HIGH-LEVEL WASTE VITRIFICATION
BY SPRAY CALCINATION/IN-CAN MELTING

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HIGH-LEVEL WASTE VITRIFICATION BY SPRAY CALCINATION/IN-CAN MELTING

INTRODUCTION

Federal regulations, Appendix F of the Code of Federal Regulations, Title 10, Part 50, require that High-Level Liquid Waste (HLLW) be converted to a solid and placed in a sealed container prior to transfer to a Federal repository. The HLLW must be solidified within 5 years after generation at a commercial nuclear fuel reprocessing plant and shipped to a Federal repository within 10 years of origination. The regulations indicate that the dry solids should be chemically, thermally, and radiolytically stable to the extent that the waste container will maintain its integrity until it is placed in a disposal site. It is the intent of the regulations to maximize the public safety by converting the HLLW to a form that will minimize radionuclide mobility and toxicity under normal and abnormal conditions. The solids are also to be isolated from the biosphere. The United States Government has conducted research and development for about three decades to provide the appropriate technology.

Solidifying radioactive wastes poses unique problems requiring specialized considerations due to the radiological, chemical, and physical properties of the waste. Under sponsorship of the United States Atomic Energy Commission (AEC) and more recently the Energy Research and Development Administration (ERDA) extensive research and development has taken place. The associated program goals were to prepare a suitable waste product form and develop processes well adapted to remote operation and maintenance. Much of the work was carried out at Battelle Pacific Northwest Laboratories (PNL) in the Waste Solidification Engineering Prototypes (WSEP) program. In this program, promising processes developed in the United States up to about 1967 were pilot plant tested and compared, using radioactive waste, except for fluidized bed calcination, which was demonstrated at the Idaho National Engineering Laboratory. The WSEP program ended in 1971 after radioactive demonstrations were completed with

the pot, spray, and phosphate glass solidification processes. A total of 33 demonstrations were completed during which more than 50 million curies of radionuclides were processed and collected in 33 canisters ranging from 6 to 12 in. in diameter by 8 ft tall. In 1972 the Waste Fixation Program (WFP) started at PNL and has continued to the present. A major objective of the WFP is to assure that suitable processes and solidified waste forms are available to industry for the fixation of HLLW.

In most countries developing nuclear power, HLLW solidification and storage programs are in progress. The more promising processes ultimately incorporate the toxic waste constituents into a highly nondispersible borosilicate glass. These processes include:

In-Canister Drying and Melting	England
Rotary Kiln Calcination with a Continuous Metallic or Ceramic Melter	France
Spray Calcination with a Continuous Metallic or Ceramic Melter	Germany

In the United States during recent years, spray and fluidized bed calcination with in-can or continuous ceramic melting to a borosilicate glass have been developed further than other methods. After extensive evaluation of the available solidification processes, PNL personnel held discussions with anticipated United States nuclear fuel reprocessors. The Spray Calciner (SC) and In-Can Melter (ICM) process was selected as the system most ready for demonstration as a production plant process. This process is now being designed for vitrification of commercial fuel reprocessing waste generated in the near future.

In 1975 PNL undertook a joint program with Nuclear Fuel Services, Inc. (NFS) to provide equipment design and a process for use by a commercial nuclear fuel reprocessor to produce solidified waste in a canister acceptable at a Federal repository. PNL was to provide the process and basic equipment design. NFS and their architect-engineering firm designed the facility together with the associated services for location at the West Valley Fuel Reprocessing Plant. This cooperative program resulted in the development of a conceptual design⁽¹⁾ and flowsheet⁽²⁾ for a commercial HLLW vitrification facility for NFS.

Although the PNL information included herein is presented using the West Valley Plant in New York as the bases, it is applicable to other fuel reprocessing plants. These include the higher capacity Allied General Nuclear Services, Barnwell plant, and the proposed Exxon plant.

This document presents information available on the Spray Calciner/In-Can Melter Vittrification process. This information is intended to provide the basis for preparation of a preliminary safety analysis and to supply information necessary for cell layout and design of process equipment. Descriptions are limited mainly to that equipment required for vittrification, including the HLLW feed system, calciner, melter, and canister post-treatment. Other systems described in less detail are an effluent treatment system, the frit feeding system, and other minor out-of-cell items.

SUMMARY

Current Federal regulations require that HLLW from a commercial nuclear fuel reprocessing plant be converted to a dry solid in a container suitable for custody in a Federal repository. PNL has developed the Spray Solidification/In-Can Melting process for producing such a waste. PNL, in cooperation with potential commercial fuel reprocessors and ERDA, is demonstrating this process for commercial application. The bases used in this document are similar to those of NFS for their plant at West Valley, New York, and to anticipated regulations for waste canister receipt at a Federal repository. The technology reported directly applies to other nuclear fuel reprocessing facilities such as Allied General Nuclear Services, Barnwell plant, and the proposed Exxon plant.

A reference NFS flowsheet has been established. This flowsheet combines plant HA Column Wastes, Low-Level Wastes, and various HLLW process recycle streams to produce a borosilicate glass with these properties:

Reference HLW Glass Properties

Calcine Content: 33 wt%

Density: 3.0 g/cm³

Volume: 3.3 ft³/MTU

Heat Generation Rate: ≤60 W/liter

Thermal Conductivity: 1.0 W/m-°K @ 200°C

Leach Rate: ~10⁻⁶ g/cm²-day

After the canister is filled and the lid is seal welded, the canister lid weld will be leak checked, visually inspected, and decontaminated prior to storage or other operations.

The equipment and instrumentation for feed supply to the calciner, calcination, melting, welding, weld inspection, canister decontamination, and in-cell canister storage are being designed and demonstrated. The equipment design is being developed to the extent that a commercial fuel reprocessor may have it designed, constructed, and licensed for operation. Process equipment development has proceeded such that partial design requirements can be designated.

Preliminary facility layouts, equipment design data, and instrumentation needs are provided for major process equipment systems. However, additional demonstration work is being performed to verify and complete the plant scale equipment design. This work includes full-scale nonradioactive equipment testing, nonradioactive facility mockup for equipment remote operation and maintenance demonstration, and pilot plant production of waste glass from actual commercial fuel HLLW. These programs are being scheduled sufficiently early that results may be used by commercial reprocessors.

The technology for spray calcination and in-can melting is well advanced and approaching readiness for commercial application. It has been demonstrated extensively in the WSEP program and other PNL programs using radioactive and nonradioactive wastes on laboratory and pilot plant scales. Additional work needed includes determining the effects of different HLLW compositions on the process, glass, and calciner off-gas. This will be done as reprocessor HLLW compositions become known.

A preliminary evaluation is made of materials that may be released from the process from normal and abnormal operations in the facility.

DESIGN BASES

The design bases used in this document are based on those of NFS for their nuclear fuels reprocessing plant in West Valley, New York. However, the material described is applicable to larger plants such as Allied General Nuclear Services, Barnwell plant, and the proposed Exxon plant. These design bases include:

- Fuel Characteristics

Type: Pressurized Water Reactor

Enrichment: 3.3% ^{235}U

Burnup: 33,000 MWD/MTU

Power: 30 MW/MTU

Neutron Flux: 2.92×10^{13} N/cm²-sec

Minimum Time Out of Reactor: 2 years

Maximum Heat Generation Rate of Resulting HLLW: 5.7 kW/MTU

- Waste Processing Facility Characteristics

Capacity (100%): 2.5 MTU/day

Operation: Remote

Automatic control where practical

Maintenance: Remote

Minimum use of manipulators

Storage: Water storage for up to 10 years in a stainless steel-lined pool where the water temperature is <105°F.

- Canister

Height: 10 ft

Diameter (I.D.): ≤20 in.

Material: 304L Stainless Steel

Capacity: Solidified HLLW from ≤5 MTU

- High-Level Liquid Waste composition (Feed to the Calcliner Feed Tank):

<u>Chemical</u>	<u>Nominal (PW-8a)</u>	<u>High Na (PW-8e)</u>	<u>Low Na (PW-8d)</u>
H, <u>M</u>	2.0	2.0	2.0
Na, <u>M</u>	0.6	0.6	0.0
Fe, <u>M</u>	0.46	0.005	0.46
Ni, <u>M</u>	0.001	0.0005	0.0005
Cr, <u>M</u>	0.003	0.0015	0.0015
F.P. (a)	100%	1%	100%
Actinides (excl. U & Pu) (b)	100%	1%	100%
NO ₃ , <u>M</u>	4.6	2.6	4.0
PO ₄ , <u>M</u>	0.026	0.026	0.026
U, <u>M</u>	0.05	0.05	0.05
Pu, <u>M</u>	0.00083	0.00021	0.00042
1/MTU	757	757	757

a. F.P. = Fission Products, excluding 100% of the Noble Gases and Bromine as well as 98% of the Iodine when 100% of the F.P. is indicated in the waste stream.

b. 1.5% Pu and 1% U present in waste.

Since waste acceptance criteria are not available for waste reception in a Federal repository, several assumptions were made as to waste form and canister requirements:

- The filled canister surface would be cleaned of radioactivity to as low as reasonably achievable without using exotic techniques.
- The canister seal weld will be leak checked.
- A glass waste form or its equivalent will be required.
- Other glass and canister characteristics will be quality or process controlled to assure acceptability to the Federal repository.

As acceptance criteria become available, comparison with the system described herein is planned. Should product modifications be required, they can be performed to assure compliance.

FLWSHEET DESCRIPTION

The flowsheet consists of basically four steps:

- Calcination
- In-Can melting
- Canister sealing, handling, and inspection, and
- Off-gas treatment.

Figure 1 is a flow diagram showing these steps. Table 1 shows the flowsheet using the nominal NFS HLLW composition.

CALCINATION

The calciner dries and decomposes the chemicals in the aqueous wastes to a metal oxide calcine suitable for vitrification.

The HLLW at $\leq 40^{\circ}\text{C}$ in the calciner feed tank is pumped at a controlled rate to the calciner through a pneumatic spray nozzle. The calciner walls are controlled at a temperature of 600 to 800°C . The waste solution is dried, and then the ionic species are converted to oxides and reaction gases. The gases from the calciner include primarily H_2O , HNO_3 , air, and NO_x . There could be some small amounts of CO_x and other gases from oxidation of organics that may be contained in the HLLW.

The calciner gases at about 350°C are filtered by sintered stainless steel filters to remove entrained calcine. Only about 0.1 wt% of the calcine passes through the filters, and $<2\%$ of the ruthenium is volatilized and escapes the calciner. Also, any iodine reaching the calciner is volatilized. The balance of radionuclides remains in the calcine. The filters are periodically blown back with air to prevent plugging with calcine fines. The off-gas from the calciner is routed to an off-gas train for radionuclide and NO_x removal.

The calcine drops into the cone below the calciner chamber, where it is combined with the glass-forming frit granules. The frit is metered into the calciner cone at a rate proportional to the calciner feed stream. About one part by weight calcine combines with two parts frit and falls through a loading chute into the canister for melting. When one canister is full, a diverter valve routes the calcine-frit mix to a second canister.

FIGURE 1. High-Level Liquid Waste Vitrification Flow Diagram

TABLE 1. High-Level Liquid Waste Vitrification Flowsheet

Solutions	(1) Calciner Feed	(2) Calciner Recycle Acid	Gases	(3) Atomizing Air	(4) Calciner OG	(5) Scrubbed Calciner OG	Solids	(6) Frit	(7) Glass
H g/l	2.0	2.74	HNO ₃ g-mole/day	0	3,780	Negligible	SiO ₂ kg/MTU	110	110
Na	13.8		H ₂ O	Negligible	80,000	8,000	B ₂ O ₃	26.2	26.2
Fe	25.7		Air	36,410	36,410	36,410	Na ₂ O	20.4	20.4
Ni	0.0587		NO _x	0	5,000	<5,000	ZnO	13.8	13.8
Cr	0.104		CO _x	0			CaO	5.52	5.52
FP	38.3		Solids g/day	0	230	23	TiO ₂	8.27	8.27
Act. ^(a)	13.8		Cs-137 Ci/day	0	257	0.257	Na ₂ O	0	14.1
U	12.6		Sr-90		185	0.185	Fe ₂ O ₃		27.7
Pu	0.176		Ce-144		467	0.467	NiO		0.056
NO ₃	292	170	Ru-106		6,840	13.7	Cr ₂ O ₃		0.115
PO ₄	2.54		I-129		9.38E-5	9.38E-7	FP _x O _y		36.1
Sugar	Some Org. Residue	Negligible	Total		9,540	16.4	Act ₂ O _q		12.4
			Temp °C	Ambient	350	55	P ₂ O ₅		1.46
			Watts/l	Negligible	Negligible	Negligible	Total	184	276
Cs-137 Ci/l	136	0.185	l/MTU @ Temp.	3.50E+5	2.56E+6	5.32E+5	Cs-137Ci/MTU	0	1.03E+5
Sr-90	97.6	0.130	l/day @ Temp.	8.76E+5	6.40E+6	1.33E+6	Sr-90		7.39E+4
Ce-144	247	0.334	Std. l/day	8.16E+5	2.80E+6	1.11E+6	Ce-144		1.87E+5
Ru-106	181	4.95					Ru-106		1.37E+5
I-129	4.96E-8	6.79E-8					I-129		Negligible
Total	1,610	6.90					Total		1.22E+6
SpG @ 4°C	1.18	1.11					SpG	1.7	3.0
Temp. °C	≤40	≤50					Temp °C	Ambient	<800
Watts/l	7.59	Negligible					Watts/l	0	61.5
l/MTU	757	552					l/MTU	108	91.9
l/day	1,890	1,380					l/day	270	230

Note:

a. Includes U and Pu.

In calculating the flowsheet the following assumptions were made:

1. Neglect process jet dilutions.
2. Neglect process air in-leakage, except assume ≤5000 g-mole/day in-leakage at calciner/melter coupling
3. Neglect instrument air volumes.
4. Air incoming to the process is dry.
5. Equipment heat losses and pickup are neglected.

Equipment decontamination factors used for the flowsheet are shown in Table 2. These decontamination factors represent somewhat conservative estimates of what the process equipment can achieve based on plant experience and/or development work.

TABLE 2. High-Level Liquid Waste-Process Equipment Decontamination Factors(a)

Equipment	Decontamination Factor			References		
	Ruthenium	Non-Volatile Elements	Iodine	Ruthenium	Non-Volatile Elements	Iodine
Calciner-Melter (incl. SS Filters)	50	1,000	1	3-5	3-5	--
Venturi Scrubber(b) Condenser Separator	500	1,000	100	4,5	4-8	6

a. Definition of Decontamination Factors (DF):

$$DF = \frac{\text{Total Contaminant in Input}}{\text{Total Contaminant in Effluent}}$$

b. System Decontamination Factor

IN-CAN MELTING

The in-can melter melts the solid calcine-frit mixture into a glass within the canister.

The calcine-frit mixture flows into the canister contained in the retort/susceptor of the multizone melter furnace. The mixture is heated to melting at about 1050°C. Once the mixture in a zone has melted to a glass, heating is terminated, and cooling air is blown on the outer retort/susceptor wall. This cools it and the canister to reduce crystalline phase settling and prevent excessive system temperatures from waste self-heating. The small volume of gas generated during the melting is routed to the calciner.

The retort is filled with an inert gas such as argon to minimize canister spalling during filling. Any spalled material is collected in a pan in the bottom of the retort. This material is removed for disposal as necessary.

The filled canister is disconnected from the calciner and the cap is screwed onto the canister. The filled canister is then removed from the furnace, seal welded, and inspected.

CANISTER OPERATIONS

The canister cap is seal welded to isolate the waste and canister interior from the outside environment. The canister weld is helium leak checked to ensure its integrity, and the canister integrity is visually inspected. The filled canister is finally decontaminated to remove any loose contamination. The canister may then be moved to interim storage. Overpacking capability will be constructed into the weld-test facility for any possible canister failure.

OFF-GAS TREATMENT

Multiple steps of off-gas treatment are employed to remove radionuclides and NO_x so that the off-gas may be released to the environment within applicable release guidelines. The effort at PNL is concentrating on characterizing the calciner off-gas to allow selection of optimum effluent treatment equipment. However, future operations will provide data on the performance of various types of effluent treatment equipment.

In the NFS reference flowsheet, calciner off-gas is initially routed through a venturi scrubber-separator and condenser system. This system is designed to remove particulates, nitric acid, water, and volatile ruthenium from the off-gas. The off-gas is also cooled to about 55°C. A negligible amount of NO_x , excluding HNO_3 , is assumed removed due to the short residence in the system. The condensed nitric acid containing the particulate and dissolved contaminants is routed to the HLLW blend/feed tank for recycle. Cooled condensate is also continuously recycled to the venturi scrubber-separator for continuous operation. The off-gas is treated later for additional NO_x , ruthenium, particulate, and possibly iodine removal in a production plant.

EQUIPMENT DESCRIPTION

Discussed here are preliminary layout and design of the equipment together with the associated instrumentation to perform the Spray Calcination/In-Can Melting production process. Efforts are in progress at PNL to provide additional data needed for final design and, where necessary, to update information contained here. These efforts include the plant equipment mockup program, cold production-scale equipment demonstration, and pilot plant processing of HLLW from spent reactor fuel in B Cell of the 324 Building. These activities are being scheduled to provide timely data to commercial fuel reprocessors for design. The "Technology" section indicates the status of equipment development.

EQUIPMENT ARRANGEMENT

An initial cell arrangement for the vitrification equipment is shown in Figures 2, 3, and 4. When the equipment was arranged, consideration was given to operation, remote maintenance, solids flow, system hydraulics, and connecting piping routings.

The major operational considerations in arranging the equipment were to provide convenient flow paths for the canisters, assure adequate viewing and, where required, in-cell crane and manipulator access. Empty canisters are transferred into the cell on the same mechanism on which the full canisters are transferred to onsite storage. The in-cell crane lifts the empty canisters and places them in the in-can melter. After filling, the canisters are moved to the welding and leak test station, then decontaminated and finally placed on the transfer mechanism for transfer to onsite storage. All these operations require close viewing, and manipulator assist may be required for operation of the welding and leak test equipment.

Considerations for remote maintenance are similar to those for operation. Most major equipment pieces are arranged for removal and installation with the in-cell crane. Overhead access to the in-can melter is achieved by moving the melters to the back of the cell on fixed rails. Shielded viewing windows and/or periscopes are provided as needed for adequate viewing.

FIGURE 2. Equipment Arrangement--Spray Calciner/In-Can Melter Process--Plan View

FIGURE 3. Equipment Arrangement--Spray Calciner/In-Can Melter Process--Elevation View of Section A-A

FIGURE 4. Equipment Arrangement--Spray Calciner/In-Can Melter Process--Elevation View of Section B-B

A major objective was to arrange the equipment to allow for gravity flow of the calcine and frit. This was accomplished by placing the in-can melters directly below the spray calciner and locating the frit addition system high enough to maintain the required slope of the frit addition line.

All process piping is sloped downward to assure free drainage. This is done to aid in decontamination of piping interiors and to assure there are no unwanted liquid holdups or places for solids to settle. Service piping is sloped from the service gallery to the cell. This is also done to assure free drainage and to impede backflow of contaminated materials from the processing equipment to the service galleries.

Removable jumpers are used to make all process and service connections to the cell equipment. An attempt was made to optimize the equipment arrangement so that the jumpers would not unduly restrict movement of equipment in the cell and that most of the jumpers could be removed without removing adjacent jumpers.

Cell dimensions are 22 ft by 50 ft long with a 40-ft working height. Head room for the in-cell crane is required above the 40-ft working height. These cell dimensions provide ample room for all required equipment plus room for an installed spare spray calciner/in-can melter unit. Also, the cell should be lined with stainless steel or the equivalent for ease of decontamination and as protection from the cell atmosphere.

Heavy duty master slave manipulators may be used to assist in welding the closure on the canister, in leak checking the canister closure weld, and for minor maintenance. If required, the manipulator will be installed, booted, and maintained in the normal manner. Labyrinth shielding will be provided in the manipulator wall penetration to prevent radiation shine into the gallery.

An automatic halon (smother gas) fire extinguishing system with heat sensors and ventilation damper controls may be installed in a commercial plant and activated if necessary.

Most of the equipment is designed to operate at very high temperatures. As a result very little combustible material is available in the cell. A safety analysis was conducted for the WSEP cell and equipment. It identified

an oil fire resulting from breakage of an oil-filled shielding viewing window as the maximum credible accident. This could be avoided by use of non-oil-filled windows or impact shields. The only other combustible material in the cell is wiring insulation and manipulator boots. Good housekeeping will prevent these items accumulating.

The floor of the solidification cell should slope a minimum of 1/8 in./ft to one corner of the cell. In this low corner of the cell will be a stainless steel-lined sump 18 by 18 by 12 in. deep. The liner will be seal welded to the stainless steel floor lines. The sump will be equipped with a liquid level detector and a steam jet for transferring any accumulation of solution. The suction of the jet will be screened to prevent plugging of the jet. The entire jet assembly will be remotely replaceable. Since high-level liquid waste could enter this sump, the discharge of the jet will be routed to an appropriate HLLW surge tank.

All cell penetrations are designed assuming the cell interior to be at a negative pressure in relation to the galleries. However, all penetrations are sealed or HEPA filtered to assure that a reversal of air flow would not cause a major contamination release from the cell.

Liquid filled, lead glass shielded windows will be used for viewing all required manipulator operations. The windows are designed to meet or exceed the shielding density of the cell wall. Standard through-wall periscopes are provided for other required viewing.

All service piping between the service gallery and the in-cell processing equipment will be installed to avoid backflow of contamination into the gallery. This is accomplished by assuring that all service lines exit the cell at an elevation higher than the vessel and by installing check valves, liquid seals, and HEPA filters or other anti-backflow devices on all service lines. Offsets or radiation bends are also provided on all service lines to maintain the shielding integrity of the cell wall.

Services such as electrical, cooling air, and instruments will be supplied to the melter furnaces through service plugs. These plugs are a part of the furnace superstructure and also serve as push rods for moving the furnace as

required for loading, filling and unloading the canisters. These plugs are similar to the existing NFS fuel shear drive rod except that the stroke will be longer. Labyrinth shielding is provided in the plugs to prevent radiation shine into the service gallery. Booting similar to manipulator booting can be provided on the gallery end of the plug to contain any contamination that may adhere to the service plugs as they move in and out of the cell.

EQUIPMENT DESIGN

The vitrification equipment is designed to be operated totally remotely with minimum aid of master-slave or electro-mechanical manipulators. Supporting equipment, such as the frit feeder, welder, and the mass spectrometer, which requires contact maintenance is located out of cell. Appropriate air locks and anti-backflow devices are provided between the in-cell and out of cell equipment to assure safe operations.

To keep personnel exposure low, all major in-cell equipment pieces are designed for remote replacement. Also, components which may wear out or fail can be remotely replaced without removing major equipment. To facilitate remote maintenance, lifting lugs are provided on the equipment so that it can be handled by the in-cell crane. Alignment dowels and fixed mounting trunions are used to assure exact positioning of equipment and components. In general, only the in-cell crane and an impact wrench are required for remote maintenance. However, provisions for master-slave manipulators are located where they could be required. Hanford type piping and electrical connectors are used for most service and process connections. Hanford type remote tank flanges are used for installation of pumps, agitators and filter assemblies. Vee flanges and other quick connective devices are used where Hanford type connections are not appropriate. Certain high-maintenance items, such as the spray calciner filter blowback valves and frit feeder air lock valves, are located in shielded wall niches and are contact maintained. These are normally nonradioactive but could become contaminated. Contact maintenance is also employed in all out of cell supporting equipment.

Some preliminary equipment design information is contained in the subsequent figures and tables:

Preliminary Design Information

<u>Equipment Item</u>	<u>Figure</u>	<u>Table</u>
Spray Calciner Feed Tank	None	3
Spray Calciner	5	4
In-Can Melter	6	5
Canister Decontamination Rack	7	6
Filled Canister Storage Rack	8	7
Empty Canister Storage, Canister Welding, Canister Leak Test Rack	8	7

TABLE 3. Preliminary Design Information,
Spray Calciner Feed Tank^(a)

Working Volume ≥ 1000 gal

Heat Dissipation Capacity ≥ 34 kW

Agitation: Provide for complete suspension of solids

(Solids: Dimension ≥ 0.5 cm

Density ≤ 3 g/cm³

Volume Percent ~ 1)

HLLW Feed Pump: Cantilever Type

~ 15 hp

160 ft maximum head

-
- a. The calciner feed tank is a standard type of equipment used in the reprocessing of spent nuclear reactor fuels. As such, it is left to the reprocessor to design it to be compatible with plant design, maintenance, and operating philosophies. The criteria stated here are needed for the spray calciner system operation.

Other tank features, including instrumentation, design, construction, materials, services and connections, are to be compatible with the calciner feed system and plant practices.

FIGURE 5. Preliminary Design Information, Spray Calciner

TABLE 4. Preliminary Design Information, Spray Calciner

Design CriteriaCalciner Chamber

Type	Right cylinder
Inside diameter	36 in.
Height	10 ft.
Total heat transfer area	94 ft. ²
Material	316 SS
Wall thickness	0.25 in.
Bottom	≥ 60° slope

Furnace

Type	Electrical resistance 3 phase, 480 V
Number of zones	4
Control	Silicon controlled rectifier
Maximum power (total)	280 kW @ 70 kW/zone
Normal operating temperature	800°C
Maximum operating temperature	1000°C

Atomizing Nozzle

Type:	Pneumatic, internal mix such as Mfg.: Spray Systems Company. Model: Setup No. 72 or equivalent
Fluid orifice	Type 304 SS, 0.375 in. I.D.
Air cap orifice	Type 303 SS with a 96% alumina insert, 0.25 in. I.D.
Atomizing gas	Ambient temperature air
Air to liquid volumetric flowrate ratio	300

Filters

Type	Sintered powder metal cylinder
Total filter area	≥ 150 ft ²
Mean pore size	65 μ
Material	316 SS
Number candles	68
Candle dimension (156 ft ²)	2 3/4 in O.D., 36 in. long, and 1/16 in. thick (reinforced)

Filter Blowback System

Type	Venturi
Blowback air pressure	60-100 psig at blowback nozzle
Blowback nozzle size	0.15-0.18 in. I.D.
Percent of filters cleaned simultaneously	20%
Blowback cycle	2-100 min
Pulse duration	0.25 sec

Vibrators

Type	Pneumatic dry lubricant such as Mfg: Cleveland Vibrator Co., Model: 1300 AC Vibramight or equivalent
Motive air pressure	40 psig
Location	Side mounted
Number	1 plus installed spare

FIGURE 6. Preliminary Design Information, In-Can Melter Schematic Diagram

TABLE 5. Preliminary Design Information, In-Can Melter

Frit Feeder (out of cell, see Figure 6)

Type - Variable speed, continuous weigh belt

Bin size - 465 kg of frit per day are required ($\sim 10 \text{ ft}^3/\text{day}$)
(Frit: size - -20/+80 mesh; Density - $\sim 100 \text{ lb/ft}^3$)

Nominal feed rate - 19.35 kg frit/hr

Control - The feeder may operate as a slave feeder by metering frit at a rate proportional to the flow rate of liquid waste to the calciner. (Possible control by canister weight.)

Maintenance - The bin, scales, and feeder will be outside the hot cell so that they need not be radiation resistant and hands-on maintenance is possible. The ducts and airlocks should be made of abrasion resistant materials.

Performance - The airlocks must minimize back migration of contamination. A duct angle of 45° from vertical is adequate for gravity flow of the frit that is -20/+80 mesh.

Spray Calciner/In-Can Melting Coupling Section (see Figures 6, 19, and 21)

Duct size - 4 in. inside diameter minimum

Minimum slope - 60° from horizontal

Operating temperature - 300°C (calcine temperature) normal and 100°C minimum

Durability - Inside must be abrasion, nitric acid, and radiation resistant. (Stainless steel may not resist abrasion well enough.)

Performance - Total section must be leakproof. Inside surfaces should be smooth with no ledges for frit/calcine to collect.

In-Can Melter

Type: To be determined (resistance or induction)

Size of furnace exterior - 12 ft high x 5 ft diameter

Size of heated chamber - 10-3/4 ft high x 3 ft diameter

Number of zones - Present experience suggests using 8 zones each approximately 15 in. high.

Power required - 30 kW/zone or 240 kW total plus safety

Cooling required - 7 kW/zone or 56 kW total plus safety

Maximum operating temperature - 1200°C

Materials - Low thermal inertia, unaffected by thermal cycling, thermal shock, and radiation

Size of susceptor/retort - 10-1/2 ft high x 28 in. max I.D.

Susceptor/retort - It must be a good susceptor material if induction heating is used. It must have good strength and oxidation resistance at 1200°C . It must be unaffected by thermal cycling and thermal shock. Hastelloy X was successfully used in both induction and resistance furnaces in WSEP. Temperature was less $\sim 1000\text{-}1050^\circ\text{C}$.

Load cell range - 0-3,500 kg

Load cell total capacity - May need to support susceptor/retort as well as can and melt

Load cell materials - Should be resistant to radiation or appropriately shielded. Should be resistant to temperature.

FIGURE 7. Preliminary Design Information, Canister Decontamination Rack

TABLE 6. Preliminary Design Information, Canister
Decontamination Rack

Washing Chamber

Height: 12 ft

Width: 3-4 ft (Depends on spray nozzle selected)

Spray Nozzles

Spray nozzles should deliver a coarse, high-velocity spray which completely covers the canister surface when the canister is rotated. The nozzles should be arranged symmetrically around the canister to prevent excessive sideways thrust on the canister rotor bearing.

Motor

Fixed speed dc motor

Material of Construction

304L stainless steel

FIGURE 8. Preliminary Design Information, Canister Storage Racks

TABLE 7. Preliminary Design Information, Canister Storage Racks for Full Canisters and Empty Canisters, Canister Welding, and Canister Leak Checking

Design Information: Full Canisters Rack

Structure

Size	60 in. wide x 60 in. long x 120 in. high
Material	Stainless steel

Coil Supports/Canister Guide

Number required	3/space
Material	304L Stainless steel

Storage Space

Number required	Suggested 4
Size	24 in. diameter (inside coil support)

Coil

Number required	4
Cooling load	28-30 kW/coil
Material	304L Stainless steel

Design Information: Empty Canisters, Canister Welding, and Canister Leak Testing Rack

Structure

Size	60 in. wide x 90 in. long x 14 ft high
Material	Stainless steel

Coil Support/Canister Guide

Number required	3/space
Material	304L Stainless steel

Storage Space

Number required	Arbitrarily: 6
Size	24 in. diameter (inside supports)

Coil

Number required	2 (one for weld station; one for leak test station)
Cooling load	28-30 kW/coil
Material	304L Stainless steel

INSTRUMENTATION

The initial process monitoring and control instrumentation necessary for the Spray Calcination/In-Can Melting process is shown below in the instrument engineering flow diagrams. The diagrams are contained in the figures indicated below:

<u>Figure Title</u>	<u>Figure Number</u>
Instrument and Engineering Flow Diagram of Spray Calciner Feed Tank	9
Instrument and Engineering Flow Diagram of Spray Calciner	10
Instrument and Engineering Flow Diagram of In-Can Melter	11
Instrument and Engineering Flow Diagram of Canister Seal Weld, Leak Test, and Empty Canister Storage Rack	12
Instrument and Engineering Flow Diagram of Filled Canister Storage Rack	13
Instrument and Engineering Flow Diagram of Canister Decontamination Rack	14
Legend for Instrument and Engineering Flow Diagram	Table 8

FIGURE 9. Instrument and Engineering Flow Diagram of Spray Calciner Feed Tank

FIGURE 10. Instrument and Engineering Flow Diagram of Spray Calciner

EQUIPMENT TO BE LOCATED IN AND OUT OF CELL WILL BE SPECIFIED IN MORE DETAILED DRAWING.

FIGURE 11. Instrument and Engineering Flow Diagram of In-Can Melter

FIGURE 12. Instrument and Engineering Flow Diagram of Canister Seal Weld, Leak Test, and Empty Canister Storage Rack

FIGURE 13. Instrument and Engineering Flow Diagram of Filled Canister Storage Rack

FIGURE 14. Instrument and Engineering Flow Diagram of Canister Decontamination Rack

TABLE 8. Legend for Instrument Engineering Flow Diagrams

Rack or panel mounted	ETM	Elapsed time meter	RC	Ratio controller
Locally or in-line mounted	FA	Flow alarm	REF	Reference pressure header
Two measured variables	FC	Flow controller	RW	Raw water (unsanitary)
Flow element	FE	Flow sensing element	SE	Sensing element
Motor	FI	Flow indicator	SS	Steam supply
Diaphragm operated valve	FT	Flow transmitter	SW	Selector switch
Solenoid operated valve	FY	Converter	SUM	Summer
Ball valve	HTA	High temperature alarm	SPL	Sampler
Needle valve	IAS	Instrument air supply	TC	Temperature controller
Reverse flow check valve	IS	Current switch	TE	Temperature sensing element
Restricting flow orifice	IC	Ionization chamber	TI	Temperature indicator
Jet pump	IY	Relay	TR	Temperature recorder
Process service lines	JR	Power recorder	TA	Temperature alarm
Pneumatic instrument lines	JS	Electrical power switch	TT	Temperature transmitter
Primary process lines	KJC	Timer	VC	Valve controller
Electronic wires or hidden lines	LLA	Low level alarm	VIB	Vibrator
AI	Amperage indicator	LLI	Liquid level indicator	WC	Weight controller
AS	Air supply	LLR	Liquid level recorder	WR	Watt recorder
ATM	Atmosphere	LC	Load cell	WS	Water supply
DPA	Differential pressure alarm	PA	Pressure alarm	Δ WA	Weight rate change alarm
DPR	Differential pressure recorder	PE	Pressure sensing element	Δ WI	Weight rate change indicator
DPT	Differential pressure transmitter	PCV	Pressure control valve	Δ WR	Weight rate change recorder
DR	Density or specific gravity recorder	PGM	Programmer	Σ WR	Weight totalizer recorder
		PI	Pressure indicator		
		PR	Pressure recorder		
		PS	Pressure switch		

TECHNOLOGY

Technology developed for the Spray Calcination/In-Can Melting process is summarized here. The references contain additional information. Process development is continuing, and this information will be revised and/or updated as new data become available.

SPRAY CALCINATION

Process Description

In spray calcination, liquid waste is pumped and metered to the spray calciner at a pressure of 1 to 2 atm. The waste is pneumatically atomized in an internal mix nozzle and sprayed into the top of a cylindrical calcination chamber. The atomized liquid waste as $\sim 70\text{-}\mu\text{m}$ -dia droplets is sequentially evaporated, dried, and calcined as it falls through the calcination chamber. The chamber walls are heated to about 700°C by an external multizone resistance furnace. Inside the chamber heat is transferred to the droplets by combined radiation and convection. This produces calcine containing typically less than 0.5% moisture. Periodic operation of side-mounted vibrators prevent significant depositions on heat transfer surfaces within the calciner. On passing through the chamber, water vapor and atomizing air entrain 15 to 50% of the calcine particles. During normal operation only 0.1% of the total particulates pass through the porous stainless steel filters. The entrained powder collects on the filters and is periodically removed by a pulse of blowback air. After this it falls into the lower calciner cone and is discharged along with that calcine falling directly from the calcination chamber.

The simplicity of the spray calciner makes it easily automated to minimize operator attention and facilitate remote operation. Successful remote operation and maintenance of a heated-wall spray calciner has been demonstrated while processing actual high-level waste.^(5,9) The calciner can be started up and shut down in less than an hour and produces no additional waste. Also during operation radionuclide volatilization is acceptably low.⁽⁹⁾

Feed System

The feed system to the calciner consists of the following subsystems: feed tank, pump, flow control, and spray nozzle. The feed system has been developed to deliver properly atomized HLLW of uniform composition to the calciner at a controlled rate. The development of these subsystems is described here. Figure 15 shows the system schematically.

FIGURE 15. Simplified Spray Calciner Feed System

Feed Tank

During normal plant operation, waste will likely be batch transferred to the calciner feed tank. If a canister of waste solid such as glass is to be produced in a batch or low-holdup melter, the liquid waste volume may be sized to produce one canister of solidified product. By this technique added assurance of canister contents can be gained because liquid sampling is normally more accurate and easier than solids sampling. Since chemical adjustment of the feedstock probably will not be necessary, a single feed tank can be used

by simply adding the next waste batch as the liquid level reaches a lower limit. This technique was routinely used in the WSEP and WFP. A tank with a working volume of 1000 gal would fulfill this need for the design bases flowsheet.

Lag storage of waste slurries is complicated by the need to prevent settling of nondissolved species. Accurate melt formulation may be dependent on a known amount of solids entering the calciner and subsequently, the melter. Also deposition of solids in waste tanks may result in plugging, eventual hot spots and accelerated corrosion. No difference in calciner performance has been observed when operating at waste concentration from 200 to over 650 liters of waste per tonne of fuel. Experience⁽¹⁰⁾ has shown that waste concentrations and/or composition may change drastically during operation without requiring corrective action.

An electric motor-driven propeller agitator for feed tank agitation has proven successful for maintaining homogeneity in waste slurry tanks. The agitator can be designed to provide the degree of mixing desired. In the WSEP, use of electric motor driven agitators has proved not only effective for solids suspension but also capable of sustained operation in high-level waste service. If desired, the agitator motor's radiation resistance can be increased by shielding the motor or other potential failure areas. Studies with simulated material have shown that agitation by air sparging is not effective in maintaining homogeneity throughout the tank. Accurate liquid sampling is thus virtually impossible. In the absence of proper agitation, suspended solids which predominate in the lower part of the tank are drawn into the calciner first, thus complicating accurate melt formation. Furthermore, pluggage of air holes in the sparge ring has been a continuing problem. A pulse type of agitation technique developed at Windscale, England, has been effective in preventing accumulation of solids in the bottom of large storage tanks. Applying this technique to feed tanks, however, can result in somewhat less than optimum performance because of the predominance of solids near the tank bottom, the frequent pulsation required, and the continually changing liquid level.

Liquid level monitoring dip tubes are accurate and effective for determining tank volumes. In the WSEP program, dip tube plugging in solutions with high solids content was negated by periodically discontinuing the air purge to the dip tube. This allowed liquid to enter the dip tube and dissolve deposits formed at the air/liquid interface. Plugging of waste tank dip tubes has not been encountered in WFP simulated nonradioactive wastes. Liquid level monitoring serves to confirm the feed rate measured by electromagnetic flowmeters on the calciner feed piping.

Maintaining the waste temperature at 40°C or lower reduces feed drying and blockage at the spray calciner atomizing nozzle. Thus, to counteract the self-heating of the calciner feeds, the feed tank(s) should have a cooling system. However, the cooling required to maintain acceptable limits will fluctuate with the quantity of feed and the specific feed heat-generating rate. Manual cooling water flow control systems can be used to compensate for fluctuating feed tank temperatures. However, an automatic control system capable of maintaining the feed within $\pm 10^\circ\text{C}$ of a set value should be considered for increased reliability and for economical use of manpower and cooling water. Neither the absolute temperature of the feed nor feed temperature fluctuations significantly affect the operation of the calciner. However, the feed should be kept cool to minimize evaporation in the feed tank and minimize corrosion of equipment.

Pump

Many types of transfer devices have been evaluated for pumping radioactive slurries. Air lift techniques have been developed and are routinely used for metering and transferring dilute suspensions. But handling concentrated slurries at low flow rates by this technique has normally not been successful. A pressure head is useful in preventing pipe and nozzle blockage and is required for some atomizing nozzles. Continuous control valve cycling normally required with air lift systems in this service is unnecessary. In the WSEP, radioactive slurries were pumped with disposable in-line centrifugal pumps. Unfortunately, their short service life limits their usefulness.

On the other hand, Savannah River Laboratory and other sites have found that concentrated radioactive slurries can be routinely pumped using vertical cantilevered shaft pumps. With this type pump all seals and bearings are above and out of the liquid. This permits long-term operation without seal replacement. Experience at Savannah River with 35 cantilever pumps in a radioactive environment has shown that in high-level waste service this type pump can be expected to operate 5 to 10 years without maintenance. These pumps typically permit high flow rates and are potentially capable of supplying feed tank mixing from a jet of recycled liquid waste.

In storage of concentrated liquid waste, at the air-liquid interface, caking on vessel walls often occurs. Dislodged caked solids in tanks and lines pose potential line blockage problems. This may be intensified in denitration vessels if the sugar denitration process is used. Restrictions in the feed lines (3/16 in. dia), the electromagnetic flowmeter, and the atomizing nozzle (1/4 in. orifice) are potential plugging points that could require shutdown if appropriate provisions are not made. To prevent blockage at these points, a solids filter may be installed in the feed system. A strainer is planned to be tested on the inlet to the cantilever pump. Since the amounts of solids material larger than 1/4 in. are likely to be very small, strainer cleaning is not expected to be necessary. Collected solids could be dissolved during system downtime. If desired, a basket type filter containing the accumulated oversize solids could also be used. In a vitrification facility the collected solids could be chemically or physically reduced in size, or it may be possible to periodically place the baskets in a canister to be filled with glass.

Flow Control

The spray calciner/in-can melter is relatively insensitive to waste feed rate fluctuations with short-term variations of as much as $\pm 50\%$ being acceptable. Since the frit flow rate is controlled so that it is proportional to the waste feed rate, proper glass formulation on melting is possible with significant feed rate fluctuations. But such variations are unnecessary since the control system described has an accuracy of about $\pm 1\%$ of the set point. The

design bases feed rate is about 80 liters/hr, but for process flexibility, the flow control system should have a usable range of from about 30 to 150 liters/hr.

A recirculation loop from the feed pump back to the feed tank, shown in Figure 15, is recommended. This accomplishes several things: it minimizes settling of undissolved solids in the feed lines when the feed rate to the calciner is low or shut off completely, and it enables the feed pressure to be adjusted to optimize the performance of the feed flow control valve. To minimize the settling of solids in the feed line, the spray nozzle, the flow sensor, the feed flow control valve, and the feed tank selector valves should be coupled as closely together as is practical, and each feed tank selector valve should be coupled as closely as practical to the respective feed recirculation loops.

A pneumatically operated flow control valve, remotely operated from a manual control station, is indicated in the feed recirculation loop for each feed tank. This valve and the recirculation loop piping should be so sized that adjusting the position of the recirculation valve permits varying the feed pressure ahead of the calciner feed flow control valve so as to keep the valve in a 60 to 80% open condition while maintaining the desired feed flow rate. This avoids the flow rate fluctuations caused by undissolved solids accumulating in the control valve when operated in its more nearly closed position. The recirculation loop control valve could conceivably be replaced with a fixed orifice if it could be assured that solids would not block the orifice and that the required calciner flow rate range is narrow enough that the feed flow control valve does not have to routinely operate outside of its 60 to 80% open condition to satisfy this flow rate range. The calciner feed flow control valve should have a linear spline plug trim, with a single tapered spline on the plug, similar to the Hammel-Dahl design. This type of trim realizes the desired flow control characteristics, and it presents the largest passage possible for undissolved solids for any given feed flow rate.

An electromagnetic flowmeter may be considered for the calciner feed flow rate sensing device. With a 1/10 in.-dia vitreous enamel-lined tube

and platinum electrodes, indicated flow rates will be accurate to within $\pm 1\%$ of the actual flow rate, from 20 to 230 liters/hr. The 1/4 in.-dia tube decreases the chance of plugging with a solid particle, but the lower flow detection limit is 30 liter/hr. The accuracy from 30 to 110 liters/hr is $\pm 2\%$, and above 110 liter/hr the accuracy improves to $\pm 1\%$. A feed metering system using the atomizing nozzle orifice as the flowmeter is being developed to potentially eliminate the need for an electromagnetic flowmeter.

It is recommended that a flush line be connected to the calciner feed line immediately ahead of the calciner feed flow control valve. This will enable the flow control valve, the flow sensor, and the spray nozzle to be flushed to the calciner, and the feed pump and recirculation line to be flushed to the feed tank when the feed to the calciner is shut down. In addition, if the flush supply is not in an adequately shielded area, it is recommended that the flush line be pressurized at all times to a value slightly in excess of the feed supply pressure. This will reduce the possibilities of feed being forced into the flush water piping system, past check valves and flow control valves that can potentially leak, or be inadvertently left open.

A conventional bourdon tube-type pressure indicator is suggested to measure the feed supply pressure ahead of the feed flow control valve. However, since the standard glass face cover will darken quickly from cell radiation, making the gage unreadable, the glass will have to be removed or replaced with radiation-resistant glass. If the gage cover glass is removed, the gage movement will be exposed to the probably corrosive environment of the cell, and gage replacement will probably be frequent. To avoid an identical problem, in indicating the feed pressure at the spray nozzle, the feed pressure can be implied by the feed flow rate, an empirical relationship developed from simulated feed compositions and prototypical nozzle assemblies.

Spray Nozzle

Proper atomization is the key to successful spray calcination. Experience⁽¹¹⁾ at PNL has shown that a droplet mass median diameter of ≤ 70 microns is sufficient for successful operation with waste compositions, chamber

configuration and temperatures studied. The required particle size may be obtained by using a commercial nozzle supplied by the Spraying System Company. The air cap has been modified by addition of an insert made of 96% alumina to avoid abrasive wear, as shown in Figure 16. A nozzle tested has logged 1000 hr of use without detectable wear. Alumina air caps are more susceptible to damage by thermal shock than are caps of stainless steel. These shocks are prevented if atomizing air flows through the nozzle during heatup to the operating temperature before the water flush is turned on, and the feed and air should not be turned off simultaneously while the calciner is hot. The atomizing air flow should also be maintained while the calciner is at the operating temperature whether or not liquid is flowing. To obtain the required atomization, a Spraying System Setup No. 72 or the equivalent can be used in a re-processing plant.

Steam, hot air, and ambient temperature air were evaluated as atomizing gases during the design verification testing (DVT) and WSEP. The steam and preheated air caused nozzle plugging because they baked waste in the orifices.

FIGURE 16. Atomizing Nozzle

Therefore a cleanout needle was designed into the nozzle assembly. At Karlsruhe, Germany, where superheated steam is used as the atomizing gas in their nuclear waste spray calciner, severe nozzle plugging problems were recently solved by cooling the liquid line and nozzle.⁽¹²⁾ Nozzle plugging has been virtually eliminated at PNL by using ambient temperature atomizing air, by placing a sieve with 0.04 in. openings in the liquid waste line before the nozzle, and by flushing the feed line and nozzle with water before each startup and after each shutdown. The only treatment given the atomizing air is filtration to remove entrained oil introduced by the compressor. Plugging is not anticipated with the Spraying Systems Co. Setup No. 72 nozzle because the minimum diameter orifice is 1/4 in. instead of the 1/8 in. nozzle used in the early tests. A remotely operated nozzle cleanout needle may not be required on a production calciner.

Atomizing air flow control is not critical in the operation of the spray calciner. To produce drops in the desirable range of 40 to 70 microns, a volumetric air-to-liquid flow rate ratio of about 300 should be used. To achieve these droplet sizes the atomizing air pressure at the nozzle should be about double the fluid feed pressure at the nozzle for feed flow rates above 40 liters/hr. Below 40 liters/hr the nozzle air pressure should be about triple the nozzle fluid pressure. To eliminate an in-cell measurement of the atomizing air pressure at the nozzle, the atomizing air pressure could be measured at some appropriate point in the out-of-cell atomizing air piping, and the piping from this point to the in-cell nozzle could be sized so as to minimize the pressure drop between this pressure measurement point and the nozzle. A pressure switch should be interlocked with the feed pump switchgear in such a way that at low atomizing air pressure values the feed pumps will be turned off. This switch would be activated by the out-of-cell nozzle atomizing air pressure and set at a pressure slightly below the minimum anticipated atomizing air pressure. This will minimize the probability of forcing feed material past potentially leakable check valves and into the out-of-cell atomizing air piping. In addition, anti-backflow devices such as check valves or filters which will not pass liquid should be installed in the atomizing air line along with a radiation alarm.

Calciner

The calciner comprises three main components: the chamber, the furnace, and the off-gas filter system. The technology for these systems is described here.

Calciner Chamber

The calcination chamber is a large, externally heated vertical tube. Atomizing liquid waste is sprayed into the top center. Combined radiant and convective heat transfer within the calcination chamber allows evaporation and calcination at a high rate. Under normal operating conditions spray particles dry before striking the wall and thus do not adhere to the wall. Calcine produced in the spray chamber falls into a conical section together with calcine blown back from the filters. It then flows by gravity to the melter below. Experience at PNL with other geometries for combining the two calcine streams has shown that the filters should be as close to the calcination chamber as possible. All surfaces are sloped ≥ 60 degrees from horizontal to avoid calcine accumulation in the cone.

Both Hastalloy and stainless steel have been used as spray chamber material. Presently, the rolled and welded stainless steel chamber has been in nonradioactive operation for over 800 hr. Spray calciner wall thickness measurements on the stainless steel chamber failed to show a detectable decrease in wall thickness. Since the instrument used was accurate to within $5\text{ }\mu\text{m}$ (0.0002 in.), a corrosion/erosion rate of less than $75\text{ }\mu\text{m}$ (0.003 in.) per year is expected.⁽¹³⁾ The 1/4-in. wall thickness in use is designed for strength with minimum concern for corrosion.

Figure 17 shows capacity data developed in 13 and 21-in.-dia spray chambers. A recent nonradioactive capacity run, using the two-zone (50 kW/zone) furnace, 21-in.-ID spray chamber heated to 700°C , and simulated clean waste, calcined waste at flow rates up to 75 liters/hr. Higher feed rates were not possible because of the limited capacity of the available calciner furnace, but scale-up calculations show that over 150 liters/hr can be processed in the full-scale unit described in the "Equipment Description" section. This unit can operate at the design bases flowsheet rate.

FIGURE 17. Spray Calciner Capacity

The calciner chamber size required, both diameter and length, has not been established. Thus a conservative size, 3 ft dia by 10 ft tall, is specified to perform the design bases flowsheet. It is anticipated that optimization will reduce the size required.

Scale (calcine and corrosion) deposits on the calciner wall can form an insulating layer which reduces calciner capacity. Experience⁽¹⁴⁾ has shown that scaling increases when wastes containing high-sodium concentrations are calcined under conditions where moist particles impinge on the wall. However, HLLW wastes containing over 2 M sodium have been satisfactorily calcined without feed additives.

Under normal operating conditions wall scale is minimal and extended operation is possible without significant scale buildup. But to ensure the flexibility and operability of the unit, vibrators have been mounted on the

calciner to minimize the possibility of scale buildup. Experience⁽¹⁵⁾ has shown that a vibrator located on the vertical center of the chamber and mounted on the furnace shell has prevented scaling even when using high-sodium-containing waste or when atomization of the feed was intentionally changed to introduce scaling conditions. Mounting the vibrator on the vertical center of the furnace outer shell has greatly reduced the required vibrator maintenance. Frequent replacement was required when the vibrator was located on the calciner top flange where it was exposed to high temperatures.

To help determine the effect of vibration on the spray calciner a 100 hr test was conducted in which the vibrators were activated frequently with the calciner at operating temperature to simulate up to 4000 hr of operation.⁽¹⁶⁾ The diameter of the spray chamber across the impact pads and at 90° to the pads was measured before and after 4000 vibrator cycles acting on 700°C calciner walls. No measurable difference in calciner shape was found when measuring to 25 μm (0.001 in.). However, the calciner must be designed to minimize the undesirable effects of vibration.

A thermal shock descaling technique for use during calciner shutdown has proved rapid and effective for removing even the most stubborn scale. A small amount of water sprayed onto the hot (500°C) calciner wall produces sufficient thermal shock to dislodge the scale. The descaling operation can be carried out with less than 40 liters (10 gal) of water, and nearly all water sprayed from a properly designed nozzle can be vaporized by the hot wall. Should it ever be needed, this descaling process requires 5 to 10 min and can be done with remotely operated equipment.

The vibrator cycle timer and solenoid operated air control valve should be adjustable for a pulse duration range of 3 to 30 sec with a 5 to 60 min cycle, depending on potential feed scaling characteristics.

Furnace

Multizone resistance furnaces have been used successfully at PNL to calcine HLLW. A ceramic fiber insulated furnace used for radioactive demonstration during the WSEP program contained three independently controlled heating

zones. The heating capacity of each zone was 15 kW. The electrical power to each heating zone was controlled by an automatic on-off controller which operated over a temperature range. A refractory brick insulated furnace used for nonradioactive demonstrations contained two independently controlled heating elements. The maximum heating capacity of each zone was 50 kW. The electrical power to each heating zone was controlled by a silicon controlled rectifier.

The recommended spray calcination chamber is heated by a resistance furnace divided into several horizontal zones. A maximum of four zones is required in the production unit, with a heating capacity of about 70 kW per zone. The electrical power to each furnace zone is controlled with a zero-crossover, silicon controlled rectifier power supply, using a thermocouple attached to the furnace side of the calcination chamber as the reference temperature. The temperature control system for each zone should be capable of maintaining the zone furnace temperature at any value within the range of 500 to 1000°C, with an accuracy of $\pm 10^\circ\text{C}$. The reference temperature should be recorded, and the alarm should be activated outside the control range to detect malfunctions of the control system. At least one redundant thermocouple for each zone should be mounted on the furnace side of the calciner opposite from the reference thermocouple. These redundant thermocouples should also be recorded and alarmed above the furnace set points to detect possible scaling within the calciner over the reference thermocouple locations.

Thermocouples should be positioned inside the calciner above the feed nozzle spray pattern, in the powder collection cone, above the powder diverter valve, and in the off-gas filter zone to monitor the calciner operation. These temperatures should be recorded to detect long-term changes.

The furnace should be encased in a material resistant to vapors and to potential spills of process solutions. Brackets should be mounted on the furnace to hold the vibrators. To reduce head room requirements the furnace may be designed capable of disassembly by zones for removal from the calciner.

Radial and longitudinal temperature uniformity does not appear to be critical to calciner operation. Longitudinal temperature differences of over

100°C have been observed at times during operation. Since the furnace will likely be held at a constant temperature of about 700°C during operation, thermal cycling will occur only at startup and shutdown. The heatup rate will likely be limited by the thermal shock resistance of furnace materials, not by the calciner.

Filter System

Early experiments⁽¹⁷⁾ with various filter types for dust removal led to the choice of sintered stainless steel filters. Various filter media tested included porous alumina, fine woven wire, fine wound wire, sintered fiber metal, and sintered metal powder. Sintered powder filters appear to exhibit the best compromise between filter efficiency and ease of cleaning by pulsed blowback air. Alumina filters have 10-mm (3/8 in.) thick walls and pore sizes ranging from 10 to 100 μm (0.0004 to 0.004 in.). They are fragile and not effectively cleaned by pulsed blowback. Wire wound and woven wire filters are not as effective as sintered filters, and sintered fiber metal filters are expensive and require high differential pressure.

The filters used in previous radioactive demonstrations as well as the present sintered filters being used in nonradioactive development testing have a mean pore size of 65 microns. They have been very effective in filtration of the calcine. A filter cross section is shown in Figure 18. However, due to the large filter pore size relative to the calcine particle size, some calcine can penetrate the filters before a layer accumulates on the filters. Thus, to avoid passage of calcine through the filtering media and particles becoming permanently lodged on the filter, filter candles having a mean pore size of 10 microns will be tested. Ten-micron seamless filters will be tested on the full-scale development spray calciner.

Pressure drop across the filters increases as the calcine accumulates on the filter candles. Pressure drop as high as 20 in. of water across the filters has shown no effects on filtration. Thus the blowback cycle is a function of the available vacuum to maintain the required 10 in. vacuum in the spray calciner unit. Accumulated filter cake is periodically dislodged from

FIGURE 18. Calciner Filter Candle

the sintered stainless steel off-gas filters by directing a short pulse of high-pressure filtered air into each filter element through a venturi nozzle in opposition to the normal off-gas flow through the unit. This blowback air is routed to each filter element venturi nozzle through a separate line controlled by a solenoid operated valve. The blowback system is analogous to a jet ejector. The venturi draws calciner off-gas from the filter off-gas plenum back into the filters to provide additional blowback air volume.

For efficient calcine cake removal and minimum calciner pressure surges, a blowback pulse of 60 to 100 psig air for 1/4 sec is used. This removes most of the cake but leaves a thin calcine layer. The layer acts as filtering media and reduces the particles that penetrate and permanently lodge in the filter.

The air to the solenoid control valves is supplied from a single manually operated pressure control valve. A cycle timer controls the operation of the solenoid valves. The cycle timer is designed so that 1) the solenoid valves are operated sequentially, 2) the period each valve remains open is adjustable from 0.25 to 5 sec, 3) the cycle time for blowing back the total complement of filters is adjustable from 1 to 100 min, and 4) any filter element may be blown back manually at any time. The time between filter blowbacks may be controlled by the filter differential pressure. The blowback piping, the solenoid valves, and the manual pressure control valve should be sized so that the pressure at the venturi nozzle will be maintained at 60 psig or greater for the duration of the blowback pulse.

The differential pressure across the sintered stainless steel off-gas filter elements should be measured and recorded to observe trends in filter performance, effects of process variations, and the effectiveness of remedial measures.

After passing through the sintered stainless steel filters, the off-gases pass directly to the off-gas cleanup system. The off-gas temperature should be measured immediately on leaving the filter plenum, and recorded, to observe trends in the calciner performance and the effects of process changes.

Calciner vacuum is normally controlled at 10 in. of water. However, during filter blowback the vacuum may only be 1 to 2 in. Internal vacuum is influenced by the interrelationships of: pressure drop across the off-gas filters, calciner feed flow rate, pressure drop through the off-gas cleanup system, and fluctuations in the volume of other gases contributing to the total flow through the vacuum source. It is recommended that the differential between the calciner operating pressure and the cell pressure be measured and recorded. The recorder should be provided with alarm contacts to warn of impending pressurizing conditions.

IN-CAN MELTING

Process Description

An empty can with a gasket in the canister mouth is transported into the hot cell where vitrification is done. An assembly consisting of the lid for the retort/susceptor (R/S), the insulating plug for the top of the furnace, and the can suspension hooks is lowered onto the top of the can with the overhead crane, and the hooks are engaged in the ears of the can. This assembly and the can are then raised by the crane and lowered into the R/S of an empty furnace. The lid assembly rests on the top flange of the R/S, and the can is suspended by the ears from the lid assembly in the R/S. Suspending the can from the top while it is in the furnace permits expansion and contraction of the can to occur during processing without affecting the connection to the calciner or the can content weight monitoring system. Suspending the can in the furnace will probably also minimize can distortion during the in-can melting process.

The present reference process designates the furnace to be at 750°C when the empty can is placed into it, but it could be at ambient temperature. Cycling the cell furnace between 750°C and the processing temperature, rather than between ambient temperature and the processing temperature, should increase the life of the furnace and significantly reduce the time required to bring an empty can to the processing temperature. However, it will also contribute to the total heat load which the cell ventilation system must remove. An additional insulating cap for the furnace will also be required for those periods when there is no can in the furnace and the furnace is idling at 750°C. Placing a can made from 304L stainless steel in the furnace at 750°C without the cover gas should not create a spall problem because scaling does not occur below 900°C.

When the can and lid assembly are in place on the furnace, the crane hook is disconnected and the furnace is rolled into position below the coupling section. Pneumatic cylinders then lower the coupling section into the top of the can to make a dust-tight seal at the gasket located there. As the cone valve is opened and lowered into the neck of the can, the pressure in the can lowers to that of the calciner. Normal operation is at a vacuum of 10 in. of water.

If the can was not already suspended on load cells when it was lowered into the R/S, this is also accomplished at this time by the action of pneumatic cylinders. The HLLW vitrification system is now assembled as shown in Figure 6.

The retort is purged with the selected cover gas to prevent canister spall formation, and the can is heated to the processing temperature. About 0.1 lb of scale per square foot of can exterior surface forms when a can made of 304L stainless steel is held at temperatures above 1000°C for more than 8 hr in an air atmosphere. Thus a 20-in.-dia by 10-ft-tall can could be coated by an oxide layer of up to 8 lb if adequate air were available to form the spall during processing. The spall can be reduced or eliminated by minimizing the air volume in the R/S or employing an inert purge gas. If the can is removed from the furnace at temperatures above 750°C for quenching, the scale is still loosely attached to the can, and the majority is deposited in the quench tank rather than in the furnace R/S. This spall is a waste to be disposed of if it is not prevented. It could be collected and placed in each canister, or could be handled as spent equipment. Alternatives to the use of a cover gas to prevent spall include 1) designing the R/S to collect spall for later disposal, 2) placing a protective coating on the can exterior such as plasma sprayed zirconia,⁽¹⁸⁾ and 3) making the can from alloys which do not form scale at the processing temperature.

The present processing temperature range is between 1050°C and 1100°C. The actual can surface temperature which the furnace must achieve depends on the batch (calcine and frit mixture) composition, the heat generation rate of the waste, and the thermal conductivity of the melt and fin design. Present batch compositions must be heated above 1025°C to melt well. WSEP experience with in-can melting showed that melt centerline temperatures of 1040°C could be obtained with self-heating waste in 8-in.-dia cans without fins by heating the can walls to between 900°C and 950°C.⁽⁴⁾ The use of larger diameter cans containing fins will require that the temperature of the can wall be much closer to the processing temperature. The maximum processing temperature is determined by the strength of the can material and its resistance to attack by the melt. The minimum temperature is determined by the batch composition

and desired melting rate. The viscosity of the melt as a function of temperature is an important consideration. When using present batch compositions and 304L can material, the best melting rates and products are obtained when temperatures are maintained as high as practical, between 1025 and 1100°C. If the cans are made from nickel base alloys, the processing temperatures may be raised to 1150°C or more. The optimum time to hold each zone at the melting temperature has not been determined. But, based on WSEP experience, it will probably not exceed by more than 2 hr the time required to fill the zone. A short time at temperature is desirable to minimize the loss of volatile species and settling of dense phases.

The rate of temperature rise of the empty can will most likely be determined by the limits of the furnace construction materials. If the furnace is an all metal induction unit, it may be heated very fast (500°C/hr). If it is a resistance-heated furnace insulated with the new fiber ceramics, the resistance elements may be the rate limiting material. It is expected that the cans used will be large enough to allow adequate cycle time for a conservative heatup rate not to exceed 200°C/hr. At a melting rate of 30 kg/hr a 20-in.-dia by 10-ft-long can will take over 50 hr to fill. By assuming 4 hr to top up and fine (remove gas bubbles) the previous can, 2 hr to cool it to 750°C, and 8 hr to change cans in the furnace, over 40 hr remain to heat the empty can to the processing temperature if desired. Thus ample time is available for the auxiliary parts of the melting process.

Carbide precipitation at grain boundaries in stainless steel alloys results in a phenomenon known as sensitization. This increases the metals' susceptibility to intergranular attack by halides. The degree of sensitization is a function of the carbon content of the metal, the temperature, and the time held at temperature. The 750°C temperature is considered by some sources to be the upper bound of the sensitization range of 304L stainless steel. The lower bound of the range is near 480°C. However, if the metal is cooled rapidly enough that transition through this range takes less than 1 hr, minimal sensitization should occur. Quenching the can of melt appears to minimize both sensitization and stress by causing the can to contract while the melt is still fluid. Presently in developmental work the canister is

immersed in flowing, cold (5 to 15°C) water. But more sophisticated spray or agitated quench systems can more easily assure uniform cooling to avoid localized stresses in the can.

When the empty can and furnace are at the processing temperature and the can in the other melter located below the calciner is nearly full, calcined waste and glass-forming frit are directed by the diverter valve down the coupling section into the empty in-can melter. The diverter is used because the heated-wall spray calciner is best operated continuously, but in-can melting is a batch process requiring periodic changing of cans in the furnace. The calciner, however, is capable of intermittent operation if desired.

Calcine is produced at a rate of about 10 kg/hr, and frit is metered into the cone below the calciner and above the diverter at a rate proportional to the calcine production rate to provide the desired batch composition. Present compositions require two parts frit to one part calcine by weight, so that the melter charging rate is about 30 kg/hr. This charging rate does not exceed the melting capacity of an 8 in. or 12-in.-dia can containing eight fins.

The in-can melter charge rate should not exceed the melting rate for most satisfactory operation. It was initially believed that the melting rate could be increased for a given diameter can by having the batch in contact with more of the hot can surface. Therefore, cans were precharged with batch or very rapidly charged with batch to the full level and then charged at a rate which maintained that level as melting proceeded. This charging method was called the batch melting method. It was found that in the relatively short, single-zone development furnace the rising level melting method resulted in higher melting rates. The batch melting rate is believed to be lower than the rising level melting rate because the NO_x and other gases released from the calcine as the batch is heated may create an insulating foam in the static batch; however, these gases are readily released at the surface of a rising level melt. The batch melting process also has been known to leave voids in the vitrified product as large as 2 in. in diameter.

As melt accumulates in the can, the temperature of the melt begins to rise above the processing temperature because of the heat generated by the waste. Power to the zones of the furnace below the melt level is switched off, and cooling of the zones is required. Forced air cooled the furnaces in the WSEP and will be used to cool the full-scale demonstration furnace. An air vacuum system gives better zone control, but a forced air system is better for hot cell application because the blowers can be located outside the cell and the hot air can either be quenched or dumped directly from the furnace to the cell.

The off-gas from the in-can melting process rises from the melter through the coupling section to the sintered metal filters of the calciner off-gas extraction system. Although characterization of the in-can melter off-gas is not yet complete, preliminary results show that cesium, boron, sodium, zinc, and molybdenum are not present, and only traces of ruthenium, zirconium, tellurium, lanthanum, praseodymium, and neodymium have been detected in the vapors to the filters. It is believed that the counter flow of batch and off-gas in the coupling section, the scrubbing effect of the calcine-coated filters, and the relatively cool, small surface of the melt in the in-can melter are responsible for the low radionuclide level of effluents from the process.

When the melt has filled the can to the desired level, the diverter directs the batch into the other melter. As the melt is fined (gas bubbles are removed), the melt level drops. If necessary to maintain the desired level, the diverter can add small quantities of batch periodically, or the melter can be overfilled initially if sufficient space is available in the heated portion of the can. Any solids accumulation in the canister section above the furnace heating sections is not completely melted due to the inability to achieve an adequate temperature.

During the fining phase of the process, off-gas from the melter must still be vented into the calciner even though the batch is being directed into the other melter. This can be accomplished within the diverter (shown in Figure 19), or a bypass line can be provided around the diverter.

FIGURE 19. Coupling Section-Concept I

Following the fining phase of the process, the inside surfaces of the unfilled portion of the can, the coupling section, and cone valve are coated with a partially melted or sintered layer of batch rich in calcine and species which have risen from the melt as volatiles and have condensed on these cooler surfaces. This coating spalls as the can is cooled following the melting process and has a leach rate about four times that of the glass. Depending on how stringent the solidified waste specifications are, this coating may have to be removed or totally vitrified. Attempts made to dislodge this material by thermal shock have not been totally successful. Other suggestions are to fill the can to the top with a glass containing no waste or to wash out the top of the can before making the closure.

After the melting is completed, the furnace and can of vitrified waste are cooled to about 750°C. The cone valve is closed, and the coupling section is disconnected from the canister. The furnace is rolled away from the coupling section to permit access to the top of the can, and the cap is placed on the can. The can is then removed from the furnace and can be water-quenched to avoid sensitization and to reduce residual stress caused by the difference in thermal expansion of the glass and steel.⁽¹⁹⁾ The quench must remove enough residual heat from the can and product that self-heating will not raise the can surface temperatures above 480°C (the sensitization range). Following the quench, the R/S lid assembly is removed from the can. The can is transferred to the closure weld station and sealed. Leak testing and decontamination of the can are then performed.

At this stage in the in-can melting process the canister may be put into water basin storage. Or it may be heat treated further at 480° to improve the canister corrosion resistance by relieving residual stresses. At this temperature the borosilicate glass will increase in density with time, and it is anticipated that as the glass volume decreases, residual stress in the can walls will also decrease. This feature is being evaluated at the present time.

The rising level method is compatible with direct coupling to a continuous calciner. To operate with the rising level melting method, the rate at which the calcine and frit enter the melter should not exceed the rate at

which they are being melted. Therefore, the melter fill rate is determined by the melting rate. Some of the variables that have been determined to increase the melting rate are:

- increased furnace temperature
- increased can diameter
- internal fins
- optimum batch feed rate to melter
- addition of reducing agent to the batch
- decreased moisture content of batch
- decreased nitrate content of calcine
- increased temperature of calcine entering melter.

Table 9 presents the melting rates demonstrated using a single-zone furnace and simulated HLLW calcine. To date both 8- and 12-in. canisters have been tested. The results are not directly comparable because some of the variables listed above were not constant for all demonstrations. But some general conclusions can be made.

Inclusion of fins in the can and use of the rising level method each had the effect of doubling the melting rate.

The effects on the melting rate of the addition of 1.5 wt% powdered silicon metal to the batch has not been quantitatively evaluated, but it has been observed to reduce the power required by the furnace to melt an equivalent amount of batch. Between 225 and 360 cal/g were required to melt batch without the additive while only 120 to 200 cal/g were required to melt the same batch with the silicon added.

Figure 20 shows some PNL experience with the effects of temperature on the melting rate. The data were obtained using the batch melting method in a 12-in.-dia can without fins.

The melting rates reported in Table 9 are considered conservative because they were established using nonradioactive, simulated waste which has no internal heat generation. High-level nuclear waste will generate from 15 to 150 W/liter of vitrified product, depending on the burnup of the fuel

TABLE 9. Melting Capacities of the In-Can Melter

CAN DIAMETER, INCH	MELTER CHARGING METHOD	NUMBER OF FINS	MELTING RATE		TIME TO MELT 100 KG, HR
			KG/HR	KG/HR-M	
8	BATCH	0		13.5	18.2
	DUMP	8		29	3.3
	RISING	0	14		7.1
	LEVEL	8	30		3.3
	RISING LEVEL CONCENTRATE	8	12		8.3
12	BATCH	0		18	6.0
	DUMP	8		21	4.2
	RISING	0	14.5		6.9
	LEVEL	8	50		2.0
	RISING LEVEL CONCENTRATE	8	13 - 19		5.3 - 7.7

FIGURE 20. The Effect of Canister Surface Temperature on Glass Melting Rate, 12 in. Canister Without Fins

processed, the age of the waste, and the waste loading in the host glass. During the radioactive in-can melting demonstrations at PNL in 1970, center-line temperatures reached 1040°C during melting in 8-in.-dia cans without fins while the walls were heated to only 900 to 950°C by the furnace. Even without the aid of this self-heating the melting rate of 30 kg/hr required for the waste from the NFS fuel reprocessing plant can be obtained with an 8-in.-dia can containing a drop-in fin assembly when coupled to a heated-wall spray calciner. This 30 kg/hr rate was determined assuming a frit-to-calcine ratio of 2:1.

Coupling Section

The coupling section conducts calcine from the calciner to the melter and melter off-gas from the in-can melter to the calciner filters. Figures 19 and 21 show some coupling section concepts. A diverter valve located immediately below the calciner directs the calcine and frit mixture to one of the two melters. Commercial diverter valves are available, but they usually provide a positive shut-off of one leg while diverting batch down the other. Application to the spray calciner/in-can melter process would thus require a bypass around the diverter valve for melter off-gas from the filled in-can melter while melting was being completed and batch was diverted to the other melter. The diverter valve shown in Figure 19 is a design which permits directing batch to one melter without restricting flow of the off-gas from the other melter to the calciner. The couplings between the valve and the calciner and legs of the coupling section are V-flange type which can be made and broken with manipulators.

The legs extending from the diverter valve to the melter are 4-in.-dia, insulated tubes which slope at a minimum of 60° from horizontal. Recent experience with uninsulated tubes has shown that moisture from the off-gas can condense in these legs and cause the calcine-frit mixture to accumulate there and partly plug the line. Insulating and heating the line to above 100°C is being investigated as a means of preventing this. This heating can be accomplished by injecting hot air into the tubes as was done in the WSEP, or

FIGURE 21. Coupling Section-Concept II

by heating the tube wall with a heat source located on the exterior of the tube. Care must be taken not to overheat the coupling section and melt or sinter the calcine-frit mixture in it.

At the lower end of the coupling section a metal bellows is used which permits the coupling to the can to be flexible so that the can is not restrained by the coupling when suspended from the load cells. A sleeve inside the bellows helps prevent accumulation in the folds, and an external shroud protects it from damage. Stops are also provided which prevent the bellows from being either over-expanded or excessively compressed.

Pneumatic cylinders are proposed in the coupling section concept shown in Figure 19 for remotely effecting the seal with the can. These cylinders are connected to the ears of the can and expand the bellows so that the lower end of the coupling section seats on the gasket located in the mouth of the can. Large clamping forces are not required because only a dust tight seal is needed, and the pressure differential is only 10 in. of water.

A cone valve is used to seal the lower end of the coupling section whenever a can is not connected. This valve also acts as a calcine-frit disperser when opened and lowered into the neck of the can. By directing batch away from the center of the can and toward the hot walls, the cone valve prevents batch bridges atop the fins and helps improve the melting rate. Experience shows that when the valve is located 12 in. above the top of the fins bridging does not occur, but when it is raised to 17 in., bridging can result within 15 min when charging at a rate of 50 kg/hr. The valve must be kept far enough above the heated part of the can so that the calcine-frit mixture does not stick to it. In the existing pilot plant unit when the valve is 12 in. above the fins, it is just at the top of the furnace vestibule. When the valve is so positioned, it acts as an insulating plug in the neck of the can to reduce heat losses during melting.

The conceptual design shows this valve being actuated by a pneumatic cylinder. The action of this cylinder must be so controlled that the position of the valve can be adjusted and the valve will not be slammed open or closed.

The valve is presently lowered and raised through a packing gland, but vapors off the melt condense on the shaft which make it too rough to pass through the gland. A concentric sheath or metal bellows are being evaluated as sealing mechanisms.

A bridge detector or some other melting process monitor may be located inside the cone valve for viewing the melt surface.

The coupling section being evaluated on an engineering scale is made from 304L stainless steel, but a more abrasion-resistant material may be required in critical wear areas such as the diverter valve and cone valve. This material must also be resistant to nitric acid at temperatures as high as 300°C and to radiation.

Retort/Susceptor

It is felt that a furnace liner is necessary to provide a secondary containment in the event of a can failure during the melting process. This liner must therefore be resistant to attack by the melt, have good strength and a low creep rate at the processing temperature, and not spall with each thermal cycle. If a cover gas is to be used, the liner then becomes a retort and must be unaffected by the cover gas. Also, if an induction furnace is used, the liner must be a good susceptor. The material selected for the retort in the full-scale demonstration furnace is Hastalloy X. The susceptor used in the six-zone induction furnace during the WSEP was made from Hastalloy X. It performed satisfactorily; however, that furnace was not used for in-can melting, and the susceptor did not serve as a retort.

The R/S should be suspended from the top in the melter furnace so that increases in linear length due to thermal expansion and creep do not affect the position of the top where the seal will be made and the can will be supported.

How well the retort will have to be sealed is not yet established, so it is assumed for present design purposes that it must be sealed tightly. It is believed that the oxygen content in the retort should be maintained below 100 ppm. This design requirement would minimize the release of radioactive material to the cell if a can did fail. But it complicates the coupling

section and retort lid design because it requires gaskets which will have to be replaced periodically and clamping forces which must be applied remotely. The inlet and outlet for the cover gas should be located at the top of the retort, but a gas distribution or exhaust manifold will be necessary inside the retort. The cover gas will be vented to the cell atmosphere.

Multizone Furnace

Whether the furnace used to heat the in-can melter should be an induction or a resistance type remains unresolved. The main criteria for making the selection are in order of importance: 1) dependability, 2) operability, and 3) maintainability. Initial cost can be insignificant compared to the cost of operation and maintenance problems in a hot cell.

The present design criteria requires a furnace having a nearly cylindrical heated chamber large enough to accept a R/S that is about 24-in.-dia by 10-ft-long. Therefore, the furnace chamber diameter should be 32-in.-dia. This heated chamber must be divided into zones, each controlled separately. The optimum zone height is not yet known. It is known that a 48-in.-high zone is too large and that overheating occurs at the bottom of the zone before batch at the top is melted. In the WSEP furnaces the zones are 14-in. high because that was a standard radiant plate size. This zone height worked well when melting self-heating HLLW. The new furnace will have 15-in.-high zones and a square heated chamber. The operation with 30-in.-high zones as well as 15-in.-high zones will be investigated. No bottom or top heaters are included in present chamber designs although one furnace supplier did recommend heaters in the lid to compensate for heat loss out the top.

The furnaces used in the WSEP were of modular construction such that each zone was a separate furnace in its own metal shell and frame. The frames interlocked so that the modules could be stacked. Such design facilitates remote maintenance or replacement of a defective zone.

The furnace assembly must be portable so that it can be moved away from the coupling section for can changes. This was accomplished in the WSEP by placing the furnace assembly on wheels and moving it on a track. The furnace connections such as power lines, cooling air lines, and thermocouple leads

telescoped in and out of plugs in the cell wall as the furnace moved. The furnace structure and wheels must be of sufficient strength to support the weight of a can full of melt and the retort/susceptor as well as the furnace itself. This weight will be near 10,000 lb excluding the furnace.

An alternative to a portable furnace with telescoping leads and a structure to support the can and R/S is a fixed furnace and a coupling section which swings or rotates clear of the top of the furnace. This design would permit the can and R/S to be supported by something other than the furnace.

The furnace should be made from materials not affected by radiation, heat, or nitric acid. The materials in the hot zone should be resistant to the effects of thermal cycling and capable of sustained service to temperatures as high as 1200°C in air. It is recommended that the shell of the furnace be constructed of 304L stainless steel. The new fiber ceramic insulations look attractive because they are not affected by thermal cycling, are very light weight, and have good insulating properties.

The furnace ordered for the full-scale demonstration has a heating capacity requirement of 30 kW exclusive of heat losses at the operating temperature for each zone and a total power rating of 180 kW for a 7 1/2-ft-high chamber. When this specification was prepared, wiped film evaporator concentrate was to be the melter feed, and the high-watt density was thought needed to both dry and melt the batch at the desired rate. However, this watt density could be achieved only in a resistance-heated furnace by using glow bar type heating elements made from SiC. Such elements do not have good service life when thermally cycled.

Melting rates of 50 kg/hr, sufficient to vitrify the HLLW from a 5 MTU/day reprocessing plant, have been sustained with a mean power consumption rate of 20.6 kW in a 48-in.-high, single-zone furnace when dry simulated HLW calcine and frit were being melted. Peak power consumption during the melting of this batch, which had no self-heating, was 26 kW including heat losses from the furnace. The resistance furnace used in the WSEP has a minimum heating capacity of 15 kW plus power capacity to compensate for heat losses at the maximum operating temperature for each 14-in.-high zone.

Temperature measurement for process monitoring and furnace control is done with thermocouples. Optical pyrometers are not recommended because the high-radiation environment darkens the view ports and lenses and damages the electronics in the instrument. The thermocouples used in the WSEP were Inconel 702 sheathed, magnesia oxide insulated, ISA type S platinum/platinum - 10% rhodium. These thermocouples were ungrounded, had a minimum sheath wall thickness of 0.024 in., and had a minimum wire diameter of 0.032 in. They gave good service. However, thermocouple materials to be used in a cover gas must be evaluated.

During development of the in-can melting process, thermocouples located inside the can have successfully monitored melting temperatures and provided information about the location of the melt level. A view port in the coupling section near the top of the can has been used to detect bridging and determine melt levels. However, in a remote production facility visual process control is not considered practical, and instrumentation of waste cans is expensive. Therefore other ways of monitoring the in-can melting process are being evaluated. The British have reported that melt level in their in-can melter is determined by monitoring the power consumed by each zone of their multizone furnace, which is controlled to maintain a constant temperature. Gamma detectors have been considered for both bridge detection and melt level determination. Thermocouples inside the retort near the can wall may provide sufficient information to control the process when this information is combined with that from the can weighing system and furnace zone power meters.

The furnace control thermocouples should be located near the center of the 4-in. gap between the retort and heating elements for best results if a resistance-heated furnace is used. They should be positioned on or very near the susceptor if induction heating is used. The process monitoring thermocouples should be located inside the retort/susceptor as near the can wall as possible. It is not expected that thermocouples will be attached to the can after processing experience has been developed. In the WSEP the thermocouples were located in a cage which could be lifted out of the furnace.

The furnace must have heat removal capabilities to prevent overheating of the can due to self-heating of the waste once melting has been completed.

In the WSEP and in the full-scale demonstration furnace this is done by blowing air into the furnace zones. Distributors made of an Inconel alloy uniformly disperse the air in each zone, which also has an exhaust port. Insulated baffles between zones prevent cooling in lower zones from interfering with melting in upper zones. An air extraction system would be more effective for isolation of zone cooling, but this would require the blower to be inside the cell and made of materials capable of operating at high temperatures. With a forced air system the blower can be located outside the cell, and the cooling air can be exhausted into the cell.

The WSEP furnace cooling system was capable of removing 4.4 kW from each zone when the R/S wall temperature was 450°C. Two compressors were used which supplied 480 cfm of ambient air at 29 psig. This was sufficient to cool 8-in.-dia by 8-ft-tall cans containing vitrified waste having heat generating rates as high as 200 W/liter. A heat removal capacity of 6 kW has been specified for each zone of the full-scale demonstration furnace in the range of 1200 to 400°C in addition to cooling sufficient to cool the empty furnace at a rate of 25°C/hr. The furnace supplier estimates 700 scfm air at 90 psig will be required to provide the specified cooling to the six zones of the furnace.

If can wall temperatures are to be maintained at 750°C following melting until the can is quenched, the cooling air flow to each zone must be controlled. This will be accomplished by using motorized adjustable port valves in the air manifold to each zone. These valves are controlled by the zone temperature controller.

Because the cooling air will be applied to the outside of the retort/susceptor, the R/S will smear the cooling across zone boundaries. This will be particularly true if the can inside the R/S has a much smaller diameter than the R/S. If this creates process control problems, it may be necessary to put washer-shaped baffles into the R/S or to use a smaller diameter R/S when small-diameter cans are being processed.

Frit Feed System

In development operations frit has been used with size ranges of -20/+80, -20/+100, and -325 mesh. A convenient size distribution for the frit supply

system being recommended is -20/+80 mesh. While the finer materials blend better with the fine calcine product and produce a homogeneous melt, the finer materials are more difficult to transfer, tending to bridge and plug the conducting piping. Coarse frits are easily transferred, but they tend to separate from the calcine as it drops into the canister, resulting in frit-rich and frit-poor zones in the melt. However, due to natural convection in the melter, this effect has not appeared detrimental to glass quality. The coarse, dry, granular characteristics of the frit materials make gravity flow systems ideal for continuous addition of frit to the canister in the glass-making step. However, the friable, abrasive characteristics of the frit limit the spectrum of solids feeding devices that can successfully control the flow rate of frit to the canister.

A reciprocating plug valve volumetric solids feeder, driven by a variable speed air cylinder, was used with some success in metering the frit flow. However, the frit's abrasiveness wore the plug and the sleeve excessively. This was particularly true at the leading edge of the plug, where the valve tended to shear the frit as the plug was moved from its filling position to its discharge position. Also, with the volumetric feeder the weight delivery rate was influenced by changes in the particle size distribution from one batch of frit to another.

Variable speed augers, feeding from vibrating or stationary hoppers, were also used with limited success in metering the frit flow. Again, with the volumetric-type feeder the weight delivery rate was influenced by changes in the frit's particle size. In addition, the vibration of the supply hopper tended to size the frit supply so that finer material was drawn out first and the coarser material last. This resulted in a higher weight flow rate with the first material out and a lower weight flow rate with the last of the frit supply, at a constant auger speed. Volumetric feeders in which the weight flow rate is influenced by the particle size of the supply frit are not recommended.

Belt feeders have been considered, and a variable speed weigh belt feeder appears adequate for frit feed rate control. A variable speed weigh belt,

solids feeder similar to a Merrick Scale Mfg. Co., Gravimerik® 950 C unit with a 12-in. belt is considered adequate for controlling the frit flow to the canister. With this unit, frit flows by gravity from a supply hopper into a distributor that spreads the frit across the moving belt in a uniform layer. A manually adjusted, fixed shear gate limits the thickness of the frit layer on the belt. A manually operated slide valve, positioned at the top of the distributor, stops the frit supply to the feeder to simplify routine maintenance of the unit. As the belt moves away from the distributor, it passes over a weigh deck where the belt and its load of frit is continuously weighed, determining the frit load per unit length of belt. This measurement is combined with a measurement of the belt speed in a multiplier module to yield a value for the weight of frit per unit of time that passes over the weigh deck. The frit is discharged from the feeder as the belt passes over the end pulley.

For an operating plant the instantaneous rate at which frit is being added to the canister is displayed in kilograms per hour in digital form on the feeder control panel. An analog value of this feed rate, suitable for a strip chart recorder, is also available at the control panel. The total weight of frit in kilograms that has been added to a canister is also displayed on a resettable digital totalizer in the feeder control panel.

The feeder is capable of being operated in an automatic, a slave, or a manual mode. In the automatic mode, the controller adjusts the belt speed of the feeder until the indicated feed rate in kilograms per hour matches the desired feed rate that has been manually positioned on the digital set point display. In the slave mode, the controller adjusts the feeder belt speed until the indicated feed rate matches a set point established by an external measurement, for example, a fixed percentage of the feed flow rate to the calciner, or a fixed percentage of the weight increase of the canister. In the manual mode, the feeder belt speed is adjusted to an appropriate constant speed by an operator at the feeder control panel. In all operating modes the instantaneous flow rate and totalizer displays function normally.

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The solids feeder is capable of delivering frit with an accuracy of $\pm 0.5\%$ of the rate set on the feeder controller.

The frit supply to the feeder flows by gravity from a supply hopper which is separately supported so that the weight of the frit supply does not rest on the feeder itself. The hopper can be sized to hold several weeks' or months' supply of frit or to hold just enough frit for a single canister of glass, thus decreasing the possibilities of overfilling the canister. A low flow rate alarm is provided on the feeder controller that can be used to indicate an empty supply hopper.

The frit feeder is located in the service gallery, where it is protected from the cell environment and is accessible for routine contact maintenance. As the frit discharges from the solids feeder, it is conveyed by gravity through the cell wall and into the calciner cone through a nominal 2-in. dia pipe. To assure smooth gravity flow, the pipe is sloped no more than 45° from vertical from the feeder to the calciner cone. To provide multiple protection against the possibility of discharging calciner gases into the service gallery, the frit conveyor pipe has an air break and an automatically operated air lock system in a shielded, ventilated niche in the cell wall (Figure 22). The currently designed airlock consists of a pair of valves, positioned in series in the frit addition pipeline below the air break funnel. The valves are operated simultaneously with a single, timer-controller, pneumatic cylinder actuator. The valves are so positioned that when one valve is open the other is closed and vice versa. In operation the frit feeder discharges continuously into the conveyor tube, through the air break funnel, and into the air lock system. With the upper air lock valve open, frit accumulates in the chamber between the two valves. With the next valve operation, the accumulated frit is discharged from the lower valve and begins accumulating on the upper valve. Since contact maintenance is used, one of many commercially available air locks could alternatively be used.

With some air lock designs there is a brief period during the valving operation when both valves are open, allowing gases to flow either into, or out of, the calciner. This feature is not desirable. Normally there is a

FIGURE 22. Schematic Drawing of the Frit Addition System

pressure difference between the calciner and the niche that results in an air flow into the calciner. This air flow is very brief and does not significantly upset the vacuum control of the calciner, nor significantly add to the noncondensable gas flow through the off-gas system. In addition, these brief pulses of air can assist in moving the frit into the calciner. If further air flow control is needed, a second, totally in-cell air break and air lock system may be added to the frit feed pipe.

The frit line from the air lock to the calciner must be maintained at a temperature above 100°C to prevent the condensation of steam from the calciner which would agglomerate the frit in the line. The line can be insulated, or hot air can be blown into it.

Canister Weighing

A system is used to continuously monitor the weight increase of the receiving canister in its filling position. It aids in detecting compromising process conditions such as overfilling of the canister, failure of the frit feeder system, plugging of the calciner discharge chute, diverter valve, or fill head assembly, or an inappropriate addition ratio of calcine to frit.

To monitor the canister weight, the canister and the retort are supported as a unit by three strain gage-type load cells, and the canister is nonrigidly attached to the canister fill head through a flexible metal bellows assembly. For a 20-in by 10-ft canister, filled to 80% of its capacity, the canister, retort, support mechanism, and glass are estimated to weigh 1200, 300, 300 and 1200 kg, respectively, for a maximum weight of about 3000 kg. Assuming a frit flow of 20 kg/hr and a maximum sensitivity of 0.1% of the total load or 3 kg, a loss of frit flow should be detected in less than 10 min. With a 1000-kg system, sensitivities of about 0.5 to 0.25 kg (0.05 to 0.025%) have been observed. Early detection of the loss of frit flow to the melter is important because tests have shown that if a layer of calcine containing no frit is deposited in the melter to a depth of 4 cm, unvitriified calcine agglomerates will result in the glass. Such a layer would be laid down in just 8 min in an 8 in.-dia can while 49 min would be required to form such a layer in a 20-in.-dia can.

Both a digital readout and an analog output, suitable for use with a strip chart recorder, are available for indicating the weight of the canister. If the canisters used are pre-weighed, the accuracy of the weighing system can be checked each time a new canister is positioned in the retort. From the control panel, the tare weight of the system can be subtracted so that the output indicates the net weight of glass within the canister, directly in kilograms. A sample-and-hold system, coupled to a calculating module, measures the system weight at discrete intervals and indicates the rate of weight increase directly in kilograms per hour. This value compared with the solids feeder frit addition rate, also in kilograms per hour, will indicate the frit-to-oxide ratio of the glass being formed and whether the frit rate or the feed rate needs adjustment.

A significant error is introduced in the indicated weight of the canister by fluctuations of the vacuum maintained in the receiving canister. While the canister/retort system "floats" and is rigidly supported only by the load cells, a portion of the system weight is supported by the canister fill head by means of the vacuum maintained in the calciner/canister system. For a development calciner/canister system using a nominal 7-in. bellows connection between the fill head and the canister, an error of 0.49 kg/in. of water pressure change was observed, with the indicated weight decreasing as the vacuum increased. An electronic vacuum compensator circuit (Figure 23), using a measurement of the differential pressure between the canister and cell atmospheres, has been successful in realizing a stable, accurate canister weight despite canister vacuum fluctuations.

FIGURE 23. Canister Weighing - Vacuum Compensator Circuit

Perhaps the greatest weakness of the standard strain gage-type load cell is its lack of resistance to heat and nuclear radiation. The effects of zero shift and calibration are temperature compensated up to 66°C. Beyond 66°C the calibration shifts about 0.1% per 38°C. Destruction temperatures are about 260°C. Specific details on the performance of strain gage load cells in a nuclear radiation environment are not known at this time. However, several manufacturers feel that radiation-hardened units, while expensive, can be realized. A trade-off then arises between periodic replacement of inexpensive standard load cells and of expensive radiation hardened units. Also, other load cells might be considered, such as the linear variable differential transformer (LVDT). This has superior radiation resistance, but a less attractive load sensitivity than the strain gage. In addition, radiation shielding and air cooling of the load cells could be provided in the design of the canister/retort support system to prolong the accuracy of the weighing system. Also, recognizing the relatively short mean-time-to-failure for strain gage load cells in nuclear radiation service, the support system should be designed to simplify their replacement.

Detection of Batch Bridging

During some of the early developmental work with internally finned receiving canisters, certain operating conditions resulted in frit/calcine mixture accumulating atop the fins. These accumulations tended to grow and to bridge from one fin top to another, eventually blocking completely the flow of powder to the lower part of the canister. Due to improved fin design and canister furnace design, this bridging problem has not been observed in recent tests. However, the possibilities and consequences of its occurrence have been recognized. With the fin tops bridged, the incoming frit/calcine mixture could build up above the bellows unit in the canister fill head assembly before the weighing system could detect a change in the normal canister rate-of-weight increase.

During normal operation of the in-can melting system, fin tops reach a steady-state temperature of about 1000°C, and with complete bridging the temperature of the powder cap may drop to 500 to 800°C. Thus noncontact temperature measuring elements, positioned to view the fin top area within the

canister, should easily detect powder accumulated atop the fins and bridging from one fin to another. A differential thermocouple system (Figure 24), positioned in the cone valve, has shown marginal success in measuring the temperature of the fin tops. The two thermocouples with their collector plates are identical, except that the upper one, positioned behind the lower one, is "shaded" from the hot fins and indicates only the ambient temperature of the thermocouple location, while the lower unit indicates this same ambient temperature plus an increase due to the radiant heat from within the canister. The two thermocouples are connected in series so that the low temperature unit opposes the voltage generated by the high temperature unit. Thus when sensing a radiant surface, such as the 1000°C fins, a temperature difference of about 100°C is realized between the two thermocouples. When calcine and frit are added to a hot canister, this temperature difference decreases by 5 to 30°C. The fluctuations of this temperature difference have not yet been correlated with process change.

FIGURE 24. Powder Bridge Detector

Two additional sensors are currently being evaluated for use as bridging detectors. One of these sensors focuses the radiation emitted from a target surface onto a detector sensitive only to a narrow band of the infrared energy spectrum. The other sensor passes the radiation from a target surface through a quartz filter, allowing only a narrow band of the infrared energy spectrum to fall on a thermopile unit. With both systems, the output of the sensor is calibrated to the temperature of the target surface.

CANISTER HANDLING AND INSPECTION

Canister handling and inspection consists of movement of the canister within the cell, canister closure welding, canister closure inspection, canister decontamination, and canister in-cell storage. These operations are described here.

Canister Movement

Canister movements between operations in the cell will be performed by the crane. At this time it is expected that ears or a holding knob will be included on the canister as part of the cap or head. A yoke or a grappling device will be placed on the cell crane hook for attachment to the canister. At this time final canister design has not been completed and evaluated to the extent that a detailed design can be designated.

Several methods of canister handling have been developed. The basic design used in the WSEP and current operations is indicated in Figure 25 and consists of ears built into the canister neck. This method has proven satisfactory in extensive experience in the nuclear industry. It has the advantages that it is simple and can pick up canisters in a horizontal position. But, depending on the neck design, the usable volume of the canister may be slightly decreased and the construction may be somewhat complicated.

Another handling method was developed at Oak Ridge National Laboratory for canister handling. It consists of a ball on the canister head, and a grappling device is used on the crane to handle the canister ball. The advantage of this system is that the lifting attachment on the canister is simple and does not significantly affect canister design and construction.

FIGURE 25. Typical In-Can Melter Test Canister

But the grappling device is mechanical equipment with many moving parts; it would have difficulty in picking up a canister in a horizontal position; and its operation would be complicated compared to using a hook. Also, there has been little experience in using this type of system in the nuclear industry.

Canister Closure Welding

The filled canisters are closed with a threaded closure. This closure is then seal welded with a 1/8 in. fusion weld fillet using a standard water-cooled

TIG welder. The welder power supply and controls are located out of cell. The welding torch, which is in-cell, is mounted on a rotating holder. During welding this holder is mounted on and indexed off a reference center point on the canister closure. Rotation is accomplished with a fractional horsepower, variable speed dc motor.

This method of remote seal welding of canister closures was developed and used in the WSEP program. As with any welding, it was found that weld joint preparation (cleanliness) is very important. This is assured by proper design of the canister neck and closure. During processing the canister is sealed below the weld joint, thus preventing contaminants from contacting or being present at the joint. With these precautions a good quality weld can be made.

Leak Test of Canister Closure Weld

It is currently planned to verify the integrity of the canister closure seal weld by a helium mass spectrometer leak test or by ultrasonic techniques. Three basic methods exist for performing the helium leak test: 1) Place a slow-release helium source in the canister and use a sniffer type of detector after closure weld. 2) Evacuate the canister through the detector, and flood the exterior of the canister with helium. 3) Place a slow-release helium source in the canister, and place the canister top in a leak chamber after closure weld.

Method 1 may not suffice due to inadequate detection sensitivity for this application. Method 2 was used for leak testing the WSEP canister closure welds. Though adequate, this method involves using an additional canister closure which must also be leak checked by another means. Outgassing the canister can be very time consuming if scale, calcine, etc., exist.

A modification of Method 3 (see Figure 26) is currently preferred. With this method a slow-release helium source is placed in the canister; the lid is placed on the canister and seal welded; a metal "bell jar" is placed over the seal weld to form the "leak chamber." A high-temperature silicone gasket is placed between the chamber and a flat on the canister neck to effect a seal. The vacuum created by the leak detector is used as the clamping force for the gasketed seal. With this method outgassing problems associated with

FIGURE 26. Canister Leak Test Method - Leak Chamber

metal scales, etc., are minimized because the only portions of the canister in the leak chamber are the closure, which has not been subjected to process heat, and the weld joint. Leak detection capability of this method is limited only by the accuracy of the mass spectrometer. The mass spectrometer is placed outside the hot cell for ease of operation and maintenance. The only equipment contained in the cell is the leak detection head.

Other methods considered to assure good closure weld integrity will be:

1. visual inspection ($\geq 7X$)
2. dye penetrant or magnetic particle test if the cap can be cooled
3. stringent welding procedures and sample testing.

But at this time the helium leak check or ultrasonic techniques appear to be the most practical and reliable.

Radiograph methods will not be practicable because of the high amount of radiation generated by the waste glass.

Canister Decontamination

Canister decontamination and smear sampling techniques and equipment have been developed at PNL as part of a program to assist in establishing waste canister acceptance criteria at the Federal repository. (20,21)

Canister decontamination is achieved by repetitively passing the canister vertically past a medium-pressure spray ring where the canister is alternately sprayed with 100 psig steam or 70 psig water. In recent tests this alternate steam/water procedure took about 140 min and used 310 gal of water and 40 lb of steam. A steam cleaning procedure required 40 min and consumed 20 lb of steam.

The spray ring is simply a toroid made of 3/4-in. stainless steel pipe with 1/16-in. holes drilled in a row on 2 1/16-in. centers, pointing toward the ring center. The ring is placed 2 in. from the canister wall during decontamination. The canister and spray ring are contained in a tank. Figure 27 shows the spray ring and canister smear apparatus used in evaluating the work.

A total of four WSEP canisters were decontaminated using the spray ring with both steam and water as cleaning agents. (21) Two additional WSEP canisters were decontaminated using the spray ring and steam only. Nearly the same level of cleaning can be done with steam in 40 min as with a dual steam and water process taking 140 min.

The major fraction of smearable contamination is removed early in the decontamination procedure. The contamination remaining seems to be a film that is removed very slowly with 100 psig steam or 75 psig water. The initial smears on the WSEP canisters showed a reading of between 8×10^5 and 5×10^6 dpm/100 cm². After decontamination, these canisters showed smear readings between 4×10^3 and 2×10^4 dpm/100 cm². Decontamination factors ranged from 139 to 950. Industrial sources indicate that these radiation levels achieved after decontamination are quite suitable for onsite storage of high-level waste canisters.

Two decontaminated canisters were recontaminated with actual high-level waste corresponding to a reactor burnup of about 54,000 MWd/MTU and an age

FIGURE 27. Spray Ring and Canister Smear Apparatus

of 2 years.⁽²¹⁾ The waste was applied in two ways to simulate an "easy" and "worst case" contamination. The "easy" case used dry waste calcine sprinkled on the canister and the "worst case" involved dissolving calcine in nitric and hydrofluoric acids and then applying the solution to the canister and letting it dry. Both cases were cleaned using the steam and water procedure. The dry calcine was easily removed to nearly the level prior to contamination. The waste acid solution, however, was left at a very high level. This is assumed to be due to the solution's actually penetrating the canister surface.

Smear samples were taken using an asbestos tape mounted to a steel frame fitting the curvature of the canister being cleaned. To take a smear, the

steel holder is mounted in a fixed position and the canister is pulled up past the asbestos tape by use of the in-cell crane. The smear sampling apparatus is shown in Figure 27.

In a production plant decontamination facility the canister would be rotated in a fixed position in front of a perforated pipe, the spray from which covers the canister length in a closed tank. This method would minimize the tank height and the escape of decontamination solution to the cell. The decontamination solution may have to be combined with other radioactive liquid wastes for treatment.

In-Cell Canister Storage

Canister storage, filled or empty, within the processing cell is not expected to be a significant or complex problem. Many proven approaches can be used and have been demonstrated in the nuclear industry. The method used will be dictated mainly by economics, reliability, simplicity, and minimization of adverse effects on the canister. Since the storage time will be for only hours or days, many long-term considerations are not applicable such as canister and storage atmosphere compatibility. In the WSEP program 33 canisters filled with radioactive materials have been stored in air and/or water for years for heat removal with only one minor canister thermowell failure attributed to stress corrosion cracking.

PNL has developed a preliminary design of a rack for canister storage as shown in Figure 8. It basically consists of a rack constructed from angle or strip 304L stainless steel. If the canister is filled and requires water cooling, a coil may be inserted in the storage position in the rack. This approach is simple and economic. However, the rack must be designed so as to prevent contamination traps which would make it difficult to decontaminate. Storage of the canister in air eliminates contaminating an additional medium such as water, which would eventually have to be treated. Also any possible adverse effects of thermal shocking the canister by placing it in water are eliminated.

CANISTER

Canister design, construction, and inspection will eventually be determined by acceptance criteria for the Federal repository. These criteria have not yet been established. PNL is therefore developing canister designs and characterizing them for possible use. The work that has been performed to date is outlined below. When criteria are available, they will be integrated into the canister design to establish an acceptable design.

Design

The can configuration currently being used for developmental work is a right circular cylinder with flat ends and a neck with a circular opening at the top. The minimum diameter of the opening is 5 in. to prevent plugging during filling and melting. Inside this opening is located a gasket groove for a metal c-ring type gasket used to effect a dust tight seal between the can and the coupling section during filling of the can. Figure 28 shows the flange design used in the in-can melter development cans at the PNL. (It is not designed for a weld closure.) A silver-plated, Inconel® X-750, c-ring gasket has been used, but a less expensive alloy can be used as long as the coupling is located outside the furnace. The gasket is made 60 mils out of round so that when it is placed in the groove it will remain in place while the can is transferred into the hot cell and coupled to the melter.

The developmental in-can melting equipment concept requires the can to have a neck of sufficient length to pass through the vestibule at the top of the furnace. This vestibule is presently 6 in. deep. Associated with this neck are the ears by which the can is handled with the crane and from which the can is suspended in the melting furnace. The exact configuration and number of these ears depend on the design of the bails and support mechanism. Two ears 180° apart are easiest to hook into with a crane, but three offer better stability. The ears and neck must be sufficiently large to adequately support the can at the melting temperature. The canister top and neck configuration will probably be changed for production canisters to allow less expensive fabrication costs and conform to final melter and coupling section design.

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FIGURE 28. In-Can Melting Canister Flange

The neck and ears of the can are extended to outside the furnace so that: 1) the closure area, which may include threads and a weld prepared area, is protected from possible distortion or oxidation by high temperature, 2) the connection between the can and coupling section will be cool, and 3) the canister supports will not be subjected to high temperatures which would cause creep, require much more material for adequate strength, and possibly spall the supports with each thermal cycle. Extending the neck through the vestibule also has disadvantages. The neck is subject, during processing, to a thermal gradient which causes sensitization of the neck material. Inside this neck calcine and frit collects on the walls and may be sintered but is likely not vitrified. Some of this spalls during cooling and collects on the surface of the glass. It is slightly less leach resistant than the glass and has a high surface area.

A drop-in, radial fin assembly, not attached to the can walls, such as the one shown in Figure 25, is recommended to improve heat dissipation from the canister contents. This drop-in design eliminates welds to the can wall. This will minimize costs of quality assurance, prevent formation of hot spots on the can walls during storage, and avoid distortion of the fins during the in-can melting process. The assembly is made from standard size materials, and the tolerances and weld quality are not critical to their performance. Computer modeling has shown that with 304L stainless steel fins the fin thickness cannot be much less than 1/4 in.. Other metals with higher thermal conductivity and lower thermal expansion are also being evaluated for this use. The fin assembly is positioned in the can by small spacers located on the outside corners of three of the fins. These spacers are rounded and must have a low modulus of elasticity so that they do not act as stress risers at the points of contact with the wall of the can. Short pieces of 0.5-in., thin wall tubing are currently used as spacers.

The number of fins required are a function of the desired can diameter; maximum allowable centerline temperature; wall temperature; heat generation rate of the waste; and heat transfer properties of the glass and the selected

fin material. A computer model is being developed to facilitate the determination of fin requirements. The assembly of eight radial fins shown in Figure 25 has proved adequate in cans up to 24 in. in diameter using present NFS design parameters.

Overall canister dimensions, material thickness, fabrication techniques, and quality assurance methods will be established directly or indirectly by the Federal repository and/or an individual fuel reprocessor. Until guidance is available in these areas, the design cannot be finalized. For the base case the right cylindrical section of the canister has been chosen to be 0.5 in. thick, seamless, 304L stainless steel pipe. It will be nominally 10 ft tall and 20 in. I.D. These design parameters were selected in conjunction with NFS, based on their planned waste handling method.

Materials

In selecting the materials for fabrication of waste storage canisters to be filled by the in-can melting process, many things must be considered, including:

- corrosion rate in the melt and vapor above the melt
- strength at the processing temperature
- creep rate at the reprocessing temperature
- spall
- corrosion resistance in various storage environments
- fabrication methods
- availability
- cost
- waste canister acceptance criteria.

All experience with the in-can melting process on an engineering scale both in the hot cell and out has been with cans made with 304L stainless steel. Figure 29 shows the results of laboratory tests to determine the corrosion rate of 304L stainless steel in contact with a simulated nuclear waste-borosilicate glass melt. Examinations of the walls and fins from processed cans verify these laboratory results, showing that the corrosion rate of 304L stainless steel is not a significant factor.

FIGURE 29. Corrosion Rate of 304L Stainless Steel in Simulated Nuclear Glass Melt

Similar laboratory corrosion rate data are also available for a number of other alloys evaluated at PNL during the metallic melter development task work. Several of these nickel base alloys are currently being considered as canister materials. Alloys such as Inconel 600 and Incolloy 801[®] may actually cost less to use than 304L stainless steel canisters due to their additional strength at glass melting temperatures. These alloys also do not spall at 1100°C, exhibit superior corrosion properties, and may be less susceptible to stress corrosion cracking. Unfortunately, little is known of their behavior under canister conditions in the nuclear industry. An evaluation of the potential use of these alloys is under way.

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The use of internal fins was originally proposed to improve heat dissipation from the canister during storage so that larger diameter canisters could be used for waste containment. Internal fins contribute significantly to the melting capacity of the in-can melter and are necessary to obtain melting rates required for the NFS design. The fin material must perform well in these areas:

- good corrosion resistance to glass and vapors during in-can melting and up to 800°C during early life
- thermal expansion rate close to glass in the temperature range below the strain point of glass, so that fractures do not develop between the glass and fins which will reduce heat transfer.

Many materials are compatible with glass from a thermal expansion standpoint but are not compatible from a corrosion standpoint. Of the fin candidate materials corrosion tested E-Brite 26-1[®] has performed well. Metals not adequately corrosion-resistant could be chrome plated. The fin material used for current developmental efforts is 304L stainless steel.

Heat Transfer and Size

Making the waste canister as large as possible saves on the cost of canisters per unit of waste processed. The size of the canister may be limited, however, either by canister temperature limits during processing or by limits imposed by transporting of waste to the Federal repository and/or Federal repository acceptance criteria.

After the canister is removed from the melting furnace, the canister wall is limited to 460°C to avoid metal sensitization. The centerline temperature is limited to 800°C, where the viscosity is high enough to reduce second phase settling, fin corrosion is minimized, and glass component volatilization is not a problem. The height of the canister has not been defined. As shown in Table 10, draft Federal repository criteria limits the length to 10 or 15 ft. It has been suggested that making the canister still shorter

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TABLE 10. Summary of Criteria Determining Canister Size

	<u>Length</u>	<u>Diameter</u>	<u>Weight</u>	<u>Heat</u>	<u>Radiation</u>																		
Truck Shipping Criteria			Gross wt trailer 35 tons, Cask and Waste 24 tons, Dry cask (J. Duckworth, NFS, personal communication)	External cask temperature should not exceed 180°C 49 CFR 173.393	200 mrem/hr at surface or cask (see 49 CFR 173.93 for other conditions)																		
Retrievable Surface Storage Facility (RSSF) Acceptance Criteria	15 ft	2 ft	6 tons	<table><tr><th>Dia (in.)</th><th colspan="2">kW/ft³</th></tr><tr><th></th><th>10 ft</th><th>15 ft</th></tr><tr><td>6</td><td>4.6</td><td>4.2</td></tr><tr><td>12</td><td>1.3</td><td>1.2</td></tr><tr><td>18</td><td>0.6</td><td>0.6</td></tr><tr><td>24</td><td>0.4</td><td>0.4</td></tr></table>	Dia (in.)	kW/ft ³			10 ft	15 ft	6	4.6	4.2	12	1.3	1.2	18	0.6	0.6	24	0.4	0.4	10 ³ rem/hr, n; 10 ⁶ rem/hr, γ at 3 ft away at mid- plane of longitu- dinal axis.
Dia (in.)	kW/ft ³																						
	10 ft	15 ft																					
6	4.6	4.2																					
12	1.3	1.2																					
18	0.6	0.6																					
24	0.4	0.4																					
Ref: O. P. Gormley "ERDA misc notice waste can etc." 8/7/75																							
Terminal Storage Criteria (Conceptual Design Report Federal Repository Lyons, Kansas. December 1971. Kaiser Engineers)	2-10 ft	(<1/8 in. variation) in diameter) (<1/2 in. axial bow) 6-14 in.	2 tons	Approx. 5 kW/can	6x10 ⁸ neutrons/sec Tightly packed array should be sub- critical even when water moderated.																		

would reduce hot cell cost by reducing the head room needed for canister handling. On the other hand, shorter canisters would be less volume efficient since canisters are filled to 80 to 90% of height and the larger number of canisters would require more frequent handling.

Table 10 summarizes the relevant existing criteria for transporting and for acceptance at a conceptual Federal repository. The truck shipping criteria are current and may not change greatly in the near future. Since the acceptance criteria for the repository are hypothetical, they may change significantly and are therefore useful only as a rough guide. Another rule that affects canister size is that the canisters must be shipped within 10 years after reprocessing. This limits the amount of initial radioactivity that may be put into a canister and still have the canister meet the heat criteria in Table 10. The maximum permissible canister dimensions according to the existing draft criteria appear to be about 2 ft dia by 15 ft high. The process equipment described in this report accommodates 2 x 10 ft canisters. Smaller canisters could also be accommodated without significant difficulty.

The maximum allowable centerline temperature for canisters of glass has been tentatively established at 800°C. The basic test for establishing this temperature is whether the canister is likely to fail at temperatures higher than the proposed limit. Possible causes of failure are pressurization of the canister due to gas generation and escape of volatile constituents. This could occur if temperatures above the processing temperature were allowed. If the temperature becomes too high, the glass may liquefy enough to allow settling of a denser insoluble phase and crystalline phases such as Ce_2O_3 . A conservative criterion for the glass viscosity might be 10^6 to 10^7 poise. At this viscosity, a particle of Ce_2O_3 1 cm in diameter will take 1 to 10 years to settle 10 ft. However, even if the one phase does settle to the bottom or float to the top, it has not been established that this would have serious consequences.

Since canisters are a major expense of waste fixation, it is desirable to reduce canister cost per unit of waste processed. One way to do this is to improve dissipation of heat from the waste so that larger canisters may be used without exceeding internal temperature limits. Larger canisters mean

small surface-to-volume ratio. This can result in lower canister cost per unit volume of vitrified waste, provided that material and fabrication costs are not increased too much. Also, the larger the canister, the fewer the canisters that are needed, thus minimizing costs.

The use of internal metallic fins has been shown to greatly improve the effective glass thermal conductivity and can roughly double the amount of waste stored in a canister if the centerline temperature is limiting, as shown in Figure 30. Space is left between the fins and the canister so that fins can easily be slipped into the canister. This somewhat reduces the heat transfer effectiveness but at the same time reduces wall temperature variations. These in turn may reduce the potential for stress corrosion cracking. The total heat in the canister may be limited by Federal regulations for waste acceptance and storage, as shown in Table 10.

FIGURE 30. Allowable Canister Diameter

Interim Canister Storage and Integrity

Canister properties after filling such as residual stress and sensitization will affect the canister integrity and its condition for interim storage. Techniques are being investigated to reduce or eliminate the residual stress in a glass filled canister, but it is doubtful that "nuclear vessel" quality can be obtained in the near future. Type 304L stainless steel currently being considered for waste canisters can withstand the processing conditions and thereafter withstand a variety of storage and shipping conditions. However, even 304L stainless steel has been known to fail under certain conditions. Stress corrosion cracking can occur if the metal has sufficient residual stress and control of the storage basin water purity is not maintained.

Since these conditions may occur, it is reasonable to assume that during water storage some canister cracks may develop. The number of cracked canisters acceptable in the storage basin will set the criteria for the measures to be taken to avoid the condition. Studies are being prepared at PNL using actual HLW canisters to evaluate contamination of the basin resulting from a crack in a glass filled canister. Since the glass inside the canister is highly leach-resistant, the amount of contamination diffusing through a crack in the canister is expected to be low. In fact, if spent fuel with partially failed cladding is stored in the same basin with the glass canisters, the increase in pool activity resulting from cracked canisters may not be detectable.

Experience with canisters filled with high-level waste glass prepared during the WSEP has shown that interim storage of such canisters is feasible. These canisters, fabricated and filled with minimum regard to integrity, have been stored up to 10 years in both water and air environments in hot cells. Some canisters have remained in continuous water storage up to 7 years. Of the 24 glass-filled canisters produced only one has been observed to crack, and this behavior was a textbook example of metal sensitization followed by stress corrosion cracking. Briefly, the 310 stainless steel canister was stored in air at 400°C for 4 years, a condition ideal for carbide precipitation at the grain boundaries of the unannealed alloy. The sensitized canister was then placed in a storage pod containing 50°C water with a significant

chloride content (13 ppm). After 6 months' water exposure, a wall penetration about 8 in. long was detected by an increase in activity of the storage pod water. Other canisters which did not receive this sensitization treatment have not cracked in water or air storage.

Depending on the assurance of canister quality required, there are many variations that can be used for processing, handling, and underwater storage of the waste canister until it is ready for shipment to a Federal repository. Some of the primary concepts for retaining glass/canister integrity and minimizing the failures in storage water are shown in Figure 31.

FIGURE 31. Canister Storage Process Options

Option A. Realize that some failures may occur during water storage, and plan accordingly to decontaminate the basin water and/or remove leaking canisters if required. Prior to shipment to terminal storage the canister is loaded into an overpack which meets the then-applicable repository requirements.

Option B. Load the melter canister into a low-cost recyclable storage can which is compatible with water and may be vented to monitor for leaks. Prior to shipment to terminal storage the melter canister is removed from the water storage canister and loaded into a virgin overpack that is compatible with the repository.

Option C. Make the melter canister with enough integrity to survive in-can melting and to provide suitable structure to support the glass monolith. Load the melter canister into an overpack designed as compatible with the melter canister and which has integrity for water storage and, if possible, terminal storage. Possibly vent the overpack to monitor for leaks.

Option D. Make a melter canister with enough integrity to survive until overpacking after 10 years or more under water.

These options are being evaluated for relative benefits.

EFFLUENT TREATMENT

Table 11 indicates the liquid and gaseous effluents generated in the process. The liquid effluents, except for HLLW, will be evaporated and sent to the low- or intermediate-level aqueous waste systems. Any liquid effluents of too high an activity for the low- or intermediate-level system will be recycled to the HLLW waste processing system. The gaseous effluents will be treated by the process off-gas system or released to the process cell. Gaseous effluent treatment will be discussed in subsequent sections.

TABLE 11. Effluent Sources in a HLLW Vitrification Cell

<u>Liquid</u>		
<u>Source Identity</u>	<u>Estimated Volume, ℓ/Day</u>	<u>Source Characterization</u>
High-Level Liquid Waste	1890	HNO ₃ based
Canister Decontamination	760	Low solids, no foaming agents
Equipment Drains	190	Acids, salts
Cell Flush	380	Low solids, nonfoaming
Silica Gel Regeneration	38	Low solids, nonfoaming
Ion Exchange Regeneration	57	Acid/base

<u>Gaseous</u>		
<u>Source Identity</u>	<u>Estimated Flow Rates, cfm</u>	<u>Source Characterization</u>
Spray Calciner	< 25	Atomizing air + NO _x + air in-leakage (excludes H ₂ O)
Tank Vent In-leakage	< 10	Cell air
Melter In-leakage	< 10	Cell air
Melter Furnace Cooling Air	≤ 700	Blower air
Inert Gas Cover from Retort/Susceptor	Negligible	Argon from pressure cylinder

Off-Gas Quantities and Compositions

At a feed rate of 80 liters/hr of HLLW to the calciner the calciner off-gas quantity at 350°C and -20 in. of H₂O pressure is equivalent to 70 scfm. Of the 70 scfm gas produced, roughly 20 scfm will be noncondensable, with the remainder condensable, mainly steam and nitrogen oxides. There will be about 50 scfm of off-gas per liter of feed at the above conditions. The volatilized fission products are of extremely small volume when compared to the total volume of the gas. As can be seen in Table 12, the gas consists of steam, nitrogen oxide, and air. The steam and the nitrogen oxides are from evaporation, the decomposition of the nitrate salts in the waste, and nitric

acid evaporation. The air is from the pneumatic atomization of the feed and vessel in-leakage. To prevent potential escape of radionuclides, the calciner is operated at less than atmospheric pressure. Some air leaks into the system through gaskets and connections.

TABLE 12. Typical Off-Gas Composition^(a)

	<u>mole %</u>
H ₂ O	64
Air	29
HNO ₃	3
NO _x ^(b)	4
CO ₂ ^(c)	Trace
CO ^(c)	Trace
CH ₄ ^(c)	Trace

a. Excluding fission products.

b. Decomposed NO₃ from metal salts in waste.

c. Organic decomposition products from plant solvent or sugar denitration.

The other very important constituent of the off-gas is the very small amounts of fission products. These fission products may be volatilized or entrained as particulate in the gas stream. The calciner-melter and filter system will have an approximate decontamination factor (DF) of 10³⁽⁴⁾ for particulates, which includes nonvolatile fission products. Therefore, some particulate will be in the gas stream. Fission products of particular concern are ruthenium, iodine, and cesium due to their volatility at high temperatures. Other potentially troublesome fission products of somewhat less concern include tellurium and selenium. To be conservative, the following discussions will use fission products levels at discharge of fuel. In an actual facility, the waste will be aged and the fission product activities will be lower.

It can safely be assumed that all iodine in the HLLW will pass through the solidification system to the off-gas cleanup system. The high-level waste may contain about 2% of the iodine in the spent fuel. The waste from the design basis PWR fuel of 33,000 MWd/MTU burnup of 30 MW power will contain about 5.5 g/MTU of iodine (2.34×10^5 Ci/MTU).⁽²²⁾ An HLLW processing rate of 80 liters/hr will therefore give 0.58 g/hr (2.47×10^4 Ci/hr) of iodine entering the off-gas system. Since these levels are at discharge, and it is improbable that any fuel this fresh will be processed, a more realistic set of values can be found by discounting the radioactivity of the short half-lived isotope ^{131}I (half-life of 8.041 day). Discounting this activity (using a waste age of 1 year) gives to the off-gas system an activity of 7.93×10^{-5} curies of iodine per hour.

Ruthenium volatility varies widely, depending upon the process, the product, and the operating conditions. The formation of borosilicate glass from waste using spray calcination and in-can melting in the WSEP program⁽⁵⁾ showed that less than 2% ruthenium volatilizes. More recent data show that about 1% ruthenium volatilization may be more characteristic. The waste from design bases PWR fuel will contain about 2.35×10^3 g/MTU⁽²²⁾ (3.71×10^6 Ci/MTU) of ruthenium. At a processing rate of HLLW at 80 liters/hr of waste, with 1% losses from the calciner, 2.48 g/hr (3.92×10^3 Ci/hr) of ruthenium will go to the off-gas system.

Using the same bases, the WSEP program⁽⁵⁾ indicates that cesium losses from volatilization range from 0.002 to 0.07%. With 0.07% losses and the same conditions for iodine and ruthenium losses, about 0.2 g/hr (5.19×10^2 Ci/hr) of cesium will go to the off-gas system.

It is assumed that the entrained particulate is a mixture of all fission products in the feed excluding the gases (H, I, and the noble gases) and the volatilized elements previously discussed. With a conservative vitrification system with a particulate DF of 10^3 , about 1.22×10^4 Ci/hr of particulate will go to the off-gas system.

Table 13 shows the typical amounts of fission products leaving the calciner-melter filters and going to the off-gas system.

TABLE 13. Fission Products Going to Off-Gas Cleanup System

<u>Element</u>	<u>Amount, g/hr</u>	<u>Activity, Ci/hr</u>
I	~0.58	7.93×10^{-5}
Ru	2.48	3.92×10^3
Cs	0.2	5.19×10^2
Other (Particulate)	--	1.22×10^4

The degree of decontamination required prior to release is based upon the amount of the isotope present and on the established effluent limit. The allowable release limits are projected as follows. The 10 CFR-20 limit may be applied to the stack concentration. Since solidification is only a part of the whole reprocessing system, its effluents should not represent more than 10% of the allowable limit. The release limit is further reduced for individual isotopes because the limit applies to the total release. Since several isotopes may be present in comparable concentrations, the limit for each is somewhat arbitrarily set at 20% of the total. From these factors the allowable stack concentration is 2% of the 10 CFR-20 limit. The DF requirements, based on a stack flow rate of 50,000 cfm are shown in Table 14.

TABLE 14. Decontamination Factor Requirements for Critical Isotopes

<u>Isotope</u>	<u>DF at 6 Months</u>	<u>DF at 2 Years</u>
I-129	2500	2500
Ru-106	2.5×10^{11}	0.9×10^{11}
Cs-137	6×10^{10}	3.5×10^{11}
Particulate	1×10^{12}	1×10^{12}

Off-Gas Treatment

The off-gas cleanup equipment supporting the waste solidification system must be designed to assure sufficient decontamination of gaseous effluent streams. The off-gas system must clean the gas sufficiently to meet stringent

release regulations on both radioactive and nonradioactive constituents. Nearly all of the gaseous effluents except air are condensable. Those that are not can be adsorbed or absorbed (excluding air from atomization, in-leakage, etc.). Both condensable and noncondensable streams need to be treated for removal of radionuclides. The noncondensable streams must be continuously discharged to the atmosphere following treatment. Liquid effluents from the off-gas cleanup system must be treated so as to be acceptable for recycle to the reprocessing plant or for final release to the environment.

Off-Gas Quenching

The first stage in the off-gas cleanup after filtration through the sintered stainless steel filters is condensation or quenching with particulate removal. The venturi scrubber can handle relatively high particulate loadings while performing some quenching and reasonable particulate removal. Pressure drop generally varies from high to less than zero, depending on the operation and the type of venturi used. Pressure drop normally varies inversely with particulate removal efficiency. Ruthenium DFs of 10 and particulate DFs of 50 to 100 are typical for the venturi scrubber.⁽⁶⁻⁸⁾ The venturi scrubber is probably the best choice for a condenser-quencher because of its ability to handle high particulate loadings. In a calciner system using sintered metal filters, the possibility of a filter candle failing does exist. The failure of a filter candle could allow relatively large volumes of particulate to pass before the equipment is shut down. The condenser-quench step must be able to handle the particulate without plugging. The use of a venturi scrubber will also require a knock-out pot to remove the mists generated in the venturi.

If a venturi scrubber followed by a knock-out pot are the first stages, the next item in the off-gas train may be a condenser. This condenser will remove any condensables left after the venturi quenching. This condenser will be a single-pass, downdraft shell and tube condenser with the process fluid on the tubeside.

Nitrogen Oxide Control

The nitrogen oxide concentration requires reduction to meet emission limits. If the oxides are recovered as an aqueous solution, the nitric acid may be recycled to a reprocessing plant. Control is obtained by one or more of these methods: absorption, conversion, and/or adsorption.

Absorption. Absorption consists of contacting the gases with water or nitric acid and absorbing the nitrogen oxides (NO_x) into the liquid. The use of other liquid scrubbing agents will generate a liquid waste stream.

Absorption of NO_2 into acid solutions takes place as follows:

NO must be oxidized to NO_2 before it can react:

N_2O_4 is an equilibrium product of NO_2 and will react in place of NO_2 in Equation (1):

The overall reaction (1) takes place in several steps. Wendel and Pigford⁽²³⁾ studied NO_2 absorption and analyzed the results using the penetration theory. The absorption process begins with the dissolution of N_2O_4 gas in water:

This reaction is considered fast; the equilibrium constant is related to the Henry's law coefficient. After entering the liquid phase, the N_2O_4 diffuses away from the gas-liquid interface and reacts with water:

This reaction is considered to be the rate limiting step in the absorption of NO_x into aqueous solutions.⁽⁸⁾ The HNO_2 is unstable in acid solutions and decomposes into H_2O , NO_2 and NO :

The NO is highly insoluble in water and escapes back to the gas phase. The evolution of NO from the liquid to the gas phase presents a significant limitation on absorption efficiency of NO_2 by acid solutions. Each absorbed mole of NO_2 produces 1/3 mole of NO which must be oxidized before it can be reabsorbed. This oxidation reaction can also be considered as a rate limiting step in the absorption of NO_x into aqueous solutions.

Peters⁽²⁴⁾ researched NO_2 absorption efficiency in various absorbers. It was found that venturis and spray towers were the poorest absorbers; packed scrubbers gave intermediate performance; and bubble cap towers and fritted bubblers gave the best performance. For all of the scrubbers, NO_x removal efficiency decreased with decreasing concentration of NO_2 in the entering gas.

Peters⁽²⁴⁾ also found that the addition of NaOH has only a minor effect on NO_x absorption efficiency. Pennak et al.⁽²⁵⁾ also found that the use of NaOH in the scrub solution gave only a minor increase in the efficiency of NO_x removal. The use of NaOH is unattractive because the acid is not recoverable and another liquid waste stream is produced with little gain in NO_x removal.

Efficiencies in removal of nitrogen oxides by aqueous scrubbing are typically low. Very few scrubbers⁽²⁴⁻²⁶⁾ have shown more than 90% removal of NO_x ; most range from 20 to 70%. Absorption will give a DF of about 10 to 10^2 for ruthenium and 10 for particulate.⁽²⁷⁾

A step to eliminate mist will be required following the absorber to remove any entrained liquid.

Conversion. NO_x may be converted to N_2 and other innocuous gases. A reactant and sometimes a catalyst are required, and acid cannot be recovered.

The three major conversion methods are thermal reduction with hydrocarbon fuel, catalytic reduction with hydrocarbon fuel, and catalytic reduction with ammonia. These processes may be used after the NO_x scrubbers for additional NO_x removal, or these processes may be used alone if nitric acid is not recovered.

Thermal reduction with hydrocarbon fuel involves reducing NO_x to N_2 and H_2O by using a fuel such as propane or natural gas. Operating temperatures are typically 1800°F to 2000°F .⁽²⁸⁾ An NO_x concentration reduction of 90% is possible using 8% combustibles (C_3H_8).⁽²⁸⁾ Fuel costs will be high because all oxygen in the stream must be consumed before the NO_x is reduced.

Gillespie et al.⁽²⁹⁾ and Reed and Harvin⁽³⁰⁾ have studied the use of natural gas in the presence of noble metal catalysts to reduce NO_x . The catalyst typically operates at temperatures of about 1200 to 1400°F (which may result in short catalyst life).

The reduction of NO_x with ammonia over a catalyst is probably the most promising conversion system. The reaction takes place at relatively low temperatures; ammonia reacts only with NO_x ; and high degrees of conversion are possible. The process consists of mixing gaseous NH_3 with the process off-gas and passing the mixture through a heated catalyst. Typical catalysts are metal-impregnated alumina and silica,^(29,30) metal exchanged zeolite,⁽³¹⁾ and hydrogen and sodium forms of zeolite.⁽²⁶⁾ The reaction forms the products N_2 and H_2O and sometimes N_2O . A system similar to this is presently used by Exxon Nuclear Company to eliminate NO_x in the off-gas from the dissolution of uranium oxides. The operation is described by Mays and Schwab.⁽³²⁾ Since the system was designed to handle NO_x fumes from the dissolution of uranium oxide, it is, from a source standpoint, much like NO_x emissions control systems for waste vitrification processes. The off-gas stream is 25 cfm, requiring a bed 10 in. in diameter and 8 in. deep. The catalyst used is 1/16-in.-dia zeolite extrusions. The off-gas is mixed with 50 to 100% excess ammonia and passes down through the bed at a temperature of 750°F . The conversion reaction^(31,32) goes as follows:

The bed temperature increases significantly during the conversion (up to 1400°F) due to the exothermic reaction. Conversion efficiencies greater than 99% have been reached.⁽³²⁾ Explosion hazards do exist due to the potential formation of NH_4NO_3 at low temperatures. Temperature controls prevent feeding of NH_3 when the bed temperature drops below a limiting temperature.

Adsorption. (24,33,34) Adsorption involves the removal of NO_x from the gas stream by uptake on the surface of solids. Since the process must be cyclic, involving solids regeneration or disposal, two or more sorption beds are required to allow simultaneous adsorption and regeneration or disposal. If the beds are regenerated, the desorbed NO_x would be of relatively high concentration, and NO_x control by absorption would be necessary. The absorption would now be of higher efficiency due to the higher NO_x concentrations. High adsorption efficiencies are possible but require large beds.

Ruthenium Control

Because wet scrubbing is an inefficient method of ruthenium removal, adsorption is generally used. The sorbent must be able to sorb large quantities of ruthenium while reducing ruthenium concentration in the off-gas effectively, must be resistant to attack from the off-gas, and must be able to withstand the radioactive environment. There are two adsorption methods: with sorbent regeneration and without regeneration. If the sorbent is to be regenerated, it must permit ruthenium desorption quite easily, be resistant to attack from the desorption agent, and have the ability to sorb effectively after regeneration. If the sorbent is not to be regenerated, it will need to be disposed of. Since the ultimate disposal would be to place the sorbent into the waste glass, the sorbent should hold most of the sorbed ruthenium at high temperatures.

Potential materials for use as ruthenium adsorbers are silica gels, ferric oxide, hydrous zirconium oxide gel, phenolic based ion exchange resins, styrene-divinyl-benzene ion exchange resins, acid-resistant molecular sieves, porous glass, impregnated alumina, copper sulfide, zirconium oxide hydrate-dithionite, etc. Of these, silica gel and ferric oxide best meet the requirements for the sorbent.

Barnes and Newby⁽³⁵⁾ studied the ruthenium adsorption characteristics of silica gel for use in the New Waste Calcining Facility at the Idaho Chemical Processing Plant. The results of the study gave the following data. Ruthenium sorption capacities greater than 4.8×10^{-3} g ruthenium/cm³ of gel (6-12 mesh particle size bed) are obtainable. Decontamination factors of 10^3 or better are possible, depending upon the depth of the bed. The silica gel can be effectively regenerated; about 80% of the ruthenium can be removed. Regenerated silica gel sorbs ruthenium as well as nonregenerated gel. The best operating conditions were found to be at a temperature slightly above the dewpoint of the gas and with a superficial velocity of about 0.4 ft/sec. Pressure drops were found to be 1.0 in. of water/in. of bed height at these operating conditions. Other reports have shown similar results.^(36,37)

Elliot et al.⁽³⁸⁾ found that DFs of 10^3 could be obtained with ferric oxide as the sorbent. The sorbent was at a temperature between 150 and 250°C, and the superficial velocity was about 3 ft/sec. The sorbent was found to have a capacity greater than 4×10^{-2} g ruthenium/cm³ of bed (18 to 25 mesh particle size bed). Elliot described a system in which the spent adsorber could be put into the glass canister. Barnes and Newby⁽³⁵⁾ found that ferric oxide cannot be effectively regenerated and that the material does not effectively sorb ruthenium after regeneration. Based on these data, ferric oxide must be used as a nonregenerable adsorber to be disposed in the glass when saturated. The cost of ferric oxide is low, allowing this type of operation.

Depending on whether adsorbent regeneration is attractive, either silica gel or ferric oxide will effectively remove ruthenium from the off-gas stream. If regeneration is used, a final method of disposal must be found for the desorbed ruthenium.

Iodine Control

Iodine control is best obtained by the use of solid adsorbents, such as silver and other metal-exchanged zeolites, silver-impregnated amorphous silicic acid, aluminum and silver oxides, and silver and other metal cation impregnated alumina.⁽³⁹⁾ Impregnated carbons may react violently with NO₂.⁽³⁹⁾

Inorganic adsorbents are chosen because they allow a simple design, are relatively noncorrosive, and can be put into permanent storage or recovered as necessary. Only about 15% of the adsorbent is utilized before breakthrough.⁽³⁹⁾ Removal of NO_2 and moisture will make the product ideal for long-term storage. Decay heat will not be a major problem since the decay energy of ^{129}I is low. If silver is used in the sorbent, high costs may warrant recovery for reuse. Recovery costs will depend upon the degree of contamination of the sorbent by other fission products, and some process for reconcentrating and encapsulating the iodine would be required. Decontamination factors of 10^3 or better are obtainable,⁽³⁹⁾ depending upon removal efficiency necessary in the specific case.

Particulate Control

Final particulate filtration is used to prevent any particles or entrained droplets from leaving the system. High-efficiency particulate filters with proved particulate DFs of 10^3 /stage are used.

Primary particulate control is effected in the wet scrubbing and condensing equipment as previously discussed. Also equipment used for NO_x , ruthenium, and iodine control as well as other pieces of equipment in the off-gas treatment system are effective in the removal of particulates.

WSEP Experience

Experience in the treatment of effluents from an HLLW solidification system was obtained in the WSEP program.⁽⁵⁾ The system is shown in Figure 32. The WSEP system was designed to:

- provide data on decontamination of solidifier off-gas
- characterize the secondary effluent streams
- evaluate the performance characteristics of individual pieces of equipment.

FIGURE 32. WSEP Auxiliary Process System

The data regarding the effluents resulting from solidification in WSEP⁽⁵⁾ can be generalized as follows:

- The immediate off-gas from the solidifiers was decontaminated by factors of 1.3 to 200 for radoruthenium and 100 to 100,000 for radio-cerium (representing nonvolatiles),* but it still remained as a highly contaminated waste.
- The radioactivity removed from the solidifier off-gases was distributed to three aqueous streams. The bulk of it remained in the evaporator bottoms where it could be recycled to the solidifier feed. About 0.1% of the ruthenium was found in the fractionator bottoms (recovered HNO_3) and less than 0.0001% in the fractionator distillate. Also about 0.0001% of the cerium was found in the fractionator bottoms and about 0.0000001% in the fractionator distillate.
- The cleanup of solidifier effluents by the WSEP effluent treatment system was adequate for the final gaseous effluent stream. Decontamination factors from the solidifier feed to the stack were 10^{10} for radoruthenium and 10^{12} for radiocerium, which represents nonvolatiles.

A summary of information on typical effluents resulting from waste solidification in WSEP is presented in Table 15.

GLASS CHARACTERISTICS

Composition

The characteristics of glass are dependent upon composition. Some properties such as leachability and viscosity are very dependent upon composition, whereas other properties such as thermal conductivity, mechanical strength, and specific heat are much less dependent.

The glass composition will vary somewhat with the waste composition, and the more variable properties can be adjusted by minor shifts in composition.

* In WSEP, $^{144}\text{CePr}$ was used as a measure of the behavior of all nonvolatile material in the effluent treatment system.

TABLE 15. Typical Effluents Resulting from Solidification of High-Level Radioactive Waste(a)

Stream	Major Constituent	Radio Ruthenium Ci/Ci in Feed(b)			Radio Cerium Ci/Ci in Feed(b)			Potential Disposal
		PC	SS	PG	PC	SS	PG	
Solidifier Condensate	1 to 6 M HNO_3	2×10^{-1}	6×10^{-1} (1×10^{-2})(c)	8×10^{-2}	6×10^{-3}	7×10^{-4}	2×10^{-3}	Recycle to solidifier feed or to fuel reprocessing plant waste concentrator.
Fractionator Bottoms	7 to 10 M HNO_3	1×10^{-3}	4×10^{-3}	2×10^{-3}	2×10^{-6}	5×10^{-6}	8×10^{-7}	Recycle for reuse in fuel reprocessing plant.
Accumulated Fractionator Distillate	0.01 to 0.1 M HNO_3	1×10^{-6} (4×10^{-4})(d)	1×10^{-5}	4×10^{-6}	1×10^{-8}	1×10^{-9}	1×10^{-8}	Recycle for reuse in fuel reprocessing plant or provide further decontamination.
Scrubber Bottoms	0 to 2 M NaOH	1×10^{-5}	4×10^{-5}	3×10^{-6}	$\sim 10^{-8}$	$\sim 10^{-8}$	$\sim 10^{-8}$	Intermediate level waste treatment or combine with high level aqueous waste.
Final Off-Gas from Scrubber	Air	$\sim 10^{-8}$	$\sim 10^{-8}$	$\sim 10^{-8}$	$\sim 10^{-9}$ (d)	$\sim 10^{-11}$	$\sim 10^{-11}$	To building ventilation filters.
Final Off-Gas to Stack	Air	$\sim 10^{-10}$	$\sim 10^{-10}$	$\sim 10^{-10}$	$\sim 10^{-12}$	$\sim 10^{-12}$	$\sim 10^{-12}$	To atmosphere.

a. Based primarily on average of typical values for all WSEP runs.

b. Total curies of radionuclide accumulated in auxiliary tank during entire run/total curies of radionuclide in feed to solidifier during entire run.

c. For in-pot melting runs SS-12 and SS-13.

d. Average value for last three pot calciner runs.

PC = pot calcination, SS = spray solidification, PG = phosphate glass solidification

Based on those properties which can be determined relatively rapidly, a glass composition termed 76-76 (shown in Table 16) was selected for the standard NFS waste PW-8a. The waste PW-8d, which would be produced when intermediate-level waste (ILW) is not available for blending with the HA column waste, can also be vitrified in this formulation by increasing the added sodium to 12.5 wt% and reducing the waste fraction. Preliminary experiments have also been made with PW-8e waste, and one possible composition is also shown in Table 16. The PW-8e waste is produced during startup and shutdown operations and is about 50 wt% Na_2O . A listing of the various waste compositions referred to in this report is shown in the "Design Bases" section.

TABLE 16. Glass Composition for NFS Wastes

Oxide	Nominal PW-8a (76-76) wt%	Low Sodium PW-8d wt%	High Sodium PW-8e wt%
SiO_2	40.0(a)	40	47
B_2O_3	9.5	9.5	10
CaO	2.0	2.0	--
Al_2O_3	--	--	2
ZnO	5.0	5.0	--
TiO_2	3.0	3.0	5.0
Na_2O	7.5(b)	12.5	--
Waste	33.0	28.0	36

a. 1.5 wt% SiO_2 is added as silicon metal powder.

b. The PW-8a waste also adds 5 wt% Na_2O for a total of 12.5 wt%.

Due to the numerous different oxides present in the waste, the specific role of each has not been fully determined. The SiO_2 , however, would provide the basic glass structure, with other oxides such as B_2O_3 and TiO_2 also acting as part of the glass network. The B_2O_3 and TiO_2 both reduce the melting point or viscosity of the glass and have demonstrated that they can enhance the chemical durability of the glass. Within specific limits B_2O_3 is also particularly effective in increasing homogeneity in the glass. Na_2O and CaO

are the main modifiers added to the glass to further reduce the viscosity and melting point and allow the 1050°C melting temperature. ZnO also acts as a modifier of glass structure and reduces viscosity and leachability in distilled water.

Part of the silica is added as silicon metal to act as a reducing agent for the MoO_3 in the waste. This is desirable since excessive molybdenum can separate from the glass as a soluble alkali molybdate containing cesium. Reducing the Mo^{+6} to a lower valence eliminates this separation. The addition of a reducing agent can also reduce other species such as ruthenium, rhodium, palladium, tellurium, and nickel. The reduced metals generally exist as fine, micron-sized particles dispersed in the glass; however, some larger spheres ~ 1 mm have also been observed. The metallic state is desirable for ruthenium since volatility is low. Addition of excessive reducing agent is to be avoided since ZnO can be reduced to zinc metal, which has a boiling point below the standard melting temperature of the glass, and zinc vapor can increase corrosion of the canisters. The second potential problem is that the reaction of the silicon powder with the waste is exothermic and, if more than about 5 wt% silicon is added, the mixture can self-heat to above the normal melting temperature. Evolution of gases and heat during the reaction could conceivably cause equipment failure if the silicon metal content is very high, greater than 15 wt%. While this possibility is not confirmed, process controls may be required to limit the silicon additions to about 1.5 wt%. The addition of 1.5 wt% silicon powder does not appear to produce enough zinc vapor to be a problem. Glass compositions are being designed which do not contain zinc oxide to further reduce this potential problem.

While the glass will generally tolerate quite wide variations in the amount of most compounds, there are several which cannot be incorporated in the glass in large quantities. These are F^- , Cl^- , I^- , $\text{SO}_4^{=}$, and mercury. Fluorine will be partially volatilized and become HF in the scrubber. The iodine, chlorine, and mercury volatilize almost completely from the melts at glass-forming temperatures and would become an off-gas disposal problem. The $\text{SO}_4^{=}$ often forms a Na_2SO_4 layer on the top surface. One solution is to reduce

the sulfate to SO_2 . However, this creates an off-gas problem. These are not glass composition problems but off-gas problems.

The additive-to-waste ratio must be controlled between an upper and a lower limit established by viscosity and leachability. The viscosity versus calcine content for the 76-76 composition without silicon metal (identified as 76-68) is shown in Figure 33. A viscosity below 200 poise at 1050°C is desirable for good melting. From Figure 33 it can be noted that about 22 wt% calcine waste would be required to reduce the viscosity below the 200 poise. As the waste loading increases, leachability gradually increases and becomes excessive with about 50 wt% waste. Thus the waste content of the glass may be able to range from 22 to 50 wt%. This is a broad range, and additional tests of these glasses will be required to verify that other properties are also acceptable. The reference composition contains 33 wt% waste and allows considerable variability in the additive-to-waste ratio. The possible variations in the waste composition due to differences caused by changes in the fuel exposure have not been tested but should not be appreciable.

FIGURE 33. Viscosity of Glass 76-68 with Variation in PW-8a-1 Calcine Content at 1050°C

At the reference conditions of 33,000 MWd/MTU and 33 wt% waste loading, the PW-8a waste glass will generate 280 kg of glass/MTU and for 2 1/2 MTU/day would generate 690 kg of glass/day. This would occupy a volume of about 230 liters (8.1 ft³).

The above data apply to the PW-8a composition. It is possible to use different waste and additive compositions to arrive at the same final glass composition, as noted in Table 16. One possible modification of interest is to incorporate additional sodium into the waste from the intermediate-level waste stream and decrease the sodium level in the additive. This has the advantage of disposing of an additional troublesome waste at a minor increase in final waste volume. The major trade-offs for this waste modification are: 1) With little or no sodium in the additive, it can not be premelted and fritted and will not produce as homogeneous a glass. This also would require the additive to be a powder mixture which would have to be prereacted, or separation of components may occur during handling. 2) With the sodium content of the glass being added with the waste stream, variation in the additive-to-waste ratio would produce larger variations in the sodium content of the glass and the associated viscosity and leachability. Therefore, the allowable range of additive/waste ratio would be significantly reduced. 3) Since specific sodium contents are required in the glass and the sodium would be a variable in the waste stream, the sodium content of the waste would require monitoring and control. 4) Calcination of the high-sodium waste composition is slightly more complex. However, spray calcination of such high sodium waste compositions has been demonstrated.

Properties

The glass properties and characteristics fall into four categories: chemical, thermal, mechanical, and radiological. The properties are somewhat interdependent; i.e., radiation damage may affect chemical, mechanical, and thermal properties. Some properties can be determined quite rapidly such as density and initial leachability; however, other properties such as damage from radiation may require years to fully determine. Long-term tests have been limited to a high-zinc glass but are currently being extended to

the NFS and other commercial waste compositions. For this reason it should be noted that any formulation will be subject to modification, depending on the data generated. Some of the data presented here are not specific to the NFS glass, but will be identified as pertaining to the high-zinc, 72-68, glass composition shown in Table 17.

TABLE 17. 72-68 Glass Composition

<u>Oxide</u>	<u>Wt%</u>
SiO ₂	27.3
B ₂ O ₃	11.1
MgO	1.5
CaO	1.5
SrO	1.5
BaO	1.5
ZnO	21.3
Na ₂ O	4.0
K ₂ O	4.0
Waste(a)	26.3

a. Waste PW-4b, which contains 6.5 wt% process inerts, 88 wt% fission products, and 5.5 wt% actinides.

Chemical Properties - Leachability

The chemical property of major current interest is leachability. Much data has been generated about commercial type glass compositions.⁽⁴⁰⁾ The leach behavior of waste glasses and proposed models has also been investigated.^(41,42) Leachability is a major function of the type of solution used, the form of the glass (crushed or cast), pH of the solution, temperature of the solution, duration of the leach test, velocity of the solution, and potential for approach to equilibrium solubility. With these major variables and other minor variables, it is difficult to detail the leach behavior of a specific glass. With this understanding, some specific leach data for the 76-76 composition can be reported, but it should be recognized that values

can vary at least an order of magnitude for conditions different from those of the specific test. For crushed samples in highly buffered room temperature solutions of pH 3.8 and 9.0, the initial 19-hr leach rates were both determined to be about 10^{-5} g/cm²-day. The leachability in 99°C distilled water was 6×10^{-5} g/cm²-day. Solid samples leach at higher rates for the first 24 hr; however, they decrease to less than 10^{-5} g/cm²-day during subsequent periods.

The other main area of chemical properties concerns corrosion of canisters by the molten glass. This is discussed elsewhere in this report.

Mechanical and Bulk Properties

The mechanical and bulk properties of major interest are the density and impact behavior. These are not highly compositional dependent.

The density of the glass can be a function of the cooling rate of the glass and the amount of residual gas or porosity trapped in the matrix. Measurements on samples of laboratory-prepared glass indicated that a typical sample would have a density of about 2.96 g/cm³. The amount of porosity in the glass is subject to variation in the melting step, with higher melting temperatures and longer hold times eliminating more of the bubbles. In the worst case, it is expected that the glasses may have as much as 2% porosity, but typically the value will probably be less than 1%.

The impact behavior of 72-68 monolithic glass castings has been documented.⁽⁴³⁾ In that study, it was shown that the glass within a canister could resist impact velocities as high as 80 mph without increasing the glass surface area more than a factor of 25. The generation of air-dispersible fines (<10 μ particles) was also low. At lower velocities (30 mph) the damage was much less.

Young's modulus, sheer modulus, and Poisson's ratio were reported⁽⁴⁴⁾ for the 72-68 glass as 11×10^{-6} , 4×10^{-6} , and 0.39, respectively, with minor temperature dependences.

Thermal Properties

The thermal properties of waste glass include a wide variety of data which can be important to the waste form.

The thermal conductivities of waste glasses are lower than for commercial glasses because of the high concentration of transition metal oxides, particularly Fe_2O_3 , which reduce radiant heat transfer. The thermal conductivity of 72-68 glass was reported⁽⁴⁵⁾ to increase with temperature from 0.84 W/m-°C at 25°C to 1.05 at 211°C and 1.21 at 403°C. The heat capacity of 72-68 type glass was also reported⁽⁴⁵⁾ to increase from 0.167 cal/g-°C at 200°C to 0.185 cal/g-°C at 400°C. It is likely that the heat capacity values would be slightly higher for the 76-76 type of glass.

The thermal expansion coefficient for the 72-68 glass was reported⁽⁴⁶⁾ to be $7.6 \times 10^{-6}/^\circ\text{C}$ from 47 to 320°C and $9.8 \times 10^{-6}/^\circ\text{C}$ from 320 to 480°C. The values for 76-76 glass are expected to be similar.

The thermal expansion, heat capacity, and thermal conductivity of the waste determine the sensitivity of the waste to thermal fracture. Thermal fracture tests⁽⁴⁷⁾ showed that for 6-in.-dia canisters of 72-68 glass water quenching would increase the surface area only a factor of about 20 and that the proposed air cooling would increase the surface area only about 12 times over that of a monolith. The resulting surface area is less than if the glass were formed into small glass shapes which could be cooled at a similar rate without fracturing.

The viscosity of a glass is important for several reasons. First, it must be low enough at the melting conditions to allow the gas bubbles to move to the top of the glass melt and escape. From industrial experience, it has been found that this requires a viscosity of 200 poise or less. During storage, it may be important that the viscosity be moderately high, at least 10^6 to 10^7 poise, to prevent settling of insoluble materials in the glass. This viscosity would be obtained at temperatures below about 700 to 800°C.

Storage of the waste glasses at temperatures above the annealing temperature (500 to 550°C) may allow some phase separation and devitrification (crystallization). The phase separation may be important if an interconnected

soluble phase forms, allowing accelerated leaching of part of the glass. The 76-76 composition is not in the composition range where significant phase separation would be expected. But some increase in leach rates (less than a factor of 3) have been noted in samples held at 550°C for 1 week. The highest concentration of crystallites from devitrification occurs at near 750°C, with the major phases being fluorite, spinel, ruthenium metal, and RuO_2 . Real wastes would probably also contain some palladium and rhodium alloys or compounds. The crystallite size is small, and it created no microcracking in the 1-week tests. Although 1 week should be sufficient to approach equilibrium, longer term tests are needed and will be performed.

Generally, crystallization or devitrification of HLW glass will result in some increase in leach rate. With the borosilicate glasses developed at PNL, this increase has been small. Typically, in Soxhlet leach tests the borosilicate glass leach rate increases by a factor of about 4 to 10 after devitrification. The devitrified glass leach rate is similar to that of bottle glass.

The volatile elements from the 72-68 composition have been determined and quantified.⁽⁴⁸⁾ The major volatile radioactive elements are cesium, tellurium, molybdenum, rubidium, and ruthenium, in a decreasing order of volatility. Cesium accounts for about 40 to 60% of the volatile material. The amount of volatile material increases exponentially with temperature from 10^{-5} g/cm²-hr at 800°C to 10^{-2} g/cm²/hr at 1200°C. The potential pressure within a canister from off-gases at temperatures below the processing temperature is very low. A test demonstrated this; pressure inside a small-scale canister was monitored at temperatures up to 900°C without a pressure increase beyond that expected from the temperature change of the gas in the system.

Radiation Properties

Changes can occur in stored glass due to radioactive decay. Radiation will induce displacement of atoms in the glass matrix. This can both induce density changes and increase the energy (stored energy) in the glass which can be released during a thermal excursion. Alpha decay will also produce

helium atoms which will both exist in the glass and diffuse into the overhead space. Alpha and beta decay changes the chemical form of the atoms involved, somewhat affecting the structure. The importance of these factors has been assessed for the 72-68 type composition and does not appear to pose significant problems.⁽⁴⁹⁾

SAFETY

The Spray Calcination/In-Can Melting process has been under development at PNL for more than a decade. The process has been shown through analysis and operation to be basically safe. But as in any industrial chemical process, it operates routinely within process limits most of the time and emits some effluents in the course of operation. There is also the situation of an abnormal operation where there may be an accident or the process goes significantly out of control. In this section a preliminary analysis is made of the immediate consequences and effluents released from normal and abnormal situations. Only the source terms from the equipment to the cell are considered.

NORMAL OPERATIONS

Normal operations consist of normal process occurrences such as a process startup, operation, and shutdown; minor equipment failure such as with valves, agitators, and seals; minor process upsets; and maintenance activities. In these operations some effluents are released from the equipment to the hot cell. These may include minor amounts of HLLW, calcine, glass, or radioactive gases. Table 18 lists the types of occurrences that may be encountered together with the associated situation and the resulting consequences. This list is not exhaustive but is intended to be "worst case," which may be used for a Preliminary Safety Analysis Report.

ABNORMAL OPERATIONS

Abnormal operations are those events not likely to occur during the life of the plant. These types of occurrences include accidents such as dropping equipment from a crane, gross vessel failure, or rapid pressurizations. In Table 19 the events, circumstances, and consequences of some "worst credible" occurrences are indicated. This list is not complete, but other situations which can be postulated may not be as severe or are not realistic to even consider. It is also assumed that the probability of these occurrences taking place simultaneously is remote.

TABLE 18. Radioactive Waste Source Terms for Normal Operations

Occurrence	Circumstances	Consequences
<u>Single Incident</u>		
HLLW Release	Connector leakage during calciner operation	<p>The HLLW would either drip or spray from a jumper connection into the cell.</p> <ul style="list-style-type: none">• Amount $\leq$ 20 gal• Composition: Table 1 - (1) HLLW• Properties: Table 1 - (1) HLLW<ul style="list-style-type: none">-Drop diameter: $\sim$3/16 in.-Drop shape: Agglomerated spheres
Calcine Release	Calciner/melter coupling section becomes inoperative or plugs with calcine and frit which are lost from the section during replacement or repair.	<p>The calcine/frit mixture drops onto the cell floor from a height of about 15 ft above the floor.</p> <ul style="list-style-type: none">• Amount = 0.5 kg• Composition: Calcine 33 wt%<ul style="list-style-type: none">-Calcine Comp: Table 20-Frit Comp: Table 1 - (6) Frit• Properties<ul style="list-style-type: none">- Frit: Particle size: -20/+80 mesh<ul style="list-style-type: none">Particle density: 2.2 g/ccBulk density: 1.7 g/cc- Calcine: Figure 34- Shape factor: Agglomerated semi-spherical particles
Glass Release	None	None
Gas Release	<ul style="list-style-type: none">• Calciner filter change• Minor calciner pressurization and system not sealed	<p>Calciner gas plus a small amount of calcine are released to the cell.</p> <ul style="list-style-type: none">• Gas<ul style="list-style-type: none">- Amount: $\leq$ 25 scfm- Composition: Table 1 - (4) Calciner Off-Gas- Properties: Initial temp. $\leq$ 350°C• Calcine<ul style="list-style-type: none">- Amount = $\sim$0.05 kg- Composition: Table 20- Properties: Figure 34
<u>Annual Release</u>		
HLLW Release	Normal operating and maintenance operations	<p>Assume the HLLW would be lost into the cell as a spray or drops</p> <ul style="list-style-type: none">• Amount: $\leq$ 5 gallons est.• Composition: Table 1 - (1) HLLW• Properties: Table 1 - (1) HLLW<ul style="list-style-type: none">-Drop diameter: $\sim$3/16 in.-Drop shape: Agglomerated spheres
Calcine Release	Normal operating and maintenance operations	<p>The calcine would drop onto the furnace or floor</p> <ul style="list-style-type: none">• Amount = $\leq$ 2.1 kg• Composition: Table 20• Properties: Figure 34
Glass Release - None	None	None
Gas Release	Normal operating and maintenance operations	<p>Calciner gas and a small amount of calcine are released to the cell.</p> <ul style="list-style-type: none">• Gas<ul style="list-style-type: none">- Amount: $\leq$ 60 scf- Composition: Table 1 - (4) Calciner Off-Gas- Properties: Initial temp $\leq$ 350°C• Calcine<ul style="list-style-type: none">- Amount = $\leq$ 0.15 kg- Composition: Table 20- Properties: Figure 34

TABLE 19. Radioactive Waste Source Terms for Abnormal Operations

Occurrence	Circumstances	Consequences
HLLW release by calciner feed tank rupture	<ul style="list-style-type: none">Equipment dropped from maintenance crane on full calciner feed tank	<p>Full tank inventory released to cell floor.</p> <ul style="list-style-type: none">Amount: 1000 galComposition and properties: Table 1 - (1) HLLWHLLW flows onto floor over short time
Calcine and gas release due to calciner rupture	<ul style="list-style-type: none">Equipment dropped from maintenance crane on calcinerCalciner pressurization due to rapid oxidization of organic or silicon metal with nitrateSteam pressurization	<p>Entire inventory of calciner released to cell. Calciner feed shuts off after 1-minute.</p> <ul style="list-style-type: none">Calcine<ul style="list-style-type: none">Amount released: 1 kgComposition: Table 20Physical Properties: Figure 34HLLW<ul style="list-style-type: none">Amount released: ~1.5 litersComposition: Table 1 - (1) HLLWProperties: Table 1 - (1) HLLW<ul style="list-style-type: none">Aerosol diameter: 70μAerosol shape: Agglomerated spheresGas<ul style="list-style-type: none">Volume: ~125 scf if not pressurized, ~150 scf if pressurizedComposition: Table 1 - (4) Calciner Off-GasOff-Gas<ul style="list-style-type: none">Properties: Initial temp: 350°CIf occurrence is vessel rupture, it is unlikely there will be flying debris or a shock wave. Assume the pressure relief tank is plugged.
Molten glass, calcine, and gas released due to canister and retort/susceptor rupture during melting operation	<ul style="list-style-type: none">The melter furnace temperature control is lost. The temperature of the canister and retort become sufficiently heated that there is a melt-through of the canister and retort.	<p>Entire inventory of the canister is lost to the cell floor. The canister is full of glass, and there is some calcine-frit present which has not been converted to glass. Material flows onto floor over short period</p> <ul style="list-style-type: none">Glass<ul style="list-style-type: none">Amount= 1500 kg (500 ℓ)Composition: Table 1 - (7) GlassProperties: Runs as a liquid (viscosity < 100 poise) onto floor.Assume solidifies in short time in a average 3/16 in. layerCalcine and Frit<ul style="list-style-type: none">Amount: 13 kg (10 ℓ)Composition: Calcine wt%: 33<ul style="list-style-type: none">Calcine Comp: Table 20Frit Comp: Table 1 - (6) FritProperties:<ul style="list-style-type: none">Frit: Particle size: -20/+80 mesh, Particle density: 2.2 g/cc, Bulk Density: 1.7 g/ccCalcine: See Figure 34Shape factor: Agglomerated semi-spherical particlesAssume mixture flows out of canister on glass surfaceGases<ul style="list-style-type: none">Amount: See Ref. 48Composition: See Ref. 48. It will contain some air, NO_x, H₂O, and fission products including Cs, Ru, and Mo oxides and possibly some other small amounts of fission products. An unrealistic worst case would assume 100% of the Cs, Ru, and Mo is volatilized.As the fluid flows out of the furnace it will form some strings and spatter, and it will crack as it cools.
Solid glass release by canister rupture during handling	<ul style="list-style-type: none">The canister is dropped on a stub or sharp metal object during handling.	<p>The canister integrity is breached. See Reference 43 for analysis of accident.</p>

TABLE 20. Design Bases Calcine Composition

Element Properties Based on One MTU

Element Oxide	Element Atomic Wt.	Elem. Oxide Molec. Wt.	g oxide MTU	Element Oxide	Element Atomic Wt.	Elem. Oxide Molec. Wt.	g oxide MTU	Element Oxide	Element Atomic Wt.	Elem. Oxide Molec. Wt.	g oxide MTU
<u>Fission Products</u>								<u>Process Chemicals</u>			
SeO ₂	79.0	111	73	I ₂	126.9	-	-	Na ₂ O	23	62	14.1
Rb ₂ O	85.5	187	368.5	Cs ₂ O	132.9	281.8	4767	Fe ₂ O ₃	55.8	159.7	27.7
SrO	87.6	103.6	1031	BaO	137.3	153.3	1675	NiO	58.7	74.7	0.056
Y ₂ O ₃	88.9	225.8	593	Re ₂ O ₃	142	332	12,203	Cr ₂ O ₃	52	152	0.115
ZrO ₂	91.2	123.2	4971	Total Fission Products			36,094	SO ₃	32	80	-
MoO ₃	95.9	143.9	5207	<u>Actinides</u>				P ₂ O ₅	31	142	1.46
Tc ₂ O ₇	99	310	1317	UO ₃	238	286	11,448				
RuO ₂	101.1	133.1	2883	NpO ₂	237	269	547				
Rh ₂ O ₃	102.9	253.8	478	PuO ₂	242	274	150				
PdO	106.4	122.4	1576	Am ₂ O ₃	243	534	234				
Ag ₂ O	107.9	231.8	64	Cm ₂ O ₃	247	542	34				
CdO	112.4	128.4	96	Total Actinides			12,453				
SnO ₂	118.7	150.7	65								
Sb ₂ O ₃	121.7	291.4	18								
TeO ₂	127.6	159.6	708								

PARTICLE DENSITY: 2-8 g/cc (AVE ~4 g/cc)
BULK DENSITY: 0.5-1.3 g/cc (AVE ~1.15 g/cc)
PARTICLE SHAPE - AGGLOMERATED SEMI-SPHERICAL PARTICLES

FIGURE 34. Spray Calcine Properties

RESEARCH AND DEVELOPMENT REQUIREMENTS

The Spray Calcination/In-Can Melting process and equipment are sufficiently developed that design for incorporation in a plant waste vitrification facility can be started. Spray calciner development is sufficiently advanced that plant design can proceed at this time. Development with the pilot-scale melter is essentially complete, and full-scale testing will provide the additional information desired to permit production facility design within a year.

Those areas needing further information include 1) equipment optimization and design normally supplied by architect engineers such as material selection, instrumentation, and maintenance features; 2) process operation optimization; and 3) characterization of the effects of off-standard operations. Although calciner effluent properties have been characterized for normal operating conditions, additional evaluation of effluent properties for various operating conditions such as process upsets will provide data for designing effluent treatment systems. Calcination techniques of high-sodium wastes should be further developed for minimizing glass volume and preventing calciner scaling. Processing procedures using a multizone in-can melter furnace should be further optimized. Techniques to prevent external canister spalling need further development. Alternative canister materials should be evaluated. Canister design for processing and subsequent storage is not complete. Also, development to date has been chiefly on a pilot-plant scale. Additional process demonstration is needed on full-scale process and equipment to show that the process can be scaled up for production plant use with easy operation and maintenance.

The program for supplying this information includes cooperation among ERDA, PNL, fuel reprocessors, and the reprocessors' architect-engineer firms. This data will be obtained during the ERDA/PNL demonstration program in which the Spray Calciner/In-Can Melting process and equipment will undergo three demonstration phases. The first phase includes full-scale (2 1/2 MTU/day and over 5 MTU/day) equipment with key items capable of remote maintenance. The second phase involves construction and operation of full-scale, fully remotely operated and maintained equipment in conjunction with reprocessor personnel.

These will be done in such a way that the facility will duplicate as nearly as possible an actual HLLW vitrification facility. The third demonstration phase will occur simultaneously with the other two and will include vitrification of actual high-level waste at rates up to 1 MTU/day.

These programs should provide sufficient characterization and optimization of variables to allow final plant design. These demonstrations will provide long-term operability and reliability data with mockup equipment. Operator training can also be conducted. Effluent characteristics with actual waste will be studied, and large-scale canisters of representative waste will be analyzed. At the program's conclusion it is anticipated that adequate data will have been developed to allow licensing of the vitrification system.

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