the major conducting ion.

TABLE 8. Combined Alkali, Iron, and Zinc Compositions for Waste Glasses

Waste	Zn wt%	Na ₂ O+K ₂ O+Cs ₂ O wt%	Na ₂ O+K ₂ O+ Cs ₂ O+ZnO wt%	Na ₂ O+K ₂ O+ Cs ₂ O+Fe ₂ O ₃ wt%	Na ₂ O+K ₂ O+Cs ₂ O+ ZnO+Fe ₂ O ₃ wt%
Frit (73-1)	28.9	11.0	40.0	11.0	40.0
ICM-0	19.3	11.5	30.8	14.4	33.7
ICM-3	21.7	11.4	33.1	13.8	35.5
ICM-6	20.9	12.7	33.6	15.1	36.0
ICM-7	19.3	11.0	30.3	13.9	33.2

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.

Along with the ongoing long-term compatibility tests designed to determine the inside corrosion of waste canisters, coupons formed into U-bend specimens are being exposed to air over a range of temperature and time. The effects of these variables on the propensity for stress corrosion cracking are being determined. These data will be useful in determining the outer surface corrosion of waste canisters during the time they are stored in water.

Specimens were fabricated from 304L, 304, 321, Incolloy 800, and Inconel 600 and are being exposed at 238, 427, 538, and 705°C. Exposure times will range from one to >10,000 hr. The degree of sensitization produced by the heat treatment is being determined by exposures to boiling 65 wt% HNO_3 or, for Inconel 600, to boiling $\text{H}_2\text{SO}_4 - \text{Fe}_2(\text{SO}_4)_3$ solution. U-bend specimens fabricated from the exposed coupons are being exposed to air-saturated water at 80°C containing 100 ppm chloride to determine the propensity for stress corrosion cracking.

Table 9 gives the sensitization data, as determined by Huey tests. One or more of the heat treatments evaluated resulted in extreme sensitization of 304, Incolloy 800, and Inconel 600. Sensitization of 321 was relatively mild, whereas sensitization of 304L was somewhat more severe. U-bend specimens with the same heat treatments given in Table 9 are being exposed to air-saturated water at 80°C containing 100 ppm chloride. Also, some specimens are being exposed which were previously exposed to one of the thermal treatments and then to $\text{HNO}_3\text{-Cr(VI)}$ solution to produce intergranular attack. Failure occurred in 2 weeks with 304 and 304L specimens subjected to a heat treatment at 1000°C for 10 and for 100 hr. No other failures have occurred after 9 weeks exposure even though other specimens showed a much higher degree of sensitization as determined by the Huey test. During the last 4 exposure weeks, the pH of the test solution was changed from 7 to 4 by adding potassium acid phthalate.

TABLE 9. Huey Tests of Candidate Canister Alloys after Heat Treatment: Corrosion Rates in Boiling 65% Nitric Acid^(a)

Heat Treatment	304 L	304	321	Inc 800	Inc 600 ^(b)
1) As mill annealed	0.5	0.7	1.8	0.2	28
2) 1 hr at 705°C	12.7	100 ^(d)	2.6	100 ^(d)	62
3) 10 hr at 705°C	12.9	100 ^(d)	2.8	12.1	2000 ^(c)
4) 100 hr at 705°C	17.2	100 ^(d)	4.3	1.7	4000 ^(c)
5) 1 hr at 538°C	0.5	0.8	2.1	0.2	39
6) 10 hr at 538°C	0.7	0.8	2.5	0.2	52
7) 100 hr at 538°C	6.0	8.2	3.7	2.9	53
8) 100 hr at 427°C	0.5	0.7	2.3	0.2	22
9) 1000 hr at 427°C	0.6	0.8	2.8	0.4	22
10) 10000 hr at 427°C	---	---	---	---	---
11) 100 hr at 238°C	0.5	0.8	2.4	0.3	26
12) 1000 hr at 238°C	---	---	---	---	---
13) 10000 hr at 238°C	---	---	---	---	---

a. Average of (five) 48-hour exposures

b. 24-hour exposure to boiling 50% H_2SO_4 containing 40 g/liter $Fe_2(SO_4)_3$

c. Three-hour exposure

d. Specimen consumed before test was completed

A specimen of Alonized mild steel (aluminum-rich layer) was obtained from the Alon Processing Company and exposed for 24 hr at 1100°C to a melt prepared from PW-4b calcine and 73-1 frit. That portion of the specimen exposed to the vapor phase was essentially unattacked, whereas the Alonized layer and about 25% of the steel was lost from that part of the specimen exposed to the melt phase. Uncoated mild steel exposed to a similar melt was attacked catastrophically in the vapor phase, the penetration rate being about 100 mils/hr.

As a part of the long-term compatibility tests in progress to determine the inside corrosion of canisters exposed to calcine and to glass, eight canisters were removed from the test for evaluation after 3-month exposure at 705°C. Severe external oxidation was noted. When the canisters were opened, it became apparent that the enclosed corrosion coupons had been exposed to a temperature in the melting range. New test canisters were prepared for exposure.

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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.

In the concept currently being developed the waste is formed into a small granule or pellet which is coated with a nonradioactive inert material to provide containment and leach resistance. The coated waste shape is then incorporated into a metal matrix which provides impact resistance and increased thermal conductivity.

DEVELOPMENT OF COATED WASTE PARTICLES - W. J. Gray

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.

Fine (probably $<10\text{ }\mu\text{m}$) calcine particles have been successfully agglomerated in a fluid-bed at Battelle-Columbus Laboratories into larger particles suitable for coating. This was done by dripping a water-glass solution into the bed, thereby producing agglomerated particles containing some SiO_2 . Work on agglomeration, as well as additional work on coatings, will continue at BCL.

Waste particles coated with nickel and Cr_7C_3 have been heated in air for one week at 800 and 500°C. The 800°C heat treatment almost totally destroyed the coatings, and there was some degradation even at 500°C. This is apparently due to formation of a nonprotective chrome oxide.

Future BCL efforts will concentrate on coatings of SiO_2 and Al_2O_3 because these two materials are geologically among the most durable.

Particles coated with SiO_2 have already been produced at BCL, but the coatings have not stood up well to 500 and 800°C heat treatments. However, there is no apparent reason why good SiO_2 coatings cannot be produced, and one of the goals in the near future will be to demonstrate this.

Meanwhile, we will try to obtain at least semiquantitative values for expected lifetimes of coatings under realistic leaching conditions. In this regard, carbon would appear to be even better than SiO_2 and Al_2O_3 ; thus carbon and perhaps SiC will be included in this evaluation.

WASTE COATING EVALUATIONS - J. J. Rasmussen

Studies have been undertaken the past quarter to evaluate the potential for applying a protective coating by plasma spraying individual waste particles. Efforts to date indicate that application of a spray coating is feasible. Calculations were made to determine the size of the waste particles that would be required to have a reasonable production rate for spray coating. It was assumed that Al_2O_3 would be a typical protective coating because of its refractory nature, low cost, and chemical inertness. This material can be sprayed typically at rates from 1 to 11 kg/hr. Assuming a spray rate of 6.8 kg/hr and a coating thickness of 0.0254 cm, the Al_2O_3 spray would cover an area of $6.734 \times 10^4 \text{ cm}^2/\text{hr}$. Using a waste-frit particle density of 2.5 g/cm^3 , Table 10 was calculated to determine the weight of waste which could be coated for different sized spherical particles.

TABLE 10. Particle Size, Waste Quantity Relationship for Spray Coatings with Al_2O_3 at 6.8 kg/hr to Thickness of 0.025 cm

Particle Diameter, cm	Number of Particles/hr	Weight of Waste/hr, kg
10^{-3}	2.14×10^{10}	2.81×10^{-2}
10^{-2}	2.14×10^8	2.81×10^{-1}
10^{-1}	2.14×10^6	2.81
1	2.14×10^4	28.1
10	2.14×10^2	281

Under the conditions assumed, 6.7 metric tons of waste could be coated per 24-hr day by a single gun for 1-cm-diam particles. To obtain the rates of production required for a waste processing facility, it is obvious that particles on the order of centimeters in diameter will be required if a plasma spray protective coating is desired.

Simulated waste-glass frit pellets were prepared by cold pressing and sintering by the Nuclear Waste Processing Section. The pellets were right circular cylinders, about 1 in. long, with curved ends, and just over 1 in. in diameter. Room temperature pellets were sprayed initially. A nickel-chromium base coat was sprayed onto a pellet without any problem. However, when the higher melting point Al_2O_3 was sprayed, the pellet literally disintegrated into powder plus a few chunks of intact material. A chromium carbide coating was then sprayed. One pellet broke up into several large fragments, and a second formed cleavage cracks without separating completely.

A second coating attempt was made using Al_2O_3 . The pellets were preheated in a small furnace to 500°C. One pellet was coated with the Ni-Cr base coat and then coated with Al_2O_3 . The Al_2O_3 appeared to bond well without producing pellet fracture. A second pellet was sprayed directly with the Al_2O_3 without using a base coat. Again the bonding appeared to be good and there was no fracture of the pellets. Apparently the preheating can overcome the problems with failure of the waste pellets by thermal shock. The pellets were returned to the furnace after coating and furnace cooled.

PELLET FORMING PROCESSES - W. A. Ross

The advanced waste form concept requires dense pellets suitable for coating and incorporation into a metal matrix. Various pellet forming methods are being developed and tested and will be compared to identify the best pellet forming process. Pellet forming by cold pressing and extrusion are reported in this section.

The extrusion process for pellet forming has several advantages which make it attractive. These include 1) the ability to work with wet materials--this avoids dusting and calcining problems, 2) the ability to process large

quantities of material in a small simple unit, and 3) the ability to make both large and small diameter pellets. A currently envisioned process flow diagram is shown in Figure 24. In the process, liquid waste is denitrated with formic acid then evaporated to a sludge. The sludge is mixed with glass frit which stiffens it and prepares it for extrusion. The extruded cylindrical column is cut into short lengths which are dumped into a rotating pan which rounds the pellets to avoid sharp corners. The formed pellets are then dried and sintered.

FIGURE 24. Process for Forming Pellets by Extrusion

Laboratory tests of the process have been conducted with both liquid waste and wiped film evaporator products. It was determined that without the denitration step, soluble nitrate salts were migrating with the water to the exterior surface of the pellets, where they were deposited as the water evaporated. This produced a very friable scum which was not adherent after drying or sintering. Denitration has prevented this from occurring.

The mixture (after the addition of about 40 wt% frit based on metal oxide content) contained about 35 wt% moisture and was sufficiently plastic that adding binders or plasticizers was unnecessary. The material appeared to extrude best at high rates, but tests to this point have been limited to a simple chamber which produces a 1/2-in.-diam column and does not have the capability for de-airing.

Drying of the pellets must occur rather slowly since they shrank about 12% diametrically as the ~35% water was removed. Rapid drying of fresh 1/2-in.-diam pellets by exposure to 120°C flowing air produced numerous cracks. Slow drying in room air was successful. An optimum drying rate will depend on the size of the product and has not yet been determined.

Sintering at 875°C produced pellets with densities of 3.0 to 3.3 g/cc. During sintering the pellets shrank about 25% diametrically. This high sintering shrinkage coupled with a high drying shrinkage produced numerous cracks. Future tests should be directed at preventing cracking.

Problems with cold pressing large (~1-1/4") spherically ended pellets have been partially solved, and pellets formed from a mixture of PW-7a-2 calcine and frit have been sintered to high density without obvious laminations or cracks. A green reaction product formed at the interface of the pellets and the Al_2O_3 setting sand has been identified as principally Na_2MoO_4 .

DISC PELLETTIZER EVALUATION - A. A. Garrett

The disc pelletizer is being evaluated to determine if it can provide a simple way to make pellets from a mixture of calcine and frit powders. The pellets would then be sintered, coated and incorporated in a metal matrix prior to terminal storage.

Pelletizing fine powders for dust control and handling convenience has been employed since the early 1900s. Today disc pelletizing has replaced older pelletizing techniques in many industries because of its high efficiency and overall simplicity. A typical disc pelletizer (as shown in Figure 25) uses a rotating, flat bottom pan inclined so as to induce the

FIGURE 25. PNL Disc Pelletizing System

feed to roll and tumble. Low-density "seeds" are formed as powdered feed enters the pan. The rolling-tumbling action plus the addition of a binder from a fine spray nozzle causes the "seed" to form tiny composted spheres. As the damp spheres roll across new feed material, they grow due to the snowballing effect. Mature pellets continuously spill from the pan's lower side.

Finished pellets are uniformly sized, tightly packed spheres. Pellet size and to some extent pellet quality are controlled by four variables: pan (disc) angle and speed, feed location, and binder spray location. All four variables depend on each other and on the feed material. Maximum unfired (green) strength results (other factors being constant) when all pore spaces in the pellet are completely filled with binder liquid (water, acrylic emulsions, etc.). The amount of liquid necessary to fill the pores is referred to as the Critical Volume (CV). A new CV must be experimentally determined whenever particle size characteristics of the feed material change.

This first phase of disc pelletizer evaluation is aimed at discovering how the four machine variables affect pellet size and quality when pelletizing various high-level waste calcine-frit feed materials and at determining the critical binder volume for those feed materials.

Run Description

Table 11 lists the conditions and objectives of the seven pelletizing runs made so far. These initial runs served to "calibrate" the pelletizer system using calcine and frit powders.

TABLE 11. Summary of Pelletizer Runs

<u>Run Number</u>	<u>Duration, hr</u>	<u>Feed Material</u>	<u>Binder</u>	<u>Objective</u>
1	3	-325 mesh frit	Water	System shakedown.
2	5	-325 mesh frit	Water	Adjust plow depth. Determine effects of disc speed.
3	2	-325 mesh frit	Water	Determine critical moisture for -325 frit, and determine effects of disc speed.
4	4	-325 mesh frit	Water	Determine effects of spray position.
5	1	-325 mesh frit	Water	Determine effects of feed input location and disc angle.
6	1	50 wt% frit 50 wt% -200 PW-4b-c	Water	Produce 1/4-in.-diam pellets for coating at Battelle Columbus. Determine Critical Moisture for 50/50 calcine-frit mixture.
7	2	50 wt% frit 50 wt% -200 PW-4b-c	Water	Produce smallest possible pellet.

Due to the high cost of feed material and the need for relatively long runs to allow equilibrium to be re-established when control changes were made, runs were designed to minimize throughput. Hence all were made at about 15 kg of solids per hour.

We used water as a binder for the first seven runs simply because it was convenient and produced satisfactory results. Future plans call for evaluating the effectiveness of other binders.

Since some constituents in the simulated calcine are somewhat toxic, pelletizing was done inside a dust hood. In general the operation produced very little dust, and finished pellets are essentially dust free.

Control Variables

Pellet size and quality are operator-controlled parameters which can be varied simply by changing one or more of the control variables: disc slope and speed, feed location, and spray location. One of our first tasks was to determine the range and effect of each variable when pelletizing a "standard" material, -325 frit. This was achieved by making small step changes in one variable while holding the others constant. After each step change and when equilibrium was reestablished, pellet samples were taken, then another step change was made. Changes in the pellet samples were correlated with the variable changes and the procedure was repeated for each variable.

- Disc Speed. Changes in disc speed cause little effect in pellet size and quality; however, speed control proved essential in regulating the amount of material reaching the plows and hence forming the desired material flow pattern in the pan. Generally higher disc speeds are required when making small pellets than when making large pellets. Acceptable disc speeds ranged from 30 rpm when producing small pellets to around 15 rpm when making large pellets.
- Pan Slope. The pan slope seems to affect pellet density more than pellet size. Decreasing the slope increases the effective pan depth, resulting in an increase in the depth of solid material in the pan. Added weight from this extra material increases the compaction forces on the pellet, resulting in a higher density product than is obtained with steeper pan slopes. Good quality, high density frit pellets were produced using pan angles between 45° and 50°. Small pellets result from larger angles, while large pellets are produced by smaller angles.
- Feed and Spray Locations mainly determine pellet size. Figure 26 shows the feed and spray locations on our pelletizer system which yield high quality pellets. "Large," "medium," and "small" refer to the pellet

FIGURE 26. Disc Pelletizer Feed and Spray Locations

size resulting from placing the feed and spray inputs in the designated areas. A large grid chart similar to Figure 26 is placed over the pelletizer pan to make feed and spray location changes. Appropriate x-y coordinates precisely define each location. For example, to make the smallest possible pellets, the feed input would be located at 4.8, (x-4.8, y-1.5) and the spray nozzle located at 5.3, 4.0. Also the pan angle would probably be set at 50° and the pan speed near 30 rpm. Generally the disc pelletizer can produce pellets as small as 0.1 cm and as large as 4.0 cm in diameter; of course in some instances, feed material characteristics may limit the possible size range.

Critical Binder Volume

The critical volume (total pore volume in a finished pellet) was calculated and determined experimentally for pure -325 mesh frit and for a

50-50 wt% mixture of -325 mesh frit and minus 200 mesh PW-4b-c calcine. These values are listed in Table 12. The calculated values are based on estimated bulk and theoretical densities for the powdered materials; consequently, some disagreement between the calculated and measured results should be expected. The low critical volume for the 50-50 mixture is attributed to the higher packing density achieved when two powders with different sized particles are mixed.

TABLE 12. Critical Binder Volume for Two Materials

Material	Critical Volume ($\frac{\text{cm}^3 \text{ pore space}}{\text{g solids}}$)	
	Calculated	Measured
100 wt% -325 mesh frit	0.35	0.14
50 wt% -325 mesh frit and 50 wt% -200 mesh PW-4b-c calcine	0.30	0.12

Fired Properties

Several batches of different sized pellets containing 50 wt% frit and 50 wt% PW-4b-c calcine were fired at temperatures between 650 and 900°C. See Table 13 for specific firing conditions, fired densities, and pellet strengths. Initially pellets were placed on an alumina bed to prevent their sticking together. However, sticking proved to be insignificant below about 850°C; thus use of the alumina bed was stopped, and the pellets were permitted to touch each other during firing. Pellet strength appears to increase with firing temperatures up to about 850°C; then slumping begins to occur. Values in Table 13 indicate that fired density is affected more by pellet size than by firing temperature. This rather unexpected result may be due to variations in the pelletizing operation rather than an actual trend. Most pellets produced to date are by-products of learning how to operate the disc pelletizer; consequently, their properties may vary unexpectedly.

TABLE 13. Firing Tests

Description	Temperature (°C)	Time at Temperature (hours)	Fired Density	Comment
5 mm pellets on alumina powder in stainless steel pan	700	3.0	2.7	Slight sticking to alumina. Requires moderate blow with 16 oz. hammer to fracture pellet.
1 cm pellets on alumina powder in stainless steel pan	680	3.0	---	No sticking - some loose calcine on surface.
7 mm pellets on alumina powder in stainless steel pan	725	2.5	2.6	Slight sticking. Requires moderate blow with hammer to fracture.
7 mm pellets in alumina crucible	725	2.5	2.6	Same as above.
1-2 mm pellets in alumina crucible	725	2.0	2.8	Slight sticking. Pellets cracked due to high heat ramp.
1-2 mm pellets in alumina crucible	800	1.0	---	Same as above.
0.75-1 mm pellets in alumina crucible	650	4.5	---	Requires light blow from hammer to fracture.
7 mm pellets in alumina crucible	825	3.0	2.6	Moderate sticking. Very hard pellets.
7 mm pellets in alumina crucible	900	3.0	---	Pellets slumped. Extensive melting - very high porosity.

Figure 27 shows photomicrographs of a 1-cm pellet fired to 700°C for 3 hr. Considerable porosity is present in the pellet; however, most of the pore cells appear to be closed, and part of the porosity resulted from grains which fell out during polishing due to insufficient sintering. Pellets sintered at 825°C show less porosity. It is also felt that the porosity may be further reduced by proper selection of frit particle sizes to insure the maximum packing density. "Grains" showing scratch marks are actually pores filled with epoxy to prevent additional grains from falling out.

FIGURE 27. Photomicrograph 1-cm Pellet of 50 wt% PW-4b-c and 50 wt% 75-75 Frit Sintered at 700°C for 3 hr

METAL MATRIX - K. R. Sump

The purpose of this study is to develop a metal matrix for increasing the thermal conductivity and impact strength of containers of high-level waste.

The metal matrix is dependent on the characterization of the waste particle and upon any coating of the particle. The selection of the matrix material is also quite dependent on the past and future thermal environments that the HLW particle has seen or will see.

The current view is that the particles will be coated, roughly spherical, 1 to 25 mm in diameter, and will have been outgassed/sintered at 900°C. The surface of the container will never exceed 815°C during storage. It also appears desirable, for optimum reaction and strength, that the matrix never be permitted to melt during storage.

Matrix Materials

Suggested matrix metals along with their melting points and relative cost per volume are given in Table 14. All of the matrix metals in Table 14 could melt during storage except for pure copper, pure iron and the steels.

TABLE 14. Matrix Melting Points and Costs

<u>Metal</u>	<u>Melting Point, °C</u>	<u>Relative Cost per Unit Volume</u> ^(a)
Aluminum	660	1.0
Antimony	630	8.0
Copper	1083	4.1
Lead	327	2.0
Manganese Bronze	870	4.3
Iron	1536	0.6
Alloy Steel	>1400	~0.7
Stainless Steel	>1400	3.8
Zinc	420	2.0

a. Based on aluminum = 1.0

Process Selection

Many processes are available for fabricating a metal matrix in an HLW container. However, the pressing or forming type processes such as extrusion, mechanical or hydraulic pressing, hot or cold isostatic pressing, swaging, high energy rate forming (HERF) and other impaction processes are quite complicated for hot cell use. The size of the HLW container (>1 ft diam x ~15 ft long) also prohibits the use of many of the above processes unless smaller containers are made and put in the large container. But small containers reduce the amount of volume available for HLW in the large container. Other considerations are the retention of the desired waste particle size and shape and integrity of the particle cladding.

The process receiving most attention is casting, mainly of aluminum. However, this may prove difficult with a large container full of 1-mm spherical particles. It is possible to cast all of the metals listed in Table 14 except for pure copper, pure iron and the steels because their melting points are greater than the sintering/outgassing temperature of the proposed HLW particles.

Gravity sintering of a metal powder matrix is a simple process and could be quite effective for this application. All the metals listed in Table 14 could be gravity sintered at or below the outgas/sintering temperature of the HLW particles. The waste particles would be loaded into the large container, and the metal powder would be loaded into the remaining void volumes by simply pouring the powder with some vibration of the container to assist in packing. A screen may be required at the container top to retain the HLW particles. The required matrix metal particle size is dependent on the HLW particle size and shape. The matrix will be 30 to 65% dense, depending on the shape and size of both the matrix and HLW particles. After loading and welding of the end closure, the container would be heated to the desired sintering temperature (maximum temperature would be the previous sintering/outgassing temperature of the HLW particles or 100°C or more below the melting point of the matrix material). This heating would occur with the stagnant air atmosphere left in the can after welding. To keep the process simple, vacuum is not used.

Experimental Results

Casting

In initial casting experiments, glass balls were clad by inserting them in molten aluminum, and Al_2O_3 grinding cylinders were cast in a manganese bronze matrix. The aluminum coating was quite adherent to the glass. The 3/4-in. Al_2O_3 grinding cylinders, used as a substitute for waste particles, were placed in a stainless steel can and heated to 900°C . Then molten manganese bronze heated to $\sim 950^\circ\text{C}$ was poured over them. No floating of the Al_2O_3 cylinders was observed. The sample has not been sectioned to examine for voids. Manganese bronze, also known as high-strength yellow brass, was chosen because its melting point of $\sim 870^\circ\text{C}$ is above the maximum container storage temperature and below the sintering/outgassing temperatures of the HLW particles. Also, it is quite resistant to saltwater and thus is normally used on exposed ship components.

Gravity Sinter

Most of the gravity sintering experiments have been made using 2 1/4-in.-diam x 3 1/2-in.-long stainless steel cans. The metal powders were loaded into the can, a lid welded in the top, and the cans heated at 900°C for 24 to 50 hr. The entrapped air caused only slight discoloration at the top of the powder compact.

During gravity sintering the material does not shrink and the particles simply bond together at their contact points. However, the particle size must be right and the appropriate temperature used. The material must not be a highly sinterable powder. Under normal conditions, the gravity sinter process also maintains good contact with the container wall.

The matrix materials that have been gravity sintered to date include the following:

- -100 and -325 mesh 316L stainless steel
- -100 mesh electrolytic iron
- -100 mesh 1040, 4600, 9400, and 4650 alloy steels
- -200 mesh 4130 alloy steel

- a bronze powder of unknown particle size
- a very fine copper powder
- -45 + 100 mesh spherical copper
- -80 + 200 mesh spherical 1018 steel.

For initial testing, the large 3/4-in. Al_2O_3 grinding cylinders were used as substitute waste particles with some -100 mesh stainless steel and the very fine copper powder. Al_2O_3 grinding balls 1/2-in. diam were used with the spherical copper and 1018 steel.

The very fine copper powder cracked and shrank badly. The bronze powder partially melted at 900°C. The 900°C temperature was somewhat low for good sinter-bonding of the alloy steels and the stainless steels. The compacts are free standing but tend to abrade easily on their surfaces. The electrolytic iron powder of irregular particle shape and the spherical copper and 1018 steel produced very good compacts.

The spherical powders lead to the highest density and are the most free flowing. The higher density promotes higher thermal conductivity and higher impact strength. The spherical powders were made by the rotating electrode process (REP). However, other atomization techniques can be used to make dense spherical particles.

Only visual examination of the gravity sintered compacts has been done. Future work includes mechanical property evaluations.

ADVANCED WASTE FORMS RESEARCH AND DEVELOPMENT (PENNSYLVANIA STATE UNIVERSITY) -

G. J. McCarthy

The objective is to develop a waste form in which all of the radioactive atoms will be isolated in thermally and chemically stable crystalline phases. Because this waste form uses the existing calcining processes with a compositionally modified waste liquid it has been termed "supercalcine." Near term objectives are 1) to determine which are the best crystalline phases for cesium, ruthenium and tellurium fixation, 2) to develop "supercalcine" formulations containing all major commercial waste atoms and 3) to demonstrate supercalcine processing on an engineering scale at PNL and develop means of consolidating the crystallized product.

PHASES FOR CESIUM AND RUTHENIUM FIXATION - S. A. Gallagher, R. G. Johnston,
D. E. Pfoertsch and G. J. McCarthy

The mineral in which cesium is found in nature is pollucite, $\text{CsAlSi}_2\text{O}_6$. Cesium is isolated in a silicate network cage and is very resistant to water leaching. Pollucite can be formed readily from solutions containing cesium and aluminum nitrates and colloidal silica by evaporating the water and firing the residue above $\sim 950^\circ\text{C}$. It also has good thermal stability at typical crystallization temperatures. Pollucite is being used as the crystalline phase for cesium fixation in supercalcine.

We have found that the phases with the nominal stoichiometries CsAlSiO_4 and $\text{CsAlSi}_2\text{O}_6$ actually show composition ranges and composition dependent phase transitions. We are studying isothermal sub-solidus sections of the system $\text{CsAlSiO}_4 - \text{Al}_2\text{O}_3 - \text{SiO}_2$, which includes both of these phases plus a third with the reported composition $\text{CsAlSi}_3\text{O}_8$. Structure, thermal stability, and leachability as a function of composition of each phase will be determined.

In the supercalcine studies discussed below, it has been shown that a solution of Al nitrate plus a suspension of silica are effective additives for cesium fixation as pollucite. A considerable excess of $(\text{Al} + 2\text{Si})$ must be added to insure complete pollucite formation. The clay minerals montmorillonite and bentonite have the appropriate aluminum to silicon ratio and are well known to have a high ion exchange affinity for cesium in waste solutions. We have obtained a number of commercial samples of these two minerals and will test them against aluminum nitrate + silica sol for their ability to fix cesium as pollucite in supercalcine.

We have nearly completed a survey of ternary oxides containing ruthenium in which high thermal stability phases are being sought. So far, it looks as though CaRuO_3 and SrRuO_3 are the best candidates. Both show no significant weight losses during firing at 1100°C for 12 hr. Compatibility studies are now in progress to obtain the thermodynamic and crystal chemical background information needed for using these phases for ruthenium fixation in supercalcine.

COMPATIBILITY STUDIES - G. J. McCarthy and M. T. Davidson

In the previous Quarterly Report* we explained the procedures used for the compatibility studies and their importance in supercalcine development.

Thirty-four compatibility reactions were studied during the last quarter. The most important information obtained from these is summarized below.

- $\text{CsAlSi}_2\text{O}_6 + \text{Nd}_2\text{O}_3$ are not compatible at typical supercalcine processing temperatures. The latter has a stronger affinity for SiO_2 to form the apatite structure phase, $\text{Nd}_{9.33}[\text{SiO}_4]_6\text{O}_2$. Thus extra SiO_2 must be added to allow the apatite phase to form with neodymium and not interfere with cesium fixation in pollucite.
- $\text{CsAlSi}_2\text{O}_6$ and Fe_2O_3 are compatible.
- $\text{CsAlSi}_2\text{O}_6 + \text{BaZrO}_3$ are compatible. When SrZrO_3 is substituted for BaZrO_3 , extra phases are formed, and some cesium is lost to volatilization. This demonstrates that BaZrO_3 is a more stable perovskite than SrZrO_3 and alerts us to the fact that excess strontium may cause problems for cesium fixation in pollucite unless a sufficient excess of (Al + Si) is also present to form strontium silicates or aluminosilicates with this excess strontium.
- $\text{CsAlSi}_2\text{O}_6$ is compatible with both scheelite structure phases CaMoO_4 and SrMoO_4 . These scheelites are used for Mo fixation.
- Nd_2O_3 has a stronger tendency to form the apatite phase than NdFeO_3 . Thus extra iron will not be effective in "pacifying" neodymium as NdFeO_3 and preventing the apatite phase.
- The stoichiometry of the apatite phase appears to be $(\text{AE})_2(\text{RE})_8[\text{SiO}_4]_6\text{O}_2$ rather than the $(\text{AE})_4(\text{RE})_6[\text{SiO}_4]_6$ suggested in several literature reports. (AE = alkaline earths, RE = rare earths).
- Ce^{4+} can be substituted in the apatite phase. $\text{Ce}(\text{AE})_3\text{Nd}_6[\text{SiO}_4]_6\text{O}_2$ (AE = Ca, Sr) have been prepared for the first time. This means that cerium may be found in the A_{ss} phase in supercalcine rather than in the familiar F_{ss} phase.

* Waste Fixation Program Quarterly Progress Report, April-June 1975, BNWL-1932, September 1975.

- When both calcium and strontium are used as supercalcine additives, strontium prefers the scheelite phase SrMoO_4 while calcium prefers the apatite phase (e.g., as $\text{Ca}_2\text{Nd}_8[\text{SiO}_4]_6\text{O}_2$). This could be important in supercalcine design if SrMoO_4 is either more or less effective for molybdenum fixation.

SUPERCALCINE DEVELOPMENT - G. J. McCarthy, D. E. Pfoertsch and W. A. Ross

The information obtained from the compatibility studies has been incorporated into new supercalcine formulations. The major phase formation proposed was $\text{CsAlSi}_2\text{O}_6$ (pollucite),* $\text{Sr}_2\text{Nd}_8[\text{SiO}_4]_{6-x}[\text{PO}_4]_x\text{O}_2(\text{A}_{\text{ss}})$, $\text{SrMoO}_4(\text{S}_{\text{ss}})$ $(\text{Ce}_{1-x}\text{Zr}_x)\text{O}_x(\text{F}_{\text{ss}})$ BaZrO_3 , NiFe_2O_4 and Fe_2O_3 .

Based on our survey of 10 new formulations using this proposed phase formation, a second supercalcine formulation was submitted to PNL for engineering-scale processing. A colloidal suspension of silica (du Pont LUDIX-AS) and solutions of aluminum and strontium nitrates were the composition modifying additives. About 50 lb of this formulation were routinely processed by spray calcining. Details are reported separately. Crystallization and consolidation studies on this product are in progress. The spray calcined product is x-ray amorphous, as expected. Initial results indicate that crystallization begins at as low as 900°C with the formation of A_{ss} + pollucite as the best crystallized phases. Weight losses recorded for 14 firings of pellets of the calcine at temperatures between 900 and 1100°C for 1 to 6 hr were $7.2 \pm 0.5\%$. Losses for five samples of powdered calcine at the same temperatures were only slightly higher at $7.6 \pm 0.6\%$. These results imply that most or almost all the weight losses on firing are due to NO_x and H_2O rather than the crystalline phases. For 1150 and 1200°C firings weight losses averaged ~1% higher. This could be due either to the last traces of NO_x and H_2O or to a small amount of volatilization of oxides. The silica tube tests for cesium fixation completed to date indicate no cesium volatilization losses after 2 hr at the highest temperature studied, 1100°C. This product then meets the thermal stability requirement for the crystalline ceramic waste form.

* Waste cations fixed in these phases are underlined.

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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, G. D. Seybold, D. L. Stevens

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 identified as constituting the dominant risk will be retained for more detailed analysis.

A rough draft report describing the failure sequence method developed to date is undergoing technical review by consultants and task contributors. Sections on dependent events/common mode failures and on sensitivity studies are included, although their procedure is not yet completely developed.

Progress has been made in placing an upper bound on the risk represented by the millions of low-probability cut sets discarded in the screening process. For a typical tree, this risk is bounded as <8% of the risk in the entire fault tree. In reality, the value is probably orders of magnitude lower than the 8% figure. However, without actually analyzing the entire tree, there is no way to precisely calculate the value. Only a bound or a very crude estimate can be given.

Some progress has been made in defining and delineating the "completeness" problem--the possible occurrence of failure sequences which do not appear

on the fault tree because of man's limited capability to conceive of every event that could occur. Of course, no solution to this problem exists. However, certain bounding values (under certain assumptions of man's degree of lack of knowledge) can be hypothesized.

RISK ASSESSMENT

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 release of radionuclides from containment/confinement barriers.

Water Basin Storage - P. J. Pelto

Initial analysis of the water basin storage fault tree has been completed using the computer programs FAULT and RAFT, and a list of important accident sequences has been generated. These computer programs are described in the previous quarterly.*

A conceptual drawing of the Water Basin Storage System is shown in Figure 28. This facility would be located adjacent to a reprocessing plant and store 4,450 canisters of vitrified high-level waste from the solidification process. The canisters are stored in nine concrete-stainless steel lined storage basins, with each basin having a separate cooling system. The basins are normally covered with metal covers and vented through the hydrogen vent system. The hydrogen vent system, consisting of two HEPA filters, a fan, and a backup fan, services all nine basins.

The building ventilation system comprises a control damper, a HEPA filter, a fan, and a backup fan. The building air is not normally filtered; a radiation detector will activate the control damper and divert the air flow to the HEPA filter.

* Waste Fixation Program Quarterly Progress Report, April-June 1975, BNWL-1932, September 1975.

FIGURE 28. Basin Storage Activity

The Water Basin Fault Tree, developed using this conceptual design, comprised about 3.5 million failure sequences (cut sets). Use of calculated probability and number of events per cut set cutoffs in FAULT resulted in about 5000 cut sets which were input to RAFT and ranked on the basis of risk. Table 15 gives the top few dominant accident sequences tentatively identified for the water basin fault tree. Loss of cooling and the resulting meltdown of the waste canisters dominate in this initial assessment. These meltdown accidents have a small probability but relatively large consequences; thus their risk is three to four orders of magnitude higher than the risk of higher probability-lower consequence accidents such as a contaminated basin in conjunction with a filter failure.

Many assumptions were needed to quantify the risk of water basin storage. Some of the major ones which affect the list of important accident sequences are discussed here. In the event of loss of water and a meltdown of the canisters, it is assumed that the hydrogen ventilation, the building ventilation, and their filters have failed by the time meltdown occurs. The steam environment, high temperatures, and filter plugging justify this

TABLE 15. Water Basin Storage Dominant Risk Accidents

- Primary failure of normal and emergency electrical power, resulting in meltdown.
- Earthquake or tornado fails both electrical supplies, resulting in meltdown.
- Earthquake or tornado fails normal power and, coupled with primary failure of emergency power, meltdown occurs.
- Earthquake or tornado fails both electrical power and basin covers, and meltdown occurs.
- Primary failure of both electrical power supplies, with basin covers removed, results in meltdown.
- Earthquake or tornado fails both electrical power supplies, and building structure and meltdown occurs.
- Primary failure of basin concrete and liner, loss of water, and meltdown.
- Primary failure of basin concrete, liner failed by corrosion, loss of water and meltdown.
- Earthquake fails basin concrete and liner, and meltdown occurs.

assumption. It is also assumed that failure of the basin concrete and liner is nonrepairable as the surface dose of the basin becomes high with the loss of water level. A final important assumption is assigning a repair time of one week to components failed by an earthquake or tornado.

Although not listed in Table 15, crude estimates of the risk from some severe external events such as a massive earthquake or a large meteor impact were made. The probabilities and consequences of these events are difficult to estimate, but the numbers picked indicate that the risks from a massive earthquake may be higher than the accidents identified in Table 15. It is emphasized that the probabilities of these events are extremely uncertain and that they have other effects which may be much more important than the radiological consequences of water basin storage.

More detailed heat transfer studies of loss of basin cooling and the effect on the canisters are needed to perform a more detailed analysis of the dominant risk cut sets for the water basin fault tree. Earlier studies indicate that if only radiative heat transfer is assumed, the canisters will remain intact. Additional information on the amounts of volatiles generated and their vapor pressures is required.

These preliminary results are being reviewed and compared with the other activities of the WFP safety reference system. The next steps in the safety analysis are a more detailed evaluation of important cut sets and an analysis of radiological consequences.

Solidification - L. V. Kimmel

Figure 29 presents a conceptual drawing of the generic spray solidification process as analyzed by the fault tree approach. The main effort of the analysis focused on such major process equipment as the surge tank, surge tank heat exchanger, calciner, calciner filters, calciner furnace, melter pot, melter furnace, canisters, and HEPA filters. Peripheral equipment such as off-gas process equipment, spray cooling chamber, welding station, and small water basin were considered in less detailed, more general terms within the tree.

The process contains the liquid, gaseous, calcine and glass forms of radioactive waste as potential source terms for accidents. The chief transport vector for accidental releases is air, with a minor potential pathway of a liquid-groundwater release.

The solidification fault tree was analyzed as three branches. These branches represented a stack release and a release from a breach in the building structure using air as the transport vector, as well as a release pathway through the building structure with a liquid transport vector. The surge tank and liquid waste piping present source terms for both air and liquid releases of liquid wastes. The calciner and off-gas process equipment and duct work are potential sources of calcine and/or gaseous releases of radioactivity, while the melter, canisters, and canister handling are source terms for glass or gaseous waste forms.

Severe environments were considered by consecutive passes through the fault tree. Earthquakes, tornados, fires, and explosions all were considered as energy sources for accident sequence initiation and common mode failures of safety equipment. Failures related to severe environments were assumed to be nonrepairable events. The question of repairability of severe

FIGURE 29. Solidification Activity

environment failures will be dealt with in detail later in the project, but for now, nonrepairable events were assumed in order to get conservative initial results.

The top risk events associated with the solidification tree are all events or ways of failing the building HEPA filters, in conjunction with failing either the off-gas cell HEPA filter or the solidification cell HEPA filter. The source term is simply the routine radioactive material concentration within the respective cells due to contamination during maintenance. Filter failure as the result of a tornado or fire is also associated with the tentatively identified dominant risk events.

The analysis of the fault tree produced over 10^7 failure sequences. About 4000 of the 10^7 sequences survived an initial screen and were ranked in terms of risk. A list of the top eight sequences follows:

- Tornado fails building and off-gas cell HEPA filters, resulting in an unfiltered release of off-gas cell contamination.
- A fire fails both the building and the off-gas cell HEPA filters, resulting in an unfiltered release of off-gas cell contamination.
- Failure of the building HEPA filters by overpressure from excessive solids or water in vent air in conjunction with the penetration of a sound hot cell HEPA filter by solidification cell contamination.
- Operator error fails off-gas cell HEPA filters, and excessive solids or moisture fails the building HEPA filters, resulting in an unfiltered release of off-gas cell contamination.
- Tornado fails building HEPA filters, and a once-filtered release of off-gas cell contamination passes through a sound off-gas cell HEPA filter.
- Failure of the off-gas cell HEPA filter and the building HEPA filter by overpressure from excessive solids or moisture in air results in an unfiltered release of off-gas cell contamination.
- Operator error fails the solidification cell HEPA filter and the building HEPA filter fails by overpressure from excessive moisture or solids resulting in an unfiltered release of the solidification cell air contamination.

- Solidification cell HEPA filter primary fails, and the building HEPA filter fails from overpressure due to excessive moisture or solids, resulting in an unfiltered release of the solidification cell air contamination.

A frequency-consequence plot for the top 80 failure sequences is shown in Figure 30. Each parallel 45° diagonal joins points of equal risk (the mathematical product of the frequency and consequence index). Comparison of the top three sequences illustrates the utility of risk assessment in placing accident sequences in perspective. Although risk values are comparable, the estimated frequency and consequences of the top three sequences span about three orders of magnitude. No estimates have yet been made of the uncertainty associated with the points plotted in Figure 30.

FIGURE 30. Frequency Consequences Plot for Dominant Sequences, Solidification Activity

As in the case of water basin storage, very rough estimates of the likelihood and consequences of a massive earthquake or large meteor impact indicate that the risk of these catastrophic events may be higher than the operations-related sequences listed above.

Transportation - E. S. Murphy

Risk assessment of transportation is based on the shipment of solidified high-level waste by rail transportation from a reprocessing plant to an interim storage facility (RSSF). The waste form is assumed to be a glass/ceramic monolith packaged in a stainless steel canister. For rail transport of the waste, canisters are placed inside massive steel and lead casks weighing about 100 tons. For a release of radioactive material to occur, both the waste canister and the shipping cask must be breached.

The method for assessing the risk in transporting high-level waste uses a fault tree to identify failure events and to specify combinations of events which could result in a breach of containment and a release of radioactive material to the environment. The dominant risk failure sequences identified for the rail transport of high-level waste are:

- Shipment of a good cask that is breached by a derailment accident involving mechanical forces only.
- Shipment of a good cask that is breached by other train accident involving fire or explosion.
- Shipment of a good cask that is breached by a derailment accident involving mechanical forces plus fire.
- Shipment of a cask with an improperly secured lid that is breached by a derailment accident involving mechanical forces only.
- Shipment of a good cask that is breached by a collision accident involving mechanical forces only.
- Shipment of a cask with an improperly secured lid that is breached by other train accident involving fire or explosion.

- Shipment of a cask with an improperly secured lid that is breached by a derailment accident involving mechanical forces plus fire.
- Shipment of a good cask that is breached by a collision accident involving mechanical forces plus fire.
- Shipment of a cask with an improperly secured lid that is breached by a collision accident involving mechanical forces only.

The sequences listed above all relate to train accidents and account for over 95% of the total transportation risk. Events of a catastrophic nature do not appear in the dominant risk sequence list developed for rail transport.

Thermal analyses of the conceptual 100-ton shipping cask and its contents have been made. Both steady-state and transient analyses were performed. The steady-state analysis under a normal transport environment was performed to determine if auxiliary cooling of the cask and canisters is required. Final temperatures indicate that auxiliary cooling will not be required and that melting of the lead shielding within the cask will be no problem under normal transport conditions.

The transient analysis with the cask exposed to a 1000°C fire was performed to determine the effects of the fire on the containment system and the canister contents. The results indicate that melting of the outer surface of the lead shield would begin after a fire duration of about 1 hr, but that exposure to the fire for periods beyond 2 hr would have no significant effect on the temperature of the canisters.

EVALUATION OF RADIOLOGICAL CONSEQUENCES

The objective of this effort is to develop information for use in estimating the radiological consequences of dominant failure sequences.

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.

Calculations have been made of climatologically averaged values of the air concentration of resuspended material. These calculations have been made for both 1- μ and 10- μ particles with a specific gravity of 3 and extend to a distance of 100 km from the original release point of the contaminant. The main conclusion from these calculations is that, except for the region within 100 m of the release point, the sum of the exposures due to resuspension and due to the direct exposure to the depositing plume is always less than the direct exposure to the nondepositing plume would have been, i.e.:

$$E_r + E_d \leq E_o$$

In other words, the exposure to the undepleted plume alone would provide a conservative upper limit to the expected sum of the exposures due to the depositing plume and due to subsequent resuspension. While these calculations ignore the effect of redeposition, i.e. deposition from the resuspended plume and subsequent additional resuspension exposure, analysis of a simplified situation indicates that this process plays only a minor role.

Characterization of Radioactive Release Forms - L. V. Kimmel

To test the viability of using grams of radioactive material released as a measure of consequence for the initial cut set screening, the Task Group Lung Model (TGLM) was applied to the different species of radionuclides expected to be available for release within the waste management processes under consideration. The model was run consecutively for a 1-g release each of ruthenium, cesium, and 1 μ mixed fission products 3, 10, 100, and 1000 years old. The purpose was to compare the doses between a volatilization of cesium and ruthenium accident and a release of mixed wastes, 3, 10, 100, and 1000 years old, respectively.

The meteorological data was from the Hanford site, using moderately stable criteria and a 1 m/sec wind speed. Dose calculations were made for 10 distance intervals of 100 m to 100,000 m from the source. The individual releases were assumed to be 1 g, and the dose calculations were made assuming both soluble and insoluble waste forms.

The 1 μ size for mixed waste was chosen for several reasons. The particle size of high-level waste from the spray calcine process is of the micron size; particles of this size are highly transportable by atmospheric processes, and deposition in the pulmonary and nasal pharynx compartments of the lung model are about equal, thus providing a complete set of pathways for radionuclide transport to the various organs of interest in dose commitment considerations.

For purposes of comparison, the results are displayed graphically for the 100-m distance. The absolute values of doses plotted are of little interest at present; rather the relative ranking of the source terms considered is of primary concern. The graphs show, where applicable, the 1- and 50-year dose commitments for the G.I. tract (GI), total body (TB), bone (B), and lungs (L).

Figure 31 gives the various dose calculations, using the assumption that the ruthenium, cesium, and mixed fission products are present in their soluble forms. While Figure 32 shows the dose calculations with the insoluble forms assumed, Figure 31 presents dose curves probably similar to what would be obtained if volatilized cesium or ruthenium is compared with a calcine or liquid spray release (again the 1- μ assumption holds). The calcine and liquid could both consist of the mixed fission products in a more soluble state than glass. If one assumes that the mixed fission products in glass are probably more or less insoluble due to the glass coating (even at the micron size), then the 3, 10, 100, and 1000-year waste dose in Figure 32 would probably be representative of the powdered glass. However, since the cesium and ruthenium will more than likely be in soluble form, a more meaningful comparison between glass and the volatiles can be seen in Figure 33. Plotted in Figure 33 are the doses for the soluble forms of cesium

FIGURE 31. Dose at 100 m for 1-g Release of Various Waste Forms (Soluble)

FIGURE 32. Dose at 100 m for 1-g Release of Various Waste Forms (Insoluble)

FIGURE 33. Dose at 100 m for 1-g Release of Various Waste Forms (Probable)

and ruthenium followed by the insoluble form of the mixed wastes. While no quantitative information exists about the solubility of micron-size particles of glass high-level waste, the assumptions underlying the interpretation of Figure 33 are at least intuitively sound. Figures 31 and 32 provide a probable lower and upper bound for the relationship that would probably occur in reality. The results indicate that in general, grams of radioactive material do provide a suitable initial measure of consequence on which to base a preliminary screening. Some caution should be exercised when young (< 10 year) waste in soluble form is being considered as a source term.

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