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Spray Calciner/In-Can Melter High-Level Waste Solidification Technical Manual

September 1980

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Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
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SPRAY CALCINER/IN-CAN MELTER
HIGH-LEVEL WASTE SOLIDIFICATION
TECHNICAL MANUAL

D. E. Larson, Editor

September 1980

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Pacific Northwest Laboratory
Richland, Washington 99352

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SPRAY CALCINER/IN-CAN MELTER
NONRADIOACTIVE PROCESS DEVELOPMENT

ABSTRACT

This technical manual summarizes process and equipment technology developed at Pacific Northwest Laboratory over the last 20 years for vitrification of high-level liquid waste by the Spray Calciner/In-Can Melter process. Pacific Northwest Laboratory experience includes process development and demonstration in laboratory-, pilot-, and full-scale equipment using nonradioactive synthetic wastes. Also, laboratory- and pilot-scale process demonstrations have been conducted using actual high-level radioactive wastes. In the course of process development, more than 26 tonnes of borosilicate glass have been produced in 75 canisters. Four of these canisters contained radioactive waste glass.

The associated process and glass chemistry is discussed. Technology areas described include calciner feed treatment and techniques, calcination, vitrification, off-gas treatment, glass containment (the canister), and waste glass chemistry. Areas of optimization and site-specific development that would be needed to adapt this base technology for specific plant application are indicated. A conceptual Spray Calciner/In-Can Melter system design and analyses are provided in the manual to assist prospective users in evaluating the process for plant application, to provide equipment design information, and to supply information for safety analyses and environmental reports. The base (generic) technology for the Spray Calciner/In-Can Melter process has been developed to a point at which it is ready for plant application.

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SUMMARY

The Spray Calciner/In-Can Melter (SC/ICM) High-Level Waste Solidification Technical Manual summarizes technology developed by Pacific Northwest Laboratory (PNL) for the Department of Energy and predecessor agencies for vitrification of high-level liquid waste (HLLW). A conceptual SC/ICM equipment design and related analyses are presented to relate PNL equipment development experience and demonstrate application of equipment concepts. The manual provides prospective SC/ICM users with source data for process application, equipment design, and safety/environmental assessments. Also, areas of system optimization and development for process application are indicated.

The process and equipment technology investigations summarized here have been conducted for over 20 years in the development of the SC/ICM Process. Process development included waste form glass chemistry, process operating techniques, and effluent treatment methods. Laboratory waste form development studies included radioactive and nonradioactive materials testing. Major process technology development systems included waste pre-treatment and process feeding, spray calcination, in-can melting (vitrification), glass processing, waste form containment (the canister), effluent treatment, and waste glass chemistry.

Equipment systems were constructed to develop and demonstrate the process on several different capacity scales using nonradioactive and radioactive waste feed material. The major nonradioactive equipment systems include laboratory-scale (about 3 L/h feed capacity), pilot-scale (about 40 L/h feed capacity), and full-scale (about 350 L/h feed capacity) units that have generated over 26 tonnes of nonradioactive glass in canisters ranging in size from 15 cm (6 in.) to 71 cm (28 in.) in diameter and up to 210 cm (7 ft) long. Radioactive demonstration work has been performed on a pilot scale in the Waste Solidification Engineering Prototypes Program, which produced two canisters [20 cm (8 in.) in diameter by 244 cm (8 ft) long] of borosilicate glass containing 4.2 MCi of radionuclide activity by the SC/ICM Process. The Nuclear Waste Vitrification Program produced two canisters containing 370 kCi of radionuclide activity in

94 L of borosilicate glass using high-level waste from commercial power-reactor fuel. Radioactive process development oriented toward off-gas treatment is being conducted in two laboratory-scale units using radioactive and nonradioactive wastes.

Bases are provided for the SC/ICM process and equipment conceptual design. Two reference HLLW immobilization flowsheets based on PNL vitrification experience are offered. One flowsheet is for neutralized waste similar to defense waste; the other is for acid waste similar to commercial waste. The selected feed rate to the calciner was 300 L/h, and the immobilization equipment is designed to be compatible with both flowsheets to the extent practical, with different requirements discussed as necessary. The technology for the process and equipment is presented in depth to make available the data used for process and equipment design and enable prospective process users to easily adapt the technology and reference design for their particular applications.

Conceptual generic equipment designs were developed for the spray calciner, in-can melter, waste canister, calciner support, and selected portions of the calciner feed system. These designs are based on PNL's SC/ICM process development program, A-E contractor equipment recommendations (based on PNL equipment development), and internal peer review of the PNL process development program. A preliminary assessment was performed to assure that remote operations and maintenance are practical under plant conditions. Related equipment and facilities needed for SC/ICM operation such as the following are indicated: hot cell; services; utilities; feed systems; canister handling, closure and inspection; calciner off-gas system; ventilation; waste handling; and effluents handling. However, design and analysis of these related systems are not within the scope of the manual. As part of the conceptual design, calculations are performed on the calciner, melter, and calciner support structure to determine their structural integrity and length of operating service.

Based on the conceptual equipment design and facility description, a preliminary safety and materials-use assessment was performed. This study provides information to potential process users for their Preliminary Safety Analysis Report and Environmental Report and indicates that process/equipment concepts can be safely applied to in an industrial facility.

This manual summarizes a major process development program at the Pacific Northwest Laboratory. The Spray Calciner/In-Can Melter process and equipment base (generic) technology has been developed such that it is available for plant application. However, additional process development related to site-specific waste characteristics and plant design/operating/maintenance philosophies is needed before the system is applied to a specific plant.

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GLOSSARY OF ACRONYMS

ADI	Alternating Direction Implicit	HLWIP	High-Level Waste Immobilization Program
ALARA	As Low as Reasonably Achievable	HLWVC	High-Level Waste Vitrification Cell
APS	Atmospheric Protection System	IAEA	International Atomic Energy Agency
ASME	American Society of Mechanical Engineers	ICM	In-Can Melter
CCS	Continuous Cooling Sensitization	ILLW	Intermediate-Level Liquid Waste
COG	Calcliner Off Gas	LVDT	Linear Voltage Differential Transducer
CFR	Code of Federal Regulations	LWR	Light-Water Reactor
DBT	Design-Basis Tornado	MFP	Mixed Fission Products
DF	Decontamination Factor	MVD	Median Volume Diameter
DOE	Department of Energy	NRC	Nuclear Regulatory Commission
DTA	Differential Thermal Analysis	NWVP	Nuclear Waste Vitrification Project
ECS	Continuous-Cooling Sensitization	OBE	Operating-Basis Earthquake
EDTA	Ethylenediaminetetraacetic Acid	OG	Off Gas
EPA	Environmental Protection Agency	ORNL	Oak Ridge National Laboratory
ERDA	Energy Research and Development Administration	PNL	Pacific Northwest Laboratory
GTA	Gas Tungsten-Arc	POG	Process Off Gas
HEPA	High-Efficiency Particulate Air	PWR	Pressurized-Water Reactor
HLLW	High-Level Liquid Waste	QA	Quality Assurance
		SC	Spray Calcliner
		SCC	Stress-Corrosion Cracking

SCR	Silicon-Controlled Rectifier	TTS	Time-Temperature-Sensitization
SEM	Scanning Electron Microscopy	WFE	Wiped-Film Evaporator
SRP	Savannah River Plant	WFP	Waste Fixation Program
SS	Stainless Steel	WSEP	Waste Solidification Engineering Prototypes
SSE	Safe-Shutdown Earthquake		
TGA	Thermo-Gravimetric Analysis		

GLOSSARY OF ABBREVIATIONS

acfm	actual cubic feet per minute	MN/m ²	meganeutons per square meter
acmm	actual cubic meters per minute	mol	mole
atm	atmosphere	MTHM	metric ton of heavy metal
Ci	curie	MTU	metric ton of uranium
cm	centimeter	MTUWE	metric ton uranium equivalent
d	day (used only in combination with other units)	MWd	megawatt-day
dia	diameter	μm	micrometer
dpm	disintegrations per minute	N	normal
ft	foot	OD	outside diameter
g	grams	Pa	pascal
gal	gallon	ppm	parts per million
gpm	gallons per minute	psig	pounds per square inch gage
μg	micrograms	R	roentgen
h	hour	rem	roentgen equivalent man
ID	inside diameter	s	second
in.	inch	SCFM	standard cubic feet per minute
kpsi	1000 lb/in. ²	sLm	standard liters per minute
L	liter	W	watt
Lpm	liters per minute	wg	water gage
<u>M</u>	molar	W/m K	watts per minute kelvin
min	minute	wt%	weight percent

1.0

INTRODUCTION

1.0 INTRODUCTION

Radioactive waste poses unique problems that require special considerations because of the radiological, chemical, and physical properties of the waste. Extensive research and development has been carried out in the United States, for more than 20 years to convert high-level liquid waste (HLLW) from the reprocessing of spent nuclear fuels to an immobile solid that is safer for handling, storage, and disposal. Much of this work has been performed by Pacific Northwest Laboratory (PNL), operated for the Department of Energy (DOE) by Battelle Memorial Institute under the Waste Fixation Program (WFP)--and subsequently the High-Level Waste Immobilization Program (HLWIP). A major HLWIP objective is to make data available on processes and solid waste forms that are suitable for plant application.

Various solidification technologies have been developed. The technique of spray calcination followed by vitrification (glass-forming) in an in-can melter is well advanced and ready for plant application. These two processes have been demonstrated on laboratory scale, pilot-plant scale and a full-size scale using nonradioactive chemicals. These same processes have also been used on a laboratory scale and pilot-plant scale using radioactive waste.

The purpose of the manual is to summarize PNL-developed spray calciner/in-can melter (SC/ICM) technology and to provide a conceptual SC/ICM system that relates PNL equipment development experience and demonstrates an application of these equipment concepts. This information is intended to provide a technical base for an actual SC/ICM plant application design. It is not intended to provide the underlying design philosophy that would normally be supplied by the user. The manual provides prospective users with source data for process adaptation, equipment design, and preparation of safety and environmental assessments. The current development status of the SC/ICM process equipment is also presented, and development areas for system optimization and for adapting a process to specific plant application are discussed.

2.0

BACKGROUND

2.0 BACKGROUND

Pacific Northwest Laboratory has been involved since the mid-1950s in developing the SC/ICM process, which converts HLLW to a solid, immobile product such as borosilicate glass. Process development was initiated on a laboratory scale and eventually developed into the Waste Solidification Engineering Prototypes (WSEP) Program. In the WSEP Program, radioactive HLLW synthesized to the composition of HLLW from power-fuel reprocessing was solidified by pilot-scale spray-calcliner, in-can melter and continuous-melter processes (Schneider 1969, Schneider and Kelley 1969, McElroy et al. 1968, Bond et al. 1970, Bond et al. 1971, McElroy et al. 1972). More than 50 million curies of radionuclides were immobilized as glass and calcine in 33 canisters that ranged in size from 15 cm (6 in.) to 30 cm (12 in.) in dia by 244 cm (8 ft) long. Two of these canisters, filled in 1970, contained borosilicate glass produced by the SC/ICM process. One 20-cm (8-in.)-dia canister contained 1.4 MCi of radionuclide activity in 54 L of glass and the other contained 2.8 MCi of radionuclide activity in 50 L of glass. The WSEP Program was terminated in 1972. The WFP (followed by the HLWIP) was subsequently initiated to further develop promising HLLW solidification processes for industrial applications.

In the HLWIP, laboratory-scale, pilot-scale (Bonner, Blair and Romero 1976; Larson and Bonner 1976), and full-scale SC's (Mikols, Romero and Bonner 1978) have been constructed and operated using nonradioactive chemicals. Also, laboratory-, pilot-, and full-scale ICM's (Larson and Bonner 1976, Blair 1976, Blair 1979) have been constructed and operated using nonradioactive chemicals. A laboratory-scale SC/ICM has been used to calcine and vitrify radioactive HLLW from power-reactor fuels (Hanson, Knox and Berger 1980; Knox and Hanson 1980).

The pilot-scale (about a 20-L/h feed capacity) SC/ICM was used to initiate nonradioactive development studies in 1974 and is still in operation. Over its operating life it has produced 42 canisters, 15 cm (6 in.) to 40 cm (16 in.) in dia by 90 cm (3 ft) to 150 cm (5 ft) high, containing a total of about 3.5 tonnes of glass. In 1977 a full-scale (about a 350-L/h feed capacity) SC/ICM initiated operation to develop scale-up information and to obtain full-scale equipment operating experience. This equipment is still in

operation and has produced about 30 canisters ranging from 30 cm (12 in.) to 71 cm (28 in.) in dia by 210 cm (7 ft) high, containing about 23 tonnes of glass. In 1980, two similar laboratory-scale (about a 2-L/h feed capacity) SC/ICM units were placed in operation to perform primarily process off-gas development studies for various types of high-level waste feed; one unit is in D-Cell for radioactive development studies using actual HLLW made up to an appropriate composition. These laboratory units will produce canisters about 12.7 cm (5 in.) in dia by 46 cm (18 in.) high.

To complete SC/ICM process development for plant application, a process verification program (Nuclear Waste Vittrification Program) was implemented. The program included processing actual HLLW from spent nuclear power-reactor fuels into two canisters as borosilicate glass in 1979 (Wheelwright et al. 1979, Bonner et al. 1980, Hanson and Bjorklund 1980). The pilot-scale unit (about a 15-L/h feed capacity) produced two canisters [20 cm (8 in.) in dia by 244 cm (8 ft) long] filled with borosilicate glass. One canister held 41.3 L of glass containing 105 kCi of radionuclide activity while the other canister contained 52.9 L of glass bearing 264 kCi of radionuclide activity. These two canisters represent the solidified borosilicate waste glass from about 1.1 MTU of spent pressurized-water-reactor (PWR) fuel.

These programs, along with associated waste-glass product development programs (Mendel et al. 1977, Mendel 1978, Ross et al. 1978, Ross 1977) and other studies (Larson et al. 1978, Barnes and Bendixsen 1977) provide basic process and equipment development technology. Process effluent treatment (Hanson 1980) equipment has been developed as an integral part of the system. Also, there has been a continuing product and package development program (Simonen and Slate 1979) to assure that the package produced by the SC/ICM process will be acceptable by the federal government for disposal.

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3.0

GENERAL SPRAY CALCINER/IN-CAN MELTER DESCRIPTION

3.0 GENERAL SPRAY CALCINER/IN-CAN MELTER DESCRIPTION

The SC/ICM process (Section 5.2) consists of two steps to convert HLLW to a glass (vitrified) product (Section 4.6) in remotely operated facilities (Section 5.3). The initial step involves calcination or conversion of soluble metal salts and solids in solution to a metal oxide powder in the SC (Sections 4.2, 5.4.3). In the second step the calcine, after being combined in the calciner with the glass-forming materials (frit), is vitrified within a container (canister) (Sections 4.5, 5.4.5.4) that functions as the melting crucible and final glass container. During the vitrification process the canister is sintered in a furnace (ICM) (Sections 4.3, 5.4.5) that supplies the heat to convert the glass-forming materials to the vitrified product. The major SC/ICM process equipment components are shown in Figure 3.1.1.

In the spray calcination process the HLLW is transferred from a feed tank (Section 4.1.2) to a spray nozzle, which atomizes the HLLW into droplets (Sections 4.2.1, 5.4.3.4). The atomized feed is sprayed into a chamber that is externally heated by a multiple-zone furnace (Sections 4.2.2, 5.4.3.2-3). A multiple-zone heater is used because the power requirements at different chamber elevations vary significantly. In the calciner chamber the heat is transferred to the atomized liquid feed, primarily by radiation and convection, which evaporates the water and other volatile materials at the calciner operating temperature (400° to 800°C). The soluble metal salts and other insoluble solids decompose primarily into metal oxides. Other salts that do not decompose at calciner operating temperatures remain unchanged. The dry calcine (less than 4 wt% moisture) either drops into a hopper (calciner cone) attached to the bottom of the calciner chamber, where it is combined with the frit, or the calcine fines are entrained into the calciner off gas (COG) and pass into the calciner filter assembly. In the filter assembly, the calcine particulates are almost totally filtered out of the off gas (greater than 99.9 wt%) by sintered-metal filter candles (Sections 4.2.3, 5.4.3.6). The off gas is then routed to an off-gas treatment system for further treatment, such as water removal, NO_x destruction, Ru removal, I removal, and further

particulate removal (Sections 4.4, 5.5). The filters are periodically blown back with a pulse of air, which knocks the calcine buildup down into the calciner cone.

Acidic SC feed may be pretreated by batch denitration or continuous treatment in the SC by the addition of a reducing agent (such as formic acid) to decrease the oxidizing potential of the feed. This treatment reduces the Ru volatilization potential from the feed as RuO_4 (Section 4.1.1).

A vibrator (Sections 4.2.2, 5.4.3.5) is attached to the calciner chamber such that it can be periodically activated to remove any calcine buildup from the calciner walls. Were this not done, calcine buildup could cause a reduction in calciner-chamber heat-transfer efficiency and would result in operating problems.

The frit is metered through a line into the calciner cone, where it is blended in the proper proportions with calcine to make glass. The calcine-frit mixture drops by gravity into a connecting section (Sections 4.3.7-8, 5.4.4), where it is diverted into one of two canisters contained in the ICM and attached to the connecting section.

In the connecting section, the diverter directs the calcine/frit mixture to the canister being filled. When one canister is full, the diverter switches positions to initiate the filling of another canister. The canister is allowed to vent to the calciner via the connecting section during filling and final out-gassing. Since the frit/calcine volume decreases as it is converted to glass, during final out-gassing some additional frit/calcine may be diverted to the canister (termed "fining") to assure a full canister. On completion of fining and canister cooldown to about 700°C , the connecting section is remotely disconnected from the canister to enable canister removal from the ICM and replacement with an empty canister. This method of operation enables continuous calciner operation, as one canister is always being filled while the second is undergoing batch or discontinuous operations. The diverter may be designed so that it may be swiveled to enable canister placement/removal from the ICM, or the ICM may be designed to enable its movement out from under the connecting section.

FIGURE 3.1.1. Spray Calciner/In-Can Melter

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In the ICM (Sections 4.3, 5.4.5) the calcine-frit mixture drops into a canister, which is heated by a multiple-zone furnace that provides enough energy to convert the mixture to glass. The multiple-zone furnace is used to supply adequate heat to each level of the canister as it is being filled. The ICM furnace radiates heat from the furnace elements, possibly via a liner, to the canister exterior walls. The heat is conducted through the canister walls and then conducted and convected in the canister interior to vitrify the calcine-frit mixture. The canister and its contents are normally maintained at between 1050° and 1150°C during filling.

Once a zone heated by the associated furnace zone is filled with glass, heating is reduced or terminated in that zone to prevent overheating, which could result in canister failure due to over-temperature, or segregation (settling) of any nonhomogeneities that may exist in the glass in that zone. It may even be necessary to actively cool a filled canister zone to prevent canister/glass overheating, should the waste glass generate too much internal heat by associated radionuclide decay.

To supplement heat transfer within the canister, a finned metal assembly may be placed within the empty canister. This finned assembly improves radial and axial heat movement via conduction within the canister. This enables increased glass-forming rates in the canister during filling and reduces the radial temperature profile. After the canister is filled and fined, it is cooled to a point at which the glass is solid and the canister has sufficient strength to withstand the stresses incurred during handling. Depending on the heat-generation rate of the glass, forced-air cooling may be used on a single zone or on the entire canister. Fairly rapid cooling of the glass between the temperatures of about 800° and 500°C is desired to prevent glass devitrification (partial crystallization). However, this cooling rate must not be too rapid, or the glass may be over-stressed by thermal gradients, which causes excessive glass-cracking. Once the filled canister is fined, the connecting section is detached and the canister may be capped and removed for subsequent operations such as placing the lid on the canister, lid seal-welding/inspection and glass/canister quality-assurance testing. During canister-filling some

canister materials such as stainless steels may oxidize; the oxide will then spall off of the canister during cooling. If canister materials of this nature are used, a pan is included in the melter furnace to collect the spall (metal oxide), or a means such as an inert-gas cover or a canister-coating bay must be provided to prevent the oxidation. Canister oxidation presents no engineering problem as long as the canister and process system are designed for it.

4.0

PROCESS TECHNOLOGY

4.0 PROCESS TECHNOLOGY

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4.0 PROCESS TECHNOLOGY

The SC/ICM process technology developed over the last two decades is summarized in this section. The section discusses the results of laboratory, equipment, and paper studies that have been performed to advance generic process technology to readiness for plant application. The technology areas discussed include:

- calciner feed
 - denitration
 - transfer
- calcination
- vitrification
- off-gas treatment
- canister
- waste glass.

Recommendations are made about additional work that may be performed for process optimization or need be performed for plant application.

The development effort and information presented is oriented toward supplying base data that provides sufficient technical material and experience to enable equipment design for plant application. However, equipment design and operation is strongly influenced by specific plant design, operating and maintenance practices--areas that are generally outside the scope of PNL's development program. This section is only intended to describe the SC/ICM development effort; extensive use is made of references that may be used to obtain more detailed information, if needed.

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4.1 CALCINER FEED

T. A. Nelson and F. A. Miller

The technology needed to prepare the calciner feed for calcination and to transfer the feed to the calciner is discussed in this section.

4.1.1 FEED TREATMENT--DENITRATION (T. A. Nelson)

4.1.1.1 Introduction

Ruthenium volatility may be suppressed during spray calcination by denitration of the HLLW. Although low ruthenium volatility is seen in the spray calciner (Hanson and McElroy 1977), consideration of the ALARA (As Low As Reasonably Achievable) clause of 10 CFR 20.1 may warrant consideration of ruthenium volatility control, such as by denitration. Denitration helps prevent ruthenium volatility by reducing the amount of nitrogen oxide produced by the HLLW. This reduces the formation of the gaseous, nitrosyl nitrate form of ruthenium and also lowers the oxidation potential of the feed solution, which helps prevent the oxidation of ruthenium to volatile RuO_4 and RuO_3 .

Denitration may also be used to adjust the pH of the HLLW without the addition of salts and the accompanying increase in the waste volume.

Several organic compounds have been used to denitrate solutions of high-level radioactive waste, including sugar, formaldehyde, paraformaldehyde and formic acid. Of these, formic acid appears to be a desirable denitrating agent. If sugar is used, reaction times are long, and the reaction products of sugar can form precipitates with the feed solution (Bradley and Goodlett 1972). Formaldehyde has a high volatility at the reaction temperature of about 90°C . This can lead to processing problems, because the denitration, with subsequent gas evolution and heat release, takes place in the downstream equipment and not under the controlled conditions of the denitrating vessel (Bradley and Goodlett 1972). However, formaldehyde has the advantage that NO_x is produced as a reaction product, which can be recovered as nitric acid. Paraformaldehyde is only 20 wt% in an aqueous solution, so it is necessary to boil off excessive amounts of water during the reaction (Bradley and Goodlett 1972).

Formic acid has the following advantages: none of the reaction products are solids; no explosive nitrate compounds can be formed; the reaction rate is relatively fast; only small amounts of water are added with the formic acid; and formic acid is not highly volatile (Hanson and McElroy 1977). The major disadvantage of formic acid is the potential for large heat releases and gas evolution if unreacted formic is allowed to accumulate in the reaction vessel. This potential problem can be overcome by slow addition of the formic to the reaction vessel.

4.1.1.2 Formic Acid/Nitric Acid Reactions

The basic reactions of formic acid and nitric acid (nitrates) are dependent upon the molarity of the nitric acid (Bradley and Goodlett 1972).

At nitric acid concentrations from 1M to approximately 4M, the reaction is reported to be

At higher nitric acid molarities, a portion of the NO is converted to NO₂:

At nitric acid molarities in excess of 14, the basic reaction becomes

with all the NO reacted to NO₂.

In the denitration process, the initial nitric acid concentration is usually between 1M and 8M, and the denitration reaction will proceed to a lower limit of about 0.5M nitric acid. In this low-acid range, both NO and NO₂ are evolved as reaction products. This variable gas mixture is referred to as NO_x. Nitrous oxide (N₂O) is also generated from batch denitration according to the following reaction:

It is possible, if not probable, that other nitrogen oxides exist in the denitration process off gas (POG), but they may not be major constituents.

The moles of formic acid added per mole of nitric acid as derived by Bradley and Goodlett (1972) is shown in Figure 4.1.1. As can be seen in the figure, the addition ratio is constant at 1.5 up to an initial concentration of approximately 6M nitric acid, indicating the predominance of Equation 4.1. At higher initial nitric acid concentrations Equations 4.2 and 4.3 enter in and lower the addition ratio. The addition ratio for any given initial nitric concentration should not be greatly exceeded, because it could lead to an accumulation of unreacted formic acid in the reaction vessel.

In adding formic acid to nitric acid, a reaction induction time has been observed (Bradley and Goodlett 1972). The induction time is dependent upon

FIGURE 4.1.1. Addition Ratio of Formic to Nitric Acid Versus Initial Nitric Acid Concentration

the temperature and the molarity of the nitric acid. The induction time is reduced as both the temperature and nitric acid molarity are increased. When the reaction is initiated, the formic acid present reacts within a short time with a sharp temperature rise in the denitrator. Therefore, the process conditions must be controlled to prevent the accumulation of a large quantity of unreacted formic acid before the reaction is started. By heating the nitric acid solution to between 90⁰ and 95⁰C, the induction period is reduced to less than 10 min in laboratory experiments when 23.5M formic acid is added to 4M nitric acid at rates of 0.025 L/min to 0.1 L/min.

A further variable that has a significant effect on the process induction time is the sparge rate of both the vapor space above the liquid and the liquid bath itself. Sparging (or other liquid-bath mixing) apparently sweeps the initial reaction products from the denitrator, thus postponing the point at which the reaction is self-supporting.

In denitration processes using formic acid, the reaction products are entirely gaseous or water, as described in the discussion of the basic reactions involved. In addition, no known explosive nitrates are produced (Bradley and Goodlett 1972). Investigations of possible catalytic agents to increase reaction rates or to decrease the induction time for the reaction have shown that the process is insensitive to catalytic or suppressant effects of reactants that may be present in high-level acid wastes. It has been speculated that organic solvents from the extraction processes may be a catalytic agent.

4.1.1.3 Process Description: Semi-Batch Denitration

After the nitrate molarity is determined, a batch of HLLW is transferred from the feed tank to the denitrator using a transfer pump. When the denitrator is filled to the proper level, the transfer pump is stopped. The preheater steam is then turned on to heat the batch to 90⁰C. An interlock is provided between the denitrator tank temperature sensor and the formic acid feed pump to prevent the addition of formic acid to the denitrator if the batch is not within the desired temperature range (between approximately 80⁰ and 100⁰C).

When the denitrator operating temperature is reached, the preheater steam is turned off and the cooling water is turned on. Cooling water flow is indicated by the cooling-water flow meters. Formic acid addition is initiated through the feed-metering pump at a rate based on the predetermined nitrate molarity of the HLLW batch. The rate of formic acid addition is controlled by the formic acid feed-metering pump. The process induction time and reaction rates are monitored by the condenser inlet off-gas temperature sensor, the denitrator liquid-temperature sensor, and the condenser DP cell across the inlet and outlet. Formic acid additions continue until a predetermined amount of acid is added through the metering pump. The denitrator is held at temperature for an additional time using the preheater steam system as necessary to maintain the denitrator at 90°C in order to permit completion of the denitration reaction. The liquor is then transferred via an air jet to the denitrated product tank. The product tank is sized to permit continuous operation of the downstream equipment.

Excessive foaming and pressurization can be controlled by closely monitoring the formic acid addition rate and maintaining the temperature of the feed at approximately 90°C. An addition rate of 0.06 mol formic acid/min/L of nitric acid (assuming an 8M initial nitric acid concentration) has been shown to limit the possibility of both pressurization and foaming if the nitric acid solution is at or above 90°C (Bradley and Goodlett 1972). However, the denitration vessel should be large enough to contain foam that may be generated. It should also include either a seal pot or rupture disk to prevent excessive pressurization. Foaming might be detected by a large pressure drop across a demister section at the denitration vessel outlet or by a change in the specific gravity if the foam has penetrated to a level between the dip legs.

During denitration, the temperature within the vessel will be lower than 120°C. At this temperature, ruthenium is the only fission product expected to be present as a volatile specie that could be removed from the liquor as a gas. Laboratory measurements with DOE defense-type zirconium wastes indicate that no detectable ruthenium is volatilized during denitration with an experimental detection limit of 2 µg total, or less than 5×10^{-5} of the total ruthenium

present during the experiment. Rapid gas evolution during the denitration process may entrain other metal nitrates or oxides as aerosols, and these species would then be carried onto the condenser and into the downstream off-gas treatment units.

4.1.1.4 Process Description: Spray Calcination Denitration

A process alternative for denitration involves mixing formic acid into the HLLW feed on a continuous basis as the feed enters a spray calciner. This process has the advantage that denitration and calcination are performed within the same process vessel, and more complete destruction of the nitrates occurs than with the semi-batch process that is carried out at 95°C. The disadvantage is that any NO_x generated during destruction is diluted with the atomizing air needed for proper operation of the spray calciner. Consequently, the off-gas process equipment used to remove NO_x must be sized to handle the additional gas.

Waste is transferred to the feed tank and sampled for nitrate molarity. Based on this analysis, the feed ratio of formic acid to HLLW feed is established. The HLLW is fed continuously to the feed nozzle at a fixed rate using a pump. An amount of formic acid slightly in excess of that needed for complete destruction of the nitrates in the HLLW solution is fed to the mixer in the calciner feed line using a metering pump. The ratio of formic acid to HLLW feed should remain fixed for the duration of a process run using HLLW of a set composition.

The formic acid/HLLW mixture is fed through the atomizing nozzle directly into an externally heated spray calciner. The formic acid, mixed into the feed, reacts with the nitrates in the HLLW as the nitrate molarity is reduced to form a mixture of metal oxides, H_2O , CO_2 , NO_x , N_2O , N_2 , and O_2 .

Since the formic acid and HLLW feed are mixed immediately at less than 50°C before the combined feed is sprayed into the calciner, no reaction of the formic acid and the HLLW is expected until the mixture is within the heated zone of the calciner. The autocatalytic induction time at 95°C is on the order of several minutes, and the mixing, atomizing, and spraying processes will occur within a few seconds.

When the continuous process for denitrating simultaneously with drying and calcination is used and is done with the process unit temperature in excess of 700°C, accumulations of unreacted formic acid cannot occur during normal operations, since the formic acid will decompose.

4.1.1.5 Effect of Denitration on Ruthenium Volatility

In German solidification processes (Krause and Randl 1972), thermal decomposition of nitrates can lead to ruthenium volatility as high as 70%, whereas chemical denitration results in ruthenium volatility of less than 1%. Typical ruthenium volatilities from the German SC/ICM process are 0.01% with batch-denitrated feed and 1% without denitration (Krause and Randl 1972). Experience at PNL using a substantially different calciner indicates that values ranging from 0.001% to 0.16% of the ruthenium are lost to the off-gas system without denitration (Hanson, Goles and Hamilton 1980). Rimshaw, Case and Tompkins (1980) report that during spray calcination at a wall temperature of 750°C an untreated 4N HNO₃ waste stream showed a RuO₄ volatility of 0.12%, and a batch-denitrated stream (2 mol formic acid/mol nitrate) showed a RuO₄ volatility of 0.013% (Rimshaw, Case and Tompkins 1980). Other denitration experience has been documented by Evans (1959), Healy (1958), Longstaff and Singer (1954).

Two SC/ICM runs done without denitration were conducted at PNL under the WSEP Program using radioactive borosilicate glass as the product. The ruthenium volatilities were 1.9% for the first run and 0.5% for the second (Bond et al. 1971). The H⁺ concentration of the feed was 0.2M in the first and 0.43M in the second, and the nitrate molarity was 5.8M in the first and 3.59M in the second. It has been postulated that these ruthenium volatility values are high because of contamination from previous runs made with the same equipment using phosphoric acid as a glass former, which leads to a much higher level of ruthenium volatilities.

An attempt was made at PNL to determine effects of H⁺ concentration on Ru volatility. One radioactive run was split into two parts. The first half of the run was made with 2M H⁺--the second half made with 6M H⁺. No differences in ruthenium volatility were noted in either half (Hanson 1980).

4.1.2 CALCINER FEED SYSTEM (F. A. Miller)

The systems used to supply feed to the spray calciner are discussed in this section.

4.1.2.1 Principles

The calciner feed system's major functions are to:

- maintain uniform waste feed composition,
- provide reliable transfer of waste feed to the calciner, and
- deliver waste feed to the calciner at an accurately controlled rate.

There are alternative components that accomplish these major functions, depending upon the type of waste feed and whether the feed stream to the calciner nozzle is pressurized or nonpressurized (see Section 4.2.1.1 for a description of internal- and external-mix nozzles). Based on a Bechtel study done for PNL (Bechtel, Inc. 1977), Table 4.1.1 lists alternative components for acidic commercial wastes and defense neutralized wastes. The alternatives listed consider a) anticipated cell radiation levels on the order of 10^6 R/h for acidic commercial waste feeds and 10^4 R/h for defense neutralized waste feeds, and b) anticipated undissolved solids of less than 2% for acidic waste feeds and of between 7% and 17% for basic waste feeds. The intense cell radiation levels with acidic wastes will require that any electric motors be shielded to provide a reasonable working lifetime; compressed air can be used instead of electric motors for feed motive energy. For basic wastes an air lift has not been satisfactorily demonstrated for wastes with very high percentages of solids in the feed. Unshielded electric motors have proven themselves satisfactory for radiation levels on the order of 10^4 R/h. These aspects are considered further in the following discussions of feed system operation, design and maintenance.

4.1.2.2 Operation

Feed system features and operations described here are those used at PNL for full-scale, nonradioactive immobilization equipment development. This experience would have to be selectively adapted for plant application, since radioactive production plant systems have safety, operating and maintenance

TABLE 4.1.1. Feed System Component Alternatives

Feed and Nozzle Type		Alternatives		
Feed	Spray Nozzle	Feed Tank Agitation	Pump Type	Flow Measurement and Control
Industrial Acidic	External-Mix (requires non-pressurized feed)	1. Air (Pachuca Tank) 2. Mixing Eductor 3. Mechanical Agitator (shielded)	1. Air-Lift 2. Centrifugal (shielded) 3. Positive Displacement (shielded)	Magnetic flowmeter and a control valve on the feed line
	Internal-Mix (requires pressurized feed)	1. Mixing Eductor 2. Air (Pachuca Tank) 3. Mechanical Agitator (shielded)	1. Centrifugal (shielded) 2. Positive Displacement (shielded)	
Defense Neutralized	External-Mix (requires nonpressurized feed)	1. Mixing Eductor 2. Mechanical Agitator 3. Air (Pachuca Tank)	1. Centrifugal 2. Positive Displacement 3. Air-Lift	
	Internal-Mix (requires pressurized feed)	1. Mixing Eductor 2. Mechanical Agitator 3. Air (Pachuca Tank)	1. Centrifugal 2. Positive Displacement	

constraints not exhibited in nonradioactive development situations. Simplified pressurized (as for internal-mix nozzle operation) and nonpressurized (as for external-mix nozzle operation) feed-system diagrams are shown in Figures 4.1.2 and 4.1.3, respectively. The pressurized feed system is that used for the full-scale, nonradioactive SC/ICM operation. The nonpressurized feed system is similar to that used on the full-scale Liquid-Fed Ceramic Melter operation at PNL. PNL has only had limited experience with this nonpressurized feed system, but it appears promising for use with an external-mix nozzle, as shown in Figure 4.1.3.

Storage of waste slurries is complicated by the need to prevent settling of nondissolved species. Although glass formulations are designed for broad composition ranges, accurate glass formulation is dependent upon a known amount of solids entering the calciner and melter. Also, deposition of solids in

FIGURE 4.1.2. Pressurized Spray Calciner Feed System (Internal-Mix Nozzle)

FIGURE 4.1.3. Nonpressurized Spray Calciner Feed System (External-Mix Nozzle)

waste tanks may result in eventual hot spots that accelerate corrosion and possible feed-transfer system plugging. Therefore, a homogeneous slurry should be maintained in the waste-holding tanks and feed tank.

The calciner feed system can be set up differently, depending on the type of atomizing nozzle used. The waste is pumped from the feed tank to the calciner through a Y-strainer (to remove large solids), a flowmeter, and a control valve when operating with a pressurized internal-mix nozzle. The largest portion of the waste flow from the pump outlet is recycled directly back to the

tank through a mixing eductor for tank agitation (Figure 4.1.2). For a non-pressurized external-mix nozzle, the waste is air-lifted to a head tank, which overflows to the feed tank. The external-mix nozzle siphons waste from the constant-head tank through a control valve and flowmeter, then into the nozzle. Since an air-lift-type feed-transfer system has not yet been demonstrated for wastes containing a high percentage of solids and would most likely be used with waste feeds containing only a few small particles, a strainer is not shown in Figure 4.1.3. The strainer is flushed when excessive pressure drop through the strainer is indicated by pressure gauges. Since only a few liters of waste are used to flush a strainer, the amount of waste generated in this manner would be small.

The flush-water lines shown in Figures 4.1.2 and 4.1.3 are used for three purposes: 1) to cool the nozzle before beginning waste-feeding in order to prevent possible plugging in the nozzle from the drying of waste in the nozzle, 2) to provide high-pressure water that will remove possible blockages in the flowmeter or feed line by back-flushing to the feed tank (pressure gauges located as shown in Figures 4.1.2 and 4.1.3 would indicate the location of the blockage), and 3) to flush the feed line after shutdown.

Experience at PNL has been primarily with the system shown in Figure 4.1.2 with, in some cases, a mechanical agitator used instead of a mixing eductor. The system has performed satisfactorily, with problems limited to the following:

- occasional plugging in the magnetic flowmeter caused by large foreign particles. [This problem was solved by reducing the size of the strainer-screen mesh to remove particles larger than the flowmeter orifice and by installing a large flowmeter that had a 0.64-cm (1/4-in.) orifice instead of the 0.40-cm (5/32-in.) opening.]
- erosion of the pump impeller housing, pipe elbows and ball valve in the feed tank's 304L stainless steel recirculation line resulting from feeds containing a high percentage of solids. (Solutions to this problem include use of a more erosion-resistant piping material, long-radius elbows or piping bends, and ball valves with port diameters at least as large as the pipe's inside diameter.)

- minor settling of solids around the outside edges on the bottom of the flat-bottomed tank. (Use of tank with a conical or dished bottom would be a solution to this problem.)

4.1.2.3 Design

The design aspects of the calciner feed system will be considered in the following categories:

A. Waste feed agitation and transfer--

Case 1. In-cell centrifugal pump and mechanical agitation

Case 2. Shielded-niche centrifugal pumps

Case 3. Air agitation and transfer

B. Feed tank design

C. Feed flow measurement and control.

This discussion is based on PNL development experience and a study of feed systems performed by Bechtel for PNL (Bechtel, Inc. 1977).

Waste Feed Agitation and Transfer--Case 1: In-Cell Centrifugal Pump and Mechanical Agitation

An electric motor used to drive a pump or agitator would limit its application to a cell environment on the order of 10^4 R/h. An electric, motor-driven agitator or centrifugal pump would be well suited for basic wastes and their relatively low radiation levels (as compared to acidic wastes) and high solids contents.

The types of centrifugal pumps that have been recommended for this application (Bechtel, Inc. 1977) are:

- Deepwell turbine-type canyon service pumps as described in Chapter XIV, Purex Plant Technical Manual (General Electric Co. 1955).
- Cantilever-type centrifugal pump as described in "Transfer of Radioactive Slurries" (Goodlett 1968).

The vertical cantilever-type pump used at PNL for transfer of feed to the calciner is mounted on a flange on top of the feed tank with the pump extending into the feed tank and the motor driver mounted over the pump on top of

the flange. With this type of pump all seals and bearings are above and out of the slurry, permitting long-term operation without seal or bearing replacement. A limitation to the use of this pump is that the maximum standard shaft lengths are approximately 1.2 m (4 ft) to 2.3 m (7.5 ft), depending on the manufacturer, which may limit the tank size that this pump can be used with. However, nonstandard pumps are available with shafts over 6 m (20 ft) long in which the shaft bearings are submerged.

With adequate capacity, a pump can be used for feed transfer and tank agitation, thus eliminating the need for a mechanical agitator. The feed tank centrifugal pump would have two head-capacity conditions to meet:

1. that required for feed to the spray calciner, which would be a relatively high head and small capacity [about 4.9 L/min (1.3 gpm)]. The required head would be approximately the following (Bechtel, Inc. 1977):

Delivery pressure @ nozzle	= 1.7 atm	25 psig
Elevation difference (allow)	= 0.34 atm	5 psig
Piping friction loss (allow)	= 0.34 atm	5 psig
Control loss (50% delivery and line loss)	= <u>1.0 atm</u>	<u>15 psig</u>
	3.4 atm	50 psig

2. that required for motive fluid to the circulation tank eductor for feed-tank agitation. At 3.4 atm (50 psig) pressure at the nozzle, one 3.8-cm (1-1/2-in.) (inlet connection) or two 1.9-cm (3/4-in.) tank eductors will require approximately 265 L/min (70 gpm) of motive fluid. The motive fluid will entrain 11.4 L (3 gal) of suction fluid for every 4 L (1 gal) of motive fluid, for a total turnover of 4 times the motive flow, or 1000 L/min (280 gpm).^(a) At this rate a full 1000-L (264-gal) feed tank will be turned over in less than 1 min. The required turnover rate depends upon the size and concentration of the solids in the feed. Therefore, to meet both of the above requirements, a centrifugal pump would need a capacity of at least 270 L/min (72 gpm) at a discharge pressure of 3.4 atm (50 psig).

(a) Data supplied by manufacturer.

For transfer of feed between waste-holding tanks and the feed tank in which the tank depth might prevent the use of a cantilevered shaft pump, or for which the use of a mechanical agitator would be more economical, diaphragm positive-displacement pumps have functioned well with simulated waste slurries. These air-operated pumps are small and can be mounted on top of the tank with a liquid suction line extending to the bottom of the tank. The air pressure to the pumps can be varied to give a wide range of flows, allowing fairly rapid tank transfer or continuous transfer to the feed tank while feeding to the calciner. These pumps are easily replaced and two pumps installed in parallel would give dependable service.

Mechanical agitation may be the most economical means of agitation for large waste-holding tanks in which radiation levels to the agitator motor are not excessive. Most manufacturers of mechanical agitators can provide detailed designs for specific applications when provided with specifications of the material to be agitated. Agitator motors receiving continuous radiation dose rates of about 10^6 R/h only lasted a few weeks to several months in continuous service while agitating radioactive cesium solutions at Hanford's B-Plant. Shielding the pump motor could extend the motor life.

Waste Feed Agitation and Transfer--Case 2: Shielded-Niche Centrifugal Pumps

For applications in which high radiation levels limit the in-cell use of electric motors and in which air lifts and air agitation are not satisfactory because of the high solids content of the waste, a shielded equipment niche can be considered for use (Bechtel, Inc. 1977). Equipment items requiring maintenance, such as pumps, flowmeters, control valves, and block and check valves can be located in the shielded niche with full viewing and handling capabilities including cranes, manipulators, and remote television. Locating centrifugal pumps in a shielded niche could allow use of mechanical joints below the liquid level of the waste-feed and waste-holding tanks. The possibility of failure of these joints requires that cell liner and sump be designed to handle the full contents of a tank and be able to jet the contents to another tank.

During the WSEP spray solidification runs, in-line centrifugal pumps with a capacity of 19 L/min (5 gpm) at a 3.8-atm (130-ft-H₂O) head was used for calciner feeding at a rate of 10 to 20 L/h. The pump experience is summarized in Table 4.1.2. The pumps contained double mechanical, water-lubricated seals with graphite rotating rings. Isolation valves were installed on the pump assembly to prevent loss of feed if the seals failed and to allow remote change-out in approximately 4 h without transferring the feed out of the feed tank. Pump life is decreased by start-and-stop operation and is substantially increased by a thorough water-flushing after each run. In an extended pump operating test with nonradioactive feed, a similar pump was operated continuously for 553 h before the seals failed.

The pumping and agitation requirements for this case could be supplied by centrifugal pumps with tank eductors to aid in agitation. The pump capacity requirements can be determined as for the calciner feed pump in Case 1.

TABLE 4.1.2. Feed Pump Experience During WSEP Spray Solidification Runs

Pump(a) No.	Service Runs	Feed Type	Duration of Run, h	Run Date	Remarks
P-12	SS-4	PW-2	42	9/12/68	P-12 failed after 297 h of operation during a flushing operation following Run SS-8.
	SS-5	PW-1	45	10/16/68	
	SS-6	PW-1	77	11/4/68	
	SS-7	PW-1	65	12/9/68	
	SS-8	PW-1	68	2/3/69	
TOTAL			297		
P-14	SS-9	PW-4m	61	2/25/69	P-14 failed during subsequent use with the phosphate glass process.
	SS-10	PW-4m	65	3/25/69	
			126		
P-17	SS-11	LMFBR	50	2/24/70	P-17 was used 68 h during Run PG-11. P-17 was not used after Run SS-12 and did not fail.
	SS-12	PW-4m	36		
			86		
P-18	SS-13	PW-4m	36	5/11/70	P-18 was used 83 h during Runs PC-7 and PC-8 and did not fail.

(a) Deanline Centrifugal Pump, Deanline Type 3/4 DL, Deanalloy Class 50, 316 SS Construction; 5 gpm at 130-ft head.

Waste Feed Agitation and Transfer--Case 3: Air Agitation and Transfer

For applications that involve high radiation levels and a low percentage of solids, the use of compressed air for agitation and feed transfer should provide reliable service. Since feed to the calciner is not sufficiently pressurized by air-lift or air-jet transfer methods, these methods cannot be used with internal-mix nozzles but are well suited for external-mix nozzles.

The design of air-agitated "pachuca" tanks has been discussed by Lament (1958). The pachuca tank is a vessel with a conical bottom (usually 60°); air can be injected at the apex of the cone. The conical bottom is intended to direct settled solids to the apex of the cone, from which they may be returned to the top of the tank by fluid currents developed by the air. Table 4.1.3 shows quantities of air required for agitation per square foot of tank cross-sectional area that have been given for a liquid depth of 9 ft (Kaufman 1930). The following equation has been suggested for use as a scale-up factor to give equal agitation at the tank bottom (Lament 1958):

$$\frac{V_a}{34 + SD_a} = \frac{V_b}{34 + SD_b}, \quad (4.5)$$

where

V = air volume rate in ft³/min at temperature and pressure of tank contents,

TABLE 4.1.3. Approximate Volume of Air Required for Tank Agitation

<u>Agitation Level</u>	<u>ft³/min Free Air per ft² Cross-Sectional Area of Tank of a 9-ft Liquid Depth</u>
Moderate agitation	0.65
Complete agitation	1.3
Violent agitation	3.1

S = specific gravity, and

D = depths at which air is released into the tank in feet
(subscripts a and b refer to tanks a and b).

Also, air-sparging has been successfully used in industrial fuels reprocessing plants for tank-liquid agitation (Nuclear Fuel Services, Inc. 1973).

For feed transfer using compressed air as the motive force, either an air-jet or an air-lift design could be used. Air jets are available commercially for a wide range of flows. An air-lift design used by Allied Chemical at Idaho Falls for a fluid-bed calciner is shown in Figure 4.1.4 (Taylor 1978). An air lift consists of a vertical pipe with the lower portion submerged in liquid and an air supply entering the bottom of the column. A rising column of liquid results from the displacement caused by rising gas. The liquid and air discharge in a head tank, which maintains a constant liquid head to the atomizing nozzle by overflowing a portion of the entering stream back to the feed tank. Previous studies have shown that pipe diameter, submergence, and liquid density affect the performance of the air lift (Kearsley 1958). As indicated previously, air lifts are also successfully being used for the full-scale Liquid-Fed Ceramic Melter feed system at PNL.

Feed Tank Design

In the Bechtel study (1977) it was recommended that the feed tanks be designed and constructed in accordance with the ASME Pressure Vessel Code, Section VIII, Division 1, and the following:

Material--Type 304L stainless steel with samples subjected to tests of corrosion resistance in accordance with ASTM A262, Practice C.

Design Temperature--The maximum temperature the tank would experience is approximately 250°F if the cooling water was lost and the feed tank self-boiled. The recommended design temperature is 150°C (300°F).

Corrosion Allowance--A minimum of a 0.32-cm (1/8-in.) corrosion allowance should be used.

FIGURE 4.1.4. Airlift Design

Nondestructive Weld Testing--All pressure-retaining welds should be 100% radiographed.

Feed-Tank Cooling--Two methods of tank-cooling were considered: external jacket and internal cooling coils. Internal cooling coils would have a higher heat-transfer coefficient and would require a smaller heat-transfer area. However, external-jacket cooling is preferred if adequate cooling capacity can be provided, since minimum obstruction to tank circulation and solids suspension is desirable. The heat release per unit volume would have to exceed 10 W/L before cooling with an external jacket becomes marginal when using a 1.5-m (5-ft)-dia feed tank.

Design Pressure--Both internal and external pressures must be considered. The controlling design pressure would likely be the maximum pressure of the cooling water.

Instrumentation--Tank instrumentation should include thermocouples for temperature measurement, pressure sensors, and liquid-level measurement. Bub-
bled air-dip tubes have proven effective for accurate liquid-level measurement
(Bonner, Blair and Romero 1976).

Feed-Flow Measurement and Control

Feed-flow measurement and control can be divided into the two categories illustrated in Figures 4.1.2 and 4.1.3: 1) pressurized calciner feed supply (internal-mix nozzle), and 2) nonpressurized calciner feed supply (external-mix nozzle). A pressurized feed control system requires a flowmeter and a control valve with pressure indicators. A flushing system should be provided to remove possible solid plugs in the flowmeter by back-flushing through the flowmeter to the feed tank with water. This system would also function to flush the feed line clean after feed to the calciner is shut off for any reason and to cool down the atomizing nozzle immediately before starting feed to the calciner. Switching from feed to flush water and vice versa can be automated to prevent both valves from being open simultaneously. The flush water should be maintained at a higher pressure than the feed to prevent feed from leaking into noncontaminated regions. Also, anti-backflow devices should be used on the flush lines for additional assurance that radioactive materials will not escape the cell.

Control of feed flow by varying the atomizing air flow in internal-mix nozzles has been tested. Since only a limited volume of air and liquid can pass through the nozzle at a certain pressure, increasing the air flow will reduce the liquid flow and reducing the air flow will increase the liquid flow. Unfortunately, control of feed flow by this method is limited to a very small flow-control range. Variations in the air flow affect the degree of atomization and can result in insufficient drying and an accumulation of calcine scale on the calciner chamber or cone sections. Although small flow adjustments are feasible with this method, controlling waste feed flow over a wide range solely by the use of atomizing air flow is not practical.

The electromagnetic flowmeter has been found to provide the best service in this application at PNL. This flowmeter is capable of accurately measuring

flow rates of corrosive liquids and slurries over wide flow ranges independent of solids loading, temperature, viscosity, or turbulence. An electromagnetic flowmeter is a volumetric fluid-flow rate device with the principle of operation based upon Faraday's Law of Induction, which states that the "voltage induced across any conductor as it moves at right angles to a magnetic field is proportional to the velocity of the conductor." The amplitude of the voltage generated is directly proportional to the flow rate of the measured fluid. An illustration of the magnetic flowmeter is given in Figure 4.1.5. The unit used in the full-scale spray calciner at PNL has a 0.64-cm (1/4-in.)-dia nominal pipe size tube with possible full-scale readings of approximately 100 to 1000 L/h. Accuracies vary between 0.5% of instantaneous flow and 2% of full-scale readings, depending on the receiving instrument selected and the calibration method used. Lower flow measurements are attainable with smaller flowmeter tube sizes, but the chance of flow blockage in the flowmeter from solid particles increases greatly as the diameter of the tube decreases. A vitreous

FIGURE 4.1.5. Magnetic Flowmeter

enamel tube liner is normally used for hot-cell applications, although fluoride attack of the enamel liner has been reported with some waste feeds (Taylor 1978). Kynar lining was used instead of enamel in this case. A drawback of the electromagnetic flowmeter is that zero-drift and calibration checks must be made routinely. Feed-tank depletion measurements provide a reliable means of checking and, if necessary, modifying the calibration of the flowmeter.

Performance of the feed control system during WSEP operations over the range of about 10 to 20 L/h was only fair because measurement of this low feed-flow rate to the solidifier with a magnetic flowmeter was frequently inadequate. The automatic feed controller receives an input signal from the magnetic flowmeter and delivers an output signal to the feed control valve. Difficulties experienced with the magnetic flowmeters occurring in many early WSEP runs included loss of signal, frequent shifts in calibration (partially due to low flow rates required), and failure of electrical wire insulation. Reliability was increased significantly by changing the electrical wire periodically. A 1/2-in. Hammel Dahl valve with a No. 5 spline trim was used to control the feed to the solidifier. Special flushing procedures were used before and after feeding to keep the feed line satisfactorily free of solids. Also, an air-operated diaphragm control valve, such as a Hammel Dahl, is used for feed-flow control in the pilot- and full-scale, nonradioactive calciner systems at PNL. Valve service has been good over an extended time of periodic operations.

4.1.2.4 Maintenance

In-cell components of the feed system requiring maintenance should be remotely replaceable, including the pumps, agitators, and piping; instrumentation is likely to be the component requiring the most maintenance. The magnetic flowmeter should be checked for zero adjustment and for calibration on about a weekly basis by using tank depletion rates. The tank's liquid-level-monitoring dip tubes have occasionally plugged, probably from a buildup of material dried by the compressed air on the dip-tube outlets. During the WSEP effort at PNL, plugging of the dip tubes was negated by periodically discontinuing the air purge to the dip tube (Bonner, Blair, and Romero 1976). This

allows liquid to enter the dip tube and redissolve deposits formed at the air/liquid interface. More stubborn plugs can be removed by high-pressure air or a small amount of acid placed in the dip tube purge line. Also, pressure sensors and gauges can become plugged with solids and require replacement. Experience at the Hanford Purex and Redox fuel chemical-reprocessing plants has indicated that the need for dip-tube cleaning can largely be eliminated by humidifying the purge air.

Major maintenance items would consist of replacing valves and piping, flowmeters, pumps, agitators, and tanks. The likely causes for replacement would be erosion/corrosion, mechanical failure and radiation damage. A pipe elbow (Sch-40), reducer, and several valves constructed of 304 stainless steel required replacement after approximately 2500 h of operation due to excessive erosion damage. Also, the cantilever pump-impeller housing required fill-welding of several gouges caused by erosion. These problems illustrate the need for highly erosion-resistant materials, especially in these susceptible areas. The only mechanical failures encountered have been a gear in a mechanical agitator, a check valve in a diaphragm pump, and several disposable in-line centrifugal pumps.

Blank

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4.2 CALCINATION

F. A. Miller

The spray calciner, used to convert the liquid feed to a dry powder, is discussed in this section.

4.2.1 ATOMIZING NOZZLE

4.2.1.1 Principles

An important phase in spray-drying is waste feed atomization. The liquid must be dispersed into droplets small enough to dry before striking the calciner wall or the cone at the bottom of the chamber in order to prevent caking on these surfaces. Good atomization increases the heat-transfer area of the droplets and increases the drying rate.

Two types of atomizing nozzles have been tested for spray-drying waste feeds--internal-mix and external-mix nozzles. An internal-mix nozzle contacts pressurized liquid with pressurized air in a small internal chamber and then sprays the fluids through an orifice, as shown in Figure 4.2.1. The air velocity is very high and the initial liquid velocity is low. Atomization occurs as a result of the shearing action of the high-speed air upon the slow-moving liquid.

An external-mix nozzle exhausts pressurized air around the liquid feed outlet and siphons the liquid through the nozzle; Figure 4.2.2 illustrates this system. The air impacts upon the liquid outside the nozzle to break the liquid into droplets.

In addition to the nozzle design, spray-droplet size is influenced by the following:

- waste feed flow rate,
- atomizing air flow rate,
- calciner temperature,
- percentage of solids in waste feed.

Kaser (1969) has shown that the mass median spray-droplet size is strongly dependent upon the ratio of liquid-to-gas flow rates, both on a mass and on a

FIGURE 4.2.1. Internal-Mix Nozzle

FIGURE 4.2.2. External-Mix Nozzle

volume basis. The droplet size decreases with higher gas-to-liquid flow ratios. The calciner temperature may influence the droplet size by causing rapid boiling and shattering of the droplets at high temperatures. A high percentage of solids in the waste feed was shown by Kaser (1969) to produce smaller droplet sizes, while filtering out solids caused the droplet sizes to approach those of water at similar flow ratios.

4.2.1.2 Operation

Steam, hot air, and ambient-temperature air have been evaluated as atomizing gases. Both steam and preheated air cause nozzle plugging in small internal-mix nozzles by drying the waste in the nozzle (Bonner, Blair and Romero 1976). Conventional external-mix nozzles are also heated excessively by hot air or steam and can plug from waste dried in the nozzle. Therefore, ambient-temperature air has been the gas used for atomization at PNL. Hot air or steam could be used for atomization with an external-mix nozzle, since the steam or hot air contacts the liquid outside the nozzle; internal nozzle cooling could prevent the feed from drying in the nozzle. This has been demonstrated at Karlsruhe, Germany (Kanfmann et al. 1976).

Nozzle cleanout assemblies have been used for nozzles with air cap orifices 0.125 in. or smaller. These assemblies have a plunger that is extended through the air cap orifice when activated by compressed air. While these cleanout assemblies have proven useful for small-scale calciners, they have never been used during operation of the full-scale calciner, which uses air cap orifices larger than 0.25 in. Nozzle plugging in the full-scale calciner has occurred only twice in 3 years of intermittent testing. The cause of those pluggages was failure to pre-cool the nozzle with demineralized water before waste feed startup. Pre-cooling the nozzle with demineralized water prevents solids formation caused by flashing of the feed when the liquid reaches the hot feed line and nozzle during startup. Plugging in full-scale nozzles is not likely to occur if the nozzle is pre-cooled. In the event that a plug did occur, replacement of the nozzle would be simpler than would providing a mechanism for cleaning the nozzle.

Accurate pressure and flow measurements of the atomizing air are important. In-cell measurements of the atomizing air pressure and flow can be eliminated by sizing the air piping to minimize pressure drop and by measuring both the pressure and flow at appropriate points in the out-of-cell air piping.

For an internal-mix nozzle, a pressure switch should be interlocked with the feed pump power supply to turn off the pump if the atomizing air pressure drops below a minimum value. This will prevent waste feed from being forced into the atomizing air line if the nozzle air cap orifice becomes plugged and the waste pressure exceeds the atomizing air pressure. In addition, an anti-backflow device should be installed in the air line. This backflow risk does not present itself with external-mix nozzles.

External-mix nozzles have a disadvantage when compared to internal-mix nozzles, in that a much higher air-to-liquid flow is required for operation--requiring larger-capacity off-gas treatment equipment. Also, external-mix nozzles tend to produce a large droplet at the center of the spray pattern at higher liquid flow rates, which may cause an accumulation of damp calcine on the calciner cone section. The number of large droplets can be reduced by maintaining a sufficient liquid siphon height, as shown in Table 4.2.1. The necessary siphon height must be determined by testing for individual calciner chamber heights and for varied flow rates. In addition, feeds with a high percentage of solids are more likely to cause plugging in external-mix nozzles than in internal-mix nozzles, since in an external-mix nozzle the waste feed must be siphoned.

Several advantages for the use of external-mix nozzles exist. A nonpressurized feed system can be used, such as air-lift-type feed system, for some waste feed types containing low solids content. This eliminates the need for a mechanical pump. Also, the risk that exists with an internal-mix nozzle of waste feed being forced into the atomizing air line is not present with the external-mix nozzle. Finally, the abrasive wear seen in external-mix nozzles is not nearly as severe with internal-mix nozzles, since the high-velocity air contacts the waste feed outside the nozzle.

TABLE 4.2.1. Flow and Droplet Size Data for External-Mix Nozzles

Nozzle Sizes		Air Pressure, psig	Air Flow, SCFM	Liquid(a) Siphon Height, in.	Liquid Flow, L/h	Estimated MVD Range, μ m	Mass Air Flow/ Mass Liquid Flow Ratio
Air Cap Orifice, in.	Fluid Cap Orifice, in.						
0.437	0.250	20	18.5	4	91	70-80	0.44
		20	18.5	8	55	50-60	0.73
		30	24.0	4	129	70-80	0.41
		30	24.0	8	98	60-70	0.54
		40	29.2	4	154	70-80	0.41
		40	29.2	8	124	60-70	0.51
1.125	0.625						
		20	105	4	452	200-250	0.51
		20	105	8	245	150-200	0.94
		25	120	8	336	150-200	0.78
		30	135	8	333	100-150	0.89
		40	165	8	429	100-150	0.84

(a) Liquid Siphon Height: height of nozzle outlet above feed tank liquid level.

Atomizing air and liquid flow data at various pressures and for various sizes of external- and internal-mix nozzles are listed in Tables 4.2.2 and 4.2.3. This data is supplied by a nozzle manufacturer for water sprayed at room temperature, but agrees closely with flow measurements made for actual calciner operation with simulated waste feeds. This data serves only as a standardized reference, since air and liquid pressure measurements for actual plant equipment will depend upon the location of the pressure sensors and upon additional system pressure drops.

The estimated median volume diameter (MVD)^(a) (Table 4.2.1) for spray droplets were also supplied by the nozzle manufacturer for water sprayed at room temperature. Since it is not practical to measure spray-droplet sizes

(a) Median Volume Diameter: 50% of the total volume of liquid sprayed is made up of droplets with diameters less than the median value and 50% with diameters greater than the median value.

TABLE 4.2.2. Flow and Droplet Size Data for Internal-Mix Nozzles

Nozzle Sizes		Liquid Pressure, psig	Liquid Flow, L/h	Air Pressure, psig	Air Flow, SCFM	Estimated MVD, μm	Mass Air Flow/ Mass Liquid Flow Ratio
Air Cap Orifice, in.	Fluid Cap Orifice, in.						
0.125	0.100	15 ^(a)		20		100	
		15 ^(a)		22		80	
		20	61	25	4.18	120	0.150
		20	32	30	5.3	50	0.362
		25 ^(a)		30		130	
		25 ^(a)		35		60	
0.312	0.251	15	309	20	17.6	200	
		15 ^(a)		25		70	
		20 ^(a)		25		200	
		20 ^(a)		30		70	
		20 ^(a)		35		50	
		25	436	30	22.5	250	0.113
		25	289	35	28.8	100	0.218
		25	173	40	35.3	50	0.446
0.547	0.437	10	546	14	51	200	0.20
		10	387	16	61	110	0.34
		10 ^(a)		20		30	
		15 ^(a)		25		70	
		20	750	26	72	255	0.210
		20	455	30	94	100	0.451
		20 ^(a)		35		35	

(a) Outside of the manufacturer's recommended operating range (high air pressures can cause discontinuous flow).

inside an 800°C calciner chamber, the flow conditions required to produce a droplet small enough to dry before striking the spray chamber wall or cone section have been determined by experiments and correlated to the droplet sizes for water at room temperature atomized at similar flow conditions. For small-scale calciners [spray chambers less than 1.8 m (6 ft) in height], nozzle flow conditions are required that produce approximately 70- μm (MVD) or smaller droplets when spraying water at room temperature. For large-scale calciners

(spray chambers greater than 10 ft high), nozzle flow conditions are required that produce approximately 100- μm (MVD) or smaller droplets when spraying water at room temperature. Table 4.2.3 indicates the air-to-liquid mass-flow ratios required to produce those droplet sizes for several atomizing nozzles.

Another factor that must be considered is that the nozzle spray pattern must be compatible with the calciner spray-chamber diameter. A wide spray pattern in a small-diameter spray chamber will cause droplets to contact the heated wall before they are dry, resulting in a scale buildup. While no rule has been developed to determine the smallest-diameter chamber compatible with a particular nozzle, the diameter of the spray chamber should at least be several inches larger than the width of the spray pattern in free air to prevent direct impingement of the spray on the chamber wall.

4.2.1.3 Design

Standard internal dimensions for the internal-mix nozzle fluid cap and air cap supplied by manufactures have been used throughout SC development. However, limited modifications have been made 1) to aerodynamically improve the

TABLE 4.2.3. Required Mass-Flow Ratios

<u>Nozzle Type</u>	<u>Nozzle Sizes</u>		<u>Droplet MVD, μm</u>	<u>Air-to-Liquid Mass Flow Ratios Required to Obtain Droplet MVD</u>
	<u>Air Cap Orifice, in.</u>	<u>Fluid Cap Orifice, in.</u>		
Internal-Mix	0.125	0.100	70	0.3
			100	0.2
	0.312	0.251	70	0.3
			100	0.2
	0.547	0.437	70	0.4
			100	
External-Mix	0.437	0.250	70	
			100	
	1.125	0.625	70	
			100	

spray pattern, which minimizes solids accumulation on the nozzle and on the top of the spray chamber and 2) to prevent abrasive wear by use of more wear-resistant materials that are also thermal-shock-resistant. These internal-mix nozzle design modifications are discussed separately.

Aerodynamic Nozzle Design

Experience has shown that certain nozzle shapes cause excessive turbulence at the nozzle-exit orifice that results in dried solid accumulations (Bonner, Blair and Romero 1976). In the same manner, nozzles that do not protrude through the top of the spray chamber at least 1 in. for full-scale calciners can also cause turbulence that results in dried solid accumulations on the top inside surface of the spray chamber. Figure 4.2.3 illustrates examples of good and poor aerodynamic nozzle designs.

FIGURE 4.2.3. Examples of Poor and Good Aerodynamically Designed Nozzles

Nozzle-Wear and Thermal-Shock Testing

Abrasive wear experienced with stainless steel internal-mix nozzle air caps prompted a search for a more wear-resistant material. Some of the materials tested are: reaction-bonded silicon nitride (Si_3N_4), 99.5% alumina, Cer-vit (a machinable glass-ceramic), and 303 stainless steel. Since these materials (except for stainless steel) are susceptible to breakage by thermal shock, tests to determine resistance to thermal shock were also completed.

Abrasive wear occurs on the upstream edges of the air cap orifices. Figure 4.2.4 illustrates the different stages of nozzle wear and locations of wear measurement. Two measurements for determining wear were taken before and after periods of simulated waste-feeding at room temperature: 1) the internal orifice diameter at the initial orifice tip length (at the initial upstream orifice edge) and 2) the orifice tip length.

Nozzle air cap wear does not significantly affect calciner performance until the diameter of the downstream edge of the air cap orifice is enlarged. The downstream edge of the orifice does not change significantly until the orifice tip has worn through. Therefore, the most important parameter for determining the amount of wear on an air cap is the percent of the orifice tip that has worn through.

The results of the abrasive-wear testing for spraying system nozzle setup #42 are shown in Table 4.2.4. Table 4.2.5 gives the composition of the feed

FIGURE 4.2.4. Location of Internal-Mix Wear Measurements Taken

TABLE 4.2.4. Results of the Abrasive-Wear Testing

Air Cap Composition	Hours Used	Internal Orifice Diameter (in.) Orientation		Average Diameter Increase, in.	Length of Orifice Tip, in.	% Orifice Tip Worn Through
		0°	90°			
Cer-vit	0	0.123	0.123	--	0.066	--
	15	0.149	0.148	0.025	0.045	32
	30	0.158	0.162	0.037	0.038	42
303SS	0	0.124	0.123	--	0.062	--
	15	0.128	0.127	0.004	0.050	19
	30	0.139	0.144	0.018	0.040	36
96% Alumina	0	0.126	0.126	--	0.068	--
	15	0.171	0.184	0.052	0.062	9
	30	0.185	0.181	0.057	0.0615	10
	45	0.180	0.180	0.054	0.061	10
	60	0.182	0.183	0.057	0.060	12
Silicon Nitride	0	0.126	0.126	--	0.069	--
	15	0.139	0.136	0.011	0.064	7
	30	0.145	0.144	0.018	0.063	9
	45	0.147	0.150	0.022	0.062	10
	60	0.150	0.150	0.024	0.062	10

slurry used for the test. The atomizing air was 25 psig and the feed pressure was 15 psig throughout the testing. A nozzle with a 0.125-in. air cap orifice was used for testing because of its relatively small air flow requirements, which simplified the test equipment and minimized the size of off-gas handling equipment. Full-size nozzles have greater orifice tip lengths and can be expected to perform longer than will small nozzles before the orifice tip is worn through and the atomization is significantly degraded.

Alumina and silicon nitride are the most wear-resistant, with only 10% to 12% of the orifice tip worn through after 60 h of operation. Cer-vit and 303 SS had 42% and 36%, respectively, of their orifice tips worn through after 30 h of operation. It is interesting that most of the wear to the alumina and

TABLE 4.2.5. Simulated Waste Feed Composition(a)

<u>Component</u>	<u>wt%</u>	<u>Chemical Form Simulated Feed</u>
Fe(OH) ₃	53.4	colloidal
Al(OH) ₃	12.4	nonsoluble powder (-200 mesh)
MnO ₂	10.5	nonsoluble powder (-200 mesh)
Zeolite	6.7	nonsoluble grit (20-50 mesh)
Ni(OH) ₂	6.1	nonsoluble powder (-200 mesh)
CaCO ₃	4.4	nonsoluble powder (-200 mesh)
SiO ₂	3.6	-40, +60 mesh sand
NaNO ₃	1.9	soluble
Na ₂ SO ₄	1.0	soluble

(a) Feed concentration: 108 g/L of the above feed chemicals.

silicon-nitride air caps occurred within the first 30 h of operation. This may indicate a decrease in wear with time.

In addition to testing for wear resistance, all these materials except 303 SS were also tested for failure caused by thermal shock. Thermal-shock failure results from stress created by a large temperature gradient across the air cap. A large temperature gradient can occur when fluid flow is interrupted or started abruptly. For example, if the atomizing air flow is off during calciner heatup and then is turned on suddenly, a cracked nozzle air cap could result. Table 4.2.6 shows the results of the thermal-shock testing.

For the rapid-cooling tests, cooling rates were varied from 440°C/min to 1790°C/min in increments of about 270°C/min using a flow of compressed air. The nozzle was inspected after each incremental change, and the rate of cooling that caused damage to the air cap, if any, was noted. Temperature-change measurements were made with a thermocouple located in the mixing chamber portion of the air cap. This location approximates the temperature of the interior surface of the air cap. In the rapid-heating test, the nozzle assembly at room temperature was placed into a 925°C furnace. The maximum initial heating rate was approximately 200°C/min.

TABLE 4.2.6. Results of the Thermal-Shock Testing

Air Cap Number	Material	Test Performed		Results
		Rapid Cooling	Rapid Heating	
1	96% Al ₂ O ₃	X		Broke at initial cooling rate of 440°C/min
2	96% Al ₂ O ₃	X		Broke at initial cooling rate of 1790°C/min
3	96% Al ₂ O ₃	X	X	Did not break
4	Cer-vit	X		Did not break
5	Cer-vit		X	Broke at initial heating rate of 200°C/min
6	Cer-vit	X	X	Did not break
7	Si ₃ N ₄	X		Did not break
8	Si ₃ N ₄	X	X	Did not break
9	Si ₃ N ₄	X	X	Did not break

As can be seen from Table 4.2.6, the alumina air caps had the greatest variation between individual air caps for breakage conditions. Possible reasons for this are quality variations or stresses induced during air cap machining. Breakage of the Cer-vit air cap in the rapid heating test may have also been due to a flaw, since the other two Cer-vit air caps tested did not break under the more rigorous rapid-cooling test. The silicon nitride air caps tested did not break under any test conditions. Figure 4.2.5 is a photograph of the three air caps that broke and an alumina air cap that broke during use with a pilot-scale calciner.

These results indicate that alumina air caps are much more susceptible to thermal-shock breakage than are air caps of Cer-vit or silicon nitride. However, breakage occurs as axial cracks, as shown in Figure 4.2.5, and does not necessarily result in performance degradation. Extensive experience with pilot-scale and full-scale atomizing nozzles has shown that alumina air caps perform as well after thermal-shock breakage as before. The large air cap

FIGURE 4.2.5. Failed Nozzles

pieces are held in place by the retaining cap and atomization continues normally. At the time of this writing there has been no experience with full-scale nozzle air caps made of silicon nitride, but the results of the test described indicate that both excellent wear and thermal-shock properties can be expected for silicon nitride.

4.2.1.4 Maintenance

Maintenance for the atomizing nozzle would consist of occasional replacement of the nozzle assembly and calibration checks of the atomizing air flowmeter and pressure indicator (liquid flow and pressure measurement is discussed in the calciner feed system section). Since the atomizing flow and pressure indicators can be located outside the cell, the consequences of maintenance

requirements are minimal. However, nozzle replacement will require that waste-feeding be stopped and that the nozzle assembly be designed for remote maintenance. The frequency of nozzle replacement required, based on the internal-mix nozzle wear measurements of 10% of the small-scale nozzle tip worn through in 60 h extrapolated to 100% of the tip worn through in 600 h, is approximately every 25 days. This is a very conservative estimate, since wear does not occur linearly with time and most of the wear takes place within the initial 30 h. Also, full-scale nozzles have thicker nozzle tips and can satisfactorily operate longer than will smaller-scale nozzles with similar feeds. Long-term tests with full-scale nozzles are necessary to determine more exactly the actual frequency of nozzle replacement that will be required.

4.2.2 SPRAY CALCINER

The spray calciner consists of a spray chamber, cone section, furnace, vibrators, and the off-gas filter assembly (a more detailed discussion of the off-gas filters is included in the next section). During operation, atomized waste feed is sprayed at the top-center of the spray chamber, which is a vertical cylinder externally heated by the concentric, cylindrical furnaces shown in Figure 4.2.6. The high velocity at which the atomizing air and waste feed droplets enter the spray chamber, in addition to the temperature difference between the chamber wall and the evaporating water droplets, creates a high degree of turbulence in the calciner.

The intensity of this turbulence was determined for an 8-in.-dia calciner using an eddy diffusivity measurement (Alleman and Johnson 1961). At a point 11 column diameters below the nozzle of the test apparatus, the Reynolds number was 80,000 to 90,000 for conditions at which the calculated Reynolds number based on the average volumetric flow rate and cross-sectional area was 260. The combination of this violent convective heat transfer with radiant heat transfer allows drying and partial calcination at a high rate.

After passing through the chamber, water vapor and atomizing air entrain a large percentage of the calcine particles. More than 99.9% of the

FIGURE 4.2.6. Spray Calciner

particulates are removed from the off gas by sintered-metal filters. A periodic pulse of blowback air removes the layer of calcine that collects on the filters. This calcine then falls into the cone section and is discharged

to the melter along with the calcine that falls directly from the calcination chamber. All surfaces are sloped at least 60° from horizontal to avoid calcine accumulation by allowing it to slide off.

Frit is added to the calciner cone section through an air-lock valve. This air-lock valve can be timed simultaneously with the filter blowbacks to obtain as much frit and calcine mixing as possible as they flow through the calciner cone into the melter.

Two vibrators are mounted 180° apart at mid-height on the calciner chamber. These vibrators are supported independently of the furnace to minimize vibration of the furnace elements and insulation. During normal calciner operation with low-sodium wastes, frequent vibration is not necessary. However, to assure the calciner is free of excess calcine powder buildup the wall is usually vibrated several times per hour.

4.2.2.1 Operation

The spray calciner operation is subsequently discussed in the following four areas:

1. calciner temperature selection
2. calciner startup and shutdown
3. steady-state calciner operation
4. calcine product.

Calciner Temperature Selection

The spray calciner has been operated at chamber wall temperatures from 400° through 900°C , depending on the type of waste feed and the feed rate. The required calciner chamber size for a desired waste feed rate can be minimized by operating at the highest temperature that will not cause the calcine to stick to the chamber wall by sintering or melting. Also, corrosion and thermal-stress concerns are more significant at higher temperatures, and must be considered in the mechanical design and temperature selection for the calciner.

Tests can be made to determine the sintering or melting temperature of a particular waste feed. Thermal-gradient feed analysis is used to determine

the maximum operating temperature for several feed types. This test involves drying an aliquot of the proposed feed solution or slurry and placing it in a thermal-gradient furnace. Physical changes in the product characteristics can be examined and related to a temperature range. The maximum calciner wall temperature should be approximately 50°C less than the point at which the product begins to stick together. Additional calcine reaction temperature data can be obtained from differential thermal analysis and thermal gravimetric analysis (MacKenzie 1970, Erdey 1965) to determine the feed behavior in the calciner.

Spray Calciner Startup and Shutdown

The spray calciner is a relatively simple piece of process equipment. The following general steps are involved in starting up a spray calciner (similar to full-scale SC at PNL):

- a. Heat the calciner furnaces to the desired temperature. For an internal-mix nozzle the atomizing air flow should be 20 to 30 SCFM during the heatup cycle to cool the nozzle and minimize thermal shock to the nozzle when waste-feeding is begun (see Section 4.2.1 for discussion of thermal shock in the atomizing nozzle).
- b. Increase the atomizing nozzle air pressure to about 35 psig.
- c. Increase the calciner vacuum to 15 to 20 in. H₂O.
- d. Slowly increase the flow of demineralized water up to the desired processing rate, allowing the vacuum controller time to react to the increase in off-gas flow.
- e. Quickly switch from demineralized water to the waste feed after the off-gas system vacuum has stabilized. (Note: Extended periods of feeding demineralized water to the calciner without a layer of calcine on the sintered-metal off-gas filters can cause plugging of the filter pores by sub-micron-size particles formed from impurities in the water.)
- f. Start flow of frit and filter blowback/vibrator timers or controllers.

- g. Make final adjustments to obtain desired atomizing air, waste feed flow rates and vacuum. A calciner vacuum of 10 in. H₂O is normally used to prevent pressurization during a filter blowback.

The following general steps are used for shutdown of the calciner:

- a. Stop flow of frit and blowback/vibrator timers or controllers.
- b. Switch from waste feed to demineralized water. Feed demineralized water for approximately 1 min to flush the feed line and prevent drying of the feed in the nozzle or piping.
- c. Shut off demineralized water.
- d. Turn off power to calciner furnace, if desired.
- e. Maintain atomizing air flow at 20 to 30 SCFM for an internal-mix nozzle to prevent thermal shock to the nozzle until the calciner temperature has dropped to about 200°C, then shut off atomizing air flow. Air flow to the external-mix nozzle can be shut off before cooldown.

Emergency shutdown of the calciner can be done simply by stopping frit and waste feed flows to the calciner and, if desired, by turning off the atomizing air flow and power to the calciner furnace.

Steady-State Calciner Operation

After waste-feeding has been started, the calciner furnace power consumption and chamber wall temperatures should reach steady-state within about 5 min with good controller response time. The cone section and off-gas temperatures require substantially more time to reach steady-state--up to several hours. The reason for this difference in time is that the furnace controllers maintain the chamber wall at a constant temperature before and after waste-feeding has been started, but the cone section and filters are cooled by the off-gas stream. The thermal inertia of the metal cone section and filters causes this cooling to occur slowly.

Typical steady-state furnace-zone power consumption and calciner temperatures for the PNL full-scale calciner are shown in Table 4.2.7 for the

TABLE 4.2.7. Typical Calciner Operating Parameters^(a)

Parameters and Units	Value
Waste Feed Rate (L/h)	300
Atomizing Air Flow Rate (SCFM)	30
Furnace Temperature ($^{\circ}\text{C}$) ^(b)	
Zone 1 (bottom)	875
Zone 2	875
Zone 3	840
Zone 4 (top)	840
Furnace Power Consumption (kW)	
Zone 1 (bottom)	90
Zone 2	92
Zone 3	55
Zone 4 (top)	53
Total	290
Calciner Chamber Wall Temperatures ($^{\circ}\text{C}$)	
Zone 1	750
Zone 2	755
Zone 3	775
Zone 4 (top)	800
Calciner Off-Gas Temperature ($^{\circ}\text{C}$)	250
Calciner Cone Temperature ($^{\circ}\text{C}$) ^(c)	230

(a) See Figure 4.2.6 for zone locations.

(b) Temperature set point maintained by controller

(c) Directly under the spray chamber centerline

indicated furnace temperatures and a feed rate of 300 L/h. These values are representative for both acid and neutralized waste at the indicated furnace temperatures.

The temperatures and furnace power consumption should be monitored closely to ensure proper calciner operation. When power is varied to maintain constant furnace or chamber wall temperatures, a rapid or gradual drop in power

consumption after the first 5 min of operation usually is an indication of a scale buildup on the inside surface of the calciner chamber. Scale buildup can be caused by moist calcine adhering to the wall or by calcine sintering to the wall if temperatures are too high. The sintering temperature of the calcine must be known to be sure which of the above possibilities is the actual cause. Moist calcine can occur when the calciner's drying capacity has been exceeded or if the atomizing nozzle is worn or damaged. Moist calcine caused by exceeding the calciner's capacity can be corrected by decreasing the feed rate of the waste, by increasing the furnace temperatures, or both. Calcine sintering to the wall can be remedied by lowering the chamber wall temperatures, and if the off-gas temperatures are lower than desired, the waste feed rate should also be lowered. An increased rate of vibrator operation is also helpful in eliminating scale buildup for the above operating problems. If vibration does not remove the scale buildup, waste-feeding can be temporarily stopped and the scale removed by washing or by thermal shock. Most scale buildup encountered to date has been encountered while processing high-sodium feed and has been readily removed by lowering a washing nozzle through the calciner spray nozzle port and spraying for a few minutes. The thermal-shock descaling technique requires that the chamber wall (and the scale) be heated up to maximum normal operating temperature and then water sprayed into the hot chamber through the atomizing nozzle for 2 to 5 min. This procedure can be repeated, if necessary. Even the most stubborn scale has been removed using this method.

Under proper operating conditions wall scale is minimal, and extended operation without use of vibration is possible. However, to assure the walls are free of powder buildup, the wall is normally vibrated several times per hour with a 2-s pulse alternated between two vibrators at equal intervals.

Calcine Product

The product of spray calcination in the heated-wall spray calciner is a very fine, dry powder that usually consists of metal oxides for the most part. Depending on the feed composition and the calcination temperature, the powder could consist of 1% to 42% alkali-metal nitrates, carbonates, sulfates, and/or waters of hydration.

Calcine particle size distribution is shown in Figure 4.2.7 (Bonner, Blair and Romero 1976) for acid-type waste and Figure 4.2.8 for neutralized waste. While 65% of the total number of particles for acid waste are in the diameter range of 1 to 5 μm , these particles account for only 15% of the mass. Only 17% of the total particles are 6 to 20 μm in dia, but they account for 75% of the mass. The large acid-waste particles (over 1 mm in dia) were analyzed and found to be of the same composition as the rest of the calcine, except for higher water and nitrate contents (Bonner, Blair and Romero 1976). For neutralized waste slurry, 88% of the total particles are less than 11 μm , but account for only 2.8% of the mass. Since the neutralized waste is a slurry rather than a solution, the larger particles in the calcine represent larger particles in the slurry. These large particles are not the same composition as the smaller calciner particles from water-soluble compounds.

Typical calcine properties are presented in Table 4.2.8 (Bonner, Blair and Romero 1976). These properties are a function of waste composition and of calciner operating parameters. The calcine moisture content is normally less than 1% but can be as high as 4% without significantly decreasing the calcine's

FIGURE 4.2.7. Acid-Waste Particle Size Distribution

FIGURE 4.2.8. Defense Waste Calcine Particle Size Distribution

ability to flow. Residual nitrate content from acid wastes is a strong function of the alkali metal content of the waste. Most nonalkali metal nitrates are converted to oxides.

The sodium nitrate content of the calcine significantly affects the sintering temperature of the calcine. Studies have shown that PW-4b (low-sodium) simulated waste is still free-flowing after being heated at 900°C, whereas PW-6 (high-sodium) simulated waste agglomerates above 310°C. Simulated Savannah River neutralized waste was also found to be free-flowing after being subjected to 900°C temperatures.

Experience with calcine shows that it does not flow freely from bulk storage, that it dusts, that it is hygroscopic, and that it has a high surface

TABLE 4.2.8. Properties of Simulated HLLW Spray Calcines

Characteristic and Units	PW-4b	PW-6	PW-7a	Defense
Aerated Bulk Density, g/cc	0.85	0.41	0.69 to 0.92	0.95
Working Bulk Density, g/cc	0.97	0.48	0.87 to 1.04	1.03
Packed Bulk Density, g/cc	1.24	0.61	1.15 to 1.33	1.27
Compressibility, %	32	33	40 to 31	25
Angle of Repose, degrees	42	39	43 to 42	27
Particle Density, g/cc	4.4	3.8	5.1	Var. (a)
Surface Area, m ² /g	20	11	14	---
Nitrate Content, wt%	<1	19 to 42	2 to 22	---
Moisture Content, wt%	<1	<1	<1 to 4	1 to 3
pH of Equilibrium Aqueous Slurry	4.5	5.0	---	7.2

(a) The calcine particle density is variable (about 4.3 g/cc average) because particles from simulated defense waste slurries remain as separate and distinct compounds--i.e., the calcine is composed of MnO₂ particles, NiO particles, zeolite particles, particles containing water-soluble compounds, etc.

activity. Bin-storage and conveyance of the calcines may be difficult. However, because the calcine is very active and presents large surface areas, it makes good feed for melting or pelletizing processes.

4.2.2.2 Design

The design of a spray calciner is discussed in the following five areas:

1. furnace
2. spray chamber size requirements
3. calciner materials experience
4. vibrators
5. alternative configurations.

Calciner Furnace

Energy needed to dry and calcine liquid waste is supplied by the calciner furnace. Also, a significant portion of the total energy supplied by the furnace is lost by conduction through the furnace walls and through the

insulation covering the top of the furnace. If induction heating is used, additional heat will be lost to the induction-coil cooling water. Therefore, both the energy used to dry the waste and the energy lost to the surrounding environment must be included for a determination of furnace power requirements.

Furnace power consumption measurements for the full-scale spray calciner have been made for various calciner feed rates at chamber wall temperatures of 750° to 800°C . These measurements are shown in Figure 4.2.9 for total power consumed and in Figure 4.2.10 for power consumption per zone. As can be seen from the figures, power consumption varies linearly with feed rate.

An excellent design method for determining the furnace power requirements for drying and heating the waste feed (calcination can be neglected) is to calculate the sensible and latent heat required to raise the inlet waste feed and atomizing air to the desired spray calciner outlet temperature. For most waste feed compositions this power requirement can be closely estimated by assuming that a liter of waste feed is a liter of water. Calculated and measured power consumption for various flow rates are shown in Table 4.2.9. Measured values compare very closely with the calculated values for the range of data available.

FIGURE 4.2.9. Calciner Furnace Total Power Consumption

FIGURE 4.2.10. Calciner Furnace Zone Power Consumption

Furnace power consumption is not axially uniform. Data from actual calciner operation, as shown in Figure 4.2.10, indicates that the lower half of the furnace (zones 1 and 2) supplies the greatest proportion of the power. Possible explanations for this occurrence are: 1) the atomizing nozzle spray pattern is wider in the lower portion of the calciner, which increases the radiative heat transfer coefficient since more particles are exposed directly to the calciner wall; 2) the convective heat transfer coefficient is greater in the lower portion of the calciner because of the high turbulence caused by the large volume of steam generated as the droplets fall through the calciner; 3) the general direction of the convection currents is upward next to the heated calciner wall and downward near the cooler center region of the calciner, which transfers heat from the lower zones to the upper zones and reduces the power required to maintain the calciner temperature set point in the upper zones. The actual explanation for the power consumption differences between the zones is most likely a combination of the above effects. These effects must be considered when calculating the calciner furnace power capacity

TABLE 4.2.9. Calculated and Measured Heating Requirements

Flowrate, L/h	Total kW(a) Used (measured)	kW Lost(b)	kW Absorbed(c) (measured)	kW Absorbed(d) (calculated)
0	60	60	0	---
200	212	60	152	158
300	290	60	230	234
400	365	60	305	310
500	---	---	---	386

- (a) Measured kW at 750° to 800°C chamber wall temperatures for a PNL full-sized spray calciner.
- (b) Kilowatts lost through the top of the furnace and the furnace walls to the cell. The kW lost could vary significantly between individual calciners. Induction-heated calciners will lose additional heat through the induction-coil cooling water.
- (c) Kilowatts absorbed by the waste feed and atomizing air (total kW used minus kW lost).
- (d) Basis for calculated kW absorbed: i) 89 kg/h of air (atomizing air, in-leakage) heated from 25° to 250°C, and ii) the indicated feed rate (assumed to be water) heated from 50° to 250°C.

per zone. For example, the total measured power consumption for 300 L/h is 290 kW, but the minimum capacity for a four-zone furnace should not be evenly divided into 72.5 kW/zone. The lower two zones each supply about 30% of the power and the upper two zones each supply about 20%. Therefore, the minimum rated capacity of the lower two zones should be 87 kW and that of the upper two should be 58 kW. Calciner designs at PNL have all the zones at equal power, which for 300 L/h should be an 87-kW minimum per zone for a four-zone furnace. In addition, a safety factor should be added to the minimum calculated power requirement.

The number of furnace zones required depends upon the desired uniformity of longitudinal chamber temperatures and the cell height available for removing and installing the furnaces if annular furnaces are used. As discussed previously, the power required to maintain a uniform chamber temperature varies axially. For maximum heat transfer into the calciner, a uniform chamber temperature at the highest operating temperature possible is desirable. Multiple

furnace zones provide the most flexibility in attaining the uniform maximum temperature. Also, if the furnace is designed for removal of individual zones, the more furnace zones for a given chamber height, the less the cell height required to lift each annular furnace zone over the spray chamber. A disadvantage of more zones is that more electrical connections and control thermocouples are required. The PNL full-scale calciner is equipped with four furnace zones and provides excellent temperature control with a manageable number of electrical connections. As few as two furnace zones could be used to provide adequate temperature control, since the power consumed by zones 1 and 2 is similar and that consumed by zones 3 and 4 is similar (Figure 4.2.10). Use of "clam shell"-type furnace zones would not require lifting over the furnace for placement.

The electrical power to each furnace zone may be controlled with a zero-crossover, silicon-controlled-rectifier (SCR) power supply, using as a reference temperature a thermocouple penetrating through the side of the furnace wall at the middle of each zone. The reference temperature should be recorded, and an alarm activated outside the control range to detect malfunctions of the control system. At least one redundant thermocouple for each zone that could be used for electrical power control should also be recorded and alarmed. Additional thermocouples to monitor the calciner operation could be positioned on the calciner spray chamber, on the cone section directly below the centerline of the spray chamber, and in the off-gas filter zone. The temperatures should be recorded to detect long-term changes that would signal buildup of scale or other operating problems.

Spray Chamber Size Determination

The calciner spray chamber heat-transfer area required to produce a dry powder depends on the following factors: 1) calciner feed rate, 2) feed atomization (drop diameter), and 3) calciner chamber temperature. The calciner feed rate is selected for process design. Feed atomization is achieved by proper nozzle operation, as discussed in the atomizing nozzle section (Section 4.2.1). Determination of the proper chamber wall temperature is discussed in the calciner operation section. On definition of these parameters, the calciner chamber heat-transfer area can be estimated.

Correlations relating capacity to spray chamber diameter, height, and wall temperature have been developed from PNL calciner operating data. Table 4.2.10 lists data that was obtained from pilot-scale and full-scale calciners. Computer regression analysis of this data yields the correlations shown in Table 4.2.11. Using the data points indicated, equations were developed to 1) relate capacity to wall temperature, chamber diameter, and chamber height; 2) relate capacity to chamber height and diameter at 700°C wall temperature; 3) relate capacity to chamber height and diameter at 550°C wall temperature; and 4) relate capacity to temperature at a chamber diameter of 91.4 cm and height of 320 cm. Capacity was defined in these tests as the maximum feed rate that produced a powder that would flow freely through the calciner cone section and melter connecting section. Based on experience, an offgas temperature of 200°C from the full-scale calciner was used as the reference process variable that would indicate a dry, "flowable" powder was being produced. Therefore, the calciner feed rate that produced an off-gas temperature of 200°C was defined as the maximum capacity at the chamber wall

TABLE 4.2.10. Calciner Capacity Data

Data Point	Wall Temp., °C	Dia, cm	Height, cm	Capacity, L/h
1(a)	700	91.4	320	315
2(a)	700	91.4	240	205
3(b)	700	53.3	198	95 ^(c)
4(b)	700	33.5	198	40
5(a)	550	91.4	320	160
6(a)	550	91.4	240	105
7(b)	550	53.3	198	62
8(b)	550	33.5	198	26
9(a)	400	91.4	320	50

(a) Data from PNL test no. FSSC 38.

(b) Data from Bonner, Blair, and Romero (1976).

(c) This capacity was estimated because furnace power capacity was not sufficient to maintain wall temperature (Bonner, Blair and Romero 1976). Deletion of this data point would not significantly affect Equation 4.6 in Table 4.2.11, but may affect Equation 4.7.

TABLE 4.2.11. Calciner Capacity Correlations

Data Points Used From Table 4.2.10	Equation	Ave. % Error in Predicting Data Points	Standard(a) Deviation From Ave. % Error
1 through 9	Capacity L/h = $7.477 \times 10^{-11} (T, ^\circ\text{C})^{2.83} (\text{Dia, cm})^{1.41} (H, \text{cm})^{0.705}$ (4.6)	12.4	9.1
1 through 4	Capacity (L/h) @ 700°C Wall Temp. = $0.0011 (\text{Dia, cm})^{1.46} (H, \text{cm})^{1.03}$ (4.7)	8.0	6.0
5 through 8	Capacity (L/h) @ 550°C Wall Temp. = $0.0048 (\text{Dia, cm})^{1.28} (H, \text{cm})^{0.793}$ (4.8)	11.6	8.6
1, 5, 9	Capacity L/h @ 91.4-cm dia, 320-cm H = $1.277 \times 10^{-7} (T, ^\circ\text{C})^{3.31}$ (4.9)	5.1	2.9

(a) Standard Deviation = $\sqrt{\frac{(\text{Ave. \% error} - \% \text{ error})^2}{\text{Degrees of Freedom}}}$

temperature. At maximum pilot-scale calciner capacity, the measured off-gas temperature was normally slightly less than 200°C (about 180°C). Therefore, the off-gas temperature for which a dry, flowable powder is produced will vary among calciners.

Other considerations, such as condensation of volatile materials from the melter (Ru, Cs, etc.), may require that an off-gas temperature higher than the minimum required to produce a flowable powder be used to prevent accumulation of volatile materials within the calciner. Each 50°C increase above the minimum off-gas temperature required to produce a flowable powder (about 200°C) will decrease the capacity indicated in the equations in Table 4.2.11 by approximately 10%. Additional long-term testing with full loadings of feed constituents (such as ruthenium) is required to determine if accumulation of volatile materials in the calciner or melter is a problem.

The correlations in Table 4.2.11 are reasonably accurate in predicting the data from Table 4.2.10. Equations 4.7 through 4.9 are more accurate in predicting the data points used (as indicated by the average percent error) than is the more general Equation 4.6.

The correlations indicate capacity is most dependent on wall temperature, with chamber diameter being the second most important, and chamber height having the least effect on capacity. While developing an accurate capacity equation based on heat-transfer theory for spray calcination would be very difficult and costly, brief consideration of simplified heat-transfer considerations shown below give some understanding of the relative importance of the variables in Table 4.2.11:

$$q_T = q_c + q_r, \quad (4.10)$$

$$q_c = UA\Delta T, \quad (4.11)$$

$$q_r = A\sigma F_{12} T_1^4 - A_2\sigma F_{21} T_2^4, \quad (4.12)$$

where

q_T = total heat flux, q_c = heat flux transferred by convection, q_r = heat flux transferred by radiation

U = overall heat-transfer coefficient

A = heat-transfer area, A_1 = heat-transfer area of hot surface, A_2 = heat-transfer area of cold surface

ΔT = temperature difference, T_1 = temperature of hot surface, T_2 = temperature of cold surface

F = view factor

σ = constant.

The drying capacity of a spray calciner is proportional to the amount of heat transferred into the spray chamber (assuming evaporation of water from the surface of the droplet is not rate-limiting, which appears to be the case for the simulated wastes tested). This heat is transferred from the chamber wall to the spray droplets by two mechanisms: 1) convective heat transfer, and 2) radiative heat transfer. Convective heat transfer, as simplistically represented by Equation 4.11, is roughly proportional to the first power of the temperature difference--whereas radiative heat transfer is proportional to the difference of the fourth powers of the temperatures. Therefore, one would expect that a combined temperature term for convective and radiative heat transfer would be between the first and fourth powers of the temperature. This is the case for Equations 4.6 and 4.9 of Table 4.2.11. Since the exponents of temperature in Equation 4.9 and Equation 4.6 are closer to four than one, radiative heat transfer appears to be the primary mode of heat transfer at these temperatures.

The diameter of the spray chamber affects the heat-transfer area and the residence time of a particle within the spray chamber. Increased residence time allows a particle to receive more of the heat flux represented in Equations 4.11 and 4.12. The heat-transfer area is proportional to the first power of the diameter ($\pi \text{ Dia} \times H$), whereas the residence time is proportional to the volume of the spray chamber ($\pi/4 \text{ Dia}^2 \times H$) and the square of the diameter.

Therefore, a single term representing the effect of diameter on capacity would be expected to be between the first and second power of the diameter. This proves to be the case in Equations 4.6 through 4.8 of Table 4.2.11.

The height of the spray chamber also affects the heat-transfer area and the residence time of a particle. Both the heat-transfer area ($\pi \text{ Dia} \times H$) and volume ($\pi/4 \text{ Dia}^2 \times H$) of the spray chamber are proportional to the first power of the height. Therefore, a single term representing the effect of chamber height on drying capacity would be expected to be approximately the first power of the height. Equations 4.6 and 4.8 in Table 4.2.11 are slightly less than the first power of the height, while Equation 4.7 is very close to the first power of the height. At lower temperatures the drying capacity appears to be less dependent on height and diameter of the spray chamber than at higher temperatures (see exponents of Equations 4.7 and 4.8 of Table 4.2.11).

Calciner Materials Experience

Experience at PNL has primarily been with 310 stainless steel spray chambers. Stainless steel 310 was selected for its high-temperature strength and oxidation resistance. Wall thickness measurements have been made on calciners operated at PNL to determine the extent of corrosion. Measurements showed no detectable corrosion when a pilot-scale, 21-in.-dia spray chamber was tested after 522 h of acid-waste calcining at 700°C that included six heatup and cooldown cycles. The instrument used for the measurements had a precision of 0.0002 in. A calciner corrosion/erosion rate of less than 0.003 in./yr was calculated based on this test (Bonner, Blair and Romero 1976).

Wall thickness measurements were made in March of 1980 on the full-scale 36-in.-dia spray chamber after 1650 h of actual operation. The operating period consisted of about 200 h with acid-type feed, 1450 h with neutralized feed, 37 heatup and cooldown cycles, and roughly 1000 h of idle time at temperatures between 700°C and 800°C. Hence, the spray calciner has been at 700°C to 800°C temperatures for about 2650 h. The differences between all thickness measurements made in April of 1977 and March of 1980 (Figure 4.2.11 and

Table 4.2.12) indicate a maximum average loss in thickness of 0.013 in. Based on the actual hours of equipment operation, a corrosion/erosion rate of 0.07 in./yr is indicated. Based on the approximate hours at operating temperatures, a corrosion/erosion rate of 0.04 in./yr is indicated. A corrosion allowance of 0.1 in. would be exceeded in 1.4 to 2.5 years at these corrosion rates.

The two sets of measurements for the pilot-scale and full-scale calciners indicate widely differing results. Additional operating time is needed to verify which of them more closely represents the actual case.

The cone section (304L SS) of the full-scale spray calciner did not show any visual corrosion after 1600 h of operation. The cone temperature varies between 200⁰ and 350⁰C during calciner feeding and ranges from 400⁰ to 700⁰C during equipment idling while at operating temperature. Comparative wall thickness measurements are not available to determine measurable corrosion rates.

To help determine the effect of vibration on the spray chamber, a 100-h test was conducted with a 21-in.-ID, 3/8-in.-wall 310 SS chamber to simulate up to 4000 h of operation (Bonner, Blair and Romero 1976; Blair 1975). The diameter of the spray chamber across the impact pads and at 90⁰ to the pads was measured before and after the 700⁰C calciner walls experienced 4000 vibrator cycles. No measurable difference in the calciner shape was found when measuring to 25 μ m (0.001 in.).

FIGURE 4.2.11. Location of Wall Thickness Measurements

TABLE 4.2.12. Wall Thickness Measurements for Spray Calciner Chamber
(see Figure 4.2.11)

Height from Bottom Flange, ft	Wall Thickness, in.							
	April 1977				March 1980			
	1	2	3	4	1	2	3	4
1	0.254	0.249	0.251	0.249	(a)	(a)	(a)	(a)
2	0.255	0.249	0.254	0.253	(a)	(a)	(a)	(a)
3	0.256	0.257	0.256	0.256	0.248	0.246	(a)	0.251
4	0.256	0.257	0.258	0.258	0.247	0.247	0.252	0.247
5	0.260	0.259	0.259	0.259	0.250	0.246	0.248	0.249
6	0.260	0.257	0.259	0.258	0.247	0.248	0.248	0.247
7	0.256	0.257	0.258	0.257	0.244	0.242	0.243	0.244
8	0.256	0.254	0.256	0.256	0.243	0.247	0.241	0.243
9	0.254	0.256	0.258	0.255	0.244	0.249	0.239	0.238
10	0.256	0.256	0.260	0.259	0.245	0.248	0.241	0.250
Avg.: 1-10	0.256	0.255	0.257	0.256				
Avg.: 3-10	0.257	0.257		0.257	0.246	0.247		0.246
Avg.: 4-10			0.258				0.245	

(a) Lower furnace zone not removed at this time; making measurements at these locations is impossible.

Average Loss in Wall Thickness (in.):

Location	April 1977	March 1980	Difference
1 (3-10 ft)	0.257	0.246	0.011
2 (3-10 ft)	0.257	0.247	0.010
3 (4-10 ft)	0.258	0.245	0.013
4 (3-10 ft)	0.257	0.246	0.011

Yearly corrosion rate based on hours of actual operation

$$\frac{0.013 \text{ in.}}{1650/\text{h operation}} \times \frac{8760/\text{h}}{\text{yr}} = 0.07 \frac{\text{in.}}{\text{yr}}$$

Yearly corrosion rate based on approximate hours at operating temperature

$$\frac{0.13 \text{ in.}}{2650/\text{h}} \times \frac{8760/\text{h}}{\text{yr}} = 0.04 \frac{\text{in.}}{\text{yr}}$$

Inconel-601 appears to be superior to stainless steel 310 in oxidation resistance, scaling resistance, and mechanical strength based on the literature (Huntington Alloys, Inc. 1973). Consideration should also be given to Inconel-625 if added corrosion resistance is determined to be necessary. While it is not quite as resistant to high-temperature (about a 1200°C limit) oxidation as Inconel-601 is, Inconel-625 would be better suited for corrosive environments containing acids, chlorides, or fluorides, and would still most likely maintain an acceptable oxidation resistance.

Vibrators

Under normal operating conditions with low-sodium feeds, calciner chamber wall scale is minimal, and extended operation without vibration is possible. But to extend the flexibility and operability of the unit, vibrators have been introduced to keep wall scale to an inconsequential level.

Successful operation has been experienced with a single vibrator mounted on top of a small-scale calciner. But vibration was quite inefficient, and vibrators had to be replaced frequently because of lubrication problems caused by the high-temperature environment (Bonner, Blair and Romero 1976). Further investigation led to use of two specially modified vibrators of the kind shown in Figure 4.2.12 mounted at mid-height on the spray chamber, 180° apart. The vibrator has an extended piston that passes through holes in the furnace and strikes on the chamber wall. This arrangement not only limits wall scaling more effectively, but also locates the vibrators where they are less likely to overheat.

Use of the impact sound intensity is the easiest way to determine whether the vibrator is hitting correctly. If the vibrator is too far from the wall, the noise of impact will of course be absent; if the vibrator is too close to the wall, the sound of impact will be muffled, since the piston is then almost always in contact with the chamber. A method of adjustment is needed to assure proper spacing between the vibrator shaft and the spray chamber.

In the past, vibrator impact pads have been welded onto the outside of the chamber wall to add strength. The weld on one of these impact pads failed

FIGURE 4.2.12. Side-Mounted Calciner Vibrator

during a test, causing the pad to fall to the bottom of the furnace and short out a furnace element. The probable cause of the weld failure was the difference in thermal expansion and heat retention between the 3/4-in.-thick pad and the 1/4-in.-thick wall. The failed impact pads were replaced by cutting 15-in.-dia holes around the pads and replacing them with circular 3/4-in.-thick plates rolled to match the diameter of the chamber (Figure 4.2.13). This new impact design was tested, but poor weld penetration made the weld insufficient. It was ground out and rewelded. After the pads were rewelded (which required several weld passes to refill the groove that had been ground out) the spray chamber surfaces around the circular impact pad became deformed. The 3/4-in. impact pad retained welding heat longer than did the 1/4-in. chamber wall, which caused the chamber to buckle slightly while cooling. Other

FIGURE 4.2.13. Modified Vibrator Impact Pad

than being slightly out-of-round, no structural damage to the spray chamber is evident, and calciner operation has been satisfactory. If the vibratory pad installation welding had been satisfactory on the first attempt, is doubtful that if the chamber distortion would have been encountered.

Alternate Configurations

Some of the high-stress areas from both concentrated support loads and thermal gradients of the spray calciner design can be minimized by alternate configurations and load supports. What follows are suggestions offered by Bechtel, Inc., which accompany their conceptual configurations shown in Figure 4.2.14 (Bechtel, Inc. 1977) that are intended to minimize high-stress areas.

1. Change the flat plate supporting the calciner chamber to a truncated cone or an ellipsoidal or flanged and dished head.
2. Develop a separate internal or external support system for the calciner chamber and connect to the remainder of the calciner with an expansion joint.

FIGURE 4.2.14. Spray Calciner Conceptual Configurations

3. Change single filter housing to multiple smaller housings symmetrically spaced around calciner shell.

A number of the configurations indicated in Figure 4.2.14 require additional cell height as compared to the reference conceptual design.

4.2.2.3 Maintenance

The components of a spray calciner should be remotely replaceable--including the furnace, filters, chamber, cone, vibrators, and thermocouples (redundant thermocouples is an alternative). The calciner chamber and cone can be designed to resist corrosion and stresses and to operate for extended periods (i.e., 5 to 20 years) and should require little or no maintenance. The amount of furnace maintenance required will depend on the design, quality of materials, and operating temperature. The low-cost, full-scale electrical-resistance furnace at PNL required replacement of coiled-wire heating elements on four occasions during 1600 h of run time and 35 heatup and cooldown cycles. The major cause of element failures was elements falling out of damaged supporting edges in the furnace-insulating fire brick and shorting out against the spray chamber or other heating elements. Fire brick in two furnace zones required replacement after the 1600 h of operation due to damage from the vibrators being mounted directly on the side of the furnace. The vibrator

supports were modified after approximately 600 h of operation to support the vibrators independently of the furnace, but the brick damage had already occurred and attempted repair of the brick at this time succeeded only temporarily in holding the heating elements in place. It is expected that appropriate furnace design and independent mounting of the vibrators would lead to an acceptable resistance-heated furnace life for plant application.

The vibrators require routine lubrication. This is most easily accomplished by using an automatic oiler in the compressed air used for vibrator operation. Occasional adjustment of the spacing between the vibrator piston and chamber wall may also be required (see Section 5.4.3.5 for method of adjustment). The required replacement period for the vibrators has not yet been established.

Maintenance for sintered-metal off-gas filters is discussed in Section 4.2.3.3.

4.2.3 SINTERED-METAL FILTERS (F. A. Miller, K. H. Oma)

Sintered-steel filters have found broad use in the nuclear industry in applications requiring high-efficiency filtration of thermally hot and/or highly radioactive vapors. Experience in SC development during the last 20 years has demonstrated high reliability and high efficiency of the filters over a wide range of operation conditions. Due to the small particle size of spray-dried calcine, much of the solid particles are entrained by the calciner off gas (COG). Sintered-metal filters have proven to be very efficient for removing these particles from the COG.

During calciner operation, a layer of powder filtered from the off gas builds on the filter's surface and forms an additional filter media. As this layer of powder becomes thicker, the filter pressure drop increases. Eventually, the pressure drop will increase until the calciner has insufficient vacuum or the desired filter pressure drop is exceeded. Before this occurs, a 0.25-s pulse of high-pressure air is directed counter-currently to the off-gas stream from above the filters. This reverse air flow, or filter blowback,

dislodges the layer of powder from the filter surface and allows it to fall to the melter below. To prevent pressurization of the calciner during filter blowback, a short air pulse is used and only a few of the filters are blown back at one time. This allows the off gas to be drawn through the remaining filters to maintain a vacuum in the calciner. This pulsed blowback is alternated between the remaining small groups of filters until all filters have been cleaned.

The blowback air is routed to each group of filters that are blown back simultaneously through a separate line controlled by a solenoid-operated valve. A small venturi is mounted at the top of each filter to draw COG back into the filters to provide additional blowback air volume.

4.2.3.1 Operation

Filter efficiency improves as a layer of calcine forms on the filter. The calcine coat acts as the filter media to prevent very small particles from reaching the sintered-metal pores, which may otherwise result in gradual plugging of the filters. Therefore, fewer filter blowbacks should increase the operating life of the filters by minimizing the time the filter surface is exposed to moving particles and very small particles.

During the first five WFP spray calcination runs at PNL (Bonner, Blair and Romero 1976) the filters were left undisturbed and the effect of calcine buildup was observed. During the first run the average filter particulate DF was about 700. During each successive run the DF steadily improved until during run 5 the DF had improved to 13,000. Following this run, tests with filter-washing were initiated that reduced the DF to near the clean-filter efficiency. Since filters will normally not be washed, it is anticipated that in an operating plant the calciner filter DF for particulates will be well above 10^3 . A filter decontamination factor of 2.7×10^4 was measured for particulates during extended full-scale tests. Actual SC permeability data is presented in Figure 4.2.15 (Bjorklund 1976).

Two basic types of blowback patterns have been used--equal and unequal intervals. These patterns are illustrated in Figures 4.2.16 and 4.2.17. The

FIGURE 4.2.15. Spray Calciner Permeability Data

filters are divided into several groups. The filters in each group are blown back simultaneously from the air supply. In the unequal filter-blowback pattern, each filter group is sequentially blown back in a short time with 1 sec between group blowbacks. Then a long interval (up to an hour) is allowed to pass before the blowback cycle is repeated. The equal-interval blowback pattern sequentially blows back each filter group with the same time period (e.g., 1 min) between each blowback.

The equal-interval blowback pattern provides a more continuous flow of calcine to the melter than does the unequal pattern because much of the calcine is entrained to the filters and remains there until blowback. Also, the equal-pattern blowbacks can be timed with the frit air-lock valve operation to allow batches of calcine and frit to fall simultaneously to the melter, thereby better mixing the calcine and frit. For the unequal-interval blowback pattern,

FIGURE 4.2.16. Unequal-Interval Filter Blowback Pattern

it is expected that calcine-frit mixing then can be accomplished by using a very fine frit that is entrained with the off gas, or the frit components can be added to the waste feed.

For the equal-interval blowback pattern, the gas velocity through the clean filters is much greater than that through the filters that are still coated after a group of filters is blown back. The filter manufacturer's maximum recommended filter-face velocity (off-gas flowrate divided by filter area) is 6 ft/min. But for a group of filters just cleaned in a filter system, the actual face velocity can approach several times the maximum recommended value due to the reduced pressure drop relative to the remaining filter groups. Excessive gas velocity may drive small particles deep into the filter pores, where they could be difficult to remove by filter blowbacks--eventually causing an increased resistance to gas flow. Of course, this high velocity drops off quickly as a layer of powder redeposits on the filter surface, but the face velocity for the recently "cleaned" filter remains higher than the average velocity for the entire filter system for a significant period. For the unequal-interval blowback pattern, all filter groups are cleaned in the

FIGURE 4.2.17. Equal-Interval Filter Blowback Pattern

shortest possible time that will not cause the calciner to lose vacuum from the air pulses. This minimizes the time that a group of clean filters will have greater-than-normal face velocities.

To summarize the advantages and disadvantages of the two filter blowback patterns, the equal-interval pattern provides a more continuous flow of calcine to the melter than does the unequal-interval pattern, whereas the unequal-interval pattern may allow longer filter life by minimizing the filter-face velocity after blowbacks.

For the unequal-interval blowback pattern, the frequency of filter blowbacks should be maintained to allow the filter pressure drop to approach the maximum desired value (about 15 to 20 in. H₂O) before blowbacks occur. For the equal-blowback pattern, a more moderate pressure drop should be maintained (about 8 to 12 in. H₂O); this will reduce the gas velocity through a group of filters after blowback.

It is desirable to minimize the calciner pressure surges caused by the pulses of blowback air. Variables that affect the magnitude of these surges

are blowback pulse duration, blowback pressure, off-gas line flow resistance, and the fraction of filters pulsed simultaneously. Experience has shown that short, 0.25-s pulses of ambient-temperature air are as effective as longer pulses for cleaning the filters. Static blowback pressures of 40 psig to 100 psig have been successfully used. One-fifth of the filters are blown back without pressurizing a pilot-scale calciner (30 to 70 L/h feed), while 1/11 of the filters in a large-scale calciner (300 to 400 L/h feed) are blown back simultaneously.

Tests have been conducted with a combination of cyclone and filters. When a cyclone was used upstream of the filters, the filter cake was not easily removed by the pulsed blowback (Kaser and Moore 1966). With the cyclone, only the finest particles reached the filter, and these particles formed an especially adherent filter cake. Preliminary tests using a cyclone alone for off-gas filtration resulted in a particulate DF of 20.

Coupling the calciner to an ICM has not been noted to affect the operation of the SC filters. Chlorides present tend to accumulate in the calciner--first being volatilized from the melt and then condensing as solids at the filters. Volatile components from the melter that are trapped in the filter cake are only a small part of the solids collected there. Hence, they are removed during filter blowbacks without noticeable effect on the filters. However, during periods of extended calciner shutdown the amount of volatiles from the melter should be minimized by lowering the melter temperature to just above the melting temperature of the glass. Also, the filters should not be blown back just prior to shutdown; a layer of calcine should be left on the filter surfaces. This layer of calcine will allow volatiles from the melter that condense on the filters to be blown off. Extended periods of shutdown with a hot melter connected to the calciner should be avoided.

The minimum off-gas temperature established by experience from which a dry, flowable powder is produced (with proper atomization) is 200°C. Other considerations, such as volatiles condensing on the filters and causing plug-gage, may increase this minimum temperature. Long-term testing with components such as mercury, ruthenium, and cesium has not been done, so it has not been

determined if an off-gas temperature higher than 200°C is necessary to allow these volatile components to pass through the filters (which prevents pluggage).

The maximum allowable filter operating temperature is determined by the limitations of the sintered-metal filter material or the powder-layer melting temperature where the powder layer begins to consolidate. After discontinuing liquid feeding, filter temperatures will increase if atomizing air flow is continued and furnace temperatures are not reduced. Therefore, it is important to monitor filter temperatures after waste-feeding to the calciner has been stopped in order to avoid exceeding the maximum recommended filter material operating temperature or the sintering powder temperature.

4.2.3.2 Design

The sintered-metal filters in use are fabricated from metal powder that is formed into a sheet and sintered. The plate formed is then rolled into a tube and welded. Another technique involves extruding the metal powder as the tube before sintering to form a seamless filter. One company grinds the external surface of the sintered filter to provide a smoother surface and to make release of the cake easier. Varying the metal particle size in fabrication alters the filter pore size. Small pores provide the best filtration efficiency but also exhibit the largest resistance to vapor flow. This layer acts as a filtering media and produces a larger differential pressure. The sintered-metal tube is welded to a venturi as shown in Figure 4.2.18. Each venturi is welded into a plate as shown to form a filter bank.

To minimize the effect of vibration or mechanical shock during installation and operation, a support rod of the type shown in Figure 4.2.19 is installed in each filter and the ends of the support rods are also connected together by reinforcing rods, as shown in Figure 4.2.20. An alternate method for reinforcing the sintered filter media is to support it with a perforated internal shell, as shown in Figure 4.2.21 (Bond et al. 1970).

Filter-face velocity (gas flow rate divided by filter area) is an important filter-design parameter. The manufacturer's maximum recommended face

FIGURE 4.2.18. Filter Element with Venturi and Blowback Nozzle

velocity is 6 ft/min. A conservative design face velocity of 3 ft/min is normally used at PNL.

Filters with nominal pore sizes of 10 and 65 μm have been tested. No conclusive results have been established as to the optimum filter pore size. A sintered-metal filter manufacturer has recommended that 10- μm filters be used instead of 65- μm filters to prevent more of the very small calcine particles from penetrating the filter pores immediately after a filter blowback when the filter surfaces are new. After a layer of calcine has formed on the filter

FIGURE 4.2.19. Filter Element with Support Rod

surfaces, the filtering efficiencies of the various pore sizes would be essentially identical, since the layer of calcine is then the primary filtering media.

A typical filter and blowback system is shown in Figure 4.2.22. The use of a venturi is intended to increase the entrainment of filtered gas by the blowback gas jet, thus decreasing the amount of external air required to clean the filters.

FIGURE 4.2.20. Filter Element Reinforcing Rods

A rapid filter pressurization is believed desirable for uniformly removing calcine cake from the filter. Consequently, during the WSEP Program at PNL (Bonner, Blair and Romero 1976), blowback air valves were located adjacent to the filters. Some problems were encountered, however, due to radiation-induced failure of the solenoid valves used. Valves that will withstand the radiation levels expected during HLLW processing are expensive and a nuisance to maintain in-cell. Therefore, out-of-cell placement of blowback valves is desirable. No significant detrimental effect on blowback efficiency is found when the valves are moved 16 ft from the filters.

The low filter differential pressure encountered in the spray calciner is only a few percent of the allowable differential for unreinforced sintered-metal filters. Therefore, it is highly unlikely that failure due to over-pressure would occur. The primary design parameter concerning the filter pressure drop is the size of the off-gas vacuum blower necessary to maintain

FIGURE 4.2.21. Spray Calciner Filter Assembly

the required calciner vacuum (10 in. H_2O). Operating parameters (Section 4.2.3.1) to minimize the filter-face velocity may limit the filter pressure drop to between 7 in. and 20 in. H_2O .

The optimum filter material has not been established. Experience has primarily been with 316 SS. One assembly of 316 SS filters was severely corroded after approximately 1600 h of run time (not including time for 34 heatup and cooldown cycles). Analysis of the metal showed that corrosion products existed not only on the filter surface, but penetrated the depth of the filter material. Metallurgical scanning electron microscope (SEM) analysis of a section of the filter material did not indicate any residual chloride or fluoride within the filter pores, or any other residual compounds. Since the corrosion

FIGURE 4.2.22. Typical Filter and Blowback System

existed throughout the thickness of the metal (though no residual compounds could be found within the filter pores), the corrosive species must have been volatile or soluble in the flush water. Chloride, fluoride and sulfate ions are likely the major cause (Dierks et al. 1980). Another contributing factor to the filter failure is that the filter temperatures exceeded 500°C during a 25-d test. The filters were at 475° to 525°C for 12 h, 525° to 575°C for 5 h and 575° to 590°C for 1 h. While these temperatures do not usually cause any problems for 316 SS, the extremely fine metal-to-metal bonds in the sintered metal are very susceptible to the slightest oxidation. A small amount of corrosion that is hardly detectable in vessels or piping can severely damage filters. Inconel-625 or Hastelloy should provide improved performance, but long-term experience with these materials has not been established for a spray calciner.

4.2.3.3 Maintenance

Sintered-metal filters may not last indefinitely in continuous service due to gradual blockage of the filter pores and/or corrosion. Since some calcine and volatilized particles are smaller than the pore size of the filter, some particles penetrate the filter and can become lodged in the pore. Unfortunately, not all particles inside the filter media are removed during blowback. The slow accumulation of particles is observed eventually as an increase in the post-blowback differential filter pressure.

Steps can be taken to partially remove particle buildup in the filter pores. With calciner feeding and melting stopped, the filters can be repeatedly blown back for approximately 24 h while the off-gas flow and filter-face velocity are at a minimum. This can remove some of the particles trapped in the filter pores and temporarily reduce the filter pressure drop. Also, washing the filters with water or nitric acid when the calciner furnaces are off has effectively cleaned the filters (Bonner, Blair and Romero 1976). The washing was done by trickling water or nitric acid into the filter from above the venturi while activating the blowback cycle. The liquid can be introduced through the blowback line. This procedure is not expected to be required routinely, but the capability should be available if needed. The wash solution can be collected in an empty canister and evaporated during the melter heat-up cycle.

The SC/ICM researchers feel that plant calciner filters should be easily replaced by remote means, especially since a reliable prediction of the operating life of the filters has not yet been established. Additional testing must be completed with more corrosion-resistant and high-temperature-resistant materials using waste compositions that include ruthenium, mercury, cesium, chloride, fluoride, sulfate, and other troublesome species. It is felt that a long (greater than a year) filter life can be achieved with appropriate materials selection.

Blank

4.78

4.3 VITRIFICATION (IN-CAN MELTING)

H. T. Blair

4.3.1 GENERAL DESCRIPTION

The ICM process shown in Figure 4.3.1 uses the waste disposal canister as the melting crucible. The canister is heated in a furnace, after which calcined HLLW and the glass-forming frit are charged into it; they then melt together and form a glass. When the canister is full of melt, the calcine and frit are diverted to another ICM and the filled canister is cooled, removed from the furnace, inspected, decontaminated, capped, and transported to a storage facility. Another empty canister is then placed in the furnace, and the cycle is repeated.

4.3.2 BATCH PREPARATION

The outlet of the calciner is coupled directly to the melter, and the glass-forming frit is added to the calcine just before it enters the melter because the properties of spray-calcined HLLW make it difficult to store or transfer (Bonner, Blair and Romero 1976). The heat generated in the calcine by the radionuclides and the poor heat-transfer properties of the fine powder may make it very difficult to prevent glass-sintering in the batch if the frit and calcine are held up in a surge bin or mixer hopper after being combined (McElroy et al. 1976). A mixer between the calciner and melter would further complicate the vitrification concept because mixers are mechanical devices that have problems with wear and remote maintenance as well as with batch holdup.

The borosilicate glass formers are added as a frit for a number of reasons. First, by premelting the mixture of compounds that make the frit, the gases that are released as the compounds decompose can be driven off and do not have to be processed through the radioactive facilities' exhaust system. Also, all of the energy required to convert these compounds to the vitreous state is expended before the frit is introduced into the ICM. The frit can be sized to be a dustless, free-flowing material, which minimizes material-handling requirements in the remote facility. The amount of boron that volatilizes

FIGURE 4.3.1. Nuclear Waste Vittrification Concept Using In-Can Melter

from the melt and condenses in the connecting section is minimized by incorporating the boron in a glass structure before putting it into the ICM. Although deposits found in the connecting section were analyzed, boron was never found to be in excess of the correct ratio to other frit constituents.

During early tests in the PNL nonradioactive facilities (Blair 1979b), all the batches charged to the pilot-scale ICM were mixed in a mechanical blender before being charged from a volumetric screw-feeder to the melter because the output of the pilot-scale spray calciner was inadequate to reach the capacity of the melter. Direct coupling of the ICM to HLLW concentrating or calcining equipment and the full-scale ICM were demonstrated with the frit added proportionally to the calcine stream as it dropped into the ICM. During these demonstrations it was observed that the calcine and frit do not flow into the melter at a continuous, uniform rate. Although calcine is continuously produced in the calciner, it is discharged into the ICM in varied quantities whenever the vibrators or filter blowback are activated. The continuous flow of the frit from the gravimetric feeder is divided into uniform, discrete quantities by the air lock. No differences in the melting rates or in the quality of the products produced by the two different batch preparation methods were observed while the batches used were composed of the highly active, calcined acid HLLW and appropriate frit compositions. However, some processing difficulties, such as the formation of refractory clinkers on top of the heat-transfer plate (fin) assemblies (Sections 4.3.17 and 4.5.2.3), may be associated with poor blending or with the difference in particle sizes of the calcine and frit. The difference in calcine and frit particle sizes may result in their separation as they enter the canister because of the difference in momentum of the particles. When the batch was agglomerated into pellets by a disc pelletizer no accumulations formed on the top of the plates.

Recent experience with neutralized defense wastes that have relatively high iron contents suggests that blending of the calcined waste and a finely ground frit may be necessary to prevent the formation of spinels, which are difficult to dissolve from the melt once formed. The frit has also been observed to melt and flow out of the batch, leaving behind refractory clinkers. Better blending should prevent this separate melting. Preliminary attempts to

achieve this blending without the introduction of a mixer into the process were made by using a microprocessor to coordinate activation of the filter blowback, vibrators, and frit chute air lock. The results were not much of an improvement because there is still a difference in the particle size of the frit and of the calcine.

4.3.3 FRIT FEEDER

Because the calciner produces calcine continuously, frit must be added to the stream of calcine flowing to the melter at a rate proportional to the rate that calcine is being generated by the calciner (Section 4.6.1.2). Experience shows that by using a frit sized to be free-flowing and a gravimetric solids feeder, the frit addition can be controlled to $\pm 0.5\%$ of the desired rate. A frit that was sized -20 mesh over 80 mesh was most frequently used. This sizing is a compromise between what is dustless and free-flowing in the storage bins, gravimetric feeder, and delivery chutes and what is quickly melted and homogenized with the calcined waste in the ICM.

The gravimetric frit-feeder is located outside the waste solidification canyon or hot cell. This permits the use of a weighed-belt or other continuous feeder that is accurate but will not endure long in a high-radiation environment and requires routine maintenance and cleaning. During a 10-d continuous demonstration of the full-scale ICM, it was learned that for the feeder used, the weighing mechanism and conveyor assembly must be cleaned in operation at least after every 48 h of operation to ensure proper frit proportioning.

4.3.4 AIR LOCKS

An air lock is necessary in the frit-delivery line between the gravimetric feeder and the spray calciner because the calciner and melter are operated with an internal pressure about 10 in. H_2O below the surrounding atmosphere. Two air locks with a space in the line between them may be desirable to assure that a pressurization of the calciner and melter would not allow radionuclides to be piped to the area outside of the cell in which the frit-feeder would be located. PNL has had experience with 1) a rotary-star valve, 2) a

motor-operated, tripping-valve air lock, 3) a pneumatic-operated reciprocating air lock, and 4) a pneumatic-operated, spherical-valve air lock in the frit-delivery line to the ICM. The rotary valve permitted inleakage to the processing envelope that was serious enough to tax the off-gas system's capacity. Fines accumulated on the sealing surfaces of the tripping valves and prevented them from sealing tightly. These surfaces were covered by an organic elastomer that would not have lasted long in a radiation environment. The reciprocating air lock also used elastomer seals that were eroded by the coarse frit.

The air lock using spherical valves incorporates metal-to-metal sealing surfaces, as shown in Figure 4.3.2. It has been used exclusively with the full-scale spray calciner for nearly 3 years. The only problems experienced with it were 1) a set screw came loose during a 10-d continuous run (such screws would be welded on a unit intended for service in a remotely maintained, radioactive facility), and 2) frit was backed up in the chute until it jammed the valve, causing some damage to a bushing during a 20-d run. Following the 10-d run, during which the air lock had been operating on a 30-s cycle, the

FIGURE 4.3.2. Air Lock Using All-Metal Spherical Valves

air lock was disassembled and inspected. The valve-to-seal clearances were still within specifications, and no other signs of wear were visible. Several pins that hold the spherical valves in place on the rotating shafts had dropped out, but these too could be welded. Of the systems assessed, the spherical valves appear to be the most promising for extended application.

4.3.5 FRIT CHUTE

The line that carries the frit from the air lock into the calciner cone below the calciner must be large, so that plugged flow does not occur when the air lock dumps a charge of frit into it. A 2-in., Sch-40S stainless steel pipe set at an angle of 60° from horizontal was used with the full-scale demonstration equipment to convey frit at rates of up to 80 kg/h. At angles less than 60° the frit will not flow freely. This frit-delivery chute must be kept hot; otherwise, steam from the calciner will condense in it and cause frit fines and calcine to accumulate. Such accumulations have completely plugged the 1-1/2-in.-dia tube on the pilot-scale equipment. Insulating the tube prevented this condensation and no additional heating was necessary. In the WSEP and NWVP the frit chute was purged with heated air to prevent condensation and overheating.

4.3.6 DIVERTER

Because continuous, uniform SC operation is considered desirable, two melter were coupled to the SC through a diverter. Thus, a filled canister could be exchanged with an empty canister without interrupting the calciner operation by diverting the calcine to the alternate ICM. The special diverter shown in Figure 4.3.3 was designed at PNL; it permits gases to flow from both melter through the diverter to the calciner gas exhaust system while the calcine and frit are directed into only one of the melter (Siemens and Bonner 1976). This two-canister handling setup is necessary, because gases continue to be released from the melt at least 2 h after batch-charging has been diverted to the other melter. The diverter is actuated by a double-acting air cylinder. This diverter has operated satisfactorily during the 3 years it has been in service on the full-scale demonstration calciner. Recently it was successfully cycled

FIGURE 4.3.3. Diverter Designed for PNL In-Can Melter

1600 times using a 20-psig air supply. Tolerances in the diverter are loose to avoid galling and jamming.

4.3.7 FIXED CONNECTING SECTION

The purpose of the connecting section is to convey the solids to be melted from the calciner to the melter and to conduct the effluents from the melter back to the spray calciner exhaust system while preventing the escape of either from the process envelope. This is easily accomplished by placing a large-diameter section of pipe between the calciner and canister in the furnace. By using a single pipe, problems with plugging of separate, smaller batch chutes and vent tubes were eliminated and design of a remote connecting section was simplified. The counter-flow of batch and effluents from the melter in a single pipe is believed to scrub the effluents and return volatiles to the melt. However, this has not been verified.

Sch-40S, 4-in.-dia stainless steel pipe was used to fabricate the connecting sections used in the nonradioactive demonstration equipment to convey as much as 120 kg of solids per hour to the ICM. This pipe has to be well

insulated to prevent the kind of condensation that leads to calcine accumulations, which can plug the pipe. No deposits occur in the connecting section when it is well insulated and the batch is dry.

The design of the connecting section became more complex when a diverter and sloping sections were introduced. Also, expansion joints were required to accommodate thermal expansion, and swivel joints, valves and metal bellows were added to permit remote canister changes and weighing of the ICM. Baffles were added to assure a uniform distribution of the batch over the top of the heat-transfer plates in the canister.

Several different ways of making the connection between the spray calciner and the canister were demonstrated at PNL. In the nuclear waste vitrification hot cell at PNL (Schneider and Kelly 1969) the top of the canister extended 14 in. out of the top of the furnace. Two ears on the sides of the canister at the top end rest on a supporting collar, such that the canister is suspended in the furnace. The connection to the calciner is made by rolling the ICM furnace, with the canister suspended in it, under the funnel beneath the calciner and then jacking the collar up so that the top of the canister is forced against the bottom of a vertical section of 6-in.-dia pipe placed between the canister and the funnel. A metal-sheathed asbestos gasket is used in the mouth of the canister to make a seal with the pipe.

The coupling arrangement used with the pilot-scale, nonradioactive SC/ICM equipment originally was similar to that used with the hot-cell ICM, except that the pipe was 4 in. in dia and a cap was placed on the canister by clamping it to the support ears. On that cap was a metal bellows that was attached to the bottom of the vertical pipe with a flange. This arrangement removed compressive forces from the pipe and accommodated thermal expansion and minor misalignments. However, it did not represent the concept using a diverter, nor did it permit weighing of the canister in the ICM. Therefore, the connecting section shown in Figure 4.3.4 was fabricated for the pilot-scale equipment. With this design, hooks were engaged in the ears on the canister as the furnace and canister were rolled under the connecting section. The joint between the canister and the connecting section was sealed by applying a clamping force with nut runners on screws attached to the hooks. A C-ring

FIGURE 4.3.4. Pilot-Scale In-Can Melter and Connecting Section With Cone Valve

gasket made from Inconel-718 alloy was used in the joint. This gasket was made out-of-round by 0.05 to 0.07 in. so that it snapped into a groove in the mouth of the canister and could not fall out. A metal bellows was placed in the connecting section to accommodate thermal expansion and to allow the

canister to hang from a load cell without restraint. This load cell arrangement permitted accurate monitoring of the ICM filling.

Experience with this sloping connecting section revealed the need to have a valve at the lower end of the connector to seal it during canister exchanges so that a vacuum was maintained in the calciner and calcined HLLW was not released. Calcine that clung to the inside surfaces of the connecting section would drop out as the bellows were compressed to retract the spout from the mouth of the canister. Therefore, the cone valve (Figure 4.3.4) was introduced into the connecting section to close the end of the spout during canister exchanges. Experience with a properly operating valve showed that about 1/2 g of calcine would be released during a canister exchange.

When the valve was opened by lowering the cone down into the neck of the canister, it deflected incoming batch away from the center of the canister toward the canister walls. The position of the cone in the neck of the canister was found to be critical to the prevention of batch accumulations at the top of the plate assembly (Blair 1979b).

In the full-scale ICM, in which the canister sits on the bottom of the furnace and does not extend through the top (Figure 4.3.5), a three-lugged twist-lock opening such as the ones shown in Figure 4.3.6 was located at the top center of the canister (Simonen and Slate 1979). The connection to the canister was made by lowering two concentric cylinders (which were hung from a metal bellows at the lower end of the sloping connecting section) through a hole in the lid of the furnace and into the mouth of the canister. The outer cylinder was made of Inconel-601 and had lugs that engaged in the twist-lock opening. The inner cylinder rested on an Inconel-718 alloy E-ring that was snapped into a groove around the opening into the canister. Clamping force was applied to the two cylinders by a bolted flange at the top end of the cylinders, thus lifting the outer cylinder against the twist lock and forcing the inner cylinder down to effect a seal at the gasket. The lower 6 in. of the spout had to be cooled by circulating water through passages in the 1/2-in.-thick wall to prevent batch from sticking there as it entered the canister. The cone valve also had to be water-cooled.

FIGURE 4.3.5. Full-Scale ICM Arrangement with Bottom-Supported Canister

This coupling arrangement was used successfully during the 10-d continuous demonstration of the full-scale SC/ICM. Twelve canister exchanges were made during this demonstration, and ensuring proper alignment of the canister with the spout on the end of the connecting section was determined to be the key to

FIGURE 4.3.6. Full-Scale In-Can Melter Canisters with Twist-Lock Openings

the successful development of a remote connecting section. The need for an expansion joint in the sloping section also became obvious while operating the full-scale equipment. The remote connecting section design that resulted from this experience also was influenced by the necessity to achieve the desired alignment without interfering with the weighing system used to monitor the filling of the canisters. Thus, the design of a remote connecting section, a canister support and alignment arrangement, and an ICM weighing system were integrated into one exercise.

One of the frequent criticisms of the present HLLW solidification concept is that the diverter and batch-delivery tubes that slope at a 60° angle from a horizontal reference between the calciner and melters require unacceptable increases in the cell height. Although not tested, it is believed that this angle may be decreased somewhat without serious consequences; however, another alternative that should be evaluated is the use of fluidized gravity conveyors. These would add little load to the exhaust system, while the angle of the legs could be reduced to only 3° to 5° from the horizontal position.

4.3.8 REMOTE CONNECTING SECTION - L. L. Petkus

Once the concept of fixed melter furnaces with the canisters totally immersed in the furnace heat zone was chosen for demonstration, a remote connecting section was constructed for testing at PNL. In addition to the SC/ICM system accommodations, other features were also incorporated into the concept. In order to facilitate the continuous weighing of canisters for process monitoring, the connecting section design needs to minimize the potential for seizing the canister, which would interfere with accurate weight assessment. "Remote," for the connecting section, indicates process-canyon operation with an overhead crane and an air wrench for any and all operations. All components of the connecting section must survive the harsh environment at the process canyon: radiation (10^6 R/h gamma, 200 R/h neutron), high humidity, sustained temperatures from 120° to 1070°C and nitric-acid contamination. Finally, canister change-out operations are to occur without serious release of calcine into the canyon.

To employ the necessary features into a connecting section, the evolved concept provided for 1) a swivel joint near the calciner that allows the connecting section to swing out of the way for canister exchange; 2) a "floating spout" that accommodates misalignment and thermal expansion with a minimum of binding; and 3) a cone valve that raises and lowers the spout, seals the delivery tube to prevent calcine leakage, and distributes the glass batch in the canister.

4.3.8.1 Connecting Section Design

A connecting section was designed to demonstrate remote operation. The new connection section was able to 1) be positioned by a remotely operated air wrench hung from a crane, 2) accommodate misalignment of the canister in the furnace, and 3) perform all the necessary movement to allow canister insertion and removal. This equipment also had to fit within PNL's existing ICM equipment. Elevation constraints between the calciner and the melter imposed design compromises that preclude the direct use of the design in a remote facility. For instance, the length of the sloped tube is considerably shorter than that required to gain overhead-crane access to the actuator or for canister exchange. Elevation constraints are also reflected in the design of the spout stroke and swivel joint.

The connecting section consists of a cone valve, spout, delivery tube, swivel joint, pivot mechanism, and a gimbaled power screw to operate the cone valve. The spout telescopes on the vertical leg of the delivery tube and is raised and lowered by the cone valve. When raised, the spout and cone valve clear the furnace elevation so the connecting section can be pivoted at the swivel joint to permit overhead crane access for canister exchange.

Principal features of the connecting section are conceptually illustrated in Figures 4.3.7 and 4.3.8. Figure 4.3.7 illustrates the connecting section engaged with a canister in the furnace. In this position the weighted spout is extended on the vertical leg of the delivery tube through the cover and supported by the canister. A flexible metal bellows seals the telescoping spout to the delivery tube. A cylindrical cage, which is integral with the delivery tube, contains two vertical ways for cam-followers attached to the

FIGURE 4.3.7. Conceptual Connecting Section Mechanism

spout weight. This arrangement prevents the bellows from being twisted by the spout during engagement with a tilted canister. For demonstration, the furnace is moved on an air pallet from the connecting section position shown to an adjacent high bay for canister exchange with an overhead crane.

FIGURE 4.3.8. Conceptual Spout and Cone-Valve Assembly

In Figure 4.3.7, the cone-valve stem extends through the vertical leg of the delivery tube and is attached to a linear slide. Another flexible metal bellows seals this slide to the vertical delivery tube. The slide moves on two vertical shafts that are contained in a frame (partially shown), which supports an actuator located on the axis of the cone-valve stem. The frame is supported by the pivot arm through a gimbal. These components are shown in Figure 4.3.8, which is a view of the upper portion of the connecting section attached to the diverter valve below the calciner funnel.

The gimbal facilitates spout alignments to the canister seal by allowing the delivery tube, which extends to the upper opening of the spout, to move universally with the spout. Clearances between the spout weight and the cage permit the required relative movement for spout alignment. The fins, on the cone-valve stem opposite the delivery tube/spout interface, approximately center the valve below the canister opening.

Universal movement of the delivery tube at the spout interface is facilitated in its sloped leg by two flexible joints. The upper joint accommodates universal pivoting and supports the weight of the sloped tube. The lower joint is a combination universal-pivoting and telescoping joint to accommodate the desired movement plus thermal expansion of the sloped tube. Both of these joints incorporate flexible metal bellows to seal the delivery tube and internal sleeves to protect the bellows from direct contact with batch flow.

A bracket extending from the pivot arm supports the upper portion of the sloped tube. This bracket also prevents transmittal of the swivel torque to the bellows in the sloped tube. An expansion bellows above the swivel joint accommodates connecting section "fit-up" to the diverter and thermal expansion of the diverter and calciner funnel. Swivel torque is isolated from this bellows by three studs, and an internal sleeve protects the bellows from direct contact with batch flow. These components can be seen in Figure 4.3.8.

The power screw illustrated in Figure 4.3.8 actuates the cone valve and spout. The power screw is advanced up and down by a nut. The nut, retained by thrust- and radial-bushings on the connecting-section frame, extends vertically with a tube that facilitates screw travel. An external torque source

(such as an air wrench or electric wrench) is positioned by an overhead crane to actuate the screw; the torque connection is at a fixed elevation for this purpose.

The power screw is attached to an upper slide that mounts a spring housing. Piston action on a compression spring retained in the housing connects a lower slide to the upper slide. The cone-valve stem is in turn attached to the lower slide. This arrangement provides a visual indication of the spout-to-canister seal prior to opening the cone valve. The lower slide stops moving when the spout seats on the canister seal. The slide position can be predetermined for a properly aligned canister. The upper slide lowers, expanding the spring and transferring the spout weight to the seal. When the spring is fully extended, the lower slide and cone valve lowers into the canister for normal operation.

Thermal expansion of the canister lifts the spout without affecting the spout-to-canister seal. The relative elevation of the cam-follower on the cage can be used to indicate this expansion. Elevation of the lower slide is adjusted accordingly to maintain the cone valve at the desired opening.

In the retracted position the connecting section may be pivoted to clear the furnace opening for canister exchange (for demonstration purposes, the furnace was moved as previously described). The pivot arm is mounted on the vertical axis of the swivel joint and driven through a worm gear. A nut on the work shaft permits pivot operation by an external torque source positioned with the overhead crane.

4.3.8.2 Connecting Section Support Equipment

For the least troubled operation, the connecting section was designed to use the minimal support equipment. However, some equipment is necessary, or may be necessary for in-cell operation. The moving components must be powered in some manner, and it is probable that extra equipment will be attached to add methods of unplugging the connecting section. It has been found that with some glass compositions, intimate mixing of glass-formers and calcine is necessary for higher rates and a more homogeneous product. Such contact between the frit and calcine would require a mixing step of some kind.

Equipment used to power the connecting section is air-driven; this is easily controlled, low-maintenance equipment. Air wrenches were originally used in the connecting section demonstration because they are common in in-cell use. Two sizes were tried--a 64-ft-lb unit and a 224-ft-lb unit. The larger-capacity unit drove the power screw faster and with less impact noise. Both units shook the connecting section violently. The acorn nut on the power screw was galled badly as a result. The use of an air-driven motor and appropriate gear reduction is being considered as a less violent alternative. Such an air motor would be mounted on the connecting section and would be remotely replaceable. The work screw for the pivot motion would be similarly driven.

There has been little attempt to develop remote unplugging methods for the connecting section. Efforts have centered on keeping plugging conditions under control. However, plugging may occur and the appropriate equipment and/or methods would be added to the connecting section. A vibrator mounted on the connecting section should remove blockages. It could be air-driven like the drive equipment. Many of the plugs experienced at PNL have been friable and are therefore susceptible to removal by vibration. Air jets were installed, but at the time of this writing had not been required. Such devices may be effective.

4.3.8.3 Operation and Maintenance

The connecting section has been used in two multiple-canister runs. In the first demonstration, four canisters were filled in 5 days. By the end of those 5 days, the unit was almost unoperable because of calcine dust collecting in the bellows and limiting movement. Efforts to make operation easier resulted in less reliable remote operation. This modification was tried in a demonstration involving only two canisters. The bellows behaved as expected, but other problems are still unresolved. The following evaluations of the unit and of several specific components will lead toward the more advanced design.

One of the improvements that was expected from the connecting section was the smoother operation of the SC/ICM system. The connecting section was to

provide for a convenient canister change-out procedure, reduced plugging problems, and better control of the ICM process through the weighing system. The smoother operation would allow more attention to be placed on central problems instead of on the hardware.

Except for the bellows problem, which will be discussed below, the connecting section has made the canister change-out a safer, more convenient job. The operation is not done remotely, but is done with minimum hands-on assistance. Plugging problems have not been eliminated, as cooling control has not been improved sufficiently and efforts to unplug remotely have not as yet been made. The weighing system is hampered by the realities of the present experimental configuration. The furnace is moved with an air pallet from underneath the connecting section to a spot where an overhead crane can reach the canister. This arrangement causes a number of canister alignment problems. The misalignment of the canister and connecting section causes interferences that result in weight fluctuations of several hundred pounds. This causes the weighing system to be useless on those runs where the furnace alignment is not good. This has not been much of an improvement for the connecting section.

Movement within the connecting section is accommodated by sliding tubes sealed by a bellows. There are four sets of tubes and bellows in the connecting section. During the first operation of the connecting section it became obvious that all of the bellows were collecting calcine. The calcine would lodge between the convolutions and prevent the full compression of the bellows. The situation was the worst for the bellows at the spout. By the end of the original 5-day run, the bellows at the spout would not retract enough to allow the spout to clear the top of the furnace for canister removal. Calcine would work past the concentric tubes and up into the bellows. The powder would then pile up behind the inside tube, restricting movement. The inner tube was removed to clean out this powder. The connecting section was used in this condition for a second set of two canisters. The bellows became slightly restricted, but could be cleaned by shaking the bellows, which dislodged the calcine. Cleaning could be done by a burst of air or by vibration. The configuration could be acceptable for the vertical bellows, but would not help the inclined bellows on the delivery leg. An alternate sliding seal will be necessary.

Operation of the power screw without lubrication was unsuccessful. The design mated a 304L stainless steel screw against a Nitronic-60[®] nut at a calculated single-thread contact pressure of 2160 psi. Schumacher (1976) indicated this combination of materials would resist galling at contact pressures in excess of 50,000 psi. Nevertheless, severe galling of the screw and nut threads occurred within three operations. The affected parts were refabricated, mating a 17-4 PH (H-1150) stainless steel screw against a Nitronic-60 nut and lubricating with "Never-Seez."[®] Based upon its performance during the 5-day run, this combination appears to be functional.

The swing movement of the connecting section will be used to remove a canister from the furnace. Because of the limited use of the swivel joint needed to effect this motion, its expected life has not been determined.

4.3.9 ICM POWER REQUIREMENTS

Experience with the nonradioactive demonstration ICM has shown that a power consumption of between 0.5 and 1.6 kW-h/kg of batch melted is required to operate an ICM. The wide range is due to a number of variables, as shown in Table 4.3.1. The first two examples listed in Table 4.3.1 illustrate the influence that batch composition can have on the power required. In Run ICM-16, the batch contained powdered silicon metal, which caused an exothermic reaction in the melt that reduced the energy the furnace had to supply to melt the batch. This cause and effect does not appear to be consistent when the power requirements of runs FS ICM-13 and FS ICM-16 are compared. The reason is that between these two runs some significant changes were made to the furnace to reduce heat losses resulting from convection. However, the values in the last column were all calculated under the assumption that 10.25 kW and 52.5 kW were being required to maintain the pilot-scale and full-scale ICMs, respectively, at the operating temperature when no batch was being melted. This basis is valid for the pilot-scale melter, but changes were constantly

[®]Armco Steel Corp., Advanced Materials Division, Baltimore, Maryland.

[®]Never-Seez Compound Corporation, Broadview, Illinois.

TABLE 4.3.1. Power Use Data from Nonradioactive ICM Demonstration

Run Number	Melter Used	Can Dia, in.	Number of Fins	Batch Composition(a)	Melting Rate, kg/h	Mean Energy Consumption, kW	Power to Operate, kW-h/kg	Power to Melt, kW-h/kg
ICM-13	Pilot-Scale	12	8	PW-7a-2(1:2.9)75-75	24	21	0.88	0.45
ICM-16	Pilot-Scale	12	8	PW-7a-2(1:2)75-75+1.5% Si	43	20.6	0.48	0.24
SRL ICM-1	Pilot-Scale	8	8	SRL 1(1:1.27)Frit 21A	12	15.5	1.29	0.44
SRL ICM-2	Pilot-Scale	8	8	SRL Sludge (1:1.27)Frit 21A	20	22	1.10	0.59
FS ICM-1c	Full-Scale	16	8	PW-7a-2(1:2.3)76-199+1.5% Si	70	64	0.9	0.16
FS ICM-13	Full-Scale	12	6	PW-7a-2(1:1.6)76-199+1.5% Si	42	68	1.6	0.37
FS ICM-16	Full-Scale	12	10	PW-7a-2(1:2.8)76-199	47	55	1.2	0.05
FS ICM-18	Full-Scale	28	16	PW-7a-2(1:2.1)76-199+1.5% Si	112	89.3	0.8	0.33
FS ICM-19	Full-Scale	24	16	SR Composite(1:3)Frit 411	50	60.2	1.2	0.15

(a) (Mendel et al. 1977)

made on the full-scale ICM to the arrangement of the canister within the furnace and the insulation, which would cause the heat losses to vary from one run to another. The value 52.5 kW is the mean of a series of values ranging from 50 to 55 kW that were obtained during run FS ICM-19.

The information presented in Table 4.3.2 shows how the power is distributed in the multizone full-scale furnace when the zones are controlled at a constant temperature as the canister is filled.

The values reported for FS ICM-18 are the hourly averages for a 10-h, 20-min period during which the batch-charging rate to the melter ranged between 107 kg/h and 117 kg/h. Those values reported for FS ICM-19 are the hourly averages for a 17-h period during which the charging rate was 50 kg/h. The wide variation in power required by the various zones of the furnace during FS ICM-19 is believed to be the result of defective SCRs in the power supplies for zones 2, 3, 4, and 5. However, the data do show that 10% to 17% more power was used in the upper half of the furnace than in the lower half during a filling cycle. This suggests that much of the batch-melting occurs before it reaches the melt surface and explains why melting rates are so high in the first half of a can-filling campaign.

Each zone of the full-scale ICM has a thermal input capacity of 30 kW, which is more than normally required, as the data in Table 4.3.2 show. This

TABLE 4.3.2. Power Requirements for Runs FS ICM-18 and FS ICM-19

<u>Zone No.</u>	<u>Required kW</u>	
	<u>FS ICM-18</u>	<u>FS ICM-19</u>
6 (top)	15.9	13.2
5	17.9	8.9
4	15.1	13.2
3	14.0	10.6
2	12.4	3.0
<u>1 (bottom)</u>	<u>14.0</u>	<u>11.3</u>
Total	89.3	60.2

much energy has only been used in the bottom zone of the furnace to obtain heatup rates of $200^{\circ}\text{C}/\text{h}$. The maximum required to obtain melting rates of 117 kg/h in a 28-in.-dia canister was 16 to 24 kW per zone, depending on which zone the melt level was in. Recent experience with accurate recording kWh meters across each zone's power supply has shown that when the zones of the furnace are controlled at a fixed temperature, a power profile is observed in which the maximum power consumption moves from zone to zone as the melt level rises in the canister. Some interesting interactions between the zones' power requirements are also observed as the control thermocouples respond to temperature changes in adjacent zones.

Power requirements to operate the in-pot melter during the WSEP were not reported, but a net power input of 0.67 to 1.0 kW-h/kg was reported for the melting of calcined waste and borosilicate glass-formers in the platinum melter. These radioactive melts had heat-generation densities as high as 204 W/L (McElroy et al. 1972).

4.3.10 IN-CAN MELTER COOLING

The ability to remove heat from the ICM is considered necessary 1) to prevent centerline temperatures of the melt from exceeding the processing temperatures due to the self-heating by the waste, and 2) to accelerate the cooling of a filled canister so that it may be removed from the furnace more quickly after filling. A cooling capability may also be useful in minimizing the results of such accidents as a leak in the wall of a canister during melting.

Provisions for forced-air cooling were built into both of the furnaces used in the WSEP (Schneider and Kelly 1969) and into the full-scale nonradioactive demonstration ICM operated at PNL since 1977. The induction furnace used in the WSEP was also cooled when the power was turned off by the water circulating in the induction coils. Blowers were used to supply 275 SCFM of forced air to the WSEP furnaces. This air was controlled with a manually operated valve in the cell gallery. It was equally distributed to the six zones of the furnace through a manifold. The air was introduced into the resistance-heated furnace around the outside of the furnace liner by an

Inconel torus located at the base of each zone. The tori were supported on insulated metal baffles that separated the zones. Holes were drilled through the inside walls of the tori so that the escaping air was directed onto the liner. The air was exhausted from the furnace into the hot cell through ten ceramic-lined ports at the top of each zone, as shown in Figure 4.3.9. An additional 50 SCFM of air was injected inside the furnace liner around the canister. This cooling in the WSEP furnaces was sufficient to maintain steady-state centerline temperatures of the 8-in.-dia canister wall and contents below 470°C and 920°C , respectively, during the processing of material that had an internal heat-generation rate of 12.7 kW. A test showed that the 50 SCFM of cooling air inside the furnace liner decreased the average canister wall temperature by 35°C (from 430° to 395°C) below that attained with only the furnace cooling (McElroy et al. 1972).

The full-scale ICM furnace was designed to provide a heat-removal capability from each zone of 6 kW plus a 25°C/h cooling rate if the furnace were empty. This was to be accomplished using 700 SCFM of air at 90 psi. A temperature differential of 93°C between the entrance and exhaust air was anticipated. The air was filtered to remove oil introduced by the compressor and distributed by a vertical manifold to the six furnace zones. At each zone a motorized adjustable port valve activated by a signal from the zone temperature controller governed the flow of air into the furnace chamber. The air was carried through the furnace wall, divided, and then taken to opposing corners of the chamber and discharged into each furnace zone in a swirling pattern by ducts made from Inconel-601 sheet. The air was removed from each zone through ports in ducts located in the two corners of the chamber not occupied by the inlet ducts. The ducts channeled the exiting air to the side of the furnace opposite the inlet manifold, where the ducts passed through the furnace insulation into an insulated exhaust stack. A valve was located on each exhaust line where it entered the stack to close it off during melting in order to minimize convection through the furnace. The zones were isolated by baffles made from Inconel sheet and a 1-in. layer of fiberceramic insulation. These baffles warped badly during the initial furnace heatups.

FIGURE 4.3.9. Resistance-Heated Furnace Used in Hot Cell for In-Can Melting

The baffles and much of the duct work was damaged while removing the furnace liner soon after the furnace became operational, so they were removed. Only the ports through the furnace insulation remained in the lower three zones. The internal duct work remained intact in the upper three zones. This experience suggests that all cooling-air duct work should be located outside the furnace chamber. It could be located between the insulation and the furnace shell or it could be outside the shell. Penetrations could then be made through the insulation into the furnace chamber from the ducts using Inconel tubing. Thus, the ducts could be constructed from inexpensive sheet metal and protected from damage due to the environment inside the furnace.

Although forced-air cooling was used to accelerate cooling of canisters filled with glass in the full-scale ICM, the programmed cooling capability using the temperature controllers and motor-controlled valves was never demonstrated. The majority of these cooling demonstrations were made without a liner in the furnace. The canister surface and the product internal cooling rates were recorded.

Attempts to cool the lower zones of the furnace while continuing to melt batch in the upper zones were unsuccessful. Whenever cooling air was introduced into a zone, the melt surface became too cool to sustain the desired processing rates. This may have been caused by the lack of baffles in the full-scale furnace. Without the baffles, the convection currents caused by the injected air were not restricted to the desired regions of the furnace chamber. Possibly a more effective method of isolating cooling to the desired zones while eliminating the need to build durable and functional baffles into the furnace to minimize convection would be to attach cooling coils to the furnace liner through which a coolant could be circulated. Sections of the coils could be isolated to define the desired zones. The stresses that such cooling would impose on the liner must be evaluated.

4.3.11 PROCESS TIME CYCLE

The in-can melting cycle for processing a canister of vitrified waste includes the following eight operations:

1. placing a cool, empty canister with a gasket secured in the opening into the ICM furnace;
2. making the connection between the canister and the calcine- and frit-delivery chute;
3. heating the empty canister to the processing temperature;
4. charging the canister with calcined waste and frit during melting;
5. fining the melt;
6. cooling the canister to the appropriate temperature for removal;
7. disconnecting the connecting section; and
8. removing the filled canister from the ICM furnace.

Numerous other peripheral pre- and post-canister treatment activities also occur, but the above eight operations are those that determine the total time required to process a canister of melt. The process turnaround time is determined by operation 4--the batch charging and melting--because all other operations are performed on the alternate canister while this operation is carried out in the primary canister. The duration of the melting operation is a function of the melting rate and the volume of the canister being filled.

Table 4.3.3 (along with Figure 4.3.10) presents estimated cycle times based primarily on PNL experience. The time estimated to place an empty

TABLE 4.3.3. Estimated ICM Process Cycle Times

<u>Operation</u>	<u>Time to Perform Operation, h</u>
Place canister in furnace	1/2
Make connection	1/4
Heat canister (100°C/h)	3-1/2
Fill canister with melt	See Figure 4.3.10
Fine the melt	2-4
Cool to 700°C (140°C/h)	2-1/2
Disconnect	1/4
Remove canister from furnace	1/2

FIGURE 4.3.10. Demonstrated Melting Rates in ICM Containing Plate Assemblies

canister into the furnace is conservative if it is assumed that the furnace cover and lifting device are already engaged in the twist-lock opening of the canister. For this to be possible, at least three furnace covers are required in the cell. Experience with the remote connecting section demonstrated at PNL in 1979 showed that the chute could normally be rotated into position and the spout lowered into the mouth of a properly positioned canister in about 5 min.

A heatup rate of 100°C was chosen to reduce the possibility of warping the furnace liner or canister. However, such caution may be redundant, since the canister could be placed in a furnace that is at 700°C to start with to obtain maximum furnace life. The furnace is expected to be at 700°C when the empty canister is placed in it because that is its temperature when the previously filled canister is removed, and the temperature range over which the furnace is cycled should be minimized. Placing a full-scale empty canister in a 700°C

furnace was never demonstrated at PNL because the facilities did not permit access to the furnace with a crane when the furnace was connected to the power supply. However, canisters were placed in furnaces at 350°C without suffering any detrimental effects.

When the empty canister has been heated to the processing temperature and the canister in the alternate ICM is filled, the diverter is activated to direct batch into the prepared canister. The rate at which the canister is charged is determined by a number of variables discussed in Section 4.3.17 of this manual concerning melting rates. The batch should not be charged to the canister faster than it is being melted. Because the melting rate is greater in an empty canister and decreases as the canister fills, and because the hot surfaces decrease where the melting occurs most rapidly, the minimum canister-filling time is achieved by charging batch to the canister at a continuously decreasing rate that always corresponds to the melting rate. However, this operation requires continuous adjustment of the spray calciner feed rate and the corresponding frit-addition rate. A constant feed rate to the calciner is considered more desirable. Thus, an average melter charging rate (Figure 4.3.10) is selected that is less than maximum for initial canister-filling and results in overcharging with unmelted batch as the canister nears the filled condition.

The use of an average charging rate requires that the contents of the canister be maintained at the melting temperature for a period of time after the batch has been diverted to the other melter. This time-at-temperature permits complete melting of the batch and refining of the melt by allowing bubbles to rise and burst at the melt surface. The time allowed for this "fining" must be limited, however, because while the bubbles are rising, undissolved dense phases are settling in the canister and corrosion of the canister walls and heat-transfer plate assemblies by the melt is continuing. Also, the bubbles carry with them to the melt surface small amounts of some materials that are better left encapsulated in the glass (such as Ru, Cs, and Te). The fining times presented in Table 4.3.3 are those found to assure complete melting and removal of all bubbles longer than 1/4 in. in dia from the

glass for two specific simulated waste compositions and the frits developed to vitrify each. The appropriate fining time for any waste melt is determined from the melting characteristics of the particular composition and the product specifications.

The cooling rate of $140^{\circ}\text{C}/\text{h}$ was demonstrated with 24-in.-dia canisters using forced-air cooling. This is the cooling rate of the canister material and not of the melt inside, which cools much more slowly. The canister is cooled at this rate to 700°C ; the 700°C level was selected as the temperature at which the canister would be removed because that was the highest temperature at which the canister design was strong enough to sustain a one-time lift. This temperature is also near the upper end of the temperature range in which sensitization of 300-series stainless steel occurs. By removing the canister from the furnace at this temperature, rapid cooling through the critical range is assured, thus minimizing the potential for sensitization of the canister material. Several filled 24-in.-dia canisters have been removed from the full-scale ICM at 700°C to demonstrate this method.

Disconnecting the chute from the canister, rotating the chute clear of the top of the furnace, engaging the lifting device into the furnace lid, and removing the canister from the furnace simply require reversing the remote operations performed at the start of the ICM cycle.

The lag time is the difference between the time required to fill a canister and the total of time required to perform all the other operations in the ICM cycle. It is the time available to make adjustments or repairs to an ICM before it would have to be operational again without disrupting operation of the rest of the waste processing system.

4.3.12 IN-CAN MELTER FURNACE

The ICM furnace provides the heat required to melt calcined HLLW and glass formers to form a homogeneous, vitrified product. Because the canisters used as the melting crucibles are right-circular cylinders having L/D ratios of 5 to 10, the furnace is usually an annulus--although box and octagonal configurations have also been used.

Both resistance heating and induction heating have been considered for in-can melting (IAEA 1977). Induction heating is believed to be more reliable and efficient than is resistance heating, but it does impose certain design constraints. The coils should be close to the work piece, though electrically isolated from it. Piping of the signal through the cell or canyon wall to the coils requires design to prevent coupling, as coupling between coils in a multizone furnace with large diameter-to-zone height ratios should be avoided.

The radioactive facilities at PNL include an induction furnace (used during the WSEP program) that is capable of processing canisters up to 12 in. in dia by 8 ft long (Schneider and Kelly 1969). The furnace is divided into six zones as shown in Figure 4.3.11 and uses a motor generator to produce a 200V, 1000-cycle output that provides 20 kW of power to each zone. This furnace was successfully used for demonstrations of the pot-calcination and rising-level phosphate-glass processes in the WSEP (McElroy et al. 1972). These results indicate the induction heating can be used to successfully heat an ICM process in a remote facility.

Resistance furnaces are easier to design than are induction units. However, because the resistance elements have a finite life, the design is complicated by the need to provide for remote replacement of the element or the entire furnace modules. Because it was felt that the processing differences were minor with either type furnace, and since resistance furnaces are more economical to obtain (with much shorter delivery times), the in-can melting of borosilicate glass compositions at PNL in both the nonradioactive demonstrations and the WSEP and Nuclear Waste Vitrification Project (NWVP) were made in resistance-heated furnaces. In addition, the furnace used by the British to demonstrate the HARVEST process was also resistance-heated (IAEA 1976).

The resistance-heated furnace used for the pilot-scale ICM at PNL is shown in Figure 4.3.4. It has a single-zone heated chamber 23 in. in dia by 48 in. high. The furnace is rated at 70 kW using 23V, 3-phase power. It was fabricated in 1961 using Kanthal resistance elements supported on dense refractory plates and refractory bricks inside a steel shell. The maximum safe working temperature is 1100°C. No element failures have occurred during 18 years of intermittent use.

FIGURE 4.3.11. Induction Furnace Used in PNL Hot Cell

The temperature in the pilot-scale furnace is monitored using Type-K thermocouples sheathed in Inconel-601 that pass through the furnace wall half way up the side of the furnace. The furnace is controlled by a solid-state, 3-mode, industrial process controller equipped with a digital set point, proportional band, automatic reset and rate. Heatup and cooldown are programmed using an electro-mechanical programmer that employs an electrostatic curve-following system. The power to the furnace is controlled by an all-solid-state, "enforced," zero-voltage firing, proportioning (CSCR) Thyristor power controller. The energy used by the furnace is displayed on a meter that is accurate to the nearest kWh.

The furnace is not satisfactory for in-can melting, however, because of the single-zone construction. When a canister being filled by the ICM process in this furnace becomes more than half full, overheating of the lower half of the canister occurs if the processing temperature is maintained at the melt surface. The necessity of having a multizone furnace for processing large canisters by the rising-level ICM process is evident even if the waste is not self-heating.

The full-scale, nonradioactive demonstration furnace at PNL is designed to operate at temperatures of up to 1200°C. It is insulated with fiberceramic materials that permit rapid cooling of the furnace because of their low heat capacity and their resistance to thermal shock. The furnace is heated with 48 SiC resistance elements. These elements are not recommended for use in a remote facility because they are easily damaged and have short service lives. However, their use in the developmental furnace provided high watt densities at a reasonable expense.

The furnace is designed to accommodate workloads up to 7 ft tall by 28 in. in dia and weighing 6600 lb in its 7-1/2-ft-tall by 31-in.-square chamber. The chamber is divided into six 15-in.-high heated zones by placing each group of eight heating rods (two on a side) on a separate power supply and temperature controller. Physically separating the zones with baffles was unsuccessful because the baffles that were used warped and broke up. The optimal zone height has not been determined. Experience with the pilot-scale melter showed

that a 48-in.-high zone is too large. There is considerable zone temperature-control interaction in the furnace with 15-in.-high zones. A zone height of 24 in. may be more satisfactory when processing waste with low heat-generation rates.

Each zone has a thermal input capacity of 30 kW, which is more than normally required, as discussed in the section on power requirements. The power is provided by Scott-connected transformers and controlled through zero-cross-over-firing SCRs. Provisions for forced-air cooling sufficient to remove 6 kW from each zone are also built into the furnace.

The temperatures in the furnace are measured by using Type-K thermocouples sheathed in Inconel cladding. Two thermocouples are located in each zone. One sensor supplies a signal to the zone temperature controller and the other is connected to a multipoint temperature recorder. The controllers are three-mode proportioning devices with current output suitable for driving SCR power control units and magnetic-amplifier/saturable-core reactor combinations. The latter is used to drive motors for opening and closing valves for control of the forced-air cooling.

The full-scale furnace was constructed so that the canister can be suspended in it from a superstructure around the furnace or set on a refractory hearth, which is a plug in a hole through the bottom of the furnace (Figure 4.3.5).

A liner 27 in. in dia by 7-3/4 ft high made of Hastelloy X was fabricated for the furnace so that canisters up to 24 in. in dia could be processed in an inert atmosphere to prevent oxidation of the canister exterior.

The resistance-heated ICM furnace in the WSEP hot cell at PNL is shown in Figure 4.3.9. The furnace consists of six identical nesting sections supported from the bottom section. Each section is a self-contained module consisting of an external shell, resistance-heating elements, element supports, insulating refractories, thermocouples, and cooling-air ducts. The shell is made from stainless steel and all penetrations are shielded so that liquid spilled from above cannot flow into the furnace. The thermocouples are Type-S, platinum/

platinum-10% rhodium, sheathed in Inconel-702 alloy. The heating elements are made from Kanthal A-1 alloy bent in a zigzag shape. They are supported in corrugated ceramic-refractory radiant plates and are arranged and connected so that two completely separate circuits or continuous heating elements exist in each of the three phases in each module. Both leads from each heating element are continued through the furnace electrical connection into the service gallery so that when any element fails the other two phases of that circuit may be disconnected to permit operation at half power with the remaining three-phase circuit or so that the remaining two elements may be reconnected to operate on single phase. The normal connection arrangement is for three-phase, grounded-wye circuits. Electrical connectors at the terminal box of each furnace module and in the electrical supply plug facilitate remote replacement of any module.

The power supplies to these furnaces were recently upgraded to zero-cross-over-firing SCR power controllers. Each zone has a power input of 15 kW.

The furnace zones are 14 in. high. They are separated by an Inconel-alloy baffle that supports 1 in. of ceramic insulation and the cooling-air duct described in the section of this manual on cooling.

4.3.13 CANISTER POSITION AND SUPPORT IN THE FURNACE

The canister may be completely contained in the ICM furnace or may extend through the top. Extending the canister through the top of the furnace has several advantages. First, it makes the opening into the canister easily accessible and relatively cool for making the connection. Second, it permits the canister to expand as it is heated without affecting the connecting hardware. Third, the canister closure area is not degraded by oxidation at high temperatures. There are also some disadvantages to having the top of the canister extend through the top of the furnace. This arrangement places the upper end of the canister in a thermal gradient ranging from 400°C to the furnace temperature of 1070°C. The temperatures in the gradient cause sensitization in even low-carbon-content 304L stainless steel during the time required to fill a canister with melt. The degree of sensitization measured in samples

from canisters processed at PNL would markedly increase the propensity for stress-corrosion cracking (SCC) if the canister were stored in a water basin (Blair 1979b).

Another problem caused by the thermal gradient is the accumulation of calcined waste on the inside surface of the canister. The material that sticks to the walls can be significant. This accumulation varies in consistency from a vitrified product at the lower end to a friable, calcined-waste-rich crust at the upper end. As the canister cools, the more vitrified material spalls onto the melt surface. As much as 938 g of this material were recovered from the tops of 8-in.-dia canisters processed in the pilot-scale melter. It has a high surface area and poor leach resistance relative to that of the glass. Because this material is deficient in frit, it will not melt at temperatures as high as 1072°C.

Various methods of eliminating the calcine that was not fixed in glass were evaluated. When the canister was full, the inside wall was sprayed with water while the canister was still hot in order to wash it and to thermally shock the accumulation off into the melt. Substantial steam was produced, but the accumulations on the walls were not significantly reduced. Cooling the canister walls from the outside by raising the canister out of the hot furnace and spraying cold water on it above the melt level was then tested. The canister cooled until the water spray no longer flashed to steam, but the deposits on the inside did not spall into the melt. Several times a frit addition of one or more kilograms was dumped into the ICM following batch-charging so that it would seal the melt surface. However, this did nothing to seal the accumulations on the canister walls up in the cooler thermal gradient. Two different graphite-mold release coatings used on glass-forming equipment were applied to the upper inside surfaces of a canister. The accumulations on the treated surfaces did not appear to be much less than those on the untreated surfaces.

Another disadvantage of extending the top of the canister out of the furnace is that the heat loss from inside the canister is great. Thus, the melting rate decreases as the canister fills, and the top of the plate assembly is so cool that batch sticks there and will not melt off. The top of the plate

assemblies has to be a minimum of 12 in. below the top of the furnace to avoid the formation of clinkers there in the pilot-scale ICM.

Stress analyses of canister designs for use in the full-scale ICM showed that the larger canisters should sit on the bottom of the furnace rather than be hung in the furnace (Simonen and Slate 1979). Bottom support made possible the design of a canister that could be located completely within the heated chamber (Figure 4.3.5). The top of the canister in the full-scale furnace was between 10 and 12 in. below the top of the furnace, or 4 to 6 in. inside the heated chamber. By using a water-cooled spout to convey the batch through the temperature gradient into the canister, accumulations of unvitified waste in the canister was reduced. The quantity of loose material that spalls from the inside surface of the canister above the melt level was reduced to 577 g in a 24-in.-dia canister, and the leach resistance of this glass spall was the same as the bulk glass in the canister (Blair 1979b). Some spalled sintered calcine-frit material is still observed in canisters. If it is determined that material is not acceptable in the product, then methods such as a vitrified frit cap on the glass may be investigated to eliminate this condition.

4.3.14 CANISTER SPALL

The operating temperature of the ICM (1050° to 1070°C) is 150°C above the maximum temperature recommended for the use of 304 stainless steel to avoid excessive spall (metal oxide scale), created by oxidation, when heated in an air environment. Therefore, when canisters made of 304L stainless steel are filled by the ICM process and allowed to cool in the furnace, accumulations of spall from the canister are deposited in the furnace or liner.

Various techniques were used to determine the amount of spall generated. The results in Table 4.3.4 show the quantities of spall collected during various ICM runs conducted at PNL.

When the first canister listed in the table was removed from the furnace following the melting test, large patches of scale were still loosely attached to the outside surface of the lower end of the canister. Samples of the scale were collected and the thickness and mass per unit area were determined. The

TABLE 4.3.4. Spall Collected from the Exterior of 304L Stainless Steel Canisters Used in the ICM Process

Canister Size		Time Heated Above 900°C, h	Hold Before Quench		Spall Collected, g	Mass of Spall per Unit Area, g/cm ²
Dia, in.	Length, in.		h	at °C		
12	60	27	0	---	---	0.078
12	49	17	11-1/2	720	513.9	0.058
12	62	20	4	675	---	0.042
8	59	14	13	810	280	0.039
8	60	16	11-1/2	755	360	0.045
8	60	15	10	765	107	0.013
8	60	11	11-1/2	755	171.3	0.021
24	84	35	0	---	3020	0.063

samples ranged in thickness from 0.007 to 0.010 in. Samples of scale were obtained from the third canister in the same way.

Numerous experiments were performed where the processed canisters of vitrified product were removed from the furnace at temperatures above 700°C and quenched to reduce the residual stress and the sensitization in the canister walls. The canisters were either immersed in water or were air-cooled by placing them in a cage made with wire mesh. The scale did not spall from the canister exterior until the canister had cooled to well below 700°C. Then the scale would pop off and be thrown as far as 5 ft from the canister. All but the very fine particles that passed through the screen were collected when a canister was air-cooled in the cage. This scale was weighed and the mass per unit area was calculated using only the surface area of the canister that had spalled.

The data presented in Table 4.3.4 do not show any correlation between the time that the canisters were exposed to high temperatures and the amount of scale collected because many other factors affecting the oxidation were not measured or held constant. One of the most important factors was the initial surface condition of the canisters. The canisters were fabricated from a wide

variety of pipe sections and rolled plates. Most of them were processed in the ICM as they were received from the fabricator without any special surface treatment.

One canister processed was an exception, for 180° of the exterior of this canister was sand-blasted before being processing. No spall was visible when the canister was removed from the furnace at 800°C, but it quickly appeared as the canister cooled. When the canister had cooled and the spalling was completed, the surface of the canister that was sand-blasted was much rougher than that which was not. It was also a rust-brown to orange color, while the unblasted surface was dark gray and smooth. The last canister listed in Table 4.3.4 was also sand-blasted by the fabricator following its assembly. The surface exposed by spalling after the canister was processed was rough and a dark, gray-brown color.

During the processing of one canister, six coupons taken from the same section of pipe that the canister was made from were suspended in the furnace along the side of the canister. Metallographic examination of these coupons after the run showed that the width of the wall of a canister made with 304L stainless steel was reduced by 0.004 to 0.006 in. by oxidation of the exterior during the ICM cycle. However, the outside diameter of the canister was actually increased by 0.002 to 0.008 in. because a layer of oxide formed that did not spall.

Because oxidation of the exterior of the canister would reduce the thickness of the canister wall and would produce 6 to 7 lb of spall to be disposed of from each 2-ft-dia by 10-ft-tall canister processed, various ways of preventing this oxidation were investigated. First, a protective coating was applied to the surface of the canister. A 4-in.-wide band of zirconia was plasma-sprayed onto the exterior of a canister. The band was prepared by grit-blasting and plasma-spraying with a base coat of Ni-Cr before the ZrO_2 was applied. The coating maintained its integrity throughout the melting process, while spalling was observed above and below the zirconia band. A section of the coated canister was removed for metallographic examination following the run. The ZrO_2 was well bonded to the metal. These results showed that various

plasma-sprayed coatings that had been studied at PNL could be applied to the ICM canisters to eliminate the external spall (Rasmussen 1975). However, the application of these coatings was expensive, and other ways of preventing the spall were sought.

A liner made from Hastelloy X was fabricated for the pilot-scale furnace and a canister was processed while protected by a cover of argon. The argon contained less than 400 ppm oxygen from the time heating was started until the canister had cooled to 400°C following filling with vitrified product. The canister exterior did not spall but had a flat, smooth, gray appearance that would assure a high emissivity to facilitate heat removal from the waste during storage. To achieve this surface finish the liner was not sealed tightly and an oxygen-getter was not used to remove all the oxygen from the atmosphere in the liner.

The first full-scale ICM run was also made using a liner and an argon atmosphere around the canister. Actually, the canister used in this test was heated to the processing temperature and then cooled again on three different occasions. During the first and second thermal cycles, the liner was tightly sealed with an argon purge. Neither of these actions was taken during the third thermal cycle. The exterior of the canister was like that described above following the first two cycles. After the third cycle was completed, the outside surface of the pipe and reducer used to fabricate the canister did not appear to have spalled. The pipe cap forming the bottom of the canister had spalled. This interesting result suggests that a spall-resistant surface may be produced on 304L stainless steel by proper heat treatment in a controlled atmosphere. Such a surface treatment, prepared and checked before the waste canister is committed to the solidification facility containment, is more desirable than using an inert cover gas during the ICM processing, because: 1) the remote processing equipment and procedures are less complicated, 2) the potential of a failure in the cover-gas control system resulting in spall is eliminated, and 3) effective advance inspection and assurance of the canister's outside surface quality is possible.

Another way to realize the advantages just listed is to make the canisters from a spall-resistant alloy. Several canisters used for ICM tests were made from Inconel-601. Following the ICM process at temperatures of 1110°C to 1155°C, the exterior of these canisters had become dark gray, but there was no spall. Inconel-601 was selected as the canister material for these tests not only because of its resistance to oxidation at high temperatures, but because of its strength at high temperatures and its resistance to corrosion by glass melts containing wastes from fuel reprocessing.

Work at PNL has demonstrated on an engineering scale a number of ways to prevent spall during the ICM process; however, during most tests the canisters were allowed to cool and spall in the furnaces. The spall was then removed from the furnace or the liners with a vacuum cleaner and disposed of. The benefits and economics of these methods for dealing with spall must be evaluated with respect to the unique operation and design philosophies of any particular application before a method of preventing the spall is selected.

4.3.15 PROCESS CONTROL

Because of the simplicity of the ICM process, there are only three critical process variables to monitor and control: 1) the temperature, 2) the rate of batch addition, and 3) the frit-to-calcine ratio. The atmosphere and pressure in the ICM canister are determined by the calciner to which it is coupled. The temperature in the ICM must be high enough to melt the batch, but it must not be allowed to exceed the safe operating temperature of the canister material. The connecting section and frit chute must be hot enough to prevent condensation. The batch must not be charged to the melter faster than it is melted or processing rates will be reduced and batch could be backed up into the connecting section. The frit-to-calcine ratio must be kept within the specified limits to produce a product with the desired quality. An excess of frit in a batch is wasteful. However, an excess of calcined waste produces a product with reduced leach resistance.

During the original ICM demonstrations made in the WSEP at PNL in 1970, the process temperatures were well monitored by thermocouples positioned inside

the canister on the central axis, at mid-radius and on the canister wall. Thermocouples were also placed between the canister and the furnace liner and between the liner and the heating elements. The rate of batch addition and frit-to-calcine ratio were determined by monitoring the flow rates of liquid waste to the calciner using a magnetic flowmeter and by weighing small batches of frit and periodically charging them into the funnel below the calciner. The melt level and the melting conditions in the canister were inferred from the responses of the thermocouples inside the canister.

When further development of the ICM process and equipment was progressing at PNL in 1975, these monitoring techniques were found to be inadequate for detecting plugs in the connecting section, frit chute, and funnel below the calciner. After heat-transfer plate assemblies were used in the canisters, problems of batch accumulations on the top of these assemblies were experienced. Without the aid of visual observation of the interior of the ICM through a viewport, the existing process-monitoring devices did not provide for timely detection of these processing problems. Process-monitoring techniques were needed that provided a measure of what was entering the ICM and where it was being deposited.

An additional requirement of these new process-monitoring techniques was that they would not use instrumentation that was built into or attached to the waste canister. A goal was set to develop methods of monitoring the ICM process that would make possible the elimination of the thermocouples from the canister design. Instrumentation on the waste canisters is not only economically undesirable--it also poses additional problems with making and breaking remote connections and sealing the filled canister. The connection was made more difficult when the complete canister was placed inside the furnace.

The first approach toward improved process monitoring was to locate several different types of thermal sensors inside the cone valve. They were evaluated for their effectiveness at detecting batch accumulations on the tops of the plate assemblies. None of the devices tested provided useful process control information (Dierks 1976).

The ability to weigh the ICM and monitor the rate of weight change was recognized as one means of obtaining needed process information. To accomplish

this with the pilot-scale ICM, the canister was suspended in the furnace from a load cell as shown in Figure 4.3.4. A vacuum compensator system supplied an additive signal to the load cell output that was proportional to the negative pressure in the process envelope. This signal compensated for the effects on the weight of the canister that fluctuations in pressure, caused by the filter blowbacks, had on the weight display. This system provided interpretation of the indicated weight to $\pm 1/4$ kg as it was displayed on a strip-chart recorder (Dierks 1976).

When the change to bottom support of the canisters in the full-scale ICM was made, three compression-type load cells were located under the hearth that supported the canister, as is shown in Figure 4.3.5. This weighing arrangement provided useful information about the accumulated weight in the canister, but it never worked satisfactorily for monitoring the rate of weight gain. Debris would drop into the gap between the hearth and the hole in the bottom of the furnace and cause binding with the hearth. Also, thermal expansion would cause the guides that were used to center the spout in the top of the furnace to bind. A blanket of ceramic fiber placed over the bottom of the furnace prevented debris from falling into the gap, but binding continued to disrupt the precision of the information obtained from the weighing system as the canister was filled with melt. Therefore, a new weighing system that combines load cells and piezoelectric force transducers to weigh the complete ICM furnace and its contents was recently installed on the full-scale demonstration equipment in conjunction with the remote connecting section.

The new weighing system has a load cell and a force transducer stacked together at each corner of the full-scale furnace. The cells are mounted in a force isolation frame to protect the devices when the furnace is moved for canister changeout. The new load cell arrangement, together with the new connecting section (described in Section 4.3.8) still has some binding problems. The movable furnace is difficult to align for proper engagement between the canister and connecting section. The signals from four load cells are scanned regularly by a digital computer, which averages several readings and adds the four readings together for the total furnace weight. An accurate total weight increase may be determined from this data, but the resolution of the load cells

is not fine enough to produce immediate rate data required for process control. The piezoelectric force transducers are capable of "zeroing out" any constant load on the transducer and then detecting small differences in force or weight. These transducers are sensitive to 1/3 lb; however, this sensitivity has made the output erratic, and attempts to produce a fill rate from its data by digital computational techniques have not been successful.

So that the required sensitivity of the weighing system could be established, an experiment was performed in the pilot-scale ICM to determine how long the frit-to-calcine ratio could be out of control before the resulting product was irrecoverable (Blair 1979b). At intervals the frit feeder was shut off for short periods of time so that layers of calcine 1 cm, 2 cm, and 4 cm thick would be deposited in an 8-in.-dia canister between approximately 10-cm layers of melt of the proper frit-to-calcine ratio. No strata of calcine were found in the cooled glass, but inclusions of calcine as large as 2 cm along their major axes were found dispersed throughout the product. There was a concentration of these inclusions near the bottom of the canister.

The weighing system is very useful for monitoring the rate of weight gain in the pilot-scale ICM to indicate problems with batch delivery or the frit-to-calcine ratioing system and for monitoring the total weight of the canister's contents. However, the weighing system does not tell the operator how melting is proceeding or when accumulations are forming on the top of the plate assembly. An approach using high-resolution gamma-ray spectroscopy of the radionuclides in the waste was developed and demonstrated to accomplish this (Bonner et al. 1980). The concept is shown in Figure 4.3.12. Because the relative intensity of a gamma ray is proportional to the quantity of the parent isotope and mass attenuation of the materials in the detector's line of sight, the intensity of the gamma-ray peaks can be used to indicate the presence of homogeneous melt and glass, voids in the product, unmelted frit, calcine, and deposits of isotopes in the processing equipment. The sensitivity of the technique is limited by the equivalent thickness of glass in the line of sight. A canister of waste-bearing phosphate glass produced during the WSEP demonstrations at PNL was used to determine this sensitivity. Useful information can be obtained as long as the line-of-sight equivalent thickness of glass is less than 8 in.

FIGURE 4.3.12. Gamma-Emission Melt-Level Detector for the ICM

The detector used is a 21% efficient, closed-end, coaxial, intrinsic, germanium diode. A 2408 channel analyzer, a linear amplifier, and a line printer comprise the electronics for the system. Access to the waste solidification equipment is through collimators placed in holes in the cell wall, as shown in Figure 4.3.12. The holes do not completely penetrate the cell wall or the stainless steel cell liner. The collimators, which range from 0.025 to

0.32 cm in dia, are interchangeable with lead plugs in the holes. With these collimators the resolution on the surface of the processing vessels is 2.5 cm in dia.

During the vitrification of two 8-in.-dia canisters of actual HLLW for the NWVP at PNL in 1979 (Bonner et al. 1980), this equipment was used to monitor the filling of the canisters, to determine the melt level in the canisters, to detect an accumulation of calcine in the funnel caused by a nozzle failure in the spray calciner, to evaluate ruthenium deposits in the filter housing, and to evaluate the homogeneity of the canister contents. The ability of the system to detect accumulations on the top of the plate assemblies has not been demonstrated because the canisters processed for the NWVP did not contain plate assemblies.

So that experience with operation of the ICM using gamma-level monitoring as a control parameter could be obtained, a gamma-transmission level-detector system was installed on the nonradioactive full-scale ICM furnace. A ^{60}Co gamma source was placed on one side of the furnace and a NaI detector was placed on the opposite side, as shown in Figure 4.3.13. Vertical scans of the furnace contents are made with the source and the detector using a motor-driven chain lift. Attenuation of the gamma radiation by the melt permits the melt level to be located. Attenuation by the plate assembly and thick plate forming the top of the canister provided a reference for determining the location of the melt level in the canister at any time during an ICM cycle. The ability to determine the melt level with a precision of ± 1 in. has been demonstrated with this device. In 12-in.-dia canisters with eight plate assemblies, the device was also able to detect accumulations of unmelted batch on the melt surface.

By combining information obtained from the weighing system about the mass of material in the canister and the rate of weight gain, and from the gamma melt-level detector about the height of fill in the canister, the rate of level rise, and the relative intensity of radiation at different levels in the canister, the operator can form an accurate picture of what is occurring inside

FIGURE 4.3.13. Gamma-Transmission Melt-Level Detection System
Used with Nonradioactive ICM

the melter. To demonstrate the operation of the ICM using these process monitors, 2 of the 12 canisters of simulated waste vitrified during a 10-day demonstration in the full-scale ICM were processed with the viewport into the melter blocked off and the recorder displaying the output from the thermocouples in and on the canister covered. The processing of the two canisters was controlled by monitoring the furnace zone temperatures, the flow rate of liquid feed to the calciner, the frit-charging rate, the weight of the ICM, and the level of the melt surface (Blair 1979a).

Experiments have also been made with thermocouples located close to the canister and shielded from the furnace heating elements so that the temperature of the canister wall may be monitored without having thermocouples attached to the canister (Blair and Mikols 1978). Monitoring the canister temperature is important when processing wastes with high heat-generation rates, which may raise temperatures in the melt above the processing temperature--as occurred in the WSEP demonstrations (McElroy et al. 1972).

The energy used by the nonradioactive ICM furnaces at PNL is displayed on kWh meters for process development purposes. However, after a more sensitive watt-hour meter was placed on the power supply of each zone of the full-scale ICM furnace and the instantaneous load displayed on a six-point strip-chart recorder, power use trends were more clearly observed. The maximum load per zone changes from zone to zone as the melt level rises in the canister when the temperature of each zone is automatically controlled to a fixed temperature. This power response, which was also observed by the British with the HARVEST furnace (IAEA 1976), may be used to monitor the melt level in the ICM, although it does not provide much precision when the zones are 15 in. or more high.

The connecting section must be monitored to detect blockage between the SC and ICM. The connecting section tends to plug in several ways. Plugs are usually caused by a slow buildup of material which then accentuates the problem, causing more plugging. Upon detection of plugging, the conditions should be corrected and the blockage removed. No remote mechanical clean-out methods have been tried on any connecting section plugs.

The first type of plugging in the connection section is caused by wet calcine coming from the calciner. Wet calcine may be produced in the calciner as a result of nozzle failure, heater failure, or inattention to proper process parameters. Whatever the cause, the condition is normally discovered and corrected at the spray calciner. A viscous mud may result if the nozzle fails and the failure is not detected. This produces an instantaneous plug that is very difficult to remove. Under less severe circumstances, the calcine can become damp and will not flow as well, causing the problem.

The connecting section may also be plugged up by dry calcine from the calciner becoming wet from condensing moisture from the melter off gas. If the connecting section is not insulated, or if the spout or cone valve cooling is excessive, water vapor can condense, leaving a place for dry powder to stick. A plug of this kind seems to grow thicker and go higher into the connecting section once it starts to form. If the heat loss from the connecting section is reduced, the calcine dries out and becomes very fragile. The dry plugs break out very easily (with little effort).

If the calcine sticks to the spout or cone valve as described above, the calcine can also act as an insulator to the cooling water. The surface of the calcine can get very hot if exposed to the radiant heat in the furnace. The lower melting components then begin to melt and get sticky on the calcine surface and a large glassy mass builds. One-eighth inch of calcine may be sufficient to cause the melting. This problem occurs mostly on the cone valve, but can happen in the spout. If the cone valve is too cool, moisture may condense and plug up with calcine; if it is too hot, frit can melt and plug with glass.

To detect the formation of a plug, a differential pressure cell has been added to the connecting section. The cell will measure the pressure difference from the canister to the calciner cone. A standard purged-air pressure-leg system is used. A plug would increase the pressure in the canister, causing a higher differential. The differential would be measured across the entire connecting section for pluggage monitoring, since the transitions at the calciner and melter are the likely locations for plugging. The differential pressure cell's output would be fed to a recorder and an alarm unit. The recorder is preferred because it allows trends to be spotted, possibly for the early detection of plugging conditions. Thus far this system has only been effective during a total blockage of the connecting section. An additional method of detection has been tried on the experimental melters. The melter weighing system will show the lack of weight gain due to blockage in the connecting section.

Temperatures at the cone valve and spout are important in the prevention of plugging, as described above. The proper operating temperature range

appears to be around 200⁰ to 300⁰C. Air-cooling was attempted, but cooling was not adequate to bring the temperature into the proper range. Water-cooling has also been used, but steps must be taken to prevent evaporation of cooling water. Surface temperatures in the flooded chamber of the cone valve were 50⁰ to 80⁰C, and 60⁰C in the spout. The exterior surface of these components remained clean during normal material flow. At one point a calciner nozzle failed, dumping moist batch through the connecting section. The batch stuck to the cone valve, forming an insulation barrier that caused subsequent melting of batch there. It is interesting to note that after the batch flow was interrupted the accumulated batch fell away from the cone valve, suggesting a potential benefit of maintaining at least the conical surface of the cone valve at a temperature considerably below the 300⁰ to 400⁰C target. To monitor the temperature, thermocouples were placed inside the cone valve. They were held in place by bending the thermocouple and using the spring tension to force them into position at the wall. The resultant temperature measurements were responsive and appeared accurate.

As described in Section 4.3.8, the lower slide, which is directly connected to the cone valve, can be used as an indicator of spout retraction, canister sealing, and cone valve position or opening. The slide position can be monitored remotely for control area information. It would be desirable to know the condition of the connecting section and canister during the operation of the power screw. Proximity indicators could be installed in appropriate locations on the slide frame to monitor the position of the slide and the condition of the spout and cone valve. A proximity indicator at the top of the slide travel would show physical presence of the slide, limiting power-screw operation, while guaranteeing sufficient retraction of the spout. Single or double indicators at the weight transition point for sealing would verify that the slide stopped in the proper position and would indicate when the slide started dropping again. Once the slide starts to drop again the canister is going to experience the calciner's environment. Finally, a series of indicators could signal cone valve opening, which will be adjusted to provide batch distribution and to prevent bridging on the fins. Alternative slide wire or Linear Voltage Differential Transducer (LVDT) systems could give a continuous

reading at position. The continuous reading with a graphical output would provide a meaningful picture of each canister fit-up.

4.3.16 HISTORY OF ICM PROCESS

One of the early solidification processes conceived of for the treatment of HLLW was the FINGAL process developed at Harwell, England (Elliot et al. 1960). This process converted the HLLW to a borosilicate glass by adding glass formers such as boron, sodium, and silicon as soluble salts or oxides to the HLLW and by feeding the slurry into a canister that was heated in a furnace. The mixture was dried, then calcined (converted to oxides), and finally melted to form a glass in the canister, which became the disposal container for the vitrified waste.

At about the same time the FINGAL process was being developed in England, the pot-calcination process and a variation of it--the rising-level glass process--were being developed at Oak Ridge National Laboratory (ORNL) in the USA (Clark et al. 1966). These processes were batch operations that included concentrating the HLLW in a heated pot to a salt cake and then denitrating the cake at high temperatures to produce porous, friable calcine. In the rising-level glass process, additives were put in to the HLLW before they were fed to the pot so that a phosphate glass melt formed when the dried cake was heated to 805°C.

Between 1966 and 1970, various waste solidification processes including the ORNL processes were demonstrated on an engineering scale with radioactive materials in the WSEP program at PNL (McElroy et al. 1972). In the spring of 1970 a variation on the ORNL rising-level glass process was demonstrated in the WSEP program. A heated-wall spray calciner was used to convert the HLLW to a calcine (Bonner, Blair and Romero 1976). The calcine flowed directly from the calciner into a heated steel pot. Borosilicate glass formers that had been premelted and cooled to form a frit were added to the pot as it filled to produce a glass melt. When the pot was filled with melt, it was cooled to produce a vitrified waste form. This innovation in the rising-level glass

process significantly improved the glass production rate. Two pots of vitrified HLLW were produced by this "in-pot melting" process in the WSEP program (McElroy et al. 1972).

In 1974, further development of the in-pot melting process (which had become known as ICM) for HLLW vitrification was undertaken as part of the WFP (now the HLWIP) at PNL. This developmental work was conducted in nonradioactive facilities at PNL using simulated HLLW.

The first objective of the ICM phase of the WFP was to demonstrate that the borosilicate glass compositions developed since 1970 for HLLW vitrification could be melted in pilot-scale canisters made of 304L stainless steel. The second objective was to evaluate compatibility of the ICM with various HLLW calciners and concentrators being developed at PNL. As Figure 4.3.14 shows, the pilot-scale ICM was demonstrated coupled to a heated-wall spray calciner, to a fluidized-bed calciner, and to a wiped-film evaporator.

The third major objective of the ICM development task at PNL was to determine what melting rate could be achieved in the ICM and what the factors were that controlled the rate. Early in the WFP the goal was to demonstrate that the process had a melting rate in excess of 48 kg/h, which was the rate required to support a reference light-water-reactor (LWR) fuel-reprocessing plant having a 5-MTU/d capacity (Larson et al. 1978). Later, as attention turned from fuel reprocessing to the vitrification of the high-level defense wastes that are presently stored in liquid form in underground tanks, melting rates of 100 kg/h became desirable.

The initial melting-rate determination tests were made in the single-zone pilot melter using 8-, 12-, and 16-in.-dia canisters. Various batch compositions, batch-charging methods and heat-transfer plate designs were used in these early tests. Because the calcine production rate of the pilot-scale spray calciner was not sufficient to match the maximum melting rate in even the 8-in.-dia canisters, the batch used for these rate-determining tests was a blend of frit and calcine produced earlier by long calciner campaigns. The portions of frit and calcine were weighed, blended in a mechanical batch-mixer and charged to the melter using a volumetric screw-feeder.

SPRAY CALCINER

FLUIDIZED-BED CALCINER

WIPED-FILM EVAPORATOR

FIGURE 4.3.14. Pilot-Scale ICM Coupled to Spray Calciner, Fluidized-Bed Calciner, and Wiped-Film Evaporator

Later, when a full-scale spray calciner and multizone ICM capable of processing 28-in.-dia, 7-ft-tall canisters became operational, the ICM was run coupled directly to the calciner because it could produce calcine at any rate required to test the capacity of the melter. The frit was added to the full-scale ICM at a rate proportional to the calcine-generation rate by a gravimetric feeder, which provided very good control of the frit-addition rate. The batch-melting rates in canisters ranging from 12 to 28 in. in dia were determined using this system. The majority of the canisters contained drop-in heat-transfer plate assemblies, although several canisters used to process simulated defense waste did not. Two simulated waste compositions were used in the full-scale melter tests. The first used was representative of wastes expected from the Allied General Nuclear Services plant in Barnwell, South Carolina (Mendel et al. 1977). The other represents the defense waste stored at the Savannah River site in South Carolina.

4.3.17 MELTING RATE

Figure 4.3.10 presents melting rates demonstrated at PNL in different-diameter canisters. Because the objective of the development program at PNL was to determine the highest processing rates possible in the ICM, the diameter of the canister is not the only variable that was changed to achieve the rates reported (Blair 1979b). The maximum rates reported are those that could be sustained while melting in the lower half of the canister when there are large areas of heated surface for the batch to melt on as it enters the canister. As the canister fills, the surface area and the melting rate decrease. The average rates presented in Figure 4.3.10 are those rates that can be sustained during the filling of a canister without overcharging the canister with unmelted batch when using the rising-level batch-charging methods. All of these rates were demonstrated in canisters containing heat-transfer plate assemblies. As the canister diameters increased, the number of radial plates inside also increased (Section 4.5). The rates demonstrated in a 24-in.-dia canister are below the curve because there were only 10 plates in the assembly, while 16 plates were used in the assemblies in the 20- and 28-in.-dia canisters. Assemblies comprised of eight plates were used in the 8-, 12- and 16-in.-dia

canisters. The batches melted during these rate demonstrations were all blends of frit and calcine obtained by spray-drying nitric acid solutions of simulated HLLW. However, the waste and the frit compositions and the calcine-to-frit ratios varied from run to run.

During the development effort to achieve maximum ICM melting rates, the following factors were determined to affect the rate:

- operating temperature
- batch preparation
- addition of reducing agents
- batch-charging methods
- canister diameter
- internal heat-transfer plates
- waste and frit composition
- distribution of batch in the canister
- zone heating of the canister.

These factors were investigated to varying degrees, depending on how significant their influences on the melting rate appeared to be.

Figure 4.3.15 presents some data obtained early in the ICM development program that shows the effect of furnace temperature on the batch-melting rate. Because it was obvious that the maximum temperature was desirable for achieving high melting rates, the highest temperature at which canisters made of Type-304 stainless steel could be safely processed was determined and all subsequent runs were made at this temperature--i.e., 1050⁰ to 1070⁰C. Some tests were made in canisters fabricated from Inconel-601 alloy at temperatures between 1100⁰C and 1150⁰C, but these were not rate-determining runs.

The degree of mixing of the calcined waste and glass-forming frit has an effect on the rate at which the batch melts (Green 1975), but the effects of batch-mixing on the melting rate were not studied in the ICM. The advantages of discharging the calciner directly into the melter and the disadvantages of having a mixer in the solidification process, which are discussed elsewhere in this document, were considered sufficient to supersede any improvements in the melting rate that may be realized by mixing the batch. Both premixed batch

FIGURE 4.3.15. Melting Rate as a Function of Surface Temperatures for a 12-in.-dia Canister

and proportionally fed streams of frit and calcine were melted in the in-can melters and no significant differences in melting rates were noted. Nor was any obvious difference observed between the melting rates of batch containing hot calcine directly from the calciner and of batch that was cool. Preheating the frit was suggested as a means of increasing the melting rate, but this was not demonstrated.

The particle size of the materials in the batch also has an effect on the melting rate. Two batches were prepared by blending the frit and calcine in a mixer. One batch contained frit that was sized -6/+20 mesh, and the other was prepared using -325 mesh frit. Batch melting rates of 5.5 kg/h and 7.7 kg/h, respectively, were demonstrated for the two batches. However, the batch containing the finer frit presented serious conveying problems. Frit sized to -20/+80 mesh is easy to meter and convey, and produces a satisfactory product.

Some tests were made using concentrated, simulated HLLW from a wiped-film evaporator (WFE) instead of calcine in the batch fed to the melter. These rates are similar to those obtained with the HARVEST process (IAEA 1976). The solids content of the concentrate used in these tests ranged between 20.5 wt%

and 36.5 wt%. The frit was proportionally added to the concentrate as it dropped from the WFE into the ICM. Liquid-batch charging to the ICM is not recommended because it greatly reduces the melting rate and causes some serious problems with entrained solids in the melter exhaust (Grover et al. 1966).

When powdered silicon metal was added to the batch to prevent the formation of alkali metal molybdate phases in the glass (Ross 1978a), an improvement in the melting rate was anticipated due to the heat released in the batch by the oxidation-reduction reaction. However, results obtained in both the pilot-scale and in the full-scale in-can melters indicated that if the addition of 1.5 wt% powdered silicon contributed to the melting rate of the batch, it was not significant enough to be detected in the process demonstration equipment. The equipment did detect a 20 to 45% decrease in the power required by the furnace to melt batches containing the additive. These results suggest that the melting rate is not just a function of heat transfer, but the mass transfer may also be a controlling factor.

How the batch is charged to the ICM does have a significant effect on the melting rate. The initial hypothesis tested was that the maximum melting rate for any diameter canister would be achieved by having the incoming batch in contact with a maximum of heated surfaces of the canister at all times during the melting operation. Therefore, canisters were either filled with batch and lowered into the preheated furnace or hot canisters were rapidly charged with batch until they were full. These levels were maintained by adding batch as the melting proceeded. This ICM charging method was called the batch-melting method. The melting rates obtained using this charging method were calculated by dividing the mass of batch charged by the time required for the centerline temperatures to reach 1000°C. These rates are presented in Table 4.3.5.

The results obtained with this batch-melting method were unsatisfactory in larger-diameter canisters, in which the melting proceeded slowly because 1) heat transfer in the powdered batch was poor, and 2) as the batch did melt, gases were generated that were then trapped in the viscous melt and created an insulating foam. Consequently, the rising-level melt-charging method was tested; this method continuously charged batch to the ICM at a rate equal to

TABLE 4.3.5. In-Can Melting Rates and the Parameters that Affect Them

Can Dia, in.	Number of Plates	Charging Method	Melting Rate, kg/h
8	0	Batch	10
8	8	Batch	29
		Rising-level	>20
8	8	Rising-level	>27.5
8	0	Rising-level	>13
8	0	Batch	5.5 to 7.7
		Rising-level	>13 < 18
12	0	Batch	17
		Rising-level	14.5
12	8	Batch	25
		Rising-level	<54
12	8	Rising-level	50
12	10	Batch	36
		Rising-level	>47

or just less than the rate at which it was melting. An insulating pile of batch was not allowed to accumulate, and the gases released during melting, which only occurred at the melt surface, easily escaped. Charging the ICM using the rising-level method resulted in melting rates higher than those achieved with the batch-charging method, as the data in Table 4.3.5 show.

Determining the exact melting rate became less quantified when using the rising-level method. The judgment of whether or not a batch-charging rate was exceeding the capacity of the ICM to melt the batch were based on: 1) what the melt-surface temperature was as it passed over a centerline thermocouple, and 2) how long it took for the melt temperature to return to the operating temperature after the thermocouple was submerged. Surface temperatures of 100°C or more below the operating temperature and one hour or more for the melt temperature to return to the operating temperature indicated that the charging rate was exceeding the melting rate. Also, the relationship between the fill height, as indicated by a thermocouple located on the central axis of the

canister, and the mass of batch charged to the canister was a good indication of whether the canister was filling with melt or with lower-density batch or foam. The melt surface was also visually observed to decide whether or not the melting capacity of the ICM was being exceeded. The gamma-emission melt-level detection system should contribute significantly to quantifying melting rate determinations because it not only locates the melt surface accurately, but also measures the thickness of unmelted material on that surface.

The data in Table 4.3.5 also shows that the melting rate is nearly doubled when radial heat-transfer plates are located inside the canister to improve heat transfer between the wall and the batch in the center of the canister. Inclusion of these plates in the canister was originally proposed to keep canister centerline temperatures down during transportation and storage, when vitrified wastes having high heat-generation rates were to be encapsulated in large-diameter canisters (Jansen and Kaser 1974).

The effect of different numbers of heat-transfer plates is presented in Figure 4.3.16. Each line represents a different-diameter canister and a different feed composition. The changes in composition make a direct comparison between the different canister diameters difficult. Also, each set of data is small, having only two or three data points. However, the slope of each line is not radically different, suggesting that overall mechanisms do not change as the canister diameter increases. The 24-in.-dia canister without fins is particularly low because the run was not rate-determining; the canister was filled at a steadier rate due to a foaming problem with this composition, as discussed below.

It was found that attaching the plates to the inside of the canister resulted in their being distorted during the ICM process because of the difference in thermal expansion between the glass and the metal and/or between the shell and fins. Therefore, the drop-in plate assembly design, such as the one made for use in a 24-in.-dia canister and shown in Figure 4.3.17, were adopted. The bends on the outside edges of the plates are intended to improve the heat transfer with the canister, and the bends were used on all plate assemblies put in canisters over 20 in. in dia.

FIGURE 4.3.16. Melting Rate with Different Canister Sizes and Numbers of Heat-Transfer Plates

To reduce the number of different-sized canisters and the variety of fin assemblies to a common parameter, the heat-transfer area has been calculated for each run. Figure 4.3.18 presents the data of peak melting rates for melter runs done either with premixed feed or with the ICM coupled to the SC. The line represents the linear regression analysis of 30 runs. As expected, the error bar showing the 2Y confidence level indicates a large scatter in the data. This scatter reflects the variability of the other parameters discussed in this section. This correlation is hampered by a lack of usable data at the high-surface-area end of the figure. The heat-transfer data was calculated from the inside diameters of the filled portions of the canisters. The portions of the canisters above the plates extending outside the furnace was not included, even though some of that area is heated. Also, both sides of the plates were included in the area, although all of this area is probably not effective heat-transfer area.

FIGURE 4.3.17. Drop-In Heat-Transfer Plate Assembly for 24-in.-dia Canister

FIGURE 4.3.18. Melter Capacity

During the development of the ICM process at PNL, over 14 different simulated waste compositions and 12 different frit compositions were used in various combinations (Blair 1979b). Most of these wastes were in the form of a nitric acid solution. When these acidic wastes were calcined, all but the alkali metal nitrates were decomposed. These residual nitrates decomposed in the melter at temperatures lower than those at which the frit began to melt. Therefore, as long as the rising-level melt-charging method was used no foaming of the melt occurred.

When the batch compositions released gases after a viscous melt had formed, as with some neutralized high-iron-content wastes and high-alkali-content frits with low softening temperatures, the melt foams and significantly reduces the melting rate. Table 4.3.6 shows the maximum melting rates obtained in 8-in.-dia canisters with eight plate assemblies when using batches that foam while melting. These rates are 1/3 to 1/2 the rates possible with a batch that

TABLE 4.3.6. Effects of Foaming Batch on Melting Rates

Run No.	Charging Period, h	Charging Rate, kg/h	Energy, kWh	Expected Melt Level, in.	Estimated Foam Level, in.
1	1-1/2	12	15.5	9.3	14
1	1/2	22	16	14.8	21
1	1/2	32	18	20.3	37
2	1/2	14	18	3.6	None
2	1/2	20	22	8.7	12-13
2	3/4	30	23	19.7	32

does not foam. Rates in large-diameter (24-in.) canisters with high-iron feed tend to be variable because of foam-induced shutdowns. The foam forms and rises up the canister enough to interfere with heat transfer and to pose a plugging threat to the canister mouth. Even the peak rates are 10% to 20% lower than in other wastes. The peak rates are usually measured as the bottom of the canister is filled, since foam is less of a problem and available heat-transfer area is greater.

During the processing of the first 12-in.-dia canister in the ICM, the need to direct the incoming batch away from the relatively cool center of the canister and towards the hotter walls was obvious. Later, when heat-transfer plate assemblies in the canisters and a sloping leg in the connecting section between the calciner and the ICM were used, the need to uniformly distribute the batch into all the sections created by the plates was recognized as being necessary to achieve the maximum melting rate. The water-cooled cone valve with deflector plates on its stem was developed to meet these needs, as well as to close off the end of the connecting section during canister exchanges so that calcined waste was not spilled. The deflectors on the stem distributed the batch uniformly over the area of the opening in the top of the canister. The cone located just inside the canister then deflected this batch away from the center and toward the walls of the canister. The effect of the cone and deflectors on the melting rate has not been evaluated independent of other variables and therefore cannot be quantified.

Early experience with the single-zone furnace used with the pilot-scale melter showed the importance of a multi-zone furnace. Multiple zones would permit compensation for heat losses through the top of the melter and maximum energy concentration at the rising melt surface without overheating that part of the canister where melting was completed. The maximum melting rate achieved in a 16-in.-dia canister was 8% better in the zoned full-scale melter than in the pilot melter.

During the initial runs in the full-scale multizoned furnace, charging was started with the top zone of the furnace off to keep the temperatures low around the load cells and connecting section hardware above the furnace. As the canister filled with melt the lower zones were turned off, and when the canister was half full the top zone was turned on. However, the best melting rates and the fewest problems with batch accumulating at the top of the plates was achieved if all the zones of the furnace were maintained at the melting temperature during the entire filling cycle.

Data from the kWh meters on the power supplies for the full-scale ICM furnace zones show that 10 to 17% more power was used in the upper half of the furnace than in the lower half during a filling cycle. This suggests that much of the batch-melting occurs before it reaches the melt surface and explains why melting rates are so high in the first half of a canister-filling campaign.

The melting rates and the techniques for obtaining them described in this report were developed using nonradioactive, simulated wastes that have no internal heat generation. High-level nuclear wastes can generate up to 150 W/L of vitrified product. The amount of heat generated depends on the burnup of the fuel processed, the age of the waste, and the waste-loading in the host glass. This self-heating will have a definite effect on the way the ICM temperature profile is controlled during a filling cycle, and it may also affect the melting rate and the power required. During a radioactive ICM demonstration at PNL in 1970 nearly 317 kg of radioactive borosilicate glass were produced in two 8-in.-dia canisters that did not contain heat-transfer plates (McElroy et al. 1972). The vitrified products of the two runs had heat-generation densities of 90 W/L and 200 W/L, respectively. Melt centerline temperatures reached 1040°C during the melting, while the furnace was operating at

only 900° to 950°C. Power to the lower zones of the furnace was shut off and the canister below the melt level had to be air-cooled to keep the melt temperature from increasing further while batch-charging and melting was still proceeding in the upper half of the canister.

4.4 OFF-GAS TREATMENT

K. H. Oma

4.4.1 GENERAL DISCUSSION

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 to meet release regulations on both radioactive and nonradioactive constituents.

Nearly all of the gaseous effluents from both neutralized and acid HLLW waste are condensable. Most effluents that are not condensable can be adsorbed or absorbed (excluding air from atomization, inleakage, etc.). Both condensable and noncondensable streams must be continuously discharged to the atmosphere following treatment. Liquid effluents from the off-gas cleanup system must be treated so they are acceptable for recycle or for final release to the environment. Radionuclide removal is complicated, and is made more difficult by the relatively large quantity of air always present in the equipment off gas.

Calcliner effluent streams from the SC/ICM flowsheets are treated initially for particulate removal and then are cooled sufficiently to remove the bulk of the condensables. Volatile ruthenium-106 may be of significant concentration in the process off-gas (POG) stream and require treatment such as adsorption for removal. Mercury vapor can be present in defense flowsheet off gas, and although no radioactive isotopes are present, special treatments consisting of condensation and sorption are required for its removal. Iodine-129 and nitric oxides are present in the acid HLLW processing and require removal by sorption or destruction.

4.4.2 SOURCE TERMS

4.4.2.1 Particulate

Due to the small particle size of the spray-dried calcine, 15 to 50% of the solids are entrained in the calciner off-gas stream. The bulk of the

larger particles are removed by sintered-metal filtration and spray-scrubbing, while the smaller particles are removed by several stages of HEPA filtration.

Typical calcine particulates formed by vitrification of caustic defense waste are of the composition presented in Table 5.2.2 and those particulates formed by vitrification of acid commercial waste are of the composition presented in Table 5.2.6. Of the total activity present in calcine described, about 40% comes from the radioisotopes ^{137}Cs , ^{90}Sr , and ^{144}Ce . It is important to note that calcine produced by the acid commercial flowsheet contains 4.42 Ci/g compared to 1.69 Ci/g for that produced by the caustic defense flowsheet.

Calcine powder particle-size distributions are shown as histograms in Figure 4.2.7 and 4.2.8. These histograms were obtained by U.S. Standard sieve analysis, Fisher subsieve analysis, Zeiss particle size analysis, and Quantimet 720 projection size distributions (Hanson 1980).

4.4.2.2 Volatile Fission Products

Elements in the HLLW that are known to be volatile include tritium, krypton and iodine. Of the tritium present in spent fuel, 8% of it is assumed to be present in the HLLW in the form of tritiated water. Because at present there are not special requirements for tritium control, no discussion on the subject will be given. The krypton content of HLLW is extremely small. Krypton control will likely not be necessary in a waste solidification facility, as the release should be negligible. The HLLW from power-reactor fuel may contain up to 27% of the iodine in spent fuel. Iodine will most likely completely volatilize in any high-temperature process. The iodine in high-level defense waste will also probably all volatilize, although some may be chemically tied up with other materials, such as mercury.

Fission products of importance that are potentially volatile in a waste solidification process include selenium, technetium, ruthenium, rhodium, antimony, tellurium, and cesium. Due to typically higher concentrations, ^{106}Ru , ^{134}Cs , and ^{137}Cs require the highest DF's. Rhodium-106 is a short-lived daughter product of ^{106}Ru ; thus, any treatment that removes ruthenium will effectively remove rhodium (^{106}Ru has a half-life of 29.9 s).

In general, it is felt that if effluent treatment systems are designed for adequate control of iodine, ruthenium and cesium, then more than sufficient cleanup will be provided for all other fission products.

Ruthenium-106 is the most important potentially volatile radionuclide present in typical HLLW since it has a high activity and because anywhere from 0.002% to virtually 100% can volatilize, depending on the processing conditions, mode of heating, cover gas composition, etc. Elemental ruthenium itself cannot be considered volatile at waste solidification temperatures, since it has a melting point of 3210°C and a boiling point of 3900°C . However, in oxidizing atmospheres at temperatures above 800°C , the formation of gaseous RuO_4 takes place. RuO_4 has a melting point of 25.5°C and a boiling point of 108°C . At higher temperatures, gaseous RuO_3 is formed by the reaction of O_2 or NO_2 with RuO_2 . The RuO_3 formation reactions become more thermodynamically favorable as the temperature increases. At temperatures below 800°C in the presence of nitric acid, ruthenium apparently forms the stable complex, nitrosyl nitrate. The vapor species can be quite stable as the gases are cooled and must be treated for removal.

M. S. Hanson (1980) performed ruthenium and cesium loss studies on the full-scale SC/ICM using commercial acid HLLW at PNL. Overall average losses through the calciner sintered-metal filters were 0.045% for ruthenium (range 0.001% to 0.16%) and 0.042% for cesium (range nondetectable to 0.132%).

4.4.2.3 Volatile Nonfission Products

Potentially volatile nonfission products of importance in defense wastes are fluoride, chloride, sulfur and mercury. The primary problem caused by volatile fluoride, chloride and sulfur is corrosion to the off-gas system, while mercury is a problem due to its toxic nature and potential sorption-bed poisoning. Removal of fluoride, chloride and mercury is readily accomplished by an ejector venturi scrubber, cyclone separator, and mercury condenser (about 10°C). To prevent chloride- and fluoride-caused corrosion, Inconel-625 or Hastelloy-B appear appropriate for construction of the sintered filters, ejector, venturi and cyclone.

Potentially volatile nonfission products of importance in acid wastes are chloride and nitric acid. Due to the potential of chloride-caused corrosion, Inconel-625 or Hastelloy-B again appear to be appropriate materials for acid-flowsheet sintered filters and the wet-scrubbing system components. Nitric acid in the waste is converted primarily to NO_x upon calcination. Up to 60% of the NO_x can be removed by the quench tower and venturi scrubber/cyclone separator. The remainder may be reacted with NH_3 to form N_2 and H_2O vapor in a NO_x destructor.

4.4.3 TREATMENT PROCESSES

4.4.3.1 Filters

High-Efficiency Particulate Air Filters

High-Efficiency Particulate Air (HEPA) filters have proven to be the most effective, reliable, and economical devices for removing low concentrations of submicron particles at extremely high (greater than or equal to 99.97% for 0.3- μm -dia particles) collection efficiency. By definition (Burchsted et al. 1976), a HEPA filter is "a throwaway, extended-medium, dry-type" filter having 1) a minimum particle removal efficiency of no less than 99.97% for 0.3- μm particles, 2) a maximum resistance (when clean) of 2.54 cm (1.0 in.) wg when operated at rated airflow capacity, and 3) a rigid casing extending the full depth of the medium, as shown in Figure 4.4.1.

Principles of Operation. Particles down to sub-micron sizes are removed from the gas stream by mechanical filtration through a special filter medium.

Engineering Data. The dimensions shown in Table 4.4.1 have been standardized for HEPA filters used in nuclear service (Burchsted et al. 1976). Other sizes can be obtained but should be considered as specials. Although the 61 x 61 x 150-cm (24 x 24 x 5-7/8-in.) size is included, it is structurally weak and should be avoided. The airflow capacities shown are nominal for the specified maximum resistance of 2.54 cm (1 in.) wg. Although some manufacturers claim substantially higher airflows at this resistance, the values shown in Table 4.4.1 should be used for design purposes.

FIGURE 4.4.1. Construction of Open-Face HEPA Filter

Decontamination factors of 10^3 for particulates and 1 for all gaseous or volatilized components have been reported for HEPA filters used during fluid-bed calcination of HLLW (Christian and Rhodes 1977).

HEPA filter papers are composed of very fine (submicron-diameter) fibers in a matrix of larger-diameter (1- to 4- μ m) fibers. An organic binder is added to hold the fibers during the papermaking process and to give added paper tensile strength. Fire-resistant filter papers are required for SC off-gas applications and are made from glass fibers, sometimes with a small percentage of asbestos added to improve resistance to hydrogen fluoride. Tensile strength of the paper is sharply reduced (about 50%) at temperatures above 400°F due to burnout of the binder (Burchsted 1968).

The usual case materials are fire-retardant exterior-grade plywood or wood-particle board and chromized or cadmium-plated carbon steel. Thickness of 1.9 cm (3/4 in.) for wood and No. 14 U.S. gage for steel are required for

TABLE 4.4.1. Standard HEPA Filters

<u>Face Dimensions, cm (in.)</u>	<u>Depth, Less Gaskets, cm (in.)</u>	<u>Design Airflow Capacity at Clean-Filter Resistance of 2.54 (1.0 in.) wg, sLm (scfm)</u>
61 x 61 (24 x 24)	29.2 (11-1/2)	28,300 (1000)
61 x 61 (24 x 24)	14.9 (5-7/8)	14,200 (500)
30.5 x 30.5 (12 x 12)	14.9 (5-7/8)	3,540 (125)
20.3 x 20.3 (8 x 8)	14.9 (5-7/8)	1,420 (50)
20.3 x 20.3 (8 x 8)	77.8 (3-1/16)	700 (25)

rigidity and to resist the compressive loads imposed when the filter is clamped to a mounting frame (axial compressive loads of 2760 kPa (400 psi) or higher may be encountered in service) (Burchsted et al. 1976).

Other factors (heat, moisture) being equal, wood-cased filters are preferred to steel-cased filters because of their greater rigidity, superior vibration-damping characteristics, greater corrosion resistance, and greater corner strength (MIL-F-51079).

Resistance to shock pressures is important in a HEPA filter because it is often the final barrier between the contaminated space and the atmosphere. The shock overpressure resistance of open-face rectangular filters, based on tests by the U.S. Navy (Anderson and Anderson 1966), is given in Table 4.4.2.

Tables 4.4.3 and 4.4.4 give limiting continuous-service temperatures for wood- and steel-cased HEPA filters, based on sealants commonly used for sealing the core into the case (Burchsted et al. 1976). Filters with both types of cases are designed to withstand temperatures to 399°C (750°F) for 5 to 10 min. Continuous operation at high temperatures is limited primarily by the sealant. At temperatures well below the char or "checkering" point, elastomeric sealants lose their shear strength [from about 5860 kPa (850 psi) at room temperature to as low as 103 kPa (15 psi) at 149°C (300°F)].

Because HEPA filters are excellent collectors of very small particles, they are likely to plug when subjected to high loadings of sensible moisture,

TABLE 4.4.2. Shock Overpressure Resistance of Open-Face HEPA Filters

Filter Dimensions, cm (in.)		Overpressure, kPa (psig)	
		Overpressure at Failure	Recommended Design Limit for Used Filters ^(a)
Face	Depth		
61 x 61 (24 x 24)	29.2 (11-1/2)	22.1 (3.2)	12.4 (1.8)
61 x 61 (24 x 24)	14.9 (5-7/8)	15.2 (2.2)	8.3 (1.2)
30.5 x 30.5 (12 x 12)	14.9 (5-7/8)	24.8 (3.6)	13.8 (2.0)
20.3 x 20.3 (8 x 8)	14.9 (5-7/8)	31.0 (4.5)	17.2 (2.5)
20.3 x 20.3 (8 x 8)	7.78 (3-1/16)	25.5 (3.7)	13.8 (2.0)

(a) Without face guards.

TABLE 4.4.3 Recommended Limiting Service Temperatures for Steel-Framed Fire-Resistant HEPA Filter Units Sealed with Elastomeric Adhesives

Sealant Used	Temperature to Which Filter Was Exposed, °C (°F)				
	Up to 10 min ^(a)	Up to 2 h	Up to 48 h	Up to 10 days	Indefinitely
HT-30-FR ^(b)	399 (750)	177 (350)	163 (325)	149 (300)	127 (260)
Z-743 ^(c)	399 (750)	163 (325)	149 (300)	135 (275)	93 (200)
EC-2155 ^(d)	399 (750)	121 (250)	104 (220)	93 (200)	93 (200)
Polyurethane foam	399 (750)	163 (325)	149 (300)	135 (275)	110 (230)

(a) Some reduction in efficiency may occur after 5 min of exposure.

(b) Goodyear.

(c) Pittsburgh Plate Glass.

(d) Minnesota Mining Manufacturing (3M).

dust or smoke. Dust plugging is reduced by the use of effective prefilters, and moisture plugging is minimized by the use of a demister and by assuring the off-gas temperature is well above the dewpoint.

Demister

The demister (mist eliminator) removes droplets from off-gas streams and will protect prefilters and HEPA filters from damage or loss of function due

TABLE 4.4.4. Recommended Limiting Service Temperatures for Wood-Framed Fire-Resistant HEPA Filter Units^(a)

Frame Material	Temperature to Which Filter Was Exposed, °C (°F)				
	Up to 10 min	Up to 2 h	Up to 48 h	Up to 10 days ^(b)	Indefinitely ^(b)
3/4-in.-thick plywood	399 (750)	149 (300)	135 (275)	93 (200)	82 (180)
3/4-in. wood-particle board ^{(c),(d)}	399 (750)	149 (300)	121 (250)	82 (180)	82 (180)

(a) Subject to sealant limitations given in Table 4.4.3.

(b) Maximum temperature of 49°C (120°F) where relative humidity is 75% or higher.

(c) Exterior-grade, fire-retardant-treated.

(d) Minimum density = 0.72 g/cc (45 lb/ft³).

to moisture entrained from off-gas equipment handling solutions such as a venturi scrubber/cyclone separator and the condenser.

Principles of Operation. Entrained liquid particles are effectively removed by passing the COG stream into the demister vessel and through a fine-meshed pad. Water particles are collected on the mesh, then form droplets that return to the demister floor and are drained to the scrubber recycle tank.

Engineering Data. With condensing steam, most of the entrained water droplets will be in the size range of 1 to 20 μm (Perry 1963). Droplets in this range pose the greatest threat to HEPA filters because droplets larger than 20 μm are readily removed, and the mass of free water represented in droplets smaller than 1 μm is too small to pose a likelihood of plugging. Within the 1- to 20- μm range, however, free water cannot be removed by inertial separation alone, and use of a more effective and higher pressure-drop devices is required.

Packed-fiber mist eliminators have given excellent performance for acid fumes in industrial service and can be tailored by selection of glass fibers and other construction materials for use.

Brink® demister designs of the type shown in Figure 4.4.2 with collection efficiencies for submicron particles up to 99.98 wt% have been demonstrated on large-scale industrial processes (Brink 1964, Brink et al. 1968). The mechanisms of mist separation for this type of element are diffusion, impaction, and inertial effects, with diffusion controlling for submicron particles.

Collection efficiencies of 100% on particles larger than 3 μm and up to 99.98% on the remaining particles 3 μm and smaller are claimed by Monsanto Enviro-Chem® for certain Brink mist eliminator designs and operating conditions.

A conservative DF of 10^2 for particulate removal (Christian and Pence 1977) has been used for the acid-waste flowsheet mist eliminator.

FIGURE 4.4.2. Brink H-E Series Mist Eliminator Element

®Monsanto Enviro-Chem Systems, Inc., Air Pollution Control Dept. Technical Bulletin BSA-1, 800 N. Lindburgh Blvd., St. Louis, Mo.

4.4.3.2 Cyclone

A cyclone separator is used to separate atomized solution and particulates from the off-gas stream. The cyclone is very efficient at removing relatively high loadings of large particles ($55\text{ }\mu\text{m}$) that exist downstream of a venturi scrubber.

Principles of Operation. Off gas and scrub solution enter the cyclone tangentially near the top. The scrub solution and larger particles are moved by centrifugal force against the cyclone wall and drain out the lower cone section, while the off gas exits through a center pipe near the top of the cyclone.

Engineering Data. The dimensions of the cyclone are specified by diameter, D , and seven dimensions ratios: a/D , b/D , D_e/D , S/D , h/D , H/D , and B/D (Figure 4.4.3). A number of cyclone "standard designs" or sets of dimension ratios have been suggested in the literature (Rao et al. 1975). Several are listed in Table 4.4.5. No single cyclone design will perform best for all particle collection problems.

High-efficiency cyclones (characteristic of designs 1 and 2, Table 4.4.5) are typically 100% efficient for removal of particles larger than $40\text{ }\mu\text{m}$, greater than 85% efficient for $10\text{-}\mu\text{m}$ particles, and greater than 60% efficient for $5\text{-}\mu\text{m}$ particles. Collection efficiencies drop off very fast for particles smaller than $5\text{ }\mu\text{m}$. Cyclone efficiencies for a given particle size increase with increased pressure drop, decrease with increased gas temperature and remain relatively constant with changing particle loadings (Rao et al. 1975).

Particulates produced by spray nozzles typically range in size from sub-micron to greater than $600\text{ }\mu\text{m}$ (Perry 1963). Anywhere from 95 wt% to 98 wt% of such particles are larger than $50\text{ }\mu\text{m}$, while over 99% are larger than $10\text{ }\mu\text{m}$.

A cyclone particulate DF of 10 is assumed for flowsheet material balance purposes (Christian and Rhodes 1977); however, the DF for entrained water is much higher.

FIGURE 4.4.3. Cyclone with Typical Design Parameters

4.4.3.3 Scrubbers

Ejector Venturi

The ejector venturi may be the first off-gas treatment device following the sintered-metal filters of the SC. The ejector performs several functions: 1) it removes entrained particulates, 2) provides a backup for particulate removal should a sintered filter fail, 3) provides initial

TABLE 4.4.5. Cyclone Standard Designs

Recommended Duty	D	a/D	b/D	De/D	S/D	h/D	H/D	B/D
1. High-efficiency	1	0.5	0.2	0.5	0.5	1.5	4.0	0.375
2. High-efficiency	1	0.44	0.21	0.4	0.5	1.4	3.9	0.4
3. General-purpose	1	0.5	0.25	0.5	0.625	2.0	4.0	0.25
4. General-purpose	1	0.5	0.25	0.5	0.6	1.75	3.75	0.4
5. High-throughput ^(a)	1	0.75	0.375	0.75	0.875	1.5	4.0	0.375
6. High-throughput	1	0.8	0.35	0.75	0.85	1.7	3.7	0.4

(a) Scroll-type gas entry used

quenching of the off-gas stream, 4) scrubs a portion of the Cl, F, Hg, and NO_x from the off gas, and 5) provides a vacuum on the calciner in the event of a power failure by using buildup water supply as a motive fluid.

Principles of Operation. A stream of scrub solution under pressure is passed through a spray nozzle. At discharge from the nozzle, the pressure decreases and velocity increases. The scrub jet mixes with the off gas and becomes entrained, passes through a venturi diffuser, and is released as a uniform mixture through a diverging section. This thorough mixing and fine liquid particle size results in good heat transfer and particulate collection.

At higher scrub pressures, the venturi ejector will provide a draft to the off-gas system.

Engineering Data. Because of their simple design, venturi ejectors have several inherent advantages over other equipment types: they have no moving parts; maintenance is simple, even in remote operation; they are self-priming, and thus well suited for intermittent operation; and they are self-cleaning, which permits high particle loadings without affecting performance.

A Schutte and Koerting (SK) 7010 10-in. ejector venturi or equivalent is appropriate for this application. Gas-handling capabilities of the SK 7010 are given in Table 4.4.6 and typical particulate removal efficiencies for the venturi with a knockout pot are presented in Figure 4.4.4.

TABLE 4.4.6. Gas-Handling Capacity of SK 10-in. Type-7010 Scrubber with Large Nozzle

Draft, mm Hg (in. of H ₂ O) Differential	Gas-Handling Capabilities in acmm (acfm)				
	Water Pressure to Nozzle, kPa (psig)				
	138 (20)	276 (40)	414 (60)	552 (80)	689 (100)
(0)	13.7 (485)	22.7 (800)	28.3 (1000)	33.7 (1190)	38.2 (1350)
0.13 (1/4)	10.8 (380)	21.8 (770)	27.8 (980)	33.1 (1170)	37.7 (1330)
0.27 (1/2)	8.78 (310)	19.7 (695)	26.9 (950)	32.3 (1140)	37.1 (1310)
0.40 (3/4)	7.22 (255)	18.3 (645)	25.8 (910)	31.4 (1110)	36.2 (1280)
0.54 (1)	5.66 (200)	16.7 (590)	24.6 (870)	30.6 (1080)	35.4 (1250)
0.80 (1-1/2)	3.26 (115)	14.7 (520)	22.1 (780)	28.3 (1000)	34.0 (1200)
1.07 (2)	---	12.7 (450)	20.2 (715)	27.3 (965)	32.6 (1150)
1.61 (3)	---	9.20 (325)	16.9 (595)	24.2 (855)	29.5 (1040)
2.14 (4)	---	6.23 (220)	14.2 (500)	21.2 (750)	26.2 (925)
3.21 (6)	---	---	9.20 (325)	16.4 (580)	20.7 (730)
4.28 (8)	---	---	4.11 (145)	12.7 (450)	16.1 (570)
5.35 (10)	---	---	---	8.78 (310)	12.3 (435)
6.42 (12)	---	---	---	2.15 (76)	9.20 (325)
7.49 (14)	---	---	---	---	5.81 (205)
Nozzle Flow in Lpm (gpm)					
---	1190 (42)	1700 (60)	2040 (72)	2350 (83)	2630 (93)

Quench Tower

A quench tower may be the first off-gas treatment device following the sintered-metal filters of the SC. Like the venturi ejector, the quench tower removes entrained particulates, could provide a backup to the sintered-filter system, could provide initial off-gas quenching, and could scrub a portion of the NO_x and volatile fission products from the off gas.

Principles of Operation. Calciner off gas enters the top of the vertical, cylindrically shaped quench tower, which has a diameter several times that of the off-gas line. Scrub spray nozzles are positioned in a series down the center axis of the tower and spray in cone-shaped patterns concurrently with the gas flow--providing both quenching and scrubbing to the gas. A narrowed

FIGURE 4.4.4. Typical Particulate Removal Efficiency of SK Type-7010 Ejector Venturi with Knockout Pot

funnel-shaped neck section below the spray nozzles near the bottom of the tower directs the liquid to the center, where it drops to a discharge point on the tower floor. Scrubbed gases pass out the side of the tower just below and behind the funnel, thus minimizing entrained liquid leaving the tower.

Engineering Data. Spray towers generally have low pressure drop, high liquid consumption, and are probably the least expensive method for achieving mass transfer. They are capable of handling large gas volumes with high particulate loadings and are suited for gas cooling and removal of gases with high liquid solubilities. Unlike the venturi ejector, this unit has a relatively high off-gas residence time. Particle collection is primarily by impaction and is generally limited by the terminal settling velocity that is related to spray-droplet diameter. Particles larger than 10 μm can typically be removed with efficiencies of up to 70% (Christian and Pence 1977). The chief disadvantage of spray towers is their relatively low scrubbing efficiency for particles in the 0- to 5- μm range. Pressure drop is very low--typically only a few centimeters H_2O (Calvert et al. 1972).

Venturi Scrubber

Venturi scrubbers may be used in POG treatment to serve three functions: 1) scrubbing particulates, 2) cooling, and 3) removing a portion of the H_2O , NO_x , halogens and volatile fission products.

Principles of Operation. Off gas is accelerated through the venturi throat, where aqueous scrub solution is injected. The scrub becomes atomized due to the high relative velocity between the gas and liquid droplets. High relative velocity promotes particle collection. Atomized droplets are carried by the off gas through a diverging section, allowing time for heat and mass transfer to take place. Droplets are subsequently removed by a cyclone separator.

Engineering Data. High off-gas velocities of 60 to 120 m/s (200 to 400 ft/s) through the venturi throat are best to assure adequate atomization.

Collection efficiency generally increases with pressure drop. High-pressure-drop, 0.10-atm (40-in. H_2O) venturi scrubbers can efficiently collect submicron particles. However, mass transfer capabilities are limited due to the concurrent nature of the gas-liquid flow (Calvert et al. 1972). Figure 4.4.5 illustrates typical collection efficiency versus particle size for venturi scrubbers having a 0.074-atm (30-in.) and 0.20-atm (80-in. wg) pressure drop (Lund 1971, Nonhebel 1964).

For best performance, the venturi should be operated at a 0.20-atm (80-in. wg) pressure drop. Scrub solution should be metered into the venturi throat at a rate of 1.07 Lpm/1000 Lpm (8 gpm/1000 acfm) of off-gas flow (Landon 1978). Modrow and Lakey (1964) reported a median diameter of $0.1 \mu m$ for particles exiting a venturi operating at 0.14 atm (60 in. wg).

Christian and Pence (1977) report particulate DF's of 100 to 600, a volatilized Ru DF of 10, and a NO_2 DF of 2 across off-gas cleanup venturi scrubbers.

FIGURE 4.4.5. Venturi Scrubber Collection Efficiency Versus Particle Size for 0.074-atm (30-in. wg) and 0.20-atm (80-in. wg) Pressure Drops

4.4.3.4 Heat Transfer Equipment

Condensers

Condensers serve to cool the off gas, remove particulates, condense water vapor, remove volatilized Ru, and condense mercury vapor.

Principles of Operation. Moisture-laden off gas enters the top of the condenser and is cooled (condensation takes place) as it flows downward through a tube bundle. Cooling water flows countercurrently on the shell side. Condensate drains out the bottom and is returned to the scrubber recycle tank.

Engineering Data. A standard tube-and-shell, single-pass condenser design with baffles and a floating head may be used for off-gas treatment. Off-gas cooling from 70°C to 40°C is required for the Section 5.2 acid flowsheet; gases in the neutralized flowsheet are cooled from 70°C to 10°C, which permits the desired mercury removal. Pressure drop across the condenser of 0.20 atm (8 in. H₂O) is expected. Most of the entrained water droplets exiting the condenser should be in the size range of 1 to 20 μm, which is typical for condensing

steam. Decontamination factors of 100 to 1000 for particulate and 200 for volatilized Ru have been reported (Christian and Pence 1977, Hanson and Kaser 1976). The neutralized flowsheet condenser should provide an elemental mercury DF of 100 based solely on the reduction in vapor pressure. At 10°C, less than 1 g/h of volatilized elemental mercury should leave the condenser for the reference neutralized waste flowsheet (Table 5.2.4).

Coolers

Standard tube and shell heat exchangers of the type used as condensers can be used to cool the scrubber recycle tank solution from off-gas treatment and to cool the iodine adsorber off gas from 150°C to 55°C prior to HEPA filtration. No effluent decontamination will be realized across the off-gas cooler.

Heaters

Heaters are used to preheat the off gas to 80°C for the ruthenium adsorbers. A second heater is required to increase the ruthenium adsorber off gas to 150°C for iodine adsorption (Landon 1979) or to maintain the off gas to the HEPA filters at 80°C (40°C above the dewpoint). No effluent decontamination will be realized across the heaters. Electric or steam heaters may be used.

4.4.3.5 Fission-Product Sorbers

Ruthenium Sorbers

A ruthenium sorber provides for removal of volatilized ruthenium prior to exiting the facility.

Principles of Operation. Off gas containing volatilized ruthenium enters the adsorber vessel from the bottom, passes through a bed support screen and upward through a silica-gel bed. Ruthenium is sorbed on the silica gel and the gases pass out the top of the bed. Once the bed is loaded, it is eluted with hot water. Design provisions are also made for change-out of bed materials. Iron oxide may also be considered as the ruthenium sorber bed material.

Engineering Data. Wet scrubbing is an inefficient method of ruthenium removal, so adsorption is preferred. The adsorbent must be able to: 1) adsorb large quantities of ruthenium in the off gas effectively, 2) be resistant to attack from the off gas, and 3) withstand the radioactive environment. There are two ways to handle the adsorption--with and without adsorbent regeneration. If the adsorbent is to be regenerated, it must permit ruthenium desorption by elution quite easily, be resistant to attack from the desorption agent, and have the ability to adsorb effectively after regeneration. If the adsorbent is not to be regenerated, it must be disposable. Since the ultimate disposal method would be to place the adsorbent into the waste glass, the adsorbent should hold most of the adsorbed ruthenium at high temperatures.

Newby and Barnes (1975) identified three adsorber materials which, under proper conditions, could reduce ruthenium concentration in COG by 1000 or more, have a high ruthenium adsorption capacity, and are resistant to attack by off gas. The three adsorbers are grade-40 silica gel, HZO-1 (a hydrous zirconium oxide gel), and ferric oxide. Grade-40 silica gel is the preferred adsorber because: 1) HZO-1 tends to cake when subjected to off gas below the dewpoint, and a high pressure drop occurs across the bed; and 2) ferric oxide requires high temperatures (greater than 300°C) for adsorption, and regeneration is not feasible.

Table 4.4.7 illustrates the effects of bed height, bed temperature and superficial vapor velocity on the ruthenium DF (Newby and Barnes 1975) using the optimum silica-gel size of 12-40 mesh (Hanson, Newby and Rhode 1959). Recommended operating conditions are: bed temperatures, 80°C; bed height, 1.32 m (52 in.); superficial vapor velocity, 0.61 m/min (0.4 ft/s). Under these conditions the capacity of grade-40 silica gel was found to be greater than 136 g Ru/ft³ (Newby and Barnes 1975). Typical pressure drop across such a bed is 0.097 atm/m (1.0 in. H₂O/in.) of bed height. Desorption (or elution) of ruthenium can be achieved effectively using water at 90°C (Hanson, Newby and Rhode 1959). Figure 4.4.6 shows the elution of ruthenium from silica gel during a laboratory study using nine column volumes of water (Newby and

TABLE 4.4.7. Effect of Sorbent Height, Sorbent Temperatures, Superficial Vapor Velocity and Sorbent Operating Time on Sorption of Ruthenium Using 12-40 Mesh Grade-40 Silica Gel

Sorbent Height, cm (in.)	Sorbent Temperature, °C	Superficial Vapor Velocity, m/s (f/s)	Ruthenium DF			
			Bed Operating Time, h			Average DF (0-3 h)
			0-1	1-2	2-3	
66 (26)	80	0.12 (0.4)	343	107	214	221
66 (26)	100	0.12 (0.4)	86	41	3.5	43
66 (26)	80	0.21 (0.7)	88	5	2	31
132 (52)	80	0.12 (0.4)	907	2297	1926	1710

Barnes 1975). The elution removed 80% of the ruthenium and after drying, the silica gel was again effective at removal of ruthenium from COG.

Iodine Sorbers

An iodine sorber provides final treatment for removal of iodine from the off-gas stream.

Principles of Operation. Off gases enter the sorbent from the top through a center pipe and pass radially outward through perforations in the pipe and through an annular bed of silver zeolite. Iodine is sorbed on the bed, and the off gas passes into an outlet annulus and exits at the bottom of the sorber.

Engineering Data. Iodine control is best obtained by using solid adsorbents. Inorganic sorbents are chosen over wet-scrubbing methods and organic sorbents because they allow a simple design, are relatively noncorrosive, and can be put into permanent storage or recovered as necessary. Silver-exchanged mordenite (AgZ) has been chosen for iodine sorption over other inorganics because of its higher DFs and its ability to be regenerated without loss in performance (Thomas et al. 1977). Mordenite is a type of zeolite having the chemical form $(Ca, Na_2, K_2)_4 Al_8 Si_{40} O_{96} \cdot 28 H_2O$.

Experiments by Murphy, Staples and Thomas (1977) show the iodine-loading on Ag^0Z in the saturation zone is 159 ± 17 mg I_2/g Ag^0Z and in the mass

FIGURE 4.4.6. Elution of Ruthenium from Grade-40 Silica Gel Using Water at 90°C

transfer zone is 69 ± 17 mg I_2 /g Ag^0Z . The overall average throughout the bed is 113 ± 12 mg I_2 /g Ag^0Z . Error limits represent a 95% confidence level. The effects and interactions of H_2O vapor, NO and NO_2 on the iodine-loading of Ag^0Z were also studied by Murphy, Staples and Thomas (1977). Table 4.4.8 shows the results of this work.

The NO effect and $NO \times NO_2$ interaction were shown to be statistically significant for increasing the iodine loading on Ag^0Z . The NO_x present in the off-gas stream should, if anything, improve the iodine sorber efficiency.

The bed temperature should be maintained high (about 150°C) during sorption to increase the loading capacity.

TABLE 4.4.8. Effects and Interactions of H₂O Vapor, NO, and NO₂ on the Iodine Loading of Ag⁰Z

<u>Gas Component(s)</u>	<u>Effect on Iodine Loading^(a) (mg I₂/g Ag⁰Z)</u>
NO	40 ± 12
NO ₂	-12 ± 12 (insignificant)
H ₂ O	-4 ± 12 (insignificant)
NO x NO ₂	25 ± 12
H ₂ O x NO ₂	11 ± 12 (insignificant)
H ₂ O x NO ₂	7.5 ± 12 (insignificant)

(a) Bed temperature, 150°C; superficial face velocity, 0.25 m/g (0.82 f/s); bed depth, 15.2 cm (6 in.).

Thomas et al. (1977) suggest that the equilibrium reaction

may be involved. The free energy of reaction is zero at 180°C and the formation of the oxide is favored at lower temperatures. Assuming similar thermodynamics for the zeolite matrix, operation at 150°C would produce a given ratio of Ag₂O/Ag⁰, and at 100°C this ratio would increase. During pretreatment or elution with hydrogen, the oxide would irreversibly react as follows:

thus the silver would exist predominantly in the metallic state.

Iodine desorption is accomplished by passing hydrogen through the bed. The reaction believed to occur is

Figure 4.4.7 shows the iodine loadings on Ag^0Z in the saturated zone versus the number of recycles. The percent iodine that can be desorbed from AgIZ with hydrogen versus number of recycles is shown in Figure 4.4.8. Data from the two figures indicate the loading and regeneration ability of Ag^0Z decreases with increased number of regeneration cycles. These effects may be due to diffusion resistance and decreasing accessibility of the silver atoms due to pore collapse (Murphy, Staples and Thomas 1977). Iodine desorbed from AgIZ using hydrogen can be effectively collected either on lead-exchanged faujsite or lead-exchanged mordenite for final storage.

Pressure drop across the AgZ bed at 150°C , 1 atm and 15-m/min (10-in./s) face velocity is 0.097 atm/m (1.0 in. H_2O /in. bed).

A flowsheet iodine DF of 1000 has been suggested across the sorber bed (Pence and Staples 1974).

4.4.3.6 Nitric Oxide Destructor

A NO_x destructor system may be used to convert NO_x to N_2 and H_2O with ammonia.

Principles of Operation. The NO_x destructor system is comprised of a heat exchanger, destructor/reactor and an ammonia feed system. Cold inlet gases to the destructor are preheated by energy exchange from the hot discharge gases in a tube and shell heat exchanger. The preheated off gases and a controlled amount of ammonia pass through the destructor bed of extrudate zeolon 900, where the NO_x and the ammonia react exothermically to form N_2 and water vapor. The bed temperature is maintained at 350°C by an electrical-resistance heater during startup and by the heat of reaction during steady-state operation.

Engineering Data. The NO_x reactor typically destroys 99% of the NO_x if a slight excess of ammonia is used (Christian et al. 1978). The bed catalyst, a hydrogen form of Zeolon 900 (hydrogen mordenite), was selected because of its high specificity for promoting the reaction between NO or NO_2 and NH_3 .

FIGURE 4.4.7. I₂ Loading Capacity on Ag₂O Versus Number of Recycles

FIGURE 4.4.8. Percent Iodine Desorption from AgIZ Using Hydrogen Versus Regeneration Cycle

Figure 4.4.9 shows the percent NO and NO₂ reacted versus the NH₃ feed rate on a stoichiometric basis for different bed temperatures (Thomas and Munger 1978). The stoichiometry is based on the reactions:

FIGURE 4.4.9. NO/ NO_2 Reaction Efficiencies Versus Stoichiometric Fraction of NH_3 at Various Bed Temperatures (dew-point 70°C)

As seen from the data, bed temperatures of between 380°C and 440°C are required to achieve greater than 99% reaction efficiency for both NO and NO_2 . Aside from the temperature effect, the most pronounced factor influencing the NO_x - NH_3 reaction efficiency is the water vapor content of the off-gas stream. Figure 4.4.10 shows the reaction efficiency of NO_2 versus stoichiometric fraction of NH_3 at various temperatures in dry air (Thomas and Munger 1978). By comparison, Figures 4.4.9 and 4.4.10 allow one to conclude that the presence

FIGURE 4.4.10. NO₂ Reaction Efficiency Versus Stoichiometric Fraction of NH₃ for Various Bed Temperatures (dry air)

of water vapor in the off gas reduces the NO₂-NH₃ reaction efficiency primarily in the lower temperature range (less than 400°C). Figure 4.4.11 shows the stoichiometric fraction of NH₃ needed for 99% reaction of NO₂ versus temperature and dew point (Pence and Thomas 1974). In a dry air stream any excess NH₃ will be converted to N₂. However, in a humid air stream, with dewpoint greater than 35°C, the excess NH₃ is not destroyed.

The NO_x destructor depicted in Section 5.5 was designed based on operating conditions recommended by Thomas and Munger (1978). The conditions are:

1. catalyst particle size = 12- to 14-mesh
2. bed temperature = 400°C
3. superficial face velocity = more than 66 m/min
4. superficial residence time = more than 0.17 s
5. NH₃/NO_x feed ratio = about 1.3 by volume.

A conservative NO_x DF of 50 may be used for flowsheet material-balance purposes, even though DFs of 100 are expected (Pence and Thomas 1974, Mays and Schwab 1975).

In addition to providing increased DFs for NO_x, ruthenium and possibly other semivolatile species from the off gas can be removed. Ruthenium DFs of approximately 300 have been observed (Newby, Barnes and Thomas 1976).

FIGURE 4.4.11. Stoichiometric Fraction of NH_3 Versus Temperature and Dewpoint for 99% Reaction of NO_2

4.5 CANISTER

S. C. Slate and F. A. Simonen

4.5.1 GENERAL DISCUSSION

Primary canister functions are to 1) provide high-integrity glass containment from processing to disposal, 2) protect the glass from physical damage, and 3) provide a means for handling the glass. The canister must be compatible with the environments it encounters during processing, handling, and storage operations. The canister development described was not oriented to provide long-term containment of radionuclides during disposal, since existing and past regulations from 10 CFR 50, Appendix F (Code of Federal Regulations, Title 10 1978) did not require significant waste containment in disposal. The recent regulatory actions of proposed 10 CFR 60 indicate that the waste will have to be contained by a high-integrity system with extended life. The canister is an element in that system. Current canister development at PNL is oriented toward higher-integrity canisters. The design of a waste canister is based on safety considerations, government regulations, facility requirements, and economics.

The basic canister design for the ICM process consists of a standard, single-wall pipe with flanged-only tank heads welded to both ends. The top may also be a standard, dished head on large-diameter canisters. The top has an opening that is carefully designed to couple to the vitrification equipment and to be reliably closed and sealed. The diameter of the canisters range from 0.3 m to 0.9 m (12 in. to 36 in.) and their length is about 3 m (10 ft). The usual construction material is stainless steel, depending on the service requirements. The current reference alloys are 304L stainless steel and Inconel-601 for ICM canisters, although other alloys have also been studied. Figure 4.5.1 shows a typical PNL ICM canister design. The internal fins are provided to achieve the increased melting rates desirable for large-scale production and for improved heat transfer through the glass during storage.

FIGURE 4.5.1. Canister Design

4.5.2 CANISTER DESIGN

Results of canister design and development are treated in this section.

4.5.2.1 Design Requirements

Designing a canister that is compatible with processing, transportation, storage and disposal requires a set of performance criteria. These criteria must be based on functional requirements, government regulations, and sound design practices. This section summarizes performance and design requirements for HLLW canisters. The relevance of the ASME Boiler and Pressure Vessel Code as it applies to the fabrication and design criteria is also reviewed.

Canister Design Criteria

At this time there are no "accepted" or established regulatory canister criteria that may be used for design purposes for currently envisioned canister life cycles. However, several DOE- and NRC-sponsored efforts are in progress. To indicate the types of canister criteria that are being considered, a preliminary draft of acceptance criteria for HLLW canisters has been developed by Moore (1978) and is summarized here. In addition to acceptance criteria, there is a need to consider anticipated requirements of processing, storage, transportation, and disposal.

Licensing. The canister and overpack must meet the requirements of the operating licenses of the waste facility, transportation system, and the federal repository.

Physical Dimensions and Weight. For canisters containing high-heat glass waste, the maximum dimensions will be 457 mm (18 in.) in OD and 4.8 m (16 ft) long, with a maximum weight of 3630 kg (8000 lb). For low-heat waste, the maximum dimensions are 610 mm (24 in.) in OD and 4.8 m (16 ft) long, with a maximum weight of 5450 kg (12,000 lb). These values include an overpack if it is used. Final limits will be established once a repository has been designed. (The 4.8-m canister length is meant to accommodate spent commercial nuclear fuel, should that be considered radioactive waste; however, the 3-m (10-ft)-long canister is most generally used for HLLW.)

Radiation Limit. The maximum radiation level 0.3 m (1 ft) from the canister midpoint must not exceed 1×10^5 rem/h total dose rate.

Surface Contamination Limit. There must be no significant removable contamination on the exterior surface of the canister. Significant levels are those levels, when averaged over any 300 cm^2 of surface, that exceed any of the values in Table 4.5.1. These limits are based on 49 CFR 173.397 (Code of Federal Regulations, Title 49 1978), which specifies contamination levels for shipping casks. The values are conservative and may be revised when facility designs are complete and operational requirements are known.

TABLE 4.5.1. Surface Contamination Limits of Canisters (49 CFR 173.397)

Source	Maximum Permissible Level	
	Ci/cm ²	dpm/cm ²
Natural or depleted uranium and natural thorium:		
beta-gamma	10 ⁻³	2200
alpha	10 ⁻⁴	220
All other beta-gamma-emitting radionuclides	10 ⁻⁴	220
All other alpha-emitting radionuclides	10 ⁻⁵	22

Design and Fabrication. The canister will be designed and fabricated to meet applicable standards of the ASME Boiler and Pressure Vessel Code, Section III, Division I. When an overpack is required, it shall meet the same requirements.

Canister Operations. The canister must be compatible with the requirements of remotely operated waste management facilities. It will be handled by a single, central handling device on the top.

The canister must protect and contain the waste glass during normal and accident conditions. The necessary canister operations must not adversely affect the glass. The canister must be compatible with a suitable overpack if one is required. An overpack may be used if the canister does not meet quality specifications, or if added protection is needed during disposal.

Waste and Canister Documentation. Each canister and its contents must be adequately documented during fabrication, processing, storage, transportation, and disposal. A permanent record is necessary to assure that the canister and glass meet all the requirements of the waste system.

Application of ASME Code. Canisters for vitrified high-level nuclear wastes will be designed and fabricated to high standards and will have strict quality assurance requirements imposed on their manufacture. However, there is presently no accepted set of rules, such as those now available for pressure vessels and piping in the ASME Boiler and Pressure Vessel Code. While

specific rules for the design and fabrication of waste canisters have not, to date, been adopted, the question of codes and standards has been the subject of review and study by PNL, as well as by others (Mecham, Seefeldt and Steindler 1976; Kaiser Engineers 1978; and Nuclear Services Corporation 1978).

It is appropriate to consider the ASME code as a guide to the design and fabrication of waste canisters for the following reasons:

- Materials, design details, and fabrication methods for canisters correspond to those for pressure vessels.
- The ASME code offers a well developed and widely accepted set of rules, which could eliminate the need to develop separate rules for waste canisters.

The ASME code has been developed over the years for vessels and piping; its main function is to guarantee safe containment of high-pressure fluids. It is not surprising that many aspects of canister usage fall outside the scope of the code. The following differences between canister requirements and normal procedures for qualifying pressure vessels have been identified:

- Internal pressures of concern to HLLW canisters are relatively low; thus, much of the emphasis of the ASME code relative to design stresses is perhaps inappropriate. Pressure requirements will not dictate canister wall thicknesses, and pressure relief devices will not be required.
- Canister wall temperatures during filling exceed those addressed by the code.
- Leakage limitations are probably of more concern to HLLW canister designers than are limitations for pressure vessels and piping. The ASME code focuses on containing high pressures and preventing failure by catastrophic burst.
- The code does not address load-handling and transportation, since it is specifically stated that the code rules do not apply to movable vessels. Supplementary design rules, such as those given in Shappert's cask designer's guide (Shappert 1970) and in federal regulations 10 CFR 71.64 (Code of Federal Regulations, Title 10 1978) covering the transport of radioactive materials, help evaluate handling and transportation loads.

- Stress-corrosion cracking (SCC) has been identified as a major concern for canisters subjected to water-basin storage. The ASME code does not address SCC in a direct and systematic manner. The canister designer will need to impose supplementary rules and rely on the results of service-type testing of canisters.
- Verification testing to validate vessel designs is allowed by the code as an alternative for qualifying vessels that do not otherwise comply, for example, with fatigue stress limits. It is likely that verification testing will play a major role in the licensing of HLLW canisters. The code provides little specific guidance in this area.

The report by Nuclear Services Corporation to Rockwell Hanford Operations (Nuclear Services Corporation 1978) discusses application of the ASME codes in detail and identifies other applicable standards and regulations. The following general conclusions on application of the ASME code are as follows:

1. Of the various sections of the ASME Boiler and Pressure Vessel Code, Section III, Division I, Class 3 provides the most appropriate set of rules for the fabrication of HLLW canisters.
2. Existing provisions of the ASME code are suitable to ensure canister quality at the time of fabrication, but are inadequate for the evaluation of canister integrity under service loadings and environments.
3. Canister integrity for handling and transportation accidents can be evaluated through application of rules for transport of radioactive materials presented by Shappert (1970) and in Appendix B of 10 CFR 71 (Code of Federal Regulations, Title 10 1978).
4. Additional research is needed for evaluating canister materials performance under service environments and for design verification by testing canisters under simulated service conditions.
5. The data developed in special research studies could form the basis of a new code subsection in subsection NH to Section III--Nuclear Power Plant Components (Nuclear Services Corporation 1978).

6. Code Case 1592-11 (Class 1 - Components in Elevated Temperature Service) provides a useful framework for evaluating canister integrity during filling at elevated temperatures. Estimated inelastic strain levels are within limits imposed by this code case. Additional materials data is required, however, to qualify materials for temperatures reached during canister processing.

4.5.2.2 Material Properties

Major candidate material attributes requiring consideration include corrosion, strength over a wide temperature range (20°C to 1150°C), reliability, metallurgical stability, fabricability, and economics. Stainless steel 304L was selected to be representative of 300-series stainless steels and Inconel-601 to be representative of a class of materials called "superalloys" that have been used for canister development studies. Less comprehensive tests have been performed on several other alloys.

Canister Corrosion

The corrosion performance of several potential canister alloys has been tested. There are three major corrosion modes that affect ICM canisters: 1) oxidation of external surfaces, 2) corrosion in the water basin (interim storage medium for HLLW), and 3) corrosion by the molten glass.

Oxidation of External Surfaces. Corrosion due to oxidation of the surfaces in contact with an oxygen-containing atmosphere is potentially of greatest concern. Rates up to 35 mm/yr have been measured on exterior surfaces of 304L SS engineering-scale canisters heated to 1075°C in air. Oxidation not only causes a loss of wall material, but also generates a significant waste stream of spall (Section 4.3.14). The scale remaining on the canister also makes decontamination difficult and may provide initiation sites for SCC during water storage. A slight oxidation of the canister is needed, however, to provide a surface with the high emissivity that is needed for good heat transfer in air.

PNL has investigated two methods of reducing canister oxidation. The first method was to protect the surface of the canister by covering the

canister with an inert gas such as argon during processing or coating the canister with a protective material. The second method was to replace 304L SS with an alloy that has a better oxidation resistance.

Nitrogen gas and an argon-hydrogen (Ar-4%H₂) mixture with various partial pressures of oxygen (O₂) were used in cover gas tests. Specimens of 304L SS were held for 48 h at 1100°C. The O₂ content in the Ar-4%H₂ atmosphere had to be near 10 ppm to reduce the oxidation rate of 304L to that of Inconel-601 in air.

There was some success with using coatings on the canisters to prevent oxidation. A plasma-sprayed coating of zirconia on the surface of an engineering-scale canister was demonstrated to effectively prevent oxidation. However, the high cost of zirconia coating provides incentive to evaluate other coatings such as aluminum paint, which worked well in laboratory tests. A coating of 4 g Al₂O₃/m² was applied (using aluminum paint) to a specimen of pickled 304L SS, which was then held for 48 h at 1100°C in air. The oxidation rate was 160 µm/yr. However, an engineering-scale test of the same coating did not indicate that the coating prevented oxidation.

A method has not been selected to prevent oxidation of a stainless steel canister. The decision would be based on which method is the most economical and beneficial from a processing standpoint.

An alternative to protecting stainless steel is to use an alloy that resists oxidation. In PNL development work and reference designs, 304L SS was used because of its relatively low cost and extensive use in the nuclear industry. The nickel-base alloy Inconel-601 has been evaluated because of its good oxidation resistance and other benefits, such as high strength at 1050°C and resistance to SCC. Figure 4.5.2 shows the oxidation resistance of some nickel-base alloys in comparison with other materials.

Corrosion in the Water Basin. The main corrosion mode predicted for a waste canister stored in a water basin is stress-corrosion cracking. PNL has researched the literature and made laboratory tests to evaluate SCC in several materials. The canister is susceptible to SCC because it will be sensitized

FIGURE 4.5.2. Comparison of Material Oxidation Rates at 1000°C
(Huntington Alloys 1973)

and its surface will be stressed to yield. Sensitization and the inducement of tensile stress in the canister is inherent in the ICM process.

Tensile stress in the canister is caused by the glass restraining the canister from contracting during cooling in the range of 500⁰ to 50⁰C. In this temperature range, the mean linear coefficient of expansion for 304L SS is $19 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ and for glass is $9 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$. Calculations show that the canister will go through plastic deformation and will be stressed to yield. Residual-stress measurements made on a canister indicate 200-MPa (30-kpsi) hoop stress and 250-MPa (36-kpsi) axial stress. Several techniques to relieve the stress in the wall of the glass-filled canister are potentially usable: 1) quench the canister to contract the metal while the glass is still able to yield, 2) cool the canister to a low enough temperature to cause sufficient yielding that it would be unstressed at normal storage temperatures, 3) place

a crushable liner between the glass and canister wall, and 4) anneal the borosilicate glass at the proper temperature to produce densification. Preliminary results from water-quenching a canister and annealing it to densify the glass show stress levels decreased by a factor of 2. The quenching operation does fracture the glass, with 96% of the pieces greater than 4.8 mm in dia and only 0.01% smaller than 180 μ m in dia.

PNL has evaluated three types of stainless steel and two nickel-base alloys in the laboratory. Specimens were fabricated from 304L, 304, 321, Incoloy-800 and Inconel-600. The specimens were held at 240⁰, 430⁰, 540⁰, and 700⁰C for exposure times ranging from 1 h to more than 10,000 hours. The degree of sensitization produced by the heat treatment was determined by exposing the specimens to boiling 65-wt% HNO₃, and exposing the Inconel-600 to a boiling H₂SO₂-Fe₂(SO₄)₃ solution. Also, U-bend specimens were fabricated from the exposed coupons and then exposed to air-saturated water at 80⁰C, containing 100 ppm chloride, to determine the propensity for SCC. Table 4.5.2 gives the sensitization results, as determined by Huey tests. One or more of the heat treatments resulted in extreme sensitization (greater than 30 mm/yr) of the 304, Incoloy-800, and Inconel-600 specimens. Sensitization of the 321 specimen was relatively mild, with the maximum rate of 1.3 mm/yr for the specimen at 700⁰C for 100 h. The sensitization of the 304L specimen was somewhat more severe, especially in those specimens held at 700⁰C. Failure occurred in two weeks with the 304 and 304L U-bend specimens that were subjected to a heat-treatment at 700⁰C for 10 and 100 hours. No other failures occurred after nine weeks of exposure, even though other specimens showed a much higher degree of sensitization. During the last four exposure weeks, the pH of the test solution was changed from seven to four by adding potassium acid phthalate.

Along with measuring the tendencies of materials to sensitize and crack, PNL is examining several methods to prevent SCC. These methods include:

- provide good water-quality control in the storage basin,
- use surface treatment before or after processing, and
- use a material that is not susceptible to SCC.

TABLE 4.5.2. Huey Tests of Candidate Canister Alloys After Heat Treatment: Corrosion Rates in Boiling 65% Nitric Acid^(a)

Heat Treatment	304L	304	321	Inc-800	Inc-600 ^(b)
1. As mill-annealed	0.15	0.21	0.55	0.06	8.5
2. 1 h at 700°C	3.87	30 ^(d)	0.79	30 ^(d)	19
3. 10 h at 700°C	3.93	30 ^(d)	0.85	3.69	600 ^(c)
4. 100 h at 700°C	5.24	30 ^(d)	1.3	0.52	1200 ^(c)
5. 1 h at 540°C	0.15	0.24	0.64	0.06	12
6. 10 h at 540°C	0.21	0.24	0.76	0.06	16
7. 1,000 h at 540°C	1.8	2.5	1.1	0.88	16
8. 100 h at 430°C	0.15	0.21	0.70	0.06	6.7
9. 1,000 h at 430°C	0.18	0.24	0.85	0.12	6.7
10. 10,000 h at 430°C	---	---	---	---	---
11. 100 h at 240°C	0.15	0.24	0.73	0.09	7.9
12. 1,000 h at 240°C	---	---	---	---	---
13. 10,000 h at 240°C	---	---	---	---	---

(a) Average of (five) 48-h exposures (mm/yr).

(b) 24-h exposure to boiling 50% H₂SO₄ containing 40 g/L Fe₂(SO₄)₃.

(c) 3-h exposure.

(d) Specimen consumed before test was completed.

Most PNL work with SCC in water-basin storage has been concerned with low-alloy stainless steels that resist sensitization because they have a low carbon content (304L) or they are stabilized (321 or 347). However, these materials still require careful process temperature control to keep sensitization low. They also need some additional method to prevent SCC, such as water quality control and surface treatment.

The control of the water quality in the basin appears to provide a good means of preventing SCC, even in partially sensitized materials. From published literature and laboratory tests, it is concluded that the probability of a 304L canister cracking during 10 years of water storage can be nearly eliminated by controlling two water conditions: 1) maintain the chloride

content of the water below 1 ppm by using ion exchangers, and 2) maintain a pH in the range of 9 to 12 by adding ammonia (McElroy 1976). Stainless steel exposed to this environment appears to form a protective film that enables it to resist SCC for a prolonged period of time under adverse conditions such as 500-ppm Cl and a pH range of 6.0 to 8.0.

Several methods of surface treatment to prevent SCC have been assessed. The first method is actually a side benefit of electropolishing decontamination that may be used. This process should eliminate chloride concentration points by removing scale and smoothing out crevices and high spots in the base metal. The second method is to apply a coating to the canister before or after processing. The coating should provide a barrier to the chloride or improve the protective action of the metal itself. PNL has made only preliminary tests in this area. One test was performed with a piece of Alonized mild steel. The accelerated test was performed by placing a specimen in air-sparged 80°C water that contained 100 ppm chloride. The Alonized layer was penetrated by pitting in one week. The final method is to shot-peen the canister after processing to place the surface in the compression. Literature suggests that this is effective in preventing SCC (Daly 1976).

The other approach to prevent problems caused by SCC in canisters is to use a material that will not crack. Specifically, PNL has started to evaluate alloys with a nickel content greater than 45%, which is the point above which there is apparent immunity to SCC under applicable conditions. This immunity can be inferred by the results of the Huey tests described in Table 4.5.2, where the highly sensitized Inconel-600 U-bend specimens did not crack.

One test canister filled with glass has failed due to SCC. This was a 310 SS canister filled with solidified nuclear waste during the WSEP Program at PNL (Bradley 1977). The canister was stored 1 year in water, 3-1/2 years in air at 400°C, and then 10 months in water at 50°C. It was at this point when the failure occurred. The water showed high amounts of dissolved oxygen and 13 ppm chloride. A Huey test was run on samples from this canister along with samples from a 304L canister that had been stored in air for 2 years at

400°C. The results (Table 4.5.3) show that both samples were severely sensitized. The samples had weight losses representing a uniform penetration rate of 12 mm/yr. The micrographs in Figure 4.5.3 indicate intergranular cracking near the fracture area. PNL anticipated that this canister might experience cracking, since the canister was stored under very adverse conditions and was severely sensitized. Canisters of 304L taken directly from the engineering-scale ICM furnace have shown much lower Huey test corrosion rates. The maximum corrosion rate for samples taken from the walls of these canisters was 0.35 mm/yr.

Another proposed solution to the SCC problem is to overpack canisters before they are stored in water. In the overpack the residual stresses are lower than in a primary canister.

In summary, the potential for SCC is greatest for low-alloy stainless steel canisters subject to water-basin storage. The potential for cracking is essentially nonexistent for low-carbon and low-alloy steel canisters and for stainless steel canisters stored in an air environment. It is believed that for water-basin storage, cracking can be eliminated by a combination by alloy selection, residual-stress reduction, control of processing conditions, and control of water chemistry of the storage basin.

TABLE 4.5.3. Huey Test Results

Material	Corrosion Rate, mm/yr ^(a)					Avg
	Period					
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	
304L ^(b)	17	47	52	51	47	43
310 ^(c)	14	55	63	68	64	53

(a) The maximum rate for acceptable material is usually 0.6 mm/yr (average).

(b) 304 specimen from WSEP SS-8 canister, 1 year in water, 2 years in air at 400°C.

(c) 310 specimen from WSEP SS-9 canister, 1 year in water, 3.5 years in air at 400°C, 10 months in water at 500°C.

Internal Surface Edge 75X

External Surface Edge 75X

Internal Surface Edge 225X

External Surface Edge 225X

FIGURE 4.5.3. Photomicrographs of Canister Wall Section from the 310 SS Canister (Oxalic Acid Electrolytic Etch)

Corrosion Effects of the Glass Melt. Corrosion rates of less than 3 mm/yr have been measured for a variety of metals in contact with several waste compositions at temperatures above 1100°C. PNL has used four wastes and two frits in laboratory tests (Table 4.5.4). In the tables and text the melt compositions are indicated by showing the waste, frit, and their ratio in the following format:

Waste- -Frit
 ↓ ↓
[PW-6 : (2:1) 72-4]
 Weight Ratio
 (Frit : Waste)

Wastes PW-6 and PW-7a are the same as PW-4b and PW-7, respectively, except that they reflect the addition of ILLW to the HLLW.

Early corrosion work at PNL was directed toward finding a material for a metallic melter. This melter received calcine and frit, melted them together, and then poured the batch into a canister. The melter required good corrosion resistance at temperatures above 1100°C for long periods of time. In contrast, the ICM process requires that materials have good high-temperature corrosion resistance for only several days. In addition, it requires that materials have high-temperature strength, resistance to corrosion in water, and low cost. The work on the metallic melter can be applied to the ICM canister.

The work with the metallic melter demonstrated the corrosion resistance of a variety of alloys under extreme melt conditions. Specimens of 15 commercial alloys were placed in [PW-6:(2:1) 72-4] at 1150°C for 425 h. The compositions of the alloys and the test results are given in Tables 4.5.5 and 4.5.6, respectively (McElroy et al. 1972). A second test (results in Table 4.5.7) was run on four of the best-performing materials and three new materials to demonstrate the effect of temperature on the corrosion rate (McElroy 1973). Inconel-601, a candidate canister material, shows good corrosion resistance.

TABLE 4.5.4. Compositions of Frits and Stimulated Wastes Used in the Tests (wt%)

Constituents	72-4 Frit	73-1 Frit	PW-4b	PW-6	PW-7	PW-7a
SiO ₂	50	37.0				
ZnO		28.9				
B ₂ O ₃	21.9	15.1				
CaO	17.5	2.0				
MgO		2.0				
Al ₂ O ₃	10.6					
K ₂ O for Rb ₂ O		5.5	0.49	0.24	1.99	1.68
Na ₂ O		5.5		33.26	0.20	10.17
SrO		2.0	2.90	1.41	1.85	1.56
BaO		2.0	4.29	2.09	2.73	2.31
ZrO ₂			13.54	6.60	8.65	7.32
MoO ₃ for Tc ₂ O ₇			17.48	8.50	11.10	9.39
Fe ₂ O ₃ for RuO ₂			9.02	23.53	8.39	7.10
Cs ₂ O			7.89			
Co ₃ O ₄ for Rh ₂ O ₃			0.83	0.40	0.53	0.45
NiO for PdO			2.86	1.96	1.82	1.54
TeO ₂			1.99	0.97	1.27	1.92
P ₂ O ₅			1.84	0.89	4.69	9.33
Cr ₂ O ₃			0.94	1.73	0.60	0.51
CdO			0.27		0.17	0.14
Ag ₂ O			0.24		0.15	0.13
Rare Earth Oxides ^(a)			35.13	18.42	37.36	31.62
Didymium Oxides ^(b)					18.48	15.64
kg/MTU			36.4	190.22	151.4	178.9

(a) Commercial rare earth mix nominal oxide composition: 0.2% Y₂O₃, 24% La₂O₃, 48% CeO₂, 5% Pr₆O₁₁, 17% Nd₂O₃, 3% Sm₂O₃, 2% Gd₂O₃, and 0.8% other rare earth oxides.

(b) Commercial didymium nominal oxide compositions: 4% Y₂O₃, 37% La₂O₃, 2% CeO₂, 10% Pr₆O₁₁, 36% Nd₂O₃, 5% Sm₂O₃, 4% Gd₂O₃, 2% Dy₂O₃, 0.2% Ho₂O₃, 0.4% Er₂O₃, less than 0.1% of each other rare earth oxides.

TABLE 4.5.5. Theoretical Compositions of All Materials Tested

Alloy	Composition, wt%					Others
	Cr	Ni	Mo	Fe	C	
304L SS	20	9	--	bal	0.03	
304 SS	20	9	--	bal	0.08	
309 SS	22	13	--	bal	0.08	
310 SS	25	20	--	bal	0.25	
316 SS	16	12	3	bal	0.08	
321 SS	18	10		bal	0.08	5 x C Ti
329 SS	25	5	2	bal		
410 SS	12	--	--	bal	0.15	1 Mn
Inconel-600	17	bal	--	10	0.15	
Inconel-601	23	60	--	14	0.15	1 Al
Inconel-617	22	54	9	--		1 Al, 12.5 Cr
Inconel-690	30	60	--	10		
Inconel-X	15	bal	--	8		2 Ti, 1 Al, 1 Nb
Incoloy-800	21	33	--	bal	0.10	
Incoloy-804	29	41	--	bal	0.10	1 Ti
D-Brite 26-1	25	--	1	bal		
20-45-5 Alloy	20	45	5	bal		
18-18-2 Alloy	18	18	--	bal		2 Si
Hastelloy X	22	bal	9	18		1 W, 2 Co
Corronel 230	35	65	--	--		
Owens-Corning Alloy	26	bal	--	3		6 W
Ra 333	25	45	3	bal		3 W, 3 Co
Supertherm	25	35	--	bal		14 Co, 5 W
Udimet 710	18	bal	3	--		15 Co, 1.5 W, 5 Ti, 2.5 Al

Also at this time, PNL evaluated the effect of four elements that were suspected to possibly accelerate corrosion: ruthenium, cesium, lead and zinc. Ruthenium and cesium are fission products that are found in all wastes, and lead and zinc are frit additions that provide desirable physical properties to

TABLE 4.5.6. Corrosion Rates of Candidate Metallic Melter Materials^(a)
in Waste Melt

Alloy	Corrosion Rate, mm/yr	
	Liquid	Interface
Corronel-230	0.64	0.20
316 SS	dissolved	dissolved
329 SS	2.0	---
309 SS	2.3	3.2
E-Brite 26-1	2.0	---
Owens Corning Alloy	1.5	1.9
20-45-5 Alloy	0.82	0.88
Inconel-601	2.0	1.7
Inconel-617	1.9	1.6
Inconel X	1.7	2.0
RA 333	3.0	4.0
Hastelloy X	1.6	1.8
18-18-2 Alloy	6.3	19.0
Supertherm	6.0	---
Udimet-710	8.4	9.8

(a) [PW-6:(2:1) 72-4] 425 h at 1150°C.

TABLE 4.5.7. Corrosiveness of Waste Melt as a Function of Temperature^(a)

Alloy	Corrosion Rate at 1150°C, mm/yr		Corrosion Rate at 1200°C, mm/yr	
	Melt	Interface	Melt	Interface
Inconel-690	1.1	0.64	1.3	1.6
Corronel-230	0.64	0.20	1.5	1.9
50 Cr - 50 Ni	1.6	1.1	---	---
Hastelloy X	1.6	1.8	7.3	8.5
Inconel-601	2.0	1.7	5.2	5.5
Inconel-617	1.9	1.6	6.4	9.8
Inconel-600	2.2	2.6	---	---

(a) [PW-6:(2:1) 72-4] 165 h at 1150°C.

the glass. In the cases of the ruthenium- and zinc-containing melts (Tables 4.5.8 and 4.5.9), the corrosion rate was only slightly increased, and there was no preferential attack. The corrosiveness of cesium-bearing glass appears to be low. Specimens of 304L were exposed for 300 h at 900°C in a melt of a zinc-bearing frit (1 part) and cesium carbonate (0.95 parts). The melt and vapor phase corrosion rates were 0.06 and 0.5 mm/yr, respectively. Intergranular attack to a depth of 130 μm was seen in specimens in the vapor phase. Some specimens were exposed to the melt for seven months at 400°C. The corrosion rate was less than 2.5 $\mu\text{m}/\text{yr}$. The melt containing lead was found to be very corrosive (Table 4.5.10). Corrosion by this melt on Inconel-601 and 20-45-5 was catastrophic, and at the melt-vapor interface was severe in all cases (McElroy 1973).

When emphasis was shifted from the metallic melter to the ICM process, new criteria came into the material selection considerations. Tests were started on materials that were hoped to be corrosion-resistant as well as inexpensive. Samples were run for 100 h in [PW-4B:(2.8:1) 73-1]. Table 4.5.11 shows the materials, the melt temperature, and the results from the test (McElroy 1975a). The specimen of 410 SS failed catastrophically in both the melt and the melt vapor. Some properties of these materials are shown in Table 4.5.12. PNL has determined the corrosion rate of 304L as a function of temperature. The test used [PW-4b:(3:1) 73-1] at the temperature and time shown in Table 4.5.13. One should note the rapid increase in the corrosion rate above 1050°C in Figure 4.5.4.

Two specially treated materials were evaluated as a canister material. A specimen of mild steel was flame-sprayed with 30% Al_2O_3 - 70% NiAl and was then exposed for 24 h at 1050°C to [PW-7a:(3:1) 73-1]. The material experienced severe corrosion (500 mm/yr) at the melt-vapor interface and in the vapor phase. The second material as Alonized mild steel that was exposed for 24 h at 1100°C to [PW-7a:(3:1) 73-1]. The part of the specimen exposed to the melt was severely corroded, losing the Alonized layer and 28% of the metal. An uncoated piece of mild steel was exposed at the same time, and it was attacked catastrophically in the vapor phase. The penetration rate was found to be about 22 m/yr.

TABLE 4.5.8. Corrosiveness of Zinc-Bearing Waste Melt(a)

Alloy	Corrosion Rate, mm/yr	
	Melt	Interface
Inconel-690	0.43 ^(b)	0.58 ^(b)
Inconel-600	2.3 ^(b)	5.0 ^(c)
20-45-5	2.4 ^(b)	1.1 ^(b)

(a) [PW-4:(3:1) 73-1] 283 h at 1150°C.

(b) Broad, shallow pit formation.

(c) Intergranular attack.

TABLE 4.5.9. Corrosiveness of Ruthenium-Bearing Waste Melt(a)

Alloy	Corrosion Rate, mm/yr	
	Melt ^(b)	Interface ^(b)
20-45-5	3.0 (0.82)	2.9 (0.88)
Corronel-230	1.5 (0.64)	1.0 (0.70)
Inconel-690	0.88 (1.1)	0.58 (0.64)

(a) [PW-6:(2:1) 72-4] plus 1 wt% ruthenium added as Ru(OH)₃, 165 h at 1150°C.

(b) Parenthetical numbers are values determined in similar tests in the absence of ruthenium.

In addition to short-term tests to evaluate glass corrosion during processing, PNL has also looked at the long-term effects. A glass compatibility test was conducted using [PW-7a:(2.8:1) 73-1] on 304L SS, Incoloy-800, and Inconel-600 (McElroy 1975a). There were 38 capsules, each containing a corrosion coupon. The capsules were held at 250°C, 550°C and 700°C for exposure periods ranging from one month for capsules at 700°C to two years for those at 250°C. Table 4.5.14 gives the program for this test. Results (Table 4.5.15), as determined by weight loss of the coupons, indicate there is no problem with long-term glass corrosion of the canister unit. Another test was run exposing 304L to PW-4 calcine. The samples were held at 60°C, 90°C, and 300°C for nine months. Attack was negligible for all cases run (about 1.3 μm/yr) (McElroy 1976).

TABLE 4.5.10. Corrosiveness of Lead-Bearing Waste Melt^(a)

Alloy	Corrosion Rate, mm/yr	
	Melt	Interface
Inconel-690	3.7	7.9 ^(b)
50 Cr - 50 Ni	2.0	13 ^(b)
20-45-5	25	dissolved
Corronel-230	2.1	7.3 ^(b)
Inconel-601	dissolved	dissolved

(a) [PW-5b:(4:1) 58.1 PbO, 6.8 K₂O, 35.1 SiO₂] 150 h at 1150°C.

(b) Severe attack at melt-vapor interface area. For Inconel-690, the penetration was about 30 mm/yr.

TABLE 4.5.11. Corrosion Rates Pertinent to In-Can Melting

Material	Melt Temp., °C	Corrosion Rate, mm/yr	
		Melt	Vapor
304L	950	1.0	1.4
310	950	0.52	0.30 pitting
304L	1000	4.6 pitting ^(b)	2.7
310	1000	0.55	1.6
410	1025	dissolved	disintegrated
304L	1050	27	10.7
Inconel-600	1050	2.3	1.4
Inconel-601	1050	1.2	1.2
Inconel-690	1050	0.76	0.76
18-18-2	1050	11	0.61
Incoloy-804	1050	0.82	0.94
Multimet	1050	0.61	disintegrated

(a) [PW-4b:(2.8:1) 73-1] 100 h at indicated temperature.

(b) About 5 mils deep.

TABLE 4.5.12. Physical Properties of Some Candidate Canister Materials

Alloy	Thermal Conductivity at 350°C, w/m K	Thermal Expansion to 1100°C, °C ⁻¹	Yield Strength, MPa	Stress Rupture @ 100 h, 1100°C, KPa
304L	20.0	19.8	275	2,700
Inconel-600	17.2	18.9	310	20,000
Inconel-601	19.8	16.7	330	9,700
Incoloy-802	16.9	14.8	275	12,000

TABLE 4.5.13. Corrosion Rate of 304L as a Function of Temperature(a)

Melt Temp., °C	Exposure, h	Corrosion Rate, mm/yr	
		Melt	Vapor
950	100	1.0	1.4
1000	100	4.6	2.7
1050	150	27	11
1100	66	---	20
1150	24	>1150	230

(a) [PW-4b:(3:1) 73-1]

PNL has examined the corrosion effect from contaminants in the melt and chemical additions that are used to improve the melting of the glass. Corrosion tests were made with 304L to determine the effect of chloride and fluoride contamination in [PW-7:(3:1) 73-1] (McElroy 1976). With chloride and fluoride additions at the 1% level (as NaCl and NaF), and with a melt temperature of 1000°C, corrosion rates were 0.64 and 5.30 mm/yr, respectively. A control specimen corroded at a rate of 0.73 mm/yr. Intergranular attack was evident only on the specimen exposed to the fluoride-bearing melt. A substance (probably MoOCl_3 and/or ZrCl_4) was volatilized from the chloride-bearing melt; the terminal chloride content was probably very low.

FIGURE 4.5.4. Corrosion Rate of 304L in [PW-4b:(3:1) 73-1] Glass as a Function of Temperature

PNL has evaluated the corrosion effect on 304L of adding strong reducing agents to the melt such as silicon metal and zircaloy cladding sections (McElroy 1976). The reducing action is needed to suppress the formation of a second-phase molybdenum compound in the glass. Zircaloy tubing may be added instead of silicon metal as a means of disposing of it. A major by-product of this reduction action is zinc vapor, which burns at the surface of the melt. Therefore, the possibility of embrittlement of the canister has been investigated.

Three specimens of 304L were exposed to [PW-7:(3:1) 73-1] for 48 h at 1050°C. For the first specimen there was no addition to the melt. For the second specimen the melt contained a 1.5 wt% silicon, and for the third the melt it contained 20 wt% oxidized Zircaloy-4 (Zry-4) tubing sections. In the presence of both reductants there was intergranular attack of the specimens,

TABLE 4.5.14. Program Plan for Glass Compatibility Test

Temp., °C	Material	Capsule Condition (a)	Glass Composition (b)	Exposure Time	No. of Capsules
700	304L, Inc-800, Inc-600	AF	A, B	1 mo	6
550	304L	AF, SR	A, B	3 mo	4
550	Inc-800, Inc-600	AF	A, B	3 mo	4
250	304L	AF, SR	A, B	1, 2, x yr	12
250	Inc-800, Inc-600	AF	A, B	1, 2, x yr	12
					38

(a) AF = as fabricated; SR = stress relieved.

(b) A = [PW-7:(2.8:1) 73-1]; B = A plus addition (= 2 x H₂O, NO₃ and halogen plus 10 wt% sodium as NaFeO₂).

TABLE 4.5.15. Glass Compatibility Tests

Material	Glass Composition (a)	Corrosion Rate, (b) $\mu\text{m}/\text{yr}$
304L	A	15
304L	B	10
Incoloy-800	A	25
Incoloy-800	B	7.6
Inconel-600	A	5.1

(a) A = [PW-7:(2.8:1) 73-1]; B = A plus addition.

(b) Samples at 700°C for one month.

particularly just above the melt-vapor interface. The depth of penetration was 50 to 75 μm and no major loss of ductility was noted. Metallography was obtained on all samples (Figure 4.5.5).

PNL has found that the corrosion effects of the melt, furnace atmosphere, and water basin on stainless steel canisters used in the ICM process are

MELT PHASE WITH NO ADDITION

100X

VAPOR PHASE WITH 1.5 WT% Si

250X

MELT PHASE WITH 1.5 WT% Si

250X

VAPOR PHASE WITH 20 WT% Zry-4

250X

MELT PHASE WITH 20 WT% Zry-4

100X

FIGURE 4.5.5. Micrographs Showing the Effects of Adding Silicon Metal and Zry-4 Tubing Sections to a Glass Melt (304L for 48 h at 1050°C)

insignificant or can be controlled. Corrosion due to the melt or its vapor is not significant for most of the examined materials at the expected temperatures and exposure times. Methods may be needed to protect the canister from oxidation, such as using an inert cover gas or surface coatings during processing. Stress-corrosion cracking in the water basin is very difficult to analyze because of the many variables. It was concluded, however, that SCC can be prevented in 304L canisters by maintaining the chloride content of the water below 1 ppm chloride and the pH in the range of 9 to 12 by adding ammonia. Additional preventive methods such as stress relief and surface treatments will add further protection but do not appear necessary. Inconel-601 is currently being evaluated at PNL. The benefits of this material are many and may well compensate for its higher costs. Some of the advantages of Inconel-601 over stainless steels are:

1. much lower corrosion rates from the melt at temperatures above 1100°C,
2. only light oxidation in an air environment for temperatures up to 1200°C,
3. immunity to SCC in the water basin.

Material Strength Evaluations

While canister materials require mechanical strength and ductility, stresses imposed on canisters in handling and storage after filling are not unusual. The strength requirements can be met by most commercial alloys.

Filling temperatures are higher than normal service temperatures for the materials of interest, so PNL has emphasized evaluation of high-temperature strength. Creep-strength data are presented below. It was found that a number of common commercial alloys can meet high-temperature strength requirements. Corrosion and melting point considerations, rather than strength, per se, probably affect upper temperature limits for potential canister materials. Ductility and toughness are required of canister materials so that they meet the impact performance requirements described in Section 4.5.2.6. In general, austenitic alloys and ferritic alloys should meet the ductility and toughness requirements of canisters for temperatures above their ductile-brittle transition range.

Creep Strength. During the filling process, canisters must contain molten glass and must minimize deformation at the high filling temperatures. Canister wall temperatures during filling exceed normal design temperatures for the materials of interest. Design data, such as those given in the ASME Boiler and Pressure Vessel Code, have not been applicable. In addition, creep-strength data reported in the literature are very limited.

The combination of corrosion test results and strength requirements focused material selection process on wrought, austenitic stainless steels and nickel chromium alloys. The alloys 304L stainless steel and Inconel-601 were selected for study because they were prime candidates for the canister application and are representative of the two ends of the spectrum of alloy content for the class of materials of interest. They were also expected to exhibit significant differences in creep strength. Therefore, a series of creep tests at ICM temperatures was conducted.

The AISI-type 304L stainless steel (18% Cr - 8% Ni) is the low-carbon (0.03 maximum) form of the standard 304 steel. The low carbon level increases corrosion resistance by reducing carbide precipitation at the grain boundaries. It can be safely welded with a minimum danger of intergranular attack. In general, its strength properties are among the lowest for the 300-series stainless steels, comparable to types 302 and 304, with normal (0.08) carbon levels (Simmons and Cross 1952).

While there is a lack of specific high-temperature strength data for the 304L steel in the very high temperature range of 950°C to 1100°C (1742°F to 2102°F), the strengths of all the 300-series steels are very nearly the same (Simmons and Cross 1952). Thus, for relating rupture strengths, a comparison with types 302 (Brickner, Ratz, and Dornagala 1965) or 310 (VanEcho, Roach, and Hall 1967) is adequate. A major drawback is a lack of oxidation resistance at very high temperatures (Allegheny Ludium Steel Corporation 1956), since even short time periods at 1100°C (2012°F) produce significant scaling.

On the other hand, Inconel-601 (60% Ni, 23% Cr) is an excellent oxidation-resistant alloy. It suffers very little weight loss when exposed for up to 500 h at 1100°C (2012°F) and 1150°C (2102°F) (International Nickel Co., Inc. 1973). It can be welded and has good high-temperature strength properties (International Nickel Co., Inc. 1973; Simmons 1968). The alloy is also resistant to carbonization, sulfidation and SCC (International Nickel Co., Inc. 1973).

The specific purpose of the creep tests was to establish the engineering creep and rupture properties of 304L stainless steel and Inconel-601 at temperatures in the range of 950° to 1150°C (1742° to 2102°F). This temperature range covered the anticipated melting conditions and also allowed evaluation of canister performance during overheating conditions. Since service exposure times are relatively short, it was necessary to establish creep performance to only about 100 h. One of the major uses of the data was to permit prediction of canister deformation under normal service conditions. Thus, many of the tests were at relatively low stress levels in order to be representative of design stress levels. These low-stress tests were discontinued after the trend of the creep curve was established, since rupture was not expected within the time frame of interest. For 304L stainless steel a few tests were performed in a vacuum to determine the effect of the air environment on creep performance. This factor is related to ICM, since an inert gas environment is a possible means of limiting the extent of external oxidation and scaling of canisters during processing. The test procedure and detailed results are presented by Simonen and Slate (1979).

Design Curves. Design curves were prepared from the results for both 304L and Inconel-601. These curves, shown in Figures 4.5.6, 4.5.7 and 4.5.8 allow a designer to select a stress that will produce a limiting amount of creep strain at a particular temperature. Creep strains of 0.2%, 0.5%, 1.0%, 2%, and 10% were chosen from the creep curves. Other creep strains can be chosen from the creep curves and similar design curves constructed. The effect of air exposure at 1100°C (2012°F) on the 304L material is evident in the 1100°C design curves (Figure 4.5.7). The slopes of the curves increase from a linear

FIGURE 4.5.6. Design Curves for 304L Stainless Steel Plate (1/2-in.) in Air

FIGURE 4.5.7. Design Curves for 304L Stainless Steel Plate (1/2-in.) in Air

FIGURE 4.5.8. Design Curves for Inconel-601 Plate (1/4-in.) at 1050°C, 1100°C and 1150°C

relationship at long times, represented by the dotted lines. The stress on the specimen, initially stressed at 1.38 MN/m^2 (200 psi) was gradually increasing as scaling progressed and creep occurred more rapidly.

Isochronous Stress-Strain Curves. For structural analysis purposes, representation of creep data using isochronous stress-strain curves is often useful. Such curves are a result of plotting the value of total strain (elastic-plus-plastic-plus-creep) as a function of stress at a given constant end-of-test time. A more complete description of the generation of isochronous stress-strain curves can be found in The Generation of Isochronous Stress-Strain Curves (ASME 1972).

Isochronous stress-strain curves for 304L stainless steel and Inconel-601 are given in Figures 4.5.9 to 4.5.15. The curves cover the temperature range of 950⁰ to 1150⁰C (1742⁰ to 2102⁰F) and the time domain of 1 h to 100 h. This range of time and temperature cover the conditions of interest to the filling phase of the ICM process.

Short-time creep and creep-rupture data were obtained for two austenitic alloys. The difference in strength of the alloys was significant, with the 304L stainless steel being about 60% as strong as Inconel-601. The effect of environment on the strength of 304L appears to be temperature-dependent. Below 1050⁰C (1922⁰F) the presence of air had a strengthening effect, which is attributed to nitrogen pickup. Above 1050⁰C, the loss of specimen cross section from oxidation was significant at test times as low as 100 h, and a noticeable reduction in life was observed.

4.5.2.3 Thermal Analysis

This section describes the studies performed on the thermal behavior of ICM canisters during filling, cooldown, and handling. Canister design and processing operations can significantly affect the temperature and condition of the glass and canister.

In the case of glass, the temperature history can significantly affect the amount of cracking and devitrification that occurs. Cracking results largely from temperature gradients that occur during cooldown and large changes in ambient temperature. In general, larger gradients mean more cracking. The consequence of cracking is that the potential for release of radionuclides by leaching or dispersion is increased. A detailed discussion of cracking is presented by Slate et al. (1979). Cracking does not appear to significantly affect heat transfer. Devitrification is the formation of crystals within the glass matrix and it is a function of the temperature history of the glass. The effect of devitrification on the quality of the glass is a matter of speculation. The consequences of devitrification are generally minor, although it is normally considered desirable to avoid.

The temperature history must be known for material selection and stress analysis. In the area of material selection the temperatures are used to

FIGURE 4.5.9. Isochronous Stress-Strain Curves for 304L Stainless Steel at 950°C

FIGURE 4.5.10. Isochronous Stress-Strain Curves for 304L Stainless Steel at 1000°C

FIGURE 4.5.11. Isochronous Stress-Strain Curves for 304L Stainless Steel at 1050°C

FIGURE 4.5.12. Isochronous Stress-Strain Curves for 304L Stainless Steel at 1100°C

FIGURE 4.5.13. Isochronous Stress-Strain Curves for Inconel-601 at 1050°C

FIGURE 4.5.14. Isochronous Stress-Strain Curves for Inconel-601 at 1100°C

FIGURE 4.5.15. Isochronous Stress-Strain Curves for Inconel-601 at 1150°C

evaluate the potential for corrosion and metallurgical changes, such as sensitization. For stress analysis, temperatures are used to select material properties and to predict strain levels. In addition, practical and efficient facility operation requires that the handling temperatures and cooldown times be known.

Computer Model

The heat transfer model CANIST, developed at PNL to assist in analyzing the effects of internal canister fins on heat transfer, was used to perform most of the analyses presented here. A two-dimensional program (r and θ), CANIST solves for the distribution of temperatures within the canister and glass under transient or steady-state conditions. It uses an Alternating Direction Implicit (ADI) method to solve the unsteady-state, heat-conduction equation. The ADI method involves solving the finite-difference equations for a single time step in one direction (r) first, and using those results to solve the other direction (θ). As a two-dimensional program, CANIST accounts for the

transfer of heat both radially and circumferentially, but assumes heat is not transferred axially. Therefore, the process of filling a storage canister with glass, or determining temperatures near either end of a canister cannot be modeled properly using CANIST. In CANIST, conduction within the canister is assumed to be the dominant mode of heat transfer; any heat that may be transferred within the canister by convection or radiation is considered to be relatively small. CANIST is also set up so that several different boundary conditions outside the canister can be modeled. These include:

- natural convection and radiation in air
- convective heat transfer in water
- interaction between canister and enclosure
- time-temperature profile of canister wall.

By taking advantage of symmetry in the θ direction, the entire radial cross section does not have to be modeled. To save computational time, CANIST is set up to model only a selected angular section of the canister. The angular section is divided into control volumes. Figure 4.5.16 shows the relationship between the canister cross section, an angular section, and a control volume.

CANIST was developed to model a variety of waste canisters. Thus, the input parameters include the diameter of the canister and the configuration and location of fins. The angle of the angular section determines the number of fins modeled. The rate at which the waste glass generates heat and the initial temperature distribution of the glass and canister are also input parameters. The thermophysical properties of the waste glass, canister, and fins are temperature-dependent and are assigned to the control volumes on the basis of the particular waste glass, storage canister, and internal fins being modeled. R. E. Taylor at Purdue University has experimentally determined the density, specific heat and thermal conductivity for BNW-76-183 and SRL Composite-411. (The compositions of these two glasses are presented in Table 4.5.16.) Shown in Figures 4.5.17 and 4.5.18 are the thermophysical properties data received from Taylor for SRL Composite-411. The large change in the experimental data for heat capacity is due to approaching the melting

FIGURE 4.5.16. Canister Cross Section

point of glass during the experimental tests. These thermoproperties were modeled (Wescott and Slate 1979) for the CANIST computer to perform heat-transfer calculations. The thermal conductivity and volumetric heat capacity values used in CANIST for 304L stainless steel canisters and fins were obtained from Touloukian (1967). The heat-generation rates of nuclear wastes from several sources are listed in Table 4.5.17. These rates are used in a number of calculations below.

Temperature-Related Phenomena

The waste glass properties influenced by the centerline temperature are devitrification, phase separation, and gravity settling. The temperature of the canister wall influences sensitization of the stainless steel, thermal stresses in the canister wall (which affects glass-cracking and SCC of the wall), and the processing time and handling considerations for the canister.

TABLE 4.5.16. Composition of Two Simulated Waste Glasses

Glass Formers	Composition, wt%	
	BNW-76-183	SRL Composite-411
SiO ₂	35.3	44.5
B ₂ O ₃	9.3	8.3
Na ₂ O, K ₂ O	10.0	9.4
CaO	2.0	5.2
TiO ₂ , CuO, LiO ₂ , etc.	10.0	9.4
<hr/>		
Waste		
Na ₂ O	3.5	--
Fe ₂ O ₃	2.4	8.0
Al ₂ O ₃	--	12.0
MuO ₂ , NiO	0.5	3.2
Rare Earth mix oxide	15.3	--
P ₂ O ₅ , ZrO ₂ , etc.	11.7	--
TOTAL	100.0	100.0

Devitrification--the formation of crystals in the glass--is a function of time and temperature. The temperature range in which rapid devitrification is most likely to occur is between 950°C and 500°C for most waste glasses. The leach rate of the glass modestly increases with the extent of devitrification. If the cooling rate is 50°C/h or more, the devitrification occurring during canister cooldown is negligible. Phase separation is another time-temperature-dependent process that increases the leach rate of the glass. The addition of reducing agents to the glass can prevent phase separation to a large extent. Gravity settling of some crystals occurs if the glass at the center of the canister stays partially melted for several or more days. By cooling the glass rapidly (more than 50°C/h) and subsequently maintaining the glass at temperatures below approximately 500°C, these phenomena should not seriously affect the glass properties and homogeneity.

FIGURE 4.5.17. Experimental Thermal Conductivity of SRL Composite-411

FIGURE 4.5.18. Experimental Volumetric Heat Capacity of SRL Composite-411

Sensitization of the stainless steel canister walls is the precipitation of chromium carbides in the grain boundaries, which usually occurs between 500° and 750°C. The walls are more susceptible to intergranular corrosion after sensitization, but the process is reversible at temperatures above

TABLE 4.5.17. Heat Outputs of Various Nuclear Wastes

Waste			Diameter (in.)	Heat Output				
			Volume (L)	6	12	16	24	36
				56	210	334	767	1727
	Watts MTU	m ³ MTU	Watts -Glass	Watts Canister	Watts Canister	Watts Canister	Watts Canister	Watts Canister
1. Commercial LWR								
a. 5-year	1,930	0.085	22.6	1,250	4,750	7,550	17,300	39,000
b. 10-year	1,090	0.085	12.7	700	2,650	4,250	9,750	22,000
c. 20-year	775	0.085	9.1	500	1,900	3,000	7,000	15,000
d. 100-year	115	0.085	1.4	80	300	450	1,100	2,400
2. West Valley								
a. With salt-cake separation	---	---	0.58	30	120	195	445	1,000
b. Without salt-cake separation	---	---	0.13	7	25	45	100	225
3. Savannah River								
a. With salt-cake separation	---	---	1.45	80	300	480	1,100	2,500
b. Without salt-cake separation	---	---	0.2 (Approx.)	12	40	60	150	340
4. Hanford								
a. With salt-cake separation	---	---	0.035	2	7	12	27	60
b. Without salt-cake separation	---	---	0.004	0.2	0.8	1.3	3.0	7.0
5. Idaho								
a. Old average	---	---	0.078	4	16	26	60	135
b. New typical	---	---	---	---	---	---	---	---

850°C. A cooldown rate of 100°C/h or greater, in the range of 750°C to 500°C, will minimize the sensitization experienced by the canister wall. Wall stresses make the canisters more susceptible to chloride-induced SCC during water-basin storage. Maintaining proper water quality at the storage basin will minimize this potential problem. Wall stresses result from the glass shrinking less than the steel does as it cools, especially below the transition temperature of the glass (the temperature at which glass changes from a plastic state to a brittle state--525°C $\pm$ 25°C for most waste glasses). If the canister and glass are cooled too rapidly (100°C/h), thermal stresses cause fracturing of the glass. Excessive cracking of the glass is undesirable, because it increases the surface area of the glass that is subject to leaching in an aqueous environment. Mendel (1978) offers more information on the phenomena described above.

As previously mentioned, cracks in the waste glass have also been a concern with respect to their effect on heat transfer. Examination of filled canisters has revealed that significant cracking does occur, especially near the canister wall and fins if the metal/glass thermal expansion mismatch is large, as shown in Figure 4.5.19. An earlier computer analysis of a 360° fracture in the glass, with only radiation heat transfer across the gap (a vacuum gap), resulted in a 120°C temperature drop across the gap and approximately the same temperature rise in the centerline temperature. Analytic evaluation showed that expressing the crack width in terms of an equivalent glass thickness was dependent only on the temperature of glass and not the width of the crack. For example, at 450°C the equivalent glass thickness is 1.4 cm, while at 50°C it was 15 centimeters. Since most cracks would not be 1.4 cm wide, the glass fractures would be less efficient than the glass at transferring heat; thus, cracks act as a barrier to heat transfer. If the gap contained helium, a comparison of thermal conductivities between the glass and the helium suggests a 1-mm-wide crack would have a heat-transfer rate equivalent to 4 mm of glass.

Fortunately, such phenomena were not observed in the experimental data from filled canisters. Two factors may be effectively nullifying the resistance to heat transfer by the cracks: contact resistance and "bridging."

FIGURE 4.5.19. Glass-Cracking Near Canister Wall and Fins

Assuming the cracks are jagged, with many points of contact, conduction should occur between the glass surfaces, thereby reducing the heat that must flow through the "void" of the crack. The fracture surfaces may also be kept in

intimate contact because the glass is under compression (Simonen and Slate 1979). The "bridging" effect implies that the crack, with its high resistance, is bypassed in a large measure as the heat flows through the surrounding glass with the lower resistance.

Limiting the Centerline Temperature During Cooldown

There are three basic approaches to limiting the centerline temperature of a waste glass with a fixed heat-generation rate. The approaches are: 1) reduce the diameter of the canister, 2) add internal fins, or 3) increase the cooldown rate. CANIST was used to predict variations in the centerline temperature as a function of the size of the canister diameter, the cooldown rate, and the addition of internal fins. Moreover, it was used to determine optimal fin volume and placement.

As an example of the effect of changing the canister diameter, Figure 4.5.20 shows the predicted centerline temperature and the temperature of the canister wall for canisters varying in diameter. These canisters contained waste with heat-generation rates of 0.58 W/L-glass and 0.13 W/L-glass. The canisters modeled had no internal fins, and the temperatures reflect a steady-state condition in 50°C ambient air. The centerline temperature dropped by a factor of two when going from a 36-in.-dia to a 12-in.-dia canister. In this particular case, the centerline temperature was not a serious problem for the 36-in.-dia canister, because it contained waste that does not generate heat at a very high rate. Figure 4.5.21 shows the effect on the centerline temperature of both reducing the diameter of and adding internal fins to a canister filled with LWR waste that was 20 years old (9.1 W/L-glass). The fins occupied 8% of the volume of the canister. The centerline temperature of the 24-in.-dia canister dropped 140°C when internal fins were added. Figure 4.5.21 also shows that the effect on the centerline temperature was about the same when the canister diameter was decreased from 36 in. to 24 in. (with no fins) and when fins were added to the 36-in.-dia canister. Figure 4.5.22 shows the temperature of increased LWR waste heat generation for comparison with Figure 4.5.21.

FIGURE 4.5.20. Canister Temperatures as a Function of Diameter
Canister With No Internal Fins

Controlling the rate at which the canister wall is cooled is another approach to limiting the centerline temperature of glasses that have high heat-generation rates. The situation modeled was the controlled cooldown of a 12-in.-dia canister containing waste glass that generates heat at a rate of 150 W/L. The canister was presumed to start with an isothermal temperature distribution of 1050°C, which is typical of ICM. The purpose of modeling this situation was to determine the rate at which the canister wall must cool to keep the centerline temperature below 1150°C. The two fin configurations modeled were the 12-in. "A" and the 12-in. "E" designs shown in Figure 4.5.23. With the 16-fin configuration, a cooling rate of 100°C/h limited the centerline temperature to 1157°C. The 8-fin configuration required a 700°C/h cooling rate to keep the centerline temperature below 1156°C. When the heat-generation rate of the waste glass was reduced to 100 W/L in the 8-fin configuration, and the

FIGURE 4.5.21. Canister Temperatures as a Function of Diameter and the Addition of Internal Fins

cooling rate was kept at 150°C/h , the maximum centerline temperature could be maintained at 1159°C . Cooling rates of 100° to 150°C/h are: 1) rapid enough to minimize the effects of devitrification and sensitization, and 2) rates that will not fracture the glass from thermal stress any more than necessary.

The steady-state temperature of the glass/canister system depends primarily on the heat-generation rate of the waste, the environment the canister is in, the diameter of the canister, and the design of the internal fins. The effect of each of these variables is discussed below.

CANIST was used to determine the centerline and canister wall temperatures in relation to different heat-generation rates, air versus water storage, and variations in the diameter of the canister. The effect of different heat-

FIGURE 4.5.22. Finned-Canister Temperatures for LWR Fuel Wastes

generation rates on the centerline and wall temperature of 12-in.-dia canisters is shown in Figure 4.5.24 for both air and water storage with an ambient temperature of 50°C . The canisters contain no fins and the temperatures are steady-state values. For a 12-in.-dia canister stored in air and containing waste glass that generated heat at 100 W/L, the centerline temperature predicted by CANIST was 990°C . The wall temperature was 345°C . Under the same conditions (except that the glass was assumed to generate heat at 10 W/L) the centerline and canister wall temperatures were 165°C and 105°C , respectively. Water storage of the waste canister with glass generating heat at 100 W/L reduced the centerline temperature by 255°C , from 990° to 735°C . Likewise, the wall temperature was reduced from 345°C to 65°C when storage was switched from

FIGURE 4.5.23. Canister Fin Designs (All Measurements in Inches)

air to water. A similar evaluation for 24-in.-dia canisters is shown in Figure 4.5.25; the 24-in.-dia canister was not evaluated for water storage. The canister wall temperature for a 24-in.-dia canister containing waste glass that generates heat at 10 W/L was 145°C, and a 12-in.-dia canister had a wall temperature of 105°C. The centerline temperature for the 24-in.-dia canister was 370°C, compared to 165°C for the 12-in.-dia canister.

The effects of fin design on cooldown and steady-state temperatures are quite complex. The variables of a fin design are fin width, fin length, distance to center, number of fins, and fin geometry. Analyzing the

FIGURE 4.5.24. Centerline and Canister Wall Temperatures as a Function of Heat-Generation Rates and Storage in Air and Water

interrelationships among these variables requires that a large number of computer runs be made. Over 120 different fin designs have been analyzed in an effort to identify the best possible candidates for demonstration.

The details of this study are discussed by Westcott and Slate (1979). They concluded that the most significant benefit on centerline temperature or cooldown can be achieved by extending the fin as close as practical to the center of the canister. Increasing the number of fins or adding flanges to their outer edges had a smaller impact on temperatures. The flanges were useful in decreasing temperature gradients in the canister wall, which reduced induced stresses. The 12 best designs are shown in Figure 4.5.23. The final

FIGURE 4.5.25. Centerline and Canister Wall Temperatures as a Function of Heat-Generation Rates for a 24-in.-dia Canister Stored in Air

selection of the fin design to be used for a particular plant would have to include careful consideration of the benefits and costs associated with a specific fin design. The costs would include not only fabrication costs but also the costs of an increased number of canisters and of different cooling equipment.

4.5.2.4 Canister Stress Analysis

The sources of stress in canisters are lifting and handling loads, internal pressure, high-temperature filling operations, transient heating and cooling, differential thermal expansions of canisters and glass, and impact

loading from low-probability accidents. The effect of these loadings have been studied by Simonen and Slate (1979), and their discussion of these considerations is summarized in the following sections.

Analysis Methods

Various computer programs and stress analysis techniques have proven useful in canister structural integrity studies at PNL. Table 4.5.18 lists specific computer programs that have been used at PNL. Program capabilities and areas of application to canister technology are noted.

Stresses and Deformation During Filling

During filling, waste canisters must serve as a mold until the glass solidifies. In this step of the processing cycle, canister wall temperatures can approach the melting points of the potential canister materials. With the loss of material strength at these temperatures, the potential for excessive creep deformation in the canister has been the focus of considerable attention at PNL and is treated in this section.

Wall Thickness -- General Considerations

There are numerous factors that can be identified as affecting the wall thickness requirements for canisters designed to contain HLLW. The focus of work at PNL has been on the conditions during filling and the potential creep deformation that can occur at the extreme temperatures of filling. Nevertheless, there are other perhaps more conventional considerations that also govern the selection of a canister wall thickness. The discussion below will briefly describe some of these considerations.

An allowance must be made for corrosion that may occur at both the inner and outer surfaces of the canister during filling. For the ICM process, both internal corrosive attack of the canister by the glass and external oxidation by the furnace environment have been observed and are discussed in Section 4.5.2.2. Experience with 304L stainless steel at ICM temperatures in an air environment suggests that an allowance for a 0.25-mm (0.010-in.) loss of oxide scale should be adequate. Corrosive attack at the canister inside surface is dependent on the composition of the waste glass. However, an allowance of

TABLE 4.5.18. Computer Codes Used in Canister Studies

Name of Code	Reference	Source of Code	Code Capability	Area of Application in Canister Studies
ANSYS	DeSalvo and Swanson 1975	Proprietary - Swanson Analysis Systems, Elizabeth, PA	General purpose finite-element code for stress and heat transfer	<ul style="list-style-type: none"> - Heat transfer and thermal stress analysis of closures - Heat transfer analysis of canister and glass residual stresses
MARC	MARC-CDC 1974	Proprietary, Marc Analysis Research Corp., Palo Alto, CA	General purpose finite-element code for stress and heat-transfer analysis	<ul style="list-style-type: none"> - Creep analysis for in-can melting conditions
HEATING-4	Turner and Simon-Tov 1971	Oak Ridge National Laboratory	Finite-difference heat transfer	<ul style="list-style-type: none"> - Heat transfer of canister closures
MONASTIFF	Lestingi 1970	Dr. J. F. Lestingi, Univ. of Akron	Multi-segment numerical integration of elastic shells of revolution	<ul style="list-style-type: none"> - Lifting stresses in closure - Discontinuity stresses in bottom and sidewall of canister
AXICRP	Sutherland 1969	Pacific Northwest Laboratory	Finite-element 2D solid for creep analysis	<ul style="list-style-type: none"> - Canister creep during filling by ICM
CRPSOL	--	Battelle Columbus Lab	Finite-element 2D solid for elastic-plastic analysis	<ul style="list-style-type: none"> - Canister creep during filling by ICM
AXISOL	Wilson and Jones 1967	Pacific Northwest Laboratory	Finite-element 2D solid for elastic-plastic analysis	<ul style="list-style-type: none"> - Canister creep during filling by ICM - Analysis of glass canister residual stresses - Analysis of glass fracturing - Calculation of stress intensity factors for weld defects
NONLEP	Gerdeen, Simonen and Hunter 1971	Battelle Columbus Lab	Multisegment numerical integration of elastic-plastic shells of revolution	<ul style="list-style-type: none"> - Canister creep during filling by ICM
WERCO	Wichman, Hopper and Mershon 1972	Proprietary, AAA Technology & Specialties, Co., Inc., Houston, TX	Local stresses in shell structures from localized external loadings	<ul style="list-style-type: none"> - Analysis of stresses at locations of canister lifting ears

0.25 mm (0.010 in.) should prove adequate for such attack. It is recommended, however, that specific corrosion tests be performed for new combinations of glass composition and canister materials on which data is not reported.

In addition to the conditions of the filling cycle, canisters must be sufficiently rugged to sustain both normal lifting loads and possible abuse from a low-probability impact load. Lifting loads are addressed in Section 4.5.2.5, which covers the subject of closure design. Impact performance is discussed in Section 4.5.2.6. Thickness requirements for impact performance are largely subject to engineering judgment. Results of impact tests suggest that wall thickness per se may not be as important as material ductility, joint design, and good welding practice. In general, PNL has specified wall thicknesses greater than those needed merely to meet creep and corrosive conditions imposed on the canister during filling. This has led to typical values of specified wall thicknesses in the range of 6.3 to 12.7 mm (0.25 to 0.50 in.), depending on the canister diameter. The greater wall thickness would correspond to a canister diameter in the 600-mm (24-in.) range.

Wall Thickness Determination. Procedures are detailed below for establishing minimum wall thickness for the ICM process based on consideration of material creep strength. The canister materials considered are 304L stainless steel and Inconel-601. These alloys tend to bound the types of alloys of interest to the ICM process in terms of strength.

Material Strength. Figures 4.5.26 and 4.5.27 give design strengths for 304L stainless steel and Inconel-601. These design curves were developed on the basis of the creep data in Section 4.5.2.2. The curves give allowable stress as a function of temperature for a criteria of 1% total creep strain. To allow for unaccounted scatter, the raw strength-data of the creep tests were reduced by a factor of two before the design strength curves of Figures 4.5.26 and 4.5.27 were plotted.

It should be noted that the curves for 304L stainless steel indicate that the strength decreases rapidly for temperatures above 1050°C (1922°F).

FIGURE 4.5.26. Design Strength of 304L Stainless Steel Based on Stress to Produce 1% Strain in a Specified Time Period

FIGURE 4.5.27. Design Strength of Inconel-601 Based on Stress to Produce 1% Strain in a Specified Time Period

Above 1100°C (2012°F), the indicated strengths become negligible. This decrease in strength is a reflection of accelerated oxidation of the test specimens. The loss of cross sections of the specimens (0.25 in. in dia) gave rise to an apparent loss of strength. With the larger stressed cross-sectional area relative to exposed surface area for a canister, a loss of surface material by oxidation will not have so profound an effect on strength. Nevertheless, 1050°C (1922°F) is probably a practical temperature limit for 304L stainless steel. The accumulation of spalled oxide scale may interfere with furnace operation.

Design Procedure. A design procedure has been developed to establish wall thicknesses for the ICM process to ensure that excessive creep deformation (i.e., diametric expansion) does not occur. The loading to the canister is due to the pressure head of the molten glass in the canister.

The procedure is intended for bottom-supported canisters. For top-supported canisters, bottom stresses and local stresses at top-support points should also be considered. These stresses for a top-supported canister can be substantial and can far exceed side-wall hoop stresses considered in the design procedure presented here.

The recommended procedure for establishing canister wall thicknesses for the ICM process is given in the following step-by-step format:

1. The relevant design conditions must be established in terms of the canister ID, fill height, total process time based on fill rate and hold time after filling, and maximum canister wall temperature during filling.
2. A 50°C (90°F) margin should be allowed for overheating, and an allowable stress level should be established for the canister material. In the example calculations that follow, this stress results in 1% total creep strain over the time span of the process cycle at a temperature equal to the process temperature, plus the 50°C (90°F) overheat allowance. The curves in Figures 4.5.26 and 4.5.27 are utilized.

3. The wall thickness should be calculated from the equations listed below:

$$t = \frac{pD_i}{2\sigma} \quad (4.18)$$

$$p = \rho h \quad (4.19)$$

where:

p = static pressure,

ρ = glass density,

h = fill height,

D_i = inside diameter of canister,

σ = design stress.

4. The thickness calculated in step 3 should prevent excessive expansion of the canister from high-temperature creep. To this thickness, a corrosion allowance must be added to account for oxidation at the canister outer surface and for glass attack at the inside surface.
5. The thickness determined in step 4 should be compared with minimum thickness requirements from impact and handling considerations. If necessary, the step 4 thickness should be increased to meet minimum thickness requirements as discussed above.

Wall Thicknesses for Typical Designs. Wall thickness requirements for bottom-supported canisters were estimated for specific filling conditions and canister sizes. The conditions were for ICM with the following design parameters:

glass density = 3.2 g/cc

melting rate = 50 kg/h

fill height = 1.98 m (6.5 ft)

hold time = 10 h

canister size = 12 in., 16 in., 20 in. and 24 in.

Based on the creep data from Section 4.5.2.2, wall thicknesses were calculated for canisters of 304L stainless steel and Inconel-601. The design curves in

Figures 4.5.26 and 4.5.27 give the design stress as a function of temperature for a criteria of 1% total creep strain within a specified period of time. (It should be recalled that to allow for unaccounted scatter, the raw strength-data from Section 4.5.2.2 were reduced by a factor of two before the design strength-curves were plotted.)

Tables 4.5.19 and 4.5.20 give the required wall thickness for a range of canister wall temperatures during filling. The actual design temperatures were 50°C (90°F) above the stated fill temperatures. The given wall thicknesses are minimum values based only on high-temperature creep considerations. These thicknesses do not include a corrosion allowance, nor do they consider handling loads or the need for impact resistance. The situation of the canister being held at an abnormally high temperature for an extended period is not taken into account.

Table 4.5.19 gives wall thicknesses for 304L for temperatures from 900°C to 1050°C (1652°F to 1922°F). For Inconel-601 (Table 4.5.20), the temperature range is 1000°C to 1150°C (1832°F to 2102°F). Above 1050°C (1922°F), the strength of 304L decreases rapidly, and it was not feasible to design a 304L canister for temperatures above this level. Within the temperature range of 1000°C to 1050°C (1832°F to 1922°F), the required wall thicknesses for the Inconel-601 canisters are 53% to 75% of those for 304L canisters.

It can be seen in Tables 4.5.19 and 4.5.20 that in several cases wall thicknesses of 2.5 mm (0.1 in.) or less are sufficient to prevent excessive

TABLE 4.5.19. Minimum Wall Thickness (304L Stainless Steel) To Avoid Excessive Creep Deformation During Filling by ICM

Canister Size ID, in.	Fill Time, h	Wall Thickness, mm (in.)			
		900°C Fill Temperature	950°C Fill Temperature	1000°C Fill Temperature	1050°C Fill Temperature
12	20	1.8 (0.070)	2.3 (0.090)	2.8 (0.112)	4.8 (0.188)
16	27	2.5 (0.100)	3.2 (0.128)	4.0 (0.158)	7.0 (0.276)
20	36	3.5 (0.136)	4.4 (0.174)	5.4 (0.212)	9.9 (0.390)
24	47	4.5 (0.178)	5.7 (0.224)	7.1 (0.278)	13.7 (0.540)

TABLE 4.5.20. Minimum Wall Thickness (Inconel-601) To Avoid Excessive Creep Deformation During Filling by ICM

Canister Size ID, in.	Fill Time, h	Wall Thickness, mm (in.)			
		1000°C Fill Temperature	1050°C Fill Temperature	1100°C Fill Temperature	1150°C Fill Temperature
12	20	1.6 (0.064)	3.6 (0.142)	4.9 (0.192)	6.3 (0.250)
16	27	2.3 (0.090)	5.0 (0.198)	6.9 (0.272)	8.9 (0.352)
20	36	3.0 (0.118)	6.6 (0.260)	9.2 (0.364)	12.0 (0.474)
24	47	3.8 (0.148)	8.4 (0.330)	11.7 (0.460)	15.2 (0.600)

creep deformation. In practice, these wall thicknesses should be increased to allow for corrosion, as well as for handling and impact loads. A typical corrosion allowance of 0.25 to 0.50 mm (0.01 to 0.02 in.) has normally been accommodated by rounding up to the next standard pipe or plate thickness. To allow for handling and impact loads, PNL has avoided wall thicknesses of less than about 6 mm (0.25 in.) for small-diameter canisters (e.g., 12 in.). For larger canisters the practice has been to increase the minimum wall thickness to about 13 mm (0.50 in.) for canisters in the 24-in. size range.

Estimated Safety Factors. The above design procedure includes a number of conservative assumptions, and safety factors associated with these assumptions have been estimated. The assumptions are listed below:

- overheat allowance of 50°C (90°F)
- 1% strain limit rather than creep rupture criterion
- derating of nominal strength properties by a factor of two to account for unknown variables in material strength
- canister is filled instantaneously
- bottom zones of furnace are not cooled as glass level rises in canister.

Numerical values of the safety factors arising from each source are estimated in Table 4.5.21. The factors are given both in terms of stress (equivalent to wall thickness) and time. The overheat allowance and assumptions on filling rate have a relatively small impact on the design. All other factors have the effect of increasing the wall thickness by a factor of two or more.

TABLE 4.5.21. Estimate of Safety Factors in Design of Canisters for ICM

<u>Design Considerations</u>	<u>Factor On Stress</u>	<u>Factor On Time</u>
Overheat allowance of 50°C	1.3	4
1% strain versus rupture	3.0	200
Design strength taken as one-half of nominal strength	2.0	20
Instantaneous filling of canister	1.1	1.5
Cooling of bottom zones	2.0	20
Composite safety factor - rupture	17.2	480,000
Composite safety factor - 1% strain	5.72	2,400

The composite safety factor on creep rupture or catastrophic failure of a canister is estimated to be 17.2 on stress, or 480,000 on a time basis. This means that the wall thickness could be reduced by a factor of about 17 before rupture of the canister wall would be considered probable.

Relative to the 1% strain limitation, the safety factor is 5.72 on stress and 2400 on the basis of time. The factor on time can be interpreted to mean that the actual creep strain will be less than 1.0% by a factor of 2400. For a 16-in.-dia canister this would amount to an actual diameter increase of 0.0017 mm (0.000066 in.).

It is concluded that the recommended design procedure provides substantial margins of safety against excess creep deformation during filling of canisters by ICM. Furthermore, unless a combination of upset events occurs simultaneously, the actual amount of creep deformation that will occur in practice will be difficult to detect through diametrical measurements.

Effect of Filling Rate. In the analyses of canister deformations, it is convenient to assume that the canister is instantaneously filled and that the load does not vary while the canister is at operating temperature. This assumption greatly simplifies and reduces the cost of the computer stress analysis. Also, the predicted results should be conservative for design purposes, since the magnitude and duration of loading is overestimated.

The effect of a uniform fill rate followed by a hold period at operating temperature was evaluated on the basis of the creep equation.

$$\sigma = 49,500 e^{0.765 t - 0.585}, \quad (4.20)$$

where:

σ = stress, psi

e = strain, mm/mm

t = time, h.

This equation was adopted to represent the behavior of a 300-series stainless steel at 1100°C (2012°F). Figure 4.5.28a defines the pressure time history and Figure 4.5.28b shows the estimated reduction in deflection that results from a gradual pressure application instead of an instantaneous application. For example, a typical canister is being filled during about half of its total hold time at maximum temperature. For this case, a computer solution that assumes the canister is filled at the start will overestimate deflections by a factor of about 30%.

For Figure 4.5.28b, the isochronous stress-strain equations were recast in the form of an incremental creep law. The creep response of a uniaxial specimen to the load time history of Figure 4.5.28a was calculated numerically for a range of maximum stress levels using a strain-hardening theory of creep. For the particular equations developed for the 300-series stainless steel at 1100°C (2012°F), the normalized response given in Figure 4.5.28b was found to be insensitive to stress level.

It was concluded that an assumption of instantaneous filling is reasonable, and will lead to conservative wall thicknesses. This, however, assumes that the entire canister is held at peak temperature throughout the actual period of filling and during subsequent hold periods at the operating temperature. It should be noted that current ICM furnaces are zone furnaces, which can allow lower portions of the canister to cool as the glass level rises. For such a mode of operation, instantaneous filling could lead to additional conservatism in creep-deformation predictions.

(a) PRESSURE TIME HISTORY

(b) FINAL DEFLECTION

FIGURE 4.5.28. Effect of Pressure History and Fill Rate on Bottom Deflection of a Canister

Local Stresses During Filling. When canisters are filled with vitrified waste, they are exposed to very high temperatures, which for ICM are in the range of 1050°C (1922°F). Material strengths at these temperatures are very low, and thus great care must be exercised in the design of canisters to minimize stress levels. For example, the desire to reduce stress levels has been a major reason for the use of the bottom-supported canister concept at PNL. In this section some specific case studies of local stress effects are

described as a means of providing insight into good canister design practice. In one of these studies, alternative bottom designs for a bottom-supported canister are evaluated. The other studies evaluate stresses and deformations due to thermal gradients in walls of canisters.

Bottom Joint Design. Figures 4.5.29 and 4.5.30 show two alternative joint designs for attachment of a flat bottom to the cylindrical body of a

FIGURE 4.5.29. Joint Stresses for Bottom-Supported Canister with Flat Bottom and Corner Weld

FIGURE 4.5.30. Joint Stresses for Bottom-Supported Canister with Flat Bottom and Turned Corner

canister. The corner weld shown in Figure 4.5.29 is simple to fabricate but was believed to be a less desirable design than the configuration shown in Figure 4.5.30. Analyses of both designs were performed to determine comparative stress states, using the shell of revolution computer program MONSASTIFF (Lestingi 1970). For both designs, the bottom was assumed to be supported by a flat, rigid base. Rotation action due to bending effects at the corners was

simulated. This resulted in a local loss of contact between the bottom plate and the supporting base. The loading to the canister had a pressure of 0.079 MN/m^2 (11.46 psi), simulating a hydrostatic head of molten glass. The canister wall was a 16-in.-dia, sch-40 pipe (0.5 in. thick), and the bottom was of 12.7-mm (0.5-in.) plate.

Figures 4.5.29 and 4.5.30 show calculated stress levels at the critical location, which is the root of the weld at the inside surface of the canister. For the simple flat bottom, the stress is 1.61 MN/m^2 (233 psi) in tension, as opposed to 0.12 MN/m^2 (17 psi) in compression for the bottom with a turned corner. The design of Figure 4.5.30 is clearly preferable, since peak stresses do not occur at the weld.

A review of closure designs in the ASME pressure vessel code indicates that the turned corner configuration of Figure 4.5.30 is recommended over the design of Figure 4.5.29. The flat plate design would be acceptable to the ASME code only with a modified weld joint, which incorporates the addition of a fillet weld at the inside location of the joint. Such a weld would be difficult to perform for canisters of any reasonable length, since access would be difficult to the inside location of the joint for welding.

The cask designer's guide (Shappert 1970) discusses the design of impact-resistant corners for nuclear shipping containers. Data show that the joint of Figure 4.5.29 is prone to cracking in corner impacts, and the joint of Figure 4.5.30, which removes the weld from the location of severe bending, corresponds to a recommended design in the cask designer's guide.

Inspection and fabrication costs are also considerations in joint design. The simple weld joint of Figure 4.5.29 will be less expensive to fabricate, but would be more difficult to inspect. It is likely that savings in fabrication costs would be consumed in higher inspection costs.

Canister Stresses at Zone Transitions. In the zone furnace for ICM, adjacent zones will maintain the canister wall at different temperature levels. At the transition between zones, longitudinal temperature gradients will be present. These gradients are a potential source of thermal stress and

permanent distortion of the canister wall. To determine the severity of these stresses, the computer program MONSASTIFF (Lestingi 1970) was applied to a postulated thermal-gradient condition.

Radial or through-the-wall temperature gradients were neglected, and a longitudinal gradient of 150°C (270°F) over 25.4 mm (1.0 in.) was assumed. This gradient was intended to bound the gradient anticipated during filling. For this analysis, elastic behavior was assumed. However, the effect of increasing temperature on material strength and resulting inelastic strain was simulated as a temperature-dependent elastic modulus. A review of estimated strengths for 304L stainless steel suggested a 4-to-1 ratio of moduli between the cold and hot zones of the canister.

Figure 4.5.31 shows predicted stress distributions in the region of the temperature gradient. Stresses have been normalized with respect to the temperature-dependent elastic modulus. The curves shown in Figure 4.5.31 can be interpreted as an estimate of the strains induced in the canister wall by the longitudinal temperature gradient. These estimated strains are on the order of 0.1%. Strains of this magnitude should not affect the structural integrity of the canister.

Figure 4.5.32 shows the estimated permanent deformation of the canister wall resulting from exposure of the narrow zone transition region to the longitudinal temperature gradient. It was assumed that local changes in canister diameter will occur as a result of differences in material strength in the thermally affected region, with the cold length of canister restraining the thermal expansion of the hot length of canister wall. The hot length is plastically deformed in compression, and this compressive strain results in a local decrease in diameter of the canister after cooling to room temperature. The computer program MONSASTIFF was used to calculate the deformation profile shown in Figure 4.5.32. This profile represents the difference between solutions with a uniform elastic modulus and a solution with a degraded modulus, as described above. As seen in Figure 4.5.32, the predicted canister deformation is a 0.058 mm (0.0023 in.) permanent change in the 203-mm (8.0-in.) nominal radius. This predicted diameter change is not considered significant and,

FIGURE 4.5.31. Canister Thermal Stresses in Region of Zone Separation in Zone-Melting Furnace, 16-in.-Dia Canister with 6.35-mm (0.25-in.)-Thick Wall

in practice, would be overshadowed by the so-called "ratchet" strain associated with the differential thermal contractions of the glass and metal canister.

Thermal Deformation in a "Banana Mode." Under the conditions of the ICM process, canisters experience unusually high temperatures and at these temperatures severe degradation of mechanical strength occurs. Such conditions would appear conducive to distortion of canisters. In this discussion a bottom-supported canister is considered, and distortion due to differential heating of the canister wall is evaluated.

FIGURE 4.5.32. Estimated Permanent Deformation of Canister Wall at Zone Separation Points of Zone-Melting Furnace, 16-in.-Dia Canister with 6.35-mm (0.025-in.)-Thick Wall

Figure 4.5.33 shows the configuration of interest. A cooled strip down the length of the canister is assumed. This cooled strip could approximate a circumferential temperature variation due, for example, to some unspecified furnace irregularity. A circumferential variation in temperature is of particular interest, since it can result in a bowing of the canister. This can be described visually as a "banana mode" of deformation. The analysis below relates the extent of deformation to the temperature differential ΔT of the cooled strip and the subtended angle θ of the strip. The results of the analysis serve to indicate the sensitivity of this deformation to small variations in temperature and to estimate allowances for thermally induced movement that must be made in the design of canister-connecting equipment.

Figure 4.5.34 shows the estimated lateral motion for the following specific parameters:

FIGURE 4.5.33. Model for Analysis of Canister Thermal Distortion by Banana Mode

$L = 3.05 \text{ m (10 ft)}$
 $D = 406 \text{ mm (16 in.)}$
 $\alpha = 5.0 \times 10^{-6} \text{ mm/mm/}^{\circ}\text{C}$
 $\Delta T = 20^{\circ}, 40^{\circ}, 60^{\circ}, 80^{\circ}, 100^{\circ}\text{C}$
 $\theta = 0 \text{ to } 360 \text{ degrees.}$

The curves show a lateral deflection approaching 25 mm (1.0 in.) for the 3.05-m (10-ft) canister for the worst combination of temperature differential ($\Delta T = 100^{\circ}\text{C}$) and circumferential distribution ($\theta = 180$ degrees). This estimate probably greatly exceeds any deflection that could occur in practice, since it is based on an improbable set of temperature conditions.

FIGURE 4.5.34. Predicted Thermal Distortion of Canister for Banana Mode

The normal lengthwise thermal expansion of the 3.05-m (10-ft) canister when heated to an ICM temperature of 1050°C (1922°F) is also of interest. This change in length is about 50 mm (2 in.), which is about twice the upper-bound estimate for lateral deflection.

It should be emphasized that the banana mode of deformation considered here is largely hypothetical. Canister distortion of this type has never been experienced in the numerous process trials performed at PNL. Canister dimensional changes from the filling process have been minor. Typically, a small increase in canister diameter and length can be detected by careful measurement. Representative diameter changes are given in Table 4.5.22. These dimensional changes are not considered to be of any consequence to the use of canisters.

Experimental Evaluation

Experimental results and service experience have been compared with analytical structural analysis models. The results of controlled creep test

TABLE 4.5.22. Calculated and Measured Diametrical Expansions of Canisters

Canister Number	Measured Diameter Change, mm (in.)	Calculated Diameter Change, mm (in.)
ICM-16	1.27 (0.050)	0.89 (0.035)
ICM-13	1.27 (0.050)	0.66 (0.026)
ICM-19	0.99 (0.039)	0.36 (0.014)
ICM-17	0.76 (0.030)	0.81 (0.032)
ICM-11	0.76 (0.030)	1.17 (0.046)
ICM-20	0.76 (0.030)	0.36 (0.014)
ICM-6	0.76 (0.030)	0.36 (0.014)
ICM-5	0.63 (0.025)	0.36 (0.014)
ICM-8	0.51 (0.020)	0.36 (0.014)
ICM-4	0.51 (0.020)	0.66 (0.026)
ICM-3	0.51 (0.020)	0.36 (0.014)
ICM-18	0.41 (0.016)	0.36 (0.014)
ICM-7	0.38 (0.015)	0.36 (0.014)

using a full-sized canister and deformation data from canisters used in ICM process demonstrations are reviewed here.

Creep Test Results. To measure creep at elevated temperatures under well controlled conditions, an empty canister was tested at PNL under an internal pressure of 0.103 MN/m^2 (15 psi) of argon. The test configuration is shown in Figure 4.5.35. In the test the canister was heated to 1050°C (1922°F), and the pressure was maintained for 24 h. The OD of the 304L stainless steel canister was 324 mm (12.75 in.), and the wall thickness was 9.5 mm (0.375 in.). The bottom was made of a 12.7-mm (0.50-in.)-thick flat plate.

The measured and predicted bottom deformations were compared using the computer program NONLEP (Gerdeen, Simonen, and Hunter 1971). Figures 4.5.36 and 4.5.37 indicate the correlation of predicted and measured bottom deformations, which attained a value of about 7.1 mm (0.28 in.) at the center of the canister bottom. Thermocouples on the canister wall registered temperatures in the 1050°C (1922°F) to 1060°C (1940°F) range. There were no thermocouples on the canister bottom. Since there is some uncertainty as to actual bottom

FIGURE 4.5.35. Canister Creep Test Configuration 304L Stainless Steel

temperatures, analyses were performed for both 1050°C (1922°F) and 1060°C (1940°F). The shape of the deformed bottom profile was measured relative to a clamped straight-rule using a vernier depth gage. As can be seen in Figures 4.5.36 and 4.5.37, the deformation pattern was nonsymmetrical along the selected diameter of the measurements. This is probably due to anisotropy of the bottom plate material associated with the rolling and transverse directions of the plate material. The correlation between the predicted and measured deformations is considered excellent.

FIGURE 4.5.36. Comparison of Predicted and Measured Canister-Bottom Deformation for Assumed Bottom Temperature of 1050°C (1922°F)

FIGURE 4.5.37. Comparison of Predicted and Measured Canister-Bottom Deformation for Assumed Bottom Temperature of 1060°C (1940°F)

Post-test diameter and length measurements were made using a micrometer and vernier caliper. The measurements indicated a reduction in length between 0.25 mm and 0.76 mm (0.010 in. to 0.030 in.), whereas the analysis predicted essentially no change in length. The measured reduction in length is attributed to the formation and the subsequent removal by sandblasting of an oxide scale on the outer surface of the canister. The measured diameter changes ranged from -0.46 mm to +0.20 mm (-0.018 in. to +0.008 in.), whereas the predicted diameter change was +0.20 mm (+0.008 in.). Again, the difference is attributed to the loss of an oxide scale.

Evaluation of ICM Trials

In the course of process development efforts at PNL, numerous 304L stainless steel canisters have been filled by the ICM furnace. Canister diameters are routinely measured before and after filling. This data base was thus available to validate analytical predictions of canister creep deformations.

A survey of processing data was made to establish time, temperature, and fill rate histories of each of 13 early canisters. Table 4.5.23 gives geometric and loading cycle parameters for these particular canisters. All the canisters had been filled in a top-supported condition so that bulging of the unsupported bottoms could occur if a sufficient static head of molten glass was present during filling. For certain canisters the bottom thicknesses were unknown except that the bottom plates were either 9.5 or 12.7 mm (3/8 or 1/2 in.) thick. For those canisters where bottom-thickness data were lacking, a 12.7-mm (0.500-in.) thickness was assumed.

For creep analyses, only the high-temperature portion of the total canister thermal history was of interest; heat-up and quenching operations were not. For the purpose of analyses, the loading cycles were simplified. The first phase consisted of a filling at a uniform rate with the canister wall at uniform and constant temperature. The second phase consisted of a hold at constant temperature after filling. In each case the analyses were for the maximum temperature in the canister wall at the critical bottom location.

TABLE 4.5.23. Canister Parameters and Loading Cycle Definition

Canister Number	Outside Diameter, mm (in.)	Wall Thickness, mm (in.)	Bottom Thickness, mm (in.)	Fill Height, m (ft)	Loading Cycle
ICM-3	219 (8.625)	8.18 (0.322)	9.52 (0.375)	0.61 (2.0)	3-h fill at 1075°C 3-h hold at 1075°C
ICM-4	324 (12.75)	9.52 (0.375)	12.70 (0.500)	1.00 (3.3)	12-h fill at 1050°C 13-h hold at 1050°C
ICM-5	219 (8.625)	8.18 (0.322)	--	0.61 (2.0)	4-h fill at 1050°C 6-h hold at 1050°C
ICM-6	219 (8.625)	8.18 (0.322)	--	0.85 (2.8)	10-h fill at 1060°C 11-h hold at 1060°C
ICM-7	219 (8.625)	8.18 (0.322)	--	0.46 (1.5)	4-h fill at 1075°C 6-h hold at 1075°C
ICM-8	219 (8.625)	8.18 (0.322)	--	0.55 (1.8)	5-h fill at 1075°C 15-h hold at 1075°C
ICM-11	324 (12.75)	9.52 (0.375)	12.70 (0.500)	0.67 (2.2)	13-h fill at 1095°C 14-h hold at 1095°C
ICM-13	324 (12.75)	9.52 (0.375)	12.70 (0.500)	0.52 (1.7)	5-h fill at 1085°C 3-h hold at 1085°C
ICM-16	324 (12.75)	9.52 (0.375)	12.70 (0.500)	0.79 (2.6)	3-h fill at 1135°C 5-h hold at 1130°C 5-h hold at 1090°C
ICM-17	324 (12.75)	9.52 (0.375)	12.70 (0.500)	0.82 (2.7)	10-h fill at 1115°C 5-h hold at 1115°C
ICM-18	219 (8.625)	8.18 (0.322)	--	0.70 (2.3)	5-h fill at 1095°C 4-h hold at 1095°C
ICM-19	219 (8.625)	8.18 (0.322)	--	0.55 (1.8)	8.5-h fill at 1075°C 5-h fill at 1085°C 7-h hold at 1085°C
ICM-20	219 (8.625)	8.18 (0.322)	--	0.76 (2.5)	3-h fill at 1075°C 4-h hold at 1075°C 40-h hold at 1025°C

Deformations were measured on a number of canisters after fill. Due to the rugged design and limited fill height, the amount of creep for all the canisters was relatively small. In addition to creep deformation, the measured diametrical expansions include effects of both 1) the loss of oxidized surface material by spalling, and 2) an increase in canister diameter due to differential thermal contraction of the glass and metal during cooling and solidification of the glass.

The calculated diameter changes were adjusted downward by 0.254 mm (0.010 in.) to account for surface spalling. An additional correction for differential thermal expansion effects between the glass and canister was made as follows. The expansion coefficients of the steel and glass were taken to be 14.4×10^{-6} mm/mm/ $^{\circ}$ C and 9.0×10^{-6} mm/mm/ $^{\circ}$ C, respectively. At 550 $^{\circ}$ C (1022 $^{\circ}$ F), the glass can be considered cool enough to behave essentially as a solid. In cooling to room temperature (21 $^{\circ}$ C or 70 $^{\circ}$ F) the glass will contract by an amount of

$$\begin{aligned}\alpha \Delta T &= (9 \times 10^{-6}) (550-21) \\ &= 4.8 \times 10^{-3} \text{ mm/mm,}\end{aligned}\tag{4.21}$$

while the steel will attempt to contract by an amount of

$$\begin{aligned}\alpha \Delta T &= (14.4 \times 10^{-6}) (550-21) \\ &= 7.6 \times 10^{-3} \text{ mm/mm.}\end{aligned}\tag{4.22}$$

The difference in contraction of the glass and steel results in a mechanical strain in the steel of

$$\begin{aligned}\epsilon &= (7.6 - 4.8) \times 10^{-3} \\ &= 2.8 \times 10^{-3} \text{ mm/mm,}\end{aligned}\tag{4.23}$$

and a tensile stress for an elastic modulus of $E = 0.193 \text{ MN/m}^2$ (28×10^6 psi) of

$$\begin{aligned}\sigma &= E \epsilon \\ &= (0.193 \times 10^6) (2.8 \times 10^{-3}) \\ &= 540 \text{ MN/m}^2 \text{ (78,400 psi).}\end{aligned}\tag{4.24}$$

The predicted diameter changes for the two canister sizes of interest are then

$$\begin{aligned}\text{8-in. Canister} - D &= (8.625 \times 2.8 \times 10^{-3}) \\ &= 0.61 \text{ mm (0.024 in.)}\end{aligned}\tag{4.25}$$

$$\begin{aligned}
 12\text{-in. Canister} - D &= (12.75 \times 2.8 \times 10^{-3}) & (4.26) \\
 &= 0.91 \text{ mm } (0.036 \text{ in.}).
 \end{aligned}$$

Table 4.5.23 gives predicted and measured diametrical expansions. The canisters are listed in order of decreasing diameter change as measured on the experimental canisters. The value listed is the maximum local expansion of the canister, which in each case was at a location near to, but slightly above the very bottom of the canister. It is apparent that none of the canisters was severely challenged structurally. Except for the few canisters listed at the top of the table, the entire measured expansion can be accounted for in terms of the differential thermal expansion effect between the glass and canister. It is apparent that the severity of the loading cycles was relatively modest compared to the canister strengths. This limits the usefulness of the measured diameter changes as a means of validating the predictive methods. It may be stated, however, that the analyses are in agreement with the test data in predicting little creep deformation and relatively small diameter changes. With one or two exceptions, the analyses correctly identified those canisters that experienced the greatest diameter changes.

Table 4.5.24 lists the experimental canisters in order of decreasing bottom deflection as predicted by the calculations. Bottom deflections were not measured on the experimental canisters. However, canister ICM-16 was identified as clearly having the greatest extent of deformation, which was reported to be roughly 8 mm (0.3 in.). The stress analyses correctly identified ICM-16 as having the greatest potential for bottom deformation. Also, insignificant bottom deformation was predicted for most of the canisters, which is in agreement with observations.

Residual Stresses and Glass Fracturing

Canister residual stresses are attributed to the differential thermal expansion coefficients of the metal canister and the glass within the canister. Since the interaction between the canister and glass is the primary source

TABLE 4.5.24. Calculated and Measured Bottom Deflection of Canisters

<u>Canister Number</u>	<u>Calculated Bottom Deflection (Relative Values)</u>	<u>Measured Bottom Deflection 10⁻³ in.</u>
ICM-16	100	300
ICM-17	71	--
ICM-11	49	--
ICM-4	16	--
ICM-13	8	--
ICM-18	5	--
ICM-19	4	--
ICM-8	3	--
ICM-20	3	--
ICM-6	3	--
ICM-7	1	--
ICM-5	1	--
ICM-3	1	--

of stress, a unified analysis procedure was used to treat both the glass and canister components. This section begins with a discussion of the effect of residual stresses on possible failure modes for canisters. Then two analytical models for predicting residual stresses and glass fracturing are described. The first utilizes a one-dimensional model, focusing on the canister and the factors that govern residual stresses in the canister wall. The second approach is a two-dimensional model focusing on the glass and factors that govern the development of cracks in the glass matrix.

Effect of Residual Stresses on Canister Integrity. The following discussion summarizes the consensus of work as reported in the literature on residual stresses. A special effort is made to interpret known trends in the context of canister residual stresses.

Existence of Residual Stresses. The existence of some level of residual stresses in engineering structures is usually a known and accepted condition. Even after stress relief, the presence of stress at some low value is

frequently assumed and is often factored into the design of the structure. However, the role of stresses on the serviceability of structures must be evaluated on a case-by-case basis.

Very high tensile residual stresses have been measured in walls of waste canisters. They are attributed to the differential thermal expansion coefficients of the metal canister and the glass within the canister. During the cooling of a canister of molten glass, the stress in the canister can build up to the extent that the canister material yields. Subsequently, the level of residual stress is limited by the material yield strength. The presence of residual stresses in canisters is not questioned. Rather, the focus has been on determining if there are possible detrimental effects of these residual stresses on the structural integrity of the canister.

Gross Distortion. Much of the literature on residual stresses relates to welding technology. Residual stresses in this context are associated with welding distortion, which can degrade the function of the component or make subsequent fit-up and welding of the structure impossible. In waste canisters, measurable changes in diameter have been observed at PNL as a result of the filling process. Typical data are given in Section 4.5.2.4 of this report. For ICM, diameter increases have not exceeded 1.27 mm (0.050 in.). No significant deviations from straightness have been observed in canister-filling trials. In no cases have dimensional changes been sufficient to affect the function of the canister to any extent. Also, observed dimensional changes per se are not believed to result in any loss of canister structural integrity.

Static Fracture. The effect of residual stresses on the static strength of structures has been subject to different interpretations in the literature. Since the residual stresses in canisters can be at the material yield strength, first-order considerations would suggest that the canister wall is in a condition of incipient fracture. Such considerations do not recognize the importance of yielding and material ductility on the occurrence of fracture and that residual stresses are of a self-limiting nature. In ductile metals, residual stresses generally cannot result in sufficient plastic deformation to cause catastrophic fracture.

Residual stresses will affect fracture under static or dynamic loadings only if the material has a low fracture toughness and if the structure has particularly large crack-like defects. However, the materials of interest to the canister application are noted for their high fracture toughness. Also, in the context of fracture mechanics, the crack-like defects that could occur in canisters are relatively small; those types of brittle fracture propagation that are of concern in large-diameter and thick-walled pressure vessels are not believed relevant to waste canisters.

At PNL, a brittle fracture of a canister due to residual stresses or imposed mechanical loadings has never been observed. In drop tests of prototypical canisters, as reported in Section 4.5.2.6, many canisters known to have high residual stresses have sustained severe impact loadings and gross plastic deformation without loss of integrity. Canisters have occasionally failed in such drop tests when they were not designed and fabricated to accepted standards. These canisters had severe plastic deformation in corner weld joints; however, even for these canisters, there is no reason to believe that residual stresses had any effect on the weld failures.

Fatigue Cracking. Residual stresses are known to have an important effect on fatigue life. Tensile residual stresses reduce fatigue life, while compressive residual stresses have been demonstrated to increase fatigue life. However, the stress cycles in the life of waste canisters are projected to be minimal. Thus, the potential for fatigue failure of waste canisters is remote, and residual stresses will have little or no potential to affect the fatigue life of canisters. Glass-filled PNL canisters have never failed because of fatigue cracking.

Stress-Corrosion Cracking. For SCC to occur, canisters having residual stresses must be associated with two other conditions: 1) the material must be susceptible to cracking (e.g., sensitized 304 stainless steel), and 2) it must be exposed to specific corrosive conditions.

Stress-corrosion cracking should not be a factor for superalloy (e.g., Inconel-600 series) canisters, or for canisters stored in air rather than in

water basins. The greatest concern at PNL has been for stainless steel canisters that are to be stored for long periods in water basins.

Stress-corrosion cracking of a stored glass-filled canister has occurred at PNL (Bradley 1977). Studies have shown that an adverse combination of stress, material characteristics, and corrosive conditions caused the cracking. It is currently recognized that material, processing, and storage conditions must be controlled to prevent SCC of canisters. It is believed that the potential for cracking can be eliminated through canister alloy selection, residual stress reduction, control of processing conditions, and control of water chemistry during water-basin storage.

Conclusions on Residual Stress Effects. Concern about residual stresses appears limited to SCC. For this failure mode, the potential damaging effect of residual stresses can be eliminated if suitable restrictions are placed on canister materials and usage. The potential for SCC is essentially nonexistent for canisters stored in an air environment. The potential is greatest for stainless steel canisters subject to water-basin storage.

One-Dimensional Analysis of Residual Stresses. It has long been recognized that stresses originate in both the glass and canister during cooling of the molten glass. Such stresses have been manifested as cracking of the glass and as tensile residual stresses in the walls of the canister. This discussion deals with the development of an analytical model to simulate the process of glass solidification and cooling, which is designed to predict time histories of stress in the glass canister system. This analytical model is based on the adaptation of finite-element computer programs. Details of this model and a collection of case studies will be described. The case studies include conditions approximating present canister experience with simulated waste, which can serve as baseline checks to evaluate the validity of the analysis. Other case studies consider internal heat generation in the radioactive waste materials. In such cases, extrapolation of experience from nonradioactive glasses can be misleading.

Thermal Analysis Model. Since all stresses of importance to the canister system are thermally induced, heat transfer is an important component of the stress analysis procedure. The thermal model is shown in Figure 4.5.38 and has been implemented with the ANSYS finite-element computer program (DeSalvo and Swanson 1975). The computer code ANSYS performs both steady-state and transient heat-transfer calculations using an implicit time-step scheme. Figure 4.5.38 illustrates an axial slice, representative of the canister, at locations removed from the ends of the canister. The glass and the metal of the canister wall were assigned individual thermal properties that are temperature-dependent; in addition, the glass could be assigned a level of internal heat generation (W/L). Tables 4.5.25 and 4.5.26 list the thermal properties for glass and 304L stainless steel that were used in the numerical studies. The glass properties should be viewed as only representative of borosilicate, waste-containing glasses and not specific to any particular composition. An ideal bond was assumed at the glass-metal interface so that the thermal impedance across this interface could be taken to be zero. Heat was transferred from the outside surface of the canister by convection and radiation.

Stress Analysis Model. Stresses were calculated with the finite-element computer program AXISOL (Wilson and Jones 1967). The element breakdown of the glass-canister structure, shown in Figure 4.5.39, matches that used in the thermal analysis that provided temperature data to the stress analysis. Detailed consideration was given to the boundary conditions imposed on the upper and lower faces of the axial slice treated in the analysis. On the lower face, nodes were constrained to remain on a plane (i.e., zero axial displacement). On the upper surface, it was necessary to use a double set of nodes so that the column of the liquid glass could rise or fall in response to thermal expansion effects. Once the glass solidified, the upper surface of the solidified mass was then constrained to displace as a plane. Within both the liquid and solid glass, radial compatibility was enforced between adjacent nodes.

The solidification of glass was treated on the basis of the instant-freezing model. Above the freezing temperature, the elements of the liquid

FIGURE 4.5.38. Thermal Analysis Model for ANSYS Finite-Element Code

glass were assigned a negligible value of elastic modulus. Stresses were calculated for a sequence of temperature states during the cooling process. After the glass passed the solidification temperature, the last recorded mechanical-strain state in the glass element was then fixed as a "locked-in" state of permanent deformation. Upon final cooling, the distribution of stress in the glass was largely determined by the distribution of such locked-in strains.

The canister was treated as an elastio-plastic solid. At each time step, the stresses were adjusted to satisfy plastic yield and flow criteria. The accumulated plastic strain at the end of each solution time step was carried over as a permanent or an initial strain to the next time step. Effects of strain reversals and residual stresses were thus taken into account. The specific mechanical properties used in the numerical studies are listed in Tables 4.5.27 and 4.5.28. Below the solidification temperature (taken as 575°C or 1067°F), variations in glass properties with temperature were neglected.

TABLE 4.5.25. Thermal and Physical Properties of Glass [Density = 3.2 g/cc (0.115 lb/in.³)]

Temperature		Conductivity		Specific Heat	
^o C	^o F	W/M- ^o C	BTU/h-in.- ^o F	Calories/g	BTU/lb
0	32	0.750	0.0361	0.084	0.152
635	1175	1.365	0.0651	---	---
727	1341	1.652	0.0795	---	---
870	1590	3.409	0.1640	---	---
2011	3652	---	---	0.171	0.309

TABLE 4.5.26. Thermal and Physical Properties of 304L Stainless Steel [Density = 7.8 g/cc (0.28 lb/in.³)]

Temperature		Conductivity		Specific Heat	
^o C	^o F	W/M- ^o C	BTU/h-in.- ^o F	Calories/g	BTU/lb
-18	0	13.0	0.625	--	--
204	400	17.9	0.861	--	--
427	800	20.2	0.972	--	--
649	1200	23.5	1.131	--	--
871	1600	26.0	1.250	--	--
1093	2000	27.4	1.319	--	--
21	70	--	--	0.060	0.108
982	1800	--	--	0.092	0.165

Glass-Hardening Behavior. The hardening behavior of glass has been discussed in the literature, particularly as it relates to the prediction of residual stresses associated with tempering of commercial plate glass. The assumption used in our numerical studies is the instant-freezing model, first proposed by Bartenev (1949). In this approach, the complex phenomena of a glass transition range is replaced by the simple concept of an instant freezing temperature, T_g . Above this temperature, the glass is considered incapable of sustaining shear stresses. While below this temperature the glass is treated as a perfectly elastic solid. The instant-freezing concept has been

FIGURE 4.5.39. Stress Analysis Model for Finite-Element Code AXISOL

successfully applied to predict residual stresses in tempered plate glass. The predicted stresses have generally been in remarkable agreement with measured stresses.

It is believed that canister-stress calculations are much less influenced by the limitations of the instant-freezing concept than calculations for plate-glass tempering. The canister and glass-tempering problems differ significantly in two ways. First, stresses in the glass-canister assembly result primarily from differences in the thermal expansion coefficients of the glass and canister material. Second, the section thicknesses in canister glass are much greater than those of interest in plate-glass tempering. Thus, temperatures can differ greatly in the interior of the canister glass relative to the softening temperature range. This is not true for tempering of plate glass.

Although the instant-freezing model appears to be an excellent approximation for canister analyses, the more complex rheological models reported in the literature have also been investigated. The application of such models to

TABLE 4.5.27. Mechanical Properties of Glass

Temperature	Elastic Modulus		Poisson's Ratio	Thermal Expansion Coefficient	
	MN/m ²	psi		°C ⁻¹	°F ⁻¹
Below Solidification Temperature, 575°C (1067°F)	75,900	11 x 10 ⁶	0.300	2.8 x 10 ⁻⁶	5 x 10 ⁻⁶
Above Solidification Temperature, 575°C (1067°F)	0.0067	1.0	0.49999	2.8 x 10 ⁻⁶	5 x 10 ⁻⁶

TABLE 4.5.28. Mechanical Properties of 304L Stainless Steel

Temperature		Modulus		Expansion		Yield Strength	
°C	°F	MN/m ²	psi	°C ⁻¹	°F ⁻¹	MN/m ²	psi
38	100	0.193 x 10 ⁶	28.0 x 10 ⁶	4.4 x 10 ⁻⁶	8.0 x 10 ⁻⁶	241	35,000
427	800	0.166 x 10 ⁶	24.1 x 10 ⁶	5.2 x 10 ⁻⁶	9.3 x 10 ⁻⁶	138	20,000
649	1200	0.145 x 10 ⁶	21.2 x 10 ⁶	5.4 x 10 ⁻⁶	9.7 x 10 ⁻⁶	103	15,000
871	1600	0.116 x 10 ⁶	16.8 x 10 ⁶	5.7 x 10 ⁻⁶	10.2 x 10 ⁻⁶	69	10,000

glass residual-stress predictions has been the subject of several papers (Narayanawamy and Gordon 1969; Wayman 1962; Lee, Rogers and Woo 1965).

The rheological behavior of glass has been treated by the theory of thermovisco-elastic stress analysis (Morland and Lee 1960; Muki and Steinberg 1961; Lee and Rogers 1963; Lee, Rogers and Woo 1965). Temperature is taken to affect the stress-relaxation process by a contraction in the time scale so that an equivalent time can be defined as

$$\zeta = t\phi(T), \quad (4.27)$$

where ζ is equivalent time, t is time and T is the temperature. Such material behavior is termed thermorheologically simple and is equivalent to a temperature change causing a shift, without a change in the shape of stress-relaxation

curves. Stress-relaxation studies by Van Zee and Noritake (1963) show that glass at elevated temperatures obeys such a law to a good approximation. For commercial soda-lime glass, the shift function can be represented as

$$\log_{10} \{ \phi(T) \} = 0.03861 (T-538) \quad , \quad (4.28)$$

where T is the temperature in $^{\circ}\text{C}$. Lee, Rogers and Woo (1965) have reported the relaxation modulus for this glass. The equations of the above rheological scheme were incorporated into our stress analysis model in a simplified manner to establish the sensitivity of glass and canister-stress predictions to visco-elastic effects. The results of these numerical studies at PNL indicated that the rheological behavior has little effect on stresses for the glass-canister situation.

Parameters for Case Study. An 8-in.-dia canister was used in initial case studies. The canister was made of 304L stainless steel, with a 203-mm (8.00-in.) ID and a wall thickness of 7.94 mm (0.3125 in.). For simplicity, there were no fins within the canister. The 8-in.-dia canister was selected partly because a larger size requires internal fins to maintain glass center-line temperatures at acceptable levels and partly because it matched the size of many existing developmental ICM canisters. These canisters have been the subject of glass-characterization and experimental residual-stress studies, and thus offered an opportunity to compare predictions with service experience.

Glass and canister stresses were calculated with two varying parameters: the internal heat-generation rate in the glass and the history of heating and cooling. Heat-generation rates from 0 to 100 W/L were considered. Thermal conditions were those of ambient air-cooling, water-cooling, and furnace-heating. Various sequences of these conditions were analyzed so that transient-stress states and residual stress levels under steady-state conditions could be determined.

Thermal Solutions. In the calculations, a canister of molten glass was assumed to be removed from an ICM furnace at a temperature of 1050°C

(1922°F) and cooled to an equilibrium temperature in air. This cooling process is shown in Figure 4.5.40 for an internal heat-generation rate in the glass of 100 W/L. Heat generation rates of 0 W/L and 50 W/L were also analyzed. The initial part of the cooling process was similar for all cases; the cooling primarily differed in the equilibrium temperature distribution. With no heat generation, the temperature eventually reached the ambient level. For

FIGURE 4.5.40. Temperature Profiles in Canister of Glass for Air-Cooling Followed by Water-Cooling from 1050°C (1922°F) - 100 W/L

50 W/L, the final canister wall temperature was 170°C (340°F), and the glass centerline temperature was 304°C (580°F) in air. For 100 W/L, the corresponding temperatures were 255°C (490°F) and 493°C (920°F).

For the heat-generating glass, thermal analyses were also performed for cooling by water immersion. As shown in Figure 4.5.40, the canister wall cools very rapidly. The canister temperature reaches a terminal level near the water temperature before the glass as a whole is able to exhibit any cooling response. Eventually, however, the glass centerline temperature reaches a reduced equilibrium temperature, which is compatible with the reduced outer wall temperature. A third transient occurs when the heat-generating canister of glass is removed from water immersion into an air-cooling environment, and this transient was also analyzed.

Canister Stresses. Canister stresses were calculated for the thermal transient conditions described above. Figure 4.5.41 shows the stress-time behavior for internal heat-generation rates in the glass, ranging from 0 to 100 W/L. For all cases, the initial air-cooling of the canister of molten glass from 1050°C (1922°F) resulted in tensile residual stress in the wall of the canister. However, the heat generation tends to reduce the level of this tensile stress. The tensile stress in the canister wall is due to the higher thermal expansion coefficient of the steel canister relative to the glass. With internal heat generation, the glass and canister never cool to ambient temperatures. As a result, the full effect of the differential thermal contraction of the metal and glass never develops.

The consequences of water-cooling on canister stress levels are dramatically shown in Figure 4.5.41. With no heat generation, the canister is initially at room temperature, and placing the canister in room-temperature water has no effect on either temperature or stress. However, when a hot canister is first placed in the water, the metal wall of the canister cools rapidly to the water temperature. The canister is thus prevented from contracting by the still hot glass; as a result, the tensile stress in the canister increases sharply, deforming the canister plastically. Eventually, as the glass also

FIGURE 4.5.41. Stress in Wall of Canister Showing Effect of Heat Generation

cools, the thermal differential between the metal and the glass decreases, and in response, the tensile stress in the canister wall decreases. For a heat rate of 100 W/L, the canister wall stress actually is predicted to become compressive. When removed from water storage, the canister wall stress tends to become even more compressive, and compressive yielding of the canister wall is predicted because both the canister and glass temperatures increase. For increasing temperatures, the higher expansion coefficient of the metal relative to the glass causes the canister stress to become compressive.

Figure 4.5.42 shows the results of calculations that include more than one cycle of the air-to-water thermal transient. The first cycle is representative of subsequent cycles, and thus, an analysis of one cycle is sufficient to characterize the cyclic stress behavior.

FIGURE 4.5.42. Stress in Canister Wall Showing Effect of Thermal Cycling

The consequences of heat treatment on a canister with a zero-heat-generation glass are shown in Figure 4.5.43. The glass is re-heated to a temperature of 427°C (800°F)--short of its 575°C (1067°F) softening temperature. The hot canister is quenched in water, and at the end of the quench a compressive canister-wall stress equal to the yield strength is predicted. However, this predicted compressive stress in the canister wall may not be realistic. If stresses in the wall of the canister are to become compressive, the glass-metal bond must support tensile stresses. Examinations of experimental canisters show evidence of fracture at or near the bond. Such bondline fractures would relieve compressive residual stresses that might develop in the canister wall.

Fractures at the bond line will affect both the thermal response and the stress response of the glass-canister system. Such fractures are normal to the path of the heat flow and will introduce gap-type resistances to heat transfer. A bond-line gap could significantly affect the temperatures in the

FIGURE 4.5.43. Effect of Water Quench on Stress in Canister Wall

system, in addition to eliminating compressive stress regime from the curves of predicted canister wall stresses. To a first approximation, the canister wall would be stress-free during the periods of predicted compressive stress, while the tensile stress regimes should be relatively unaffected by the presence of bond-line fractures.

Residual Stress Reduction. Numerous procedures have been tested for reducing residual stresses in canisters. Thermal treatments include quenching and subcooling. In quenching trials at PNL, a hot canister was rapidly cooled in water. Thermal stresses resulting from the quench were expected to deform the canister and relieve residual stresses. However, the measured reduction in stresses was marginal (much less than anticipated). In subcooling tests at PNL, subscale canisters of glass were cooled below room temperature in a cold bath. Reductions in measured residual stress were observed that were almost as predicted. However, the bath temperature was not cold enough to entirely eliminate the tensile residual stresses. Although thermal treatments show promise of reducing canister residual stresses, they may have detrimental

effects on glass quality. The extent of cracking in the glass is likely to increase because of shock-type thermal stressing of the glass.

Changes in the design of the canister and packaging system can also be used to reduce residual stresses. Ferritic stainless steels have thermal-expansion coefficients that more closely match expansion coefficients of waste glasses. The alloy E-Brite 26-1 has been considered for this reason and also because of its good corrosion characteristics. However, ferritic stainless steels can have low impact-toughness at room temperature and poor creep strengths (relative to austenitic materials) at ICM temperatures.

Compliant liners have been evaluated at PNL as a means of reducing canister residual stresses. In this concept, the liner will crush with little resistance as the canisters tend to shrink around the glass. Porous metal materials have been considered for this purpose. However, these materials have not been considered particularly desirable. They tend to be attacked by the molten glass and also seriously impede the removal of heat from the glass.

Overpacks have been evaluated as a means of achieving an outer containment that is relatively free of residual stresses. It is concluded that residual stresses in overpacks will be much less severe than in primary canisters, although stresses from final closure welding will no doubt still be present in overpacks.

Glass Stresses. Stresses in the glass arise from two sources. The first source is the differential thermal expansion of the glass relative to the canister, which results in a radial loading to the glass at the glass-metal interface. Stresses from this source cannot exceed about 19 MN/m^2 (2700 psi), since greater stresses in the glass would imply a stress in the canister wall greater than the material yield strength of 241 MN/m^2 (35,000 psi). The second source of stress is the glass monolith itself, which develops residual stresses because of temperature differentials in the glass as it cools through its softening temperature range. For glass with internal heat generation, thermal stress patterns (from steady-state cooling) are superimposed on these locked-in stresses.

Three components describe the state of stress in the glass: stresses in the radial, axial, and hoop (or circumferential) directions. The predicted axial- and hoop-stress components have been found to have roughly equivalent distributions, which are greater in magnitude than the corresponding radial component of stress. In general, the central portion of the glass is in a state of tension while the outer region is in a state of compression. Maximum tensile and compressive stresses were calculated to be on the order of 207 MN/m^2 (30,000 psi). The following figures show the significant trends of the predicted axial-stress components.

Figure 4.5.44 shows the effect of heat content of the glass (0 W/L and 100 W/L) on the stress in the glass. The calculated stress is lower for the heat-generating glass. Changes in stress as the heat-emitting glass is transferred from air storage to water storage are also indicated. Stresses are lowest following the initial air-cooling of the molten glass from the melting temperature of 1050°C (1922°F). Glass stress level increases when the canister is quenched during transfer to water storage. The glass stress increases even further when the canister is later removed from the water; it again attains a steady-state thermal condition in the air-cooling environment.

Figure 4.5.45 shows the change in glass stress predicted over a long period, as the level of radioactive decay heat decreased from 100 W/L to a level of zero heat-generation. The stress for the self-heating glass tends to increase with time and eventually exceeds the level predicted for a nonheating glass.

Figure 4.5.46 indicates that process conditions can have an important effect on the stress level in the glass. In this study, a nonheating glass was considered. In one case, the glass was simply air-cooled from a molten state at 1050°C (1922°F). In the other case, the glass was water-quenched from a temperature of 650°C (1200°F), which is above its softening point. The development of stress during the cooling period of the quench was indicated. It was also shown that the rapidly cooled glass has significantly higher stresses than the air-cooled glass.

FIGURE 4.5.44. Effect of Heat Content on Glass Stress

It should be emphasized that the results shown in Figures 4.5.44 to 4.5.46 do not consider glass fracture. The estimated tensile fracture strength of the glass of interest will be on the order of 35 MN/m^2 (5000 psi) or lower. It is clear for the heating and cooling conditions considered here that the glass in the canisters will crack. After the glass has cracked, the stress will be redistributed in both the glass and canister wall.

Conclusions and Recommendations. Analytical models of residual stresses and glass cracking have proven useful in the interpretation of experimental trends and as a guide to process improvements. The predictions of canister residual stress calculations agree with experimental data, which

FIGURE 4.5.45. Change in Glass Stress as Heat Content of Glass Decreases During Period of Storage

show residual stresses of the material yield strength in the walls of canisters. Predictions of glass stresses and cracking patterns are consistent with the types of cracking observed in experimental canisters.

Slate et al. (1979) have addressed the causes and consequences of glass cracking in depth. They concluded that thermal and residual stresses are the major causes of cracking in glass waste. The major consequences of cracking are the increase in surface area, which may result in more leaching, and the production of respirable-size particles. Slate et al. (1979) concluded, however, that the amount of cracking in HLLW glass can be controlled.

FIGURE 4.5.46. Effect of Cooling Rate on Glass Stress (Zero-Heat-Generation Glass)

4.5.2.5 Closure Design

The major role of the closure is to seal the glass inside the canister and to remain a durable and reliable barrier during subsequent handling operations. PNL has developed the twist-lock closure by the systematic application of the following design criteria. Besides providing a reliable barrier, the closure must connect with remotely operable process equipment for filling. Therefore, the closure opening in the canister top may require special configurations and features beyond those needed simply to secure and seal the lid. The lid must be seal-welded and inspected by remote operations. These operations are discussed in detail in Section 4.5.3.3. The connecting device by which the canister is lifted should be an integral part of the closure. A

centrally positioned attachment point at the top of the canister adapts itself readily to remote connecting devices for lifting the canister. Canisters go through a decontamination operation after closure. The canister and closure configuration should avoid features such as recesses or pockets that are difficult to decontaminate. Also, allowance must be made to overpack each canister. Thus, projections that would prevent a convenient fit of a canister into an overpack should be avoided.

PNL has conducted several stress analyses on the twist-lock closure. The first analysis was on the stresses that resulted from lifting the canister. This study is discussed below. In order to establish criteria for the ultrasonic weld inspection, PNL has analyzed thermal stress and have made a detailed fracture-mechanics analysis of the closure. A summarized discussion of this work is below. Finally, stresses from internal pressures and impacts are discussed in Section 4.5.2.6.

Twist-Lock Design

The twist-lock design is shown schematically in Figure 4.5.47, with prototype lids shown in Figure 4.5.48. In this design, lifting loads are carried through lugs of the twist-lock rather than through the minimum section of the seal plate and closure weld. The 3.2-mm (0.125-in.)-thick seal plate was selected as a convenient section limit for the GTA-type fusion weld and to provide required flexibility to the plate. For ultrasonic inspection, flat surfaces are present for positioning of transducers. The stud on the canister lid is designed to remotely connect to a lifting device. The twist-lock design has been integrated with process equipment to make the glass-filling and off-gas connection.

Application of the lid to the filled canister and the seal-welding operation must be performed remotely. Closure designs have avoided filler metal in welding to simplify the design of equipment for remote welding. If a fusion weld without filler metal is used, the weld cross section will tend to be relatively small. Careful configuring of the closure weld ensures that the weld is not stressed excessively during handling of the canister.

FIGURE 4.5.47. Schematic Drawing of the Twist-Lock Closure

The remote welder developed at PNL is shown in Figure 4.5.49. The GTA process is the most common method in use today for welding nuclear equipment. It has been carefully studied and the techniques for making high-quality welds are well understood. The welder shown makes an autogenous fillet that can range from 3.2 to 6.4 mm (1/8 to 1/4 in.) thick. Tight tolerances are maintained on the lid dimensions to maintain the appropriate gap between the welding tip and the lid. The welder is positioned off a hole in the center of the lid, so that the only fit-up requirement is to minimize the gap between the lid and the canister top. The welder and the sealing process are described in detail in Section 5.5.3.3.

Lifting Stresses on Twist-Lock Closures

After the waste canisters are filled, they will be subjected to lifting stresses from special-purpose, remote-connecting devices. It is the objective here to illustrate methods that can ensure that over-stress conditions do not

FIGURE 4.5.48. Prototype Twist-Lock Closure

occur during handling. The rules given in the cask designer's guide (Shappert 1978) were found to be appropriate for HLLW canisters. The main requirement of this guide is that there be a safety factor of 3.0 with respect to yield for static 1.0-g loads. This safety factor evidently provides suitable provision to account for dynamic contributions to lifting loads during handling.

FIGURE 4.5.49. PNL Prototype Canister Closure Welder Using the GTA Welding Process

In this study, canisters 12, 16, 20 and 24 in. in dia were analyzed for stresses after being lifted by the center of the lid. In analyses of preliminary designs the lids were first found to be under-stressed. Further stress analyses showed that section sizes could be substantially reduced. Minimum member sizes are given below for the four canister designs, and stress levels in the optimal closure designs are reported.

The closures were designed for lifting loads at 400°C (750°F). A one-time lift of the canister from the ICM furnace at a temperature as high as 700°C to 800°C (1290°F to 1470°F) was also considered. A safety factor of 3.0 with respect to yield during normal handling at 400°C (750°F) was adopted as a design criterion. This safety factor is in accordance with recommendations of the cask designer's guide (Shappert 1978) for lifting loads applied to shipping containers for nuclear applications. With this safety factor, the design stresses were 50.5 MN/m² (7320 psi) and 73.0 MN/m² (10,590 psi), respectively, for 304L stainless steel and Inconel-601.

The computer program MONSASTIFF (Lestingi 1970) was used for the stress calculations. Figure 4.5.50 shows how the configuration was modeled as shell segments in the computer stress analyses. The lugs were assumed to support no stress in the circumferential direction, with a zero value of elastic modulus assigned to this direction. Also, the lugs were assumed to extend around 50% of the circumference of the twist-lock configuration, with a 10% clearance for assembly. Thus, calculated lug stresses from the axisymmetric analyses were multiplied by a factor of 2.22 to account for the three-dimensional nature of the twist-lock configuration. It was believed that this was a reasonable approximation, provided that a minimum of four lugs are employed in the twist-lock design. The three-dimensional, finite-element calculations described below show that the approximation is reasonable even for a three-lug configuration.

Vertical lifting loads equal to the estimated canister weights were applied to the center of the canister lids. The weights for the four canister sizes were 840 kg, 1316 kg, 2130 kg and 3090 kg (1850 lb, 3000 lb, 4700 lb and 6800 lb). Because of possible lateral loads applied to the canister lifting

(a) MODEL OF TWIST-LOCK CLOSURE FOR MONSASTIFF STRESS ANALYSIS

(b) MODEL OF TWIST-LOCK LID FOR MONSASTIFF STRESS ANALYSIS

FIGURE 4.5.50. Shell-Segment Model of Twist-Lock Closure

device, the closure was analyzed for downward, as well as upward, loading. Upward and downward loads from canister-handling are indicated as F_1 and F_2 , respectively, on Figure 4.5.50.

The load F_3 indicated in Figure 4.5.50 is a 3430 N/m (20 lb/in.) seal compression load. This seal is a ring with a C-shaped cross section, which is used when the canister is connected to the spray calciner. Bending stresses in the lug loaded by the seal are much below yield strength levels for the design temperature of 400°C (750°F). At canister fill temperatures of 1050°C (1922°F), creep deformation would occur in the lug at the calculated stress levels. However, in actual practice, it is expected that any relaxation in sealing preload would occur by plastic deformation or creep in the metallic seal rather than in the canister lug.

The dimensions given in Figures 4.5.50 through 4.5.55 are for optimal designs and are intended to serve as a basis for selecting minimum dimensions consistent with structural integrity requirements. Dimensions are given only for 304L stainless steel. The thickness for Inconel-601 can be reduced by about 17% due to its higher yield strength compared to 304L. The designs for all but the 24-in.-dia canister were developed for a flat-ended top closure. For the 24-in.-dia canister both a flat-ended and a contoured-ended closure were designed. A comparison of Figures 4.5.54 and 4.5.55 shows that wall thickness can be considerably reduced by the more structurally efficient contoured end. However, structural efficiency and weight reduction are relatively low-priority considerations compared to ease of assembly, ease of closure welding, and the ability to perform nondestructive inspection. These other factors tend to favor the flat-ended configuration. The stresses shown in Figures 4.5.50 through 4.5.55 are the maximum values calculated at each of the indicated locations for all three loading conditions (F_1 , F_2 and F_3). Stress levels at the various locations are at or near the design stress of $50.5 \text{ MN}/\text{m}^2$ (7320 psi) for the optimal designs. The dimensions of these optimal designs were determined by adjusting member thicknesses and performing stress analyses in an iterative manner. The actual dimensions used in the fabrication of prototype canisters at PNL were rounded up slightly from the minimum dimensions given in the figures.

The actual dimensions were standardized so that common connecting equipment and lids could be used on all canister sizes. The dimensions of the

(a) CLOSURE DIMENSIONS

(b) CLOSURE STRESSES

FIGURE 4.5.51. Dimensions and Lifting Stresses for Twist-Lock Closure for 12-in.-Dia Canister

(a) CLOSURE DIMENSIONS

(b) CLOSURE STRESSES

FIGURE 4.5.52. Dimensions and Lifting Stresses for Twist-Lock Closure for 16-in.-Dia Canister

FIGURE 4.5.53. Dimensions and Lifting Stresses for Twist-Lock Closure for 20-in.-Dia Canister

(a) CLOSURE DIMENSIONS

(b) CLOSURE STRESSES

FIGURE 4.5.54. Dimensions and Lifting Stresses for Twist-Lock Closure for 24-in.-Dia Canister of Flat-Ended Configuration

(a) CLOSURE DIMENSIONS

(b) CLOSURE STRESSES

FIGURE 4.5.55. Dimensions and Lifting Stresses for Twist-Lock Closure for 24-in.-Dia Canister of Contoured-Ended Configuration

final twist-lock closure for various-diameter canisters are shown in Figures 4.5.56 and 4.5.57. The groove on the bottom part of the closure is for an E-ring metallic gasket. This E-ring is used to seal the canister to the connecting section.

Three-Dimensional Analysis of Lid

In the design analyses described above, the calculation of stresses in the twist-lock closure was based on simplified assumptions. In particular, the twist-lock was treated as an axisymmetric shell structure using linear shell-bending theory. As such, aspects of stress distributions in the individual lugs of the twist lock were ignored. For more realistic stress data, the twist-lock lid was analyzed with three-dimensional, solid-type elements. For comparison purposes, one set of analyses will retain the assumption of axisymmetry. To consider circumferential variations in stress, a finite-element model was designed to use the eight-node isoparametric element in the computer program ANSYS (DeSalvo and Swanson 1975) for treating general three-dimensional solids.

Figure 4.5.58 shows the finite-element model of the twist-lock lid used for analysis of stresses from lifting loads. Three-dimensional solid or brick-type elements are used to model a three-lug design. Due to geometric symmetry, only one-sixth (a 60° sector) of the lid was included in the model. In the model, the gaps between the lugs were filled with elements that will be deleted during the stress solution.

Figure 4.5.59 shows the calculated variation in deflection around the circumference of the lid, as would be produced by a 1316-kg (3000-lb) lifting load. The results show that the deflection at the lugs is over twice that at locations midway between the lugs.

Figures 4.5.60 to 4.5.62 show contours of stress (two times maximum shear stress) at the upper and lower surfaces of the lid and at the midplane of the lid. The dashed contours correspond to the axisymmetric solution (neglecting lugs) for the same geometry. Calculated stresses are clearly higher for the nonsymmetric loading and geometry. The design stress for the lid was

FIGURE 4.5.56. Basic Dimensions of a 24-in.-Canister Top

FIGURE 4.5.57. Basic Dimensions of 12-in.- and 16-in.-Canister Tops

50.5 MN/m² (7320 psi), whereas the maximum stress shown in Figures 4.5.60 to 4.5.62 is about 27.6 MN/m² (4000 psi). As has been stated, approximation methods were used to calculate stress levels for lid design, and it was concluded that these methods were conservative. Also, the actual lid and twist-lock thickness of a prototype canister were used in the three-dimensional analyses. These values were greater than the minimum values established by the design calculations.

Analysis of Closure by Damage-Tolerance Concepts

At the conclusion of the vitrification process the canister is sealed with a lid and the final closure weld is made. This final closure must be

FIGURE 4.5.58. Finite-Element Model of Twist-Lock Canister Lid

FIGURE 4.5.59. Calculated Rim Displacement for Canister Lid

FIGURE 4.5.60. Calculated Stress Contours (2x Max. Shear) on Lower Surface of Lid

welded in a hot-cell environment. The weld must also be inspected by remote means. This section summarizes a fracture-mechanics analysis of the twist-lock closure design. The structural integrity of a weld under projected service conditions is studied, based on damage-tolerance concepts. Admissible defect sizes and inspection requirements are thereby established. These sizes will provide the acceptance criteria for preservice and in-service ultrasonic inspection.

The method of damage-tolerance analysis has been developed extensively within the aerospace industry, and detailed design procedures based on the method have been formulated (Military Specification MIL-A-8344). Such methods utilize fracture mechanics concepts and involve the prediction of in-service

FIGURE 4.5.61. Calculated Stress Contours (2 x Max. Shear) on Midplane of Lid

crack extension. Various forms of structural damage are considered, such as material flaws, manufacturing defects, and in-service cracks from such mechanisms as fatigue. Initial defect sizes are established by estimates of the size of the largest crack that could go undetected during inspection of the component. It is then required that this crack will not grow to a critical size in service. Alternatively, in-service inspection intervals may be established so that the component can be replaced or repaired before a defect can grow to critical size.

In the present application, the defects of concern were in a seal weld of a canister closure system. The proposed inspection method was thought to be capable of detecting cracks that extended through one-half or more of the net

FIGURE 4.5.62. Calculated Stress Contours (2 x Max. Shear) on Upper Surface of Lid

section of the weld. The purpose of this study was to consider the growth of various postulated defects and to determine by analysis if such defects would grow in-service to a size that would result in a leakage path or lead to a gross fracture through the closure weld.

A review of the canister service conditions was conducted to identify sources of stress in the weld. Stresses due to lifting were insignificant. However, the canister was expected to suddenly change in temperature during service. It is expected that a water basin will be used for interim storage. Also, a water spray may be used to decontaminate the outer surface of the canister. The vitrified radioactive waste will produce internally generated heat, possibly at a rate as high as 100 W/L. For analysis purposes, this

level of heat generation was assumed. When stored in air, the heat from the vitrified waste will cause the temperature to rise in the top and lid of the canister. When immersed in water, the temperature of the top will approach that of the water. During the thermal transient, it was evident that the potential existed for substantial thermal stress. The review of service conditions concluded that such transient thermal stresses would govern the structural integrity of the closure weld. Subsequently, detailed heat-transfer and stress analyses of the canister closure design were undertaken.

Heat Transfer. The computer codes HEATING4 (Turner and Simon-Tov 1971) and ANSYS (DeSalvo and Swanson 1975) were used to analyze steady-state and transient temperatures in the canister top region. The canister material was assumed to be 304L stainless steel. Due to ease of input data preparation, the HEATING4 code was used in preliminary scoping studies. Once heat-transfer conditions and thermal-solution trends were established, the canister was modeled with the finite-element computer program ANSYS. This code permitted a unified thermal and stress analysis to be performed with automated transfer of thermal solution data to the stress analysis phase of the calculation.

Two steady-state and two transient temperature states were considered. The steady-state conditions were radiation and free convection in 49°C (120°F) ambient air, and submersion in 21°C (70°F) water. The transients corresponded to an instantaneous transfer of the canister from one medium to the other. By far the most severe thermal gradients resulted from the quench of the hot canister at a temperature of about 260°C (500°F) into the water.

Figure 4.5.63 shows the finite-element model used in the ANSYS thermal and stress analysis. Only the upper 305 mm (12 in.) of the canister that extended above the glass level were modeled. Previous HEATING4 analyses included the heat-emitting glass, and results of these analyses provided glass surface temperatures for use as boundary conditions to the ANSYS thermal analyses. Calculated glass-surface temperatures ranged from 482°C (900°F) at the centerline of the canister to 205°C (400°F) at the outer surface. Using these temperatures as boundary conditions, heat transfer from the glass surface to the top

FIGURE 4.5.63. Finite-Element Model for Thermal Structural Analysis

and sides of the canister was accounted for by the mechanism of radiation. A form factor of 1.0 was assumed for radiation to the top of the canister, and a factor of 0.2 for radiation to the side walls of the canister. A factor of 1.0 for the top was assumed to be conservative, since this would maximize top temperatures and thus overestimate the severity of the conditions for the water quench. Emissivities within the range of 0.6 to 0.8 were used for the radiation calculations. A form factor of 1.0 was assumed for radiation from the outer surfaces of the canister to the environment.

During the water quench, the heat transfer will be governed by complex phenomena, as discussed by Chen (1955). The film coefficient for pool-boiling conditions reported by Forster and Zuber (1955, pp. 531-535) was used in the present calculations. This coefficient was a strong function of film temperature, giving very high cooling rates early in the quench, and then showing a rapid decrease with film temperature as the quench proceeded.

Gaps between parts of the twist-lock lid were modeled in detail for the thermal analysis. However, the geometry of the twist lock was idealized to be axisymmetric. Heat transferred across the gaps by the combined mechanisms of radiation and heat conduction through air.

During the water quench, the most significant aspect of the transient thermal solutions was the rapid cooling of the thin seal-plate relative to the more massive parts of the canister top and lid. Thermal contraction of this

plate induced tensile stresses that were transmitted through the closure weld. Figure 4.5.64 indicates temperatures at selected nodes of the finite-element model for a time of 4.6 s into the water quench, which corresponded to the maximum tensile stresses adjacent to the weld.

Stress Analysis. The finite-element model of Figure 4.5.63 was utilized to calculate transient thermal stresses. Of critical concern were the stresses in the seal plate at the location of the closure weld. Figure 4.5.65 shows the calculated variation in these stresses during transient heating and cooling.

During rapid cooling, two critical times were identified. At 0.39 s into the water quench, the thermal differential through the thickness of the seal plate resulted in a maximum tensile stress at the outer surface location. At a much later time (4.6 s), the temperature differential between the thin seal-plate and the more slowly cooling portions of the canister top resulted in the predicted maximum tensile stresses that were adjacent to the weld at the inner surface of the seal plate.

Transient heating of the canister top upon removal from the water-cooling environment resulted in no critical stresses of interest. Rather, it was the steady-state condition of air-cooling for which stresses at the closure weld attained their maximum compressive values.

The nominal stresses shown in Figure 4.5.65 were not used directly in evaluating the integrity of the closure weld. Rather, these results were used to identify the specific times for evaluating stress intensity factors for postulated weld defects. For stress intensity factor evaluations, more refined finite-element models of the closure weld were used. These stress intensities were calculated for equivalent, purely mechanical loading states, which were determined from solutions for the first-level finite-element model shown in Figure 4.5.63. This model had a provision to introduce a cut adjacent to the closure weld. In this way, a complete fracture across the seal plate could be simulated and the relative displacement of the parts across the fracture plane were determined. Stress intensity factors were determined on the basis of the mechanical loadings required to eliminate the calculated displacement

FIGURE 4.5.64. Temperature Distribution at 4.6 s into Water Quench

discontinuity across the artificial cut in the thermal structural model. With this procedure, it was not necessary to transpose the temperature distributions onto the refined model used in the fracture mechanics analysis. Details of the calculation of the stress intensity factors are presented by Simonen and Slate (1979).

The calculation of stress intensity factors was used with canister service life data to estimate crack growth in the seal weld. A theoretical and actual weld bead configuration was considered. The conclusion of this study was that initial defects of substantial and detectable size could be tolerated in the weld. The anticipated ultrasonic inspection system can reliably detect defects extending through about one-half of the weld's cross section. Defects well in excess of this size can be safely tolerated.

FIGURE 4.5.65. Transient Thermal Stress in Seal Plates Adjacent to Closure Weld

4.5.2.6 Performance Testing and Accident Evaluation

The evaluation of canister stresses and structural integrity, both for design and licensing purposes, will be partly based on validation of canister performance by structural testing. This section summarizes PNL efforts to evaluate canister performance under normal operating conditions and hypothetical accident conditions.

Evaluation of Process Trials

Over 20 full-scale canisters have been filled by the ICM process at PNL. In addition, two nearly full-scale canisters of radioactive waste glass were produced in WSEP program at PNL in 1970, and two more were filled in the NWVP in 1979. These canisters have provided data on canister performance, under

both filling and storage conditions, which support the stress-analysis and structural-integrity evaluations.

Characterization of ICM canisters has been emphasized, because of the severe service conditions. Measured diameter increases have been relatively small and have not exceeded 1.27 mm (0.050 in.). Most of this change is attributed to the differential thermal expansion coefficients of the canister and glass, rather than stress-induced creep. There have been no instances at PNL of canister structural failure that resulted in released glass during filling.

The long-term integrity of canisters in storage environments is less certain, particularly for water-basin storage. Bradley (1977) reports the SCC in one of the canisters filled in 1970 with radioactive waste. This canister developed a crack in the water environment of a test pod. The canister material was determined to be extremely sensitized by an adverse thermal history; the combination of residual stress and water chemistry was particularly conducive to SCC. The conditions for this canister were not typical of anticipated canister conditions.

Accident Considerations

Various hypothetical accidents have been studied for canisters during processing, handling, storage, and transportation. In general, the accidents involved either impacts or overheating.

In evaluating the consequences of accidents, it should be recognized that the canister will never be the sole or final barrier to the release of radioactive material. In addition, the solid form of the waste glass will greatly minimize the amount of release in accidents. Radiation-shielding requirements will dictate that canisters be confined at all times in either a shielded facility (i.e., processing cell) or a shielded container (i.e., transportation cask). Such facilities by themselves will be capable of containing any release of material from the canister. Nevertheless, an objective in canister design has been to maximize the performance of the canister itself and to demonstrate

the ability of the primary canister to meet accident criteria. Accident-resistant canisters will provide additional margins of safety and, perhaps, ease requirements on processing, storage, and transportation facilities.

Impact performance has received the greatest emphasis in work done at PNL. Lacking specific design criteria for HLLW canisters, research at PNL and elsewhere (Kaiser Engineers 1977 and 1978, Nuclear Services Corporation 1978) has used the federal regulations from 10 CFR 71.64 (Code of Federal Regulations, Title 10 1978). These criteria define test requirements for fire, impact, and submersion in water. The submersion requirement is essentially trivial for glass in canisters and will not be discussed further here.

One of the standard criteria imposed on containers for shipment of radioactive materials is its ability to survive a fire of 800°C (1475°F) for 0.5 h 10 CFR 71, Appendix B (Code of Federal Regulations, Title 10 1978). Such a temperature is not high enough for a canister to fail by overheating (melting or oxidation). The primary concern is pressure that may build up from the heating of gases that may be in the void space at the top of the canister. (Such internal pressure stresses are evaluated below for the PNL twist-lock closure design). It is believed that the canister will not lose integrity unless a substantial quantity of water is present in the canister top void because of leakage during water storage. It is also felt to be impractical to design canisters that will sustain the very high pressures of such rapid heating of entrapped water. However, it is doubtful if a high pressure could be achieved, since if the water leaked in the canister there would be a path for steam escape.

The other mode of overheating failure is that of an uncontrolled temperature excursion during processing. Hypothetical causes of such an excursion could be a malfunction of an ICM furnace, or a high-heat-generating glass placed in an insulated enclosure that does not allow adequate cooling of the canister.

Process overheating has been studied at PNL in a canister-overheat test. In this test, glass in a canister was heated by electrical resistance heating of fins imbedded in the glass. The glass and canister were heated to temperatures above normal ICM temperatures (i.e., 1050°C or 1922°F). Melting of the heated fins terminated the test before any noticeable damage occurred to the canister. Further testing of canisters under overheating conditions is needed to establish the temperature and failure mode for catastrophic failure of a canister during processing. Possible failure modes are stress-induced creep rupture, catastrophic corrosion of the canister wall, and melting of the canister wall. It is anticipated that the ultimate failure will not occur until temperatures at or near the canister melting temperature are reached.

Impact Strength of Canisters

Canisters for vitrified high-level nuclear waste must be rugged to sustain loads of handling and transportation. Under normal conditions, such loads will be relatively modest and will not tax the integrity of the canister. However, under accident conditions (dropping during handling, collision accidents during shipment, etc.) loadings can be severe, and breaching of the canister must be considered a possibility.

Specific design criteria for accident conditions have not yet been adopted for waste canisters. However, it is expected that future criteria will be similar to the highly developed rules presently in force for the transportation of radioactive materials. The approach at PNL to the design of canisters for impact loadings has been to follow, as much as possible, the design practices recommended for shipping containers for radioactive materials. These recommended practices cover materials selection, joint design, welding techniques, and quality assurance. Due to the difficulty of predicting the structural response of containers under impact conditions, stress calculations have been minimal. Rather, efforts have been directed to evaluation of designs using full-scale drop tests.

Evidence both from PNL impact tests and data reported in the literature, indicates no inherent technical problems relative to bottom and side impact of

filled canisters. In fact, data suggests that waste canisters could be designed to sustain bottom and side impact velocities in the 20- to 90-m/s (100- to 300-ft/s) range (Teledyne Isotopes 1974; General Electric Space Division 1975), which is well above any of the present criteria for transportation of radioactive materials. In contrast, little is known of the consequences of an impact on a canister top and the subsequent integrity of the canister closure system. The impact capabilities of specific closure concepts are expected to vary greatly. Depending on details of the design, the closure could fail in an impact from a drop of a few feet, or could sustain impacts approaching the canister capability under bottom and side impact.

Design Criteria. Lacking specific design criteria for HLLW canisters, PNL and other companies (Nuclear Services Corporation 1978; Kaiser Engineers 1977) have applied the federal criteria of 10 CFR 71, Appendix B (Code of Federal Regulations, Title 10, 1978). These requirements apply to containers for the transport of radioactive materials. For impact, engineering analyses or actual tests must show that the containers can be subjected to the following hypothetical accident conditions without releasing radioactive materials:

- Free Drop: Free drop through a distance of 9 m (30 ft) onto a flat, essentially unyielding surface, striking the surface in a position for which maximum damage is expected.
- Puncture: Free drop through a distance of 102 cm (40 in.) onto the top end of a vertical, cylindrical, mild-steel bar mounted on and perpendicular to an essentially unyielding horizontal surface. The bar shall be 15 cm (6 in.) in dia, with its top horizontal and its edge rounded to a radius of not more than 0.64 cm (1/4 in.). It shall be of a length that causes maximum damage to the package, but shall not be less than 20.3 cm (8 in.) long. The container striking the bar shall be in a position for which maximum damage is expected.

The practice has been to impose these impact requirements on the waste package itself, even though in transport the canister will necessarily be

within a massive shielded cask to meet radiation requirements. Neglect of the impact protection provided by the cask insures a conservative approach to canister design and also dictates a measure of ruggedness to the canister against accidents that may occur in handling the canister outside a shipping cask. Handling of exposed canisters will occur within the processing plant and at the geological disposal site. The question has not been resolved whether impact accident criteria from the general transportation field should be applied to handling operations conducted within the controlled environment of the processing plant or disposal site.

Other accident scenarios have been proposed by Kaiser Engineers (1977). The most severe of these is probably a canister drop of several thousand feet down a mine shaft at the geological disposal site. As in the case of a shielded transportation cask, impact requirements on the canister could be greatly decreased if energy absorption is provided as part of the mine shaft handling system.

In addition to or as a replacement for the above federal criteria, a detailed evaluation of accident possibilities in the life cycle of a canister should be performed. For specific canisters and processing facilities, maximum drop heights can be determined. Also, items could be established in the plant that could act as penetrators if struck by a falling canister. Evaluations of this type would more realistically govern canister impact strength requirements. The consequences of a canister breach could also be factored into such evaluations, although in the controlled environment of the processing plant such breaches could be of minor significance.

Impact Tests

Two series of impact tests on glass-filled canisters have been conducted at PNL. These test series were performed in 1975 and 1977. The main objective of the 1975 series was to evaluate the extent of glass fracturing as a result of impact (Smith and Ross 1975). The quantity of respirable glass fines produced and the increase in glass surface area were measured. As a secondary factor, the impact resistance of the filled canisters was considered. Breaches of certain canisters were observed only at relatively high velocities of 20

and 36 m/s (66 and 117 ft/s) and not at a 13.4-m/s (44-ft/s) velocity corresponding to a 9-m (30-ft) drop. Both full-scale and subsized canisters were tested.

The more recent 1977 test series involved full-scale canisters and the focus was on canister integrity. Figures 4.5.66 and 4.5.67 show the mobile crane and the test pad used for the drop test. The specially constructed test pad consisted of a 178-mm (7-in.)-thick steel plate set into a 1.2 x 1.2 x 3-m (10 x 10 x 4-ft) reinforced concrete mass. At the maximum crane height, a drop from 32 m (104 ft) above the pad could be achieved. A quick-release hook allowed canisters to be dropped without imparting an impulse at the time of release. By suitable positioning of the cable sling along the length of the

FIGURE 4.5.66. Mobile Crane and Canisters in Position for Impact-Testing

FIGURE 4.5.67. View of Impact Pad with Canister Number 5 About to Impact

canister, the canister could be dropped with a corner impact point in line with the canister's center of gravity. This impact results in maximum damage to the canister.

Table 4.5.29 lists the results of impacts on canisters of various designs. Some canisters were filled with simulated waste of nonradioactive borosilicate

TABLE 4.5.29. Description of Canisters Impacted in 1977-Series Drop Tests

Canister Number	Diameter, in.	Length, m (in.)	Wall Thickness, mm (in.)	Material	Weight, kg (lb)	Bottom Design	Top Design	Contents
8	12.75	2.13 (84)	6.3 (0.25)	304L	592 (1305)	Formed head with flat end; weld about 50 mm (2 in.) from end	Twist-lock	Nearly 2.13 m (84 in.) glass
45	16	2.13 (84)	7.9 (0.312)	304L	917 (2020)	Formed head with flat end; weld 50 to 75 mm (2 to 3 in.) from end	Twist-lock	1.93 (76 in.) glass
3	12.75	2.95 (116)	9.5 (0.375)	Carbon Steel	754 (1660)	Flat plate welded to end of pipe	Pipe flange	Filled to top with concrete
4	18	2.95 (116)	14.3 (0.562)	Carbon Steel	1507 (3320)	Flat plate welded to end of pipe	Pipe flange	Filled to top with concrete
7	24	2.95 (116)	6.3 (0.25)	Carbon Steel	2165 (4770)	Formed head with flat end; weld about 75 mm (3 in.) from end	Pipe flange; flat plate bolted to flange	Filled to top with concrete
18	24	2.95 (116)	6.3 (0.25)	Carbon Steel	2192 (4830)	Flat plate welded to end of pipe	Pipe flange	Filled to top with concrete
1	24	2.84 (112)	6.3 (0.25)	Carbon Steel	2176 (4795)	Formed head with flat end; weld about 75 mm (3 in.) from end	Formed head of dished shape; pipe flange welded to head	Filled to top with concrete
29	24	1.52 (60)	9.5 (0.375)	Carbon Steel	944 (2080)	Formed head of dished shape; cylindrical skirt welded to head	Formed head of dished shape; projection of 150 to 200 mm (6 to 8 in.) dia welded to top	Glass
30	24	2.84 (112)	6.3 (0.25)	Carbon Steel	2176 (4795)	Formed head with flat end; weld about 50 mm (2 in.) from end	Formed head of dished shape; pipe flange welded to head	Glass
46	20	2.13 (84)	25.4 (1.00)	304L	1725 (3800)	Flat plate welded to pipe with multipass fillet weld	Twist-lock	Glass
5	24	2.84 (112)	9.5 (0.375)	Carbon Steel	2365 (5210)	Flat plate welded to end of pipe	Flat plate with 6-in. pipe flange	0.46 m (18 in.) glass; 2.39 m (94 in.) concrete
42	24	2.45 (116)	9.5 (0.375)	Carbon Steel	2431 (5355)	Flat plate welded to end of pipe	Flat plate with 6-in. pipe flange	Filled to top with concrete
2	24	2.84 (112)	9.5 (0.375)	Carbon Steel	2406 (5300)	Flat plate welded to end of pipe	Flat plate with 6-in. pipe flange	1.32 m (52 in.) glass; 1.52 m (60 in.) concrete

glass. Some canisters were partially filled with glass and then topped off with concrete, while others were filled entirely with concrete. The latter were used primarily for practice drops. All tests were conducted during the month of December, with near-freezing temperatures prevailing.

Canisters selected for these tests included some that potentially could meet criteria for packaging of HLLW in terms of design characteristics and fabrication quality. On the other hand, a number of canisters had been fabricated to meet short-term needs of nonradioactive process development trials at PNL. The design and fabrication quality of these canisters did not meet the criteria for HLLW packaging. The drop-test results for these canisters nevertheless provided valuable data on failure thresholds.

Table 4.5.30 summarizes the drop heights and observed condition of the canisters after the impacts. Figure 4.5.68 shows the result of a typical bottom-impact test. Canister condition after impact was evaluated on the basis of visual inspection and in several cases by metallographic sectioning to check for cracks. No cracks were observed in bottom impacts for canisters that followed accepted design and fabrication practices. Cracking was observed in carbon-steel canisters with flat-plate bottoms welded to a length of pipe that served as the canister body. Of these, only canister No. 5 exhibited a gross breach that resulted in visible ejection of glass, and in this case the glass was ejected after two 9-m (30-ft) drops. Later, metallographic inspection of the bottom welds in canister 5 and other cracked canisters showed a lack of weld penetration. A bottom corner joint of the design used on canister 5 is not recommended for low-carbon steel, and partial-penetration welds are to be avoided at all joints subject to impact damage.

Top impacts for some of the canisters were performed, with typical results shown in Figure 4.5.69. The consequences of top impact were expected to be more severe than for bottom impact. The void at the top of the canisters does not provide the restraining effect that glass provides at the canister bottom. The observed impact performance in the top drops was not satisfactory, since cracking occurred at welds. It is believed, however, that optimization of the

TABLE 4.5.30. Results of the 1977-Series Canister Impact Tests

Canister Number	Drop Height	Damage	Comments
8	9.1 m (30 ft) on bottom corner	No visible cracks; minimum deformation of bottom with no buckling of canister wall.	
45	31.7 m (104 ft) on bottom corner	No visible cracks; extensive corner deformation; slight buckling of canister wall near bottom.	
3	6.1 m (20 ft) on bottom corner	No visible external cracks; metallography showed no breach of canister, but some cracking starting at root of partial-penetration weld.	Severe local buckle of side wall, probably due to lack of full curing of concrete.
4	9.1 m (30 ft) on bottom corner	Cracked part through, but no breach of canister; metallography showed poor weld penetration with some cracking starting from internal surface.	Severe local buckling of side wall, probably due to lack of full curing of concrete.
7	9.1 m (30 ft) on bottom corner	No visible external cracks; metallography showed no breach of canister, but some cracking starting at root of partial-penetration weld.	Damage at two impacted bottom corners appears to be independent of each other.
	9.1 m (30 ft) on (opposite) bottom corner	No visible external cracks; metallography showed no breach of canister, but some cracking starting at root of partial-penetration weld.	
	9.1 m (30 ft) on top flange	Cracking of flange to head weld; canister breached; bolts dented head, but did not penetrate.	
18	Not dropped		
1	15.2 m (50 ft) on bottom corner	No visible external cracks; metallography showed good welds with full penetration; no evidence of crack growth from inside surface.	Corner flattening extended into weld.
29	15.2 m (50 ft) on bottom corner	No breach of canister; cracking of welds joining skirt to bottom; no metallography performed.	
	12.2 m (40 ft) on top	Cracking of joint between top and welded projection.	
30	7.6 m (25 ft) on bottom corner	Canister breached; cracks in both weld and base metal; metallography showed good weld quality, but large grain size in heat-affected zone.	A dent near the bottom appears as if the canister struck the corner of the impact pad.
	6.1 m (20 ft) on top	Cracking of flange to head weld; canister breached.	
46	9.1 m (30 ft) on bottom corner	No visible external cracks; minimal deformation; no metallography.	Massive canister, but with less than optimum bottom corner joint design.
5	9.1 m (30 ft) on bottom corner	Corner probably cracked and canister breached; weld cracking and canister breach evident during sectioning; metallography showed poor weld with lack of penetration.	
	9.1 m (30 ft) on (opposite) bottom corner	Cracking and breach of impacted corner; gross opening of opposite corner, which had been cracked in previous impact.	Glass fragments ejected from crack during second drop.
42	6.1 m (20 ft) on bottom corner	Cracking of corner weld through full thickness; metallography showed poor weld penetration resulting in weld cracking along heat-affected zone.	
2	9.1 m (30 ft) on bottom corner	Cracking of corner weld through full thickness; metallography showed poor fit-up at joint leading to incomplete weld penetration.	Buckling of side wall near bottom. Concrete flowed plastically due to incomplete curing; more extensive bottom deformation seen on concrete-filled canister than glass-filled canister.

FIGURE 4.5.68. Canister 45 Showing Bottom Deformation Following 31.7-m (104-ft) Drop onto Corner

weld-joint configurations can correct the deficiencies in impact performance. Impact strengths could be increased by reinforcement of the critical weld-joint region to force plastic deformation to be distributed into the head, rather than be localized in the joint area. Also, alternative closure designs can eliminate the projection associated with the flange-type closure by bringing the closure flush with the top (as in the case of the twist-lock closure designed at PNL).

The parameters of the canister wall thickness and drop height were not varied sufficiently in the test matrix to clearly identify trends in impact performance relative to these parameters. However, the results are consistent with evidence presented, for example, by Shappert (1970). This evidence suggests that bottom impact performance is strongly influenced by material toughness and joint design. Wall thickness and drop height are less important.

PNL has not tested canister puncture resistance as defined by the above criteria. Performance data from shielded shipping casks shows a clear

FIGURE 4.5.69. Top of Canister Number 30 Following Drop from 6.1 m (20 ft)

relationship between puncture resistance (as measured by allowable drop height) and wall thickness. It is likely that puncture resistance criteria will impose definite limits on minimum canister wall thicknesses.

It was concluded that HLLW canisters can sustain severe bottom impacts and that no unusual design features are required.

Internal Pressure Stresses

In the design of HLLW canisters, stresses due to internal pressure have been viewed as being of secondary importance. Nevertheless, PNL has identified possible sources of internal pressure, and has evaluated the consequences of pressurization of the canister closure after seal-welding.

After closure-welding there will be a volume of gas within the top cavity of the canister. It was estimated that heating of contained gases will result in a pressure increase of 0.012 MN/m^2 (1.79 psi) for each 56°C (100°F) change in temperature. A typical temperature rise was estimated to be 177°C

(350°F), for which the increase in pressure would be 0.043 MN/m^2 (6.26 psi). This normal internal pressure increase is of negligible significance.

Heating of any water entrapped in the top cavity of the canister can have far more serious consequences. If water were present in sufficient quantity, the pressure during heating would equal the vapor pressure of the water at the temperature in question. For example, heating to 371°C (700°F) would result in a pressure of 22 MN/m^2 (3200 psi). The most likely source of water is thought to be leakage through a defect in the closure weld during periods of water-basin storage. In the event of relatively slow heating, it is likely that vapor pressure would vent itself through the same defect that permitted entry of water into the canister in the first place. Catastrophic pressurization is anticipated primarily in connection with very rapid heating, such as if the canister were exposed to a fire.

Stress calculations have helped to establish the pressure capability of the twist-lock closure system. Figure 4.5.70 shows the results of a finite-element stress analysis of a top and twist-lock closure of a 406-mm (16-in.)-dia canister. An internal pressure of 0.69 MN/m^2 (100 psi) was selected for purposes of calculating relative stress levels in different components of the canister. The inner hub of the 3.2-mm (1/8-in.)-thick seal plate is the most highly stressed location. The outer portion of the canister top has stresses at levels of approximately one-half of the stress levels in the seal plate. Stresses in the canister sidewall are relatively low.

For initial design purposes, a material yield strength of 207 MN/m^2 (30,000 psi) and an ultimate strength of 414 MN/m^2 (60,000 psi) were assumed for 304L stainless steel. The yield strength is a function of temperature, and at higher temperatures than used here, lower values should be used. Pressure ratings were estimated for: 1) initial yielding, 2) gross plastic deformation, and 3) bursting. At sufficiently high pressures the canister top and seal plate will burst like a rupture disc. This bursting pressure (as given in Table 4.5.31) was estimated to be twice that which produced gross plastic deformation.

FIGURE 4.5.70. Calculated Stresses in Canister Closure System for Internal Pressure of 0.69 MN/m^2 (100 psi)

The seal plate was clearly the weak link in the twist-lock design. However, it has more than adequate strength to sustain pressure increases during normal heating cycles. On the other hand, if large amounts of entrapped water are heated rapidly (such as during a fire), even the relatively high pressure rating of the canister sidewall would be exceeded. In this event, the seal

TABLE 4.5.31. Pressure Ratings of Canister Top

Test Parameter	Canister Side Wall	Canister Top	Seal Plate
Initial Yield	9.2 MN/m ² (1330 psi)	1.31 MN/m ² (190 psi)	0.60 MN/m ² (87 psi)
Gross Plastic Deformation	9.2 MN/m ² (1330 psi)	2.76 MN/m ² (400 psi)	1.24 MN/m ² (180 psi)
Burst	18.3 MN/m ² (2650 psi)	5.52 MN/m ² (800 psi)	2.48 MN/m ² (360 psi)

plate would perform like a rupture disk and vent the pressure once a level of about 2.48 MN/m² (360 psi) was reached. It would be preferable if the canister top failed at this lower pressure. The release of energy would be less at the lower pressure, and there would be less dispersion of contamination.

4.5.2.7 Conclusions and Recommendations for Canister Design

Many conclusions and recommendations have been incorporated in this section on canister design. A summary of the major conclusions and recommendations that will advance the state of canister stress analysis are included below:

1. No formal and comprehensive criteria or codes have been adopted for the design and fabrication of waste canisters, although a number of existing codes and regulations provide valuable guidance. The ASME Boiler and Pressure Vessel Code is suitable for canister fabrication and quality assurance, but important aspects of canister processing and loadings fall outside the scope of the ASME code. Methods proposed in this section provide preliminary design rules for processing conditions, and existing federal regulations on transportation of nuclear materials provide guidance on handling and transportation stresses.
2. The factors of materials performance, fabrication methods, and nondestructive inspection methods cannot be separated from stress analysis and

structural design. In particular, the requirements for remote welding and inspection of the final seal weld will largely dictate canister closure configurations.

3. The high temperatures experienced by canisters, along with the requirement to contain molten glass during filling, falls outside the scope of conventional engineering practice. However, PNL studies have shown that canisters can be designed for the extreme conditions encountered during filling.
4. The feasibility of interim storage of canisters in water-basin environments is not in question, provided suitable measures are taken to preclude cracking (i.e., alloy selection, metallurgical controls, water chemistry control, and residual stress reduction). Uncertainty exists as to what trade-offs and compromises can be made to minimize costs and to simplify processing.
5. The evaluation of canister impact strength should be based on full-scale drop tests rather than on stress calculations. Tests at PNL have shown that canisters can sustain severe bottom impacts without releasing contained waste.

4.5.3 CANISTER OPERATIONAL ANALYSIS

This section describes the life cycle of the canister from initial fabrication through disposal. The canister's service life has been studied to identify the effect of operations on the design, the canister integrity, and the vitrified waste. The canister and glass have a close interrelationship that must be considered during all canister processing operations. The important effects of each operation on the canister and glass are discussed in the following pages.

There are many operations that must be performed on the waste canister through its service life. These operations have been grouped as follows:

- fabrication and preparation for filling
- glass-filling

- canister closure
- decontamination
- quality verification
- repair (overpack or recycle)
- interim storage
- transportation to disposal
- disposal.

4.5.3.1 Fabrication and Preparation for Filling

Canisters must provide the desired level of containment of the waste glass. Thus, the strict fabrication and quality-assurance requirements for nuclear components will, in general, apply to canisters.

While to date no specific rules or regulations for the fabrication of canisters have been formally adopted, there are several reasons for adopting existing standard codes. Such codes have both governmental and public acceptance because of their demonstrated reliability. Also, potential vendors are accustomed to working with the standard codes, and this will expedite procurement and decrease costs of canister fabrication and inspection. Fabrication of a well characterized, reproducible, high-quality canister will also greatly assist quality verification of the packaged HLLW. Such quality verification will be necessary to meet criteria for acceptance of the packaged waste at the geologic repository.

The rules of the ASME Boiler and Pressure Vessel Code, Section III, Nuclear Power Plant Components (as discussed in Section 4.5.2.1), are considered appropriate to the fabrication and quality-assurance aspects of waste canisters. Although it is recognized that the service stresses and functional requirements of canisters are, in many respects, different from those addressed by the ASME code, waste canisters are generally within the scope of the ASME code. Low-carbon steel, low-alloy steel, stainless steels, and nickel-based alloys are all recognized and approved for coded vessels. Canister designs and fabrication methods are also within the scope of the code, although it may be desirable to amend existing code requirements, where such changes will further improve canister integrity. Canister fabrication may also need

to be responsive to the quality-assurance requirements of 10 CFR 50 Appendix B (Code of Federal Regulations, Title 10 1978) and defect-reporting requirements of 10 CFR 21 (Code of Federal Regulations, Title 10, 1978).

Specific fabrication and quality assurance measures will apply to the general areas listed below:

- material specifications and certification
- specifications concerning welding procedures, welding materials, and qualification of welding personnel
- heat treatment
- inspection of welds by approved methods, such as ultrasonics
- identification, standards and associated conformance documentation.

Documentation begins at the time of canister material production/fabrication and continues through the life cycle of the canister.

Preparation for Filling

After the canister is received at the waste-processing facility, it is prepared for filling. It is inspected and the quality-assurance records are examined to determine if the canister meets the design specifications. All fabrication records are included in the Quality Verification file. This permanent file is kept for each canister and serves as a basis for canister and glass quality verification. The preparation step is important because it is the final opportunity for detailed inspection of the canister and lid before filling, and it is the initial condition of the canister that is the basis for determining its performance and integrity.

Currently, no requirements have been established on inspection and record-keeping.

4.5.3.2 Glass-Filling

The glass-filling process is briefly reviewed here with emphasis on canister effects. The filling operation consists of three main steps: canister emplacement, glass-filling, and cooldown.

Canister Placement

The canister-placement sequence has been tested at PNL. The reference process, for placing the canister and connecting the waste processing equipment to it, is described in detail in Section 4.3.7. The sequence starts by connecting to the canister a guide that is part of the furnace top. The canister top must be designed to remotely accept this guide and be able to be carried by it. A conceptual design for this guide is shown in Section 5.4.4. This operation is necessary to properly align the canister in the furnace. Guides in the furnace are not practical because of the high temperatures involved. The guide/canister assembly is then placed in the furnace with the canister sitting on the bottom of the furnace chamber. Bottom support allows the canister design to be greatly simplified with respect to top-supported designs. The bottom-support designs have thinner walls and fewer fabrication steps, which mean lower costs and perhaps greater reliability (see Section 4.5.2.4). Figure 4.5.71 shows the entire canister inside the furnace. This is necessary to allow complete vitrification of all the canister contents and to prevent large temperature gradients on the canister that occur when part of the canister is outside the furnace. The connection to the solidification equipment is completely automatic for remote operations; thus, alignment of the canister is important. The connection is dust-tight, and the inside of the canister is maintained at the processing pressure of 10 in. H₂O vac. It is very important that the canister be designed with this connection in mind.

The ICM furnace provides a number of monitoring and process-control capabilities. Active capabilities include temperature control (i.e., heating and cooling), canister alignment and connection, atmosphere control, and contamination protection for the canister. Monitoring capabilities include temperature measurement, level detection, weight measurement, internal pressures, and perhaps visual observation. The monitoring functions are very important in providing a record of process parameters to be used in quality verification of the glass and canister. The enclosure will also provide a second level of containment if there is a process failure.

FIGURE 4.5.71. Canister-Handling for the ICM Process

It is primarily the active functions that affect the canister. The effect of the support and alignment function are discussed above. Temperature control, as well as heating or cooling rates, affect the canister in the areas of creep strength, corrosion, deformation, and metallurgical changes. Details on this are discussed in the glass-filling section. Another function is contamination control. The enclosure will be designed to prevent contamination of the canister as much as possible. For example, the ICM connecting guide will shield the canister from calcined waste that may fall from the connecting section. The last major function affecting the canister is the use of a controlled atmosphere, such as argon, to prevent oxidation of the canister exterior if necessary. Oxidation is not severe, but it can cause minor operational problems. For example, spalling (Section 4.3.14) creates an additional waste

stream to handle, and the rough surface is more difficult to decontaminate. The decision to use a controlled atmosphere depends on the process used and the canister material. Engineering tests to date have not indicated the need for such controls.

In-Can Melting Sequence

The filling operation places greater requirements on the canister than any other processing step. The canister must provide adequate containment of the glass during processing without adversely affecting it. The canister itself must survive the filling operation without excessive corrosion, deformation, or loss of integrity.

The filling process will be controlled and monitored to assure repeatable quality in the glass product and the canister. The parameters that may be monitored as part of the canister quality verification are maximum temperature, filling time, and cooling rate. Other parameters may be included in verifying glass quality.

The canister is placed in the furnace, which is at 700°C. The entire canister is then heated to 1050°C, at which point the feeding of the waste calcine and frit is started. Temperatures are measured by thermocouples in the furnace. Engineering tests have shown furnace and canister temperatures to be within 5°C.

The filling operation progresses at a rate that maintains a molten-glass surface. There are two major concerns during canister filling:

1. The canister must be able to exist at these temperatures without excessive deformation. A 1% permanent strain limit is suggested for process operations (Section 4.5.2.4).
2. Corrosion by the waste glass and the furnace atmosphere should not be excessive. For most canister materials corrosion has not been a problem (Section 4.5.2.2).

As the canister fills, heating in the lower zones of the melter is reduced and cooling may be started, if necessary, to prevent the glass from

exceeding 1100°C because of heat generation. This cooling of the lower zones has the added advantage of reducing corrosion and deformation of the canister. Engineering tests and analyses have shown that temperature gradients do not adversely affect the canister (Section 4.5.2.4).

After the canister has been filled, the bulk of the glass will be held at 1050°C for 2 h to allow the glass to fine. The actual canister temperature at this time depends on the temperature gradient of the glass which occurs due to heat generation. For low-heat generating glass, the canister would be near 1050°C, and for high-heat-generating glass the canister might be as low as 850°C. At this time additional batch may be added to "top off" the canister. This allows the canister to be filled to its maximum. Because of the reduced temperature, deformation and corrosion rates are reduced; however, they still have finite values and must be considered.

The canister is cooled uniformly to near 700°C at a rate dependent on the glass heat-generation rate, and is then removed from the furnace. The major concern during this step is the possibility of sensitizing the canister. Sensitization has an impact on the corrosion resistance of the canister in water storage (Section 4.5.3.7). A wall-cooling rate in the range of 100°C/h is recommended to minimize sensitization of the canister. The center-line of the glass will cool much more slowly. The actual rate will depend on canister size and the furnace design. The canister is cooled in the furnace; there it can be controlled and monitored, and it can be removed at a lower temperature. This is desirable because the material strength is a strong function of temperature, and a large increase in yield strength can be realized by cooling to 700°C. Thus, the material thicknesses of the canister can be reduced to values that are required for normal operation.

Cooldown

When the canister is filled with glass and removed from the furnace, it is at a high temperature in the range of 500° to 700°C, with the glass at a somewhat higher temperature of 600° to 900°C. Controlled cooling appears to be necessary to maintain the quality of both the canister and the glass. The major question to be resolved is what cooling sequence should be used. Care

must be taken in selecting a cooling rate based only on either glass or canister requirements so that adverse conditions are not created in the other. PNL studies have shown that the glass has the rate-determining requirements.

The major concerns in cooling the glass are minimizing devitrification and preventing cracking due to thermal stresses. Devitrification is a structural change in the glass and can potentially decrease the durability of the glass (Mendel 1978) (Section 4.6.3.2). The amount of devitrification depends on time and temperature. The temperature range of greatest concern is 950⁰ to 550⁰C for most glasses. In this range, devitrification may occur in a period of hours to months, depending on the glass. The concern arises when the glass must be cooled in a matter of hours. Excessive cracking of the glass is undesirable because it increases the available surface area of the glass that is subject to leaching in an aqueous environment. Cracking will occur when the glass is cooled below its transition temperature ($525^{\circ}\text{C} \pm 25^{\circ}\text{C}$ for most waste glasses) and when large gradients are present (100⁰C/in.).

If a glass is subject to rapid devitrification, the bulk of the glass in the canister should be cooled as rapidly as possible to about 600⁰C. Rapid cooling of the glass centerline is difficult because of the high heat capacity and low conductivity of the glass. The gradients seen during cooling can be large. To bring the glass temperatures down to about 600⁰C, the glass near the canister wall drops below 525⁰C, which results in some cracking. This illustrates the tradeoff between preventing devitrification and minimizing cracking of the glass. The temperature gradients can be decreased by canister design. For example, internal fins or a smaller diameter could be used. This type of behavior is present in all glasses, whether or not heat is being generated. The minimum cooling rate to prevent significant devitrification is dependent on the glass composition, but a minimum cooling rate of 50⁰C/h is frequently used.

Cooling below the transition point is controlled by the acceptable amount of cracking that can take place. The glass and canister are cooled to

approximately the steady-state temperature incurred during handling. For example, canisters containing high-heat glass may be cooled to the temperatures they will be at during water storage, or low-heat canisters may be cooled to ambient air temperatures. The cooling rates can range from those found in water- or air-quenching to those necessary for annealing. Current thought suggests a compromise approach between these two extremes, which would maintain a wall-cooling rate in the range of 50° to 100°C/h . At these rates, cracks caused by thermal stresses will occur at approximately 2-in. intervals. Glass-cracking is also caused by the bond between the glass and the canister. During cooling the canister moves relative to the glass. When bonding is present this movement causes significant fracturing in a surface layer of glass about 1 cm deep. This cracking cannot be easily prevented. A discussion of glass-cracking is presented by Slate et al. (1979).

The impact of the cooling rates selected for the glass must be evaluated on the canister. The two major concerns are sensitization and residual stress in the canister wall. Both of these things have an impact on the canister's susceptibility to SCC when in water storage. When air storage is used, sensitization and residual stress conditions are not of major importance.

Sensitization results from depletion of chromium at the grain boundaries caused by the grain-boundary precipitation of chromium carbides. It occurs in austenitic stainless steels and many other high-alloy metals. Sensitization is a reversible time-temperature dependent phenomenon. For canisters, there is a concern with continuous-cooling sensitization (CCS). Sensitization by CCS can be predicted from standard time-temperature-sensitization (TTS) curves (Figure 4.5.72) (Solomon 1978). To prevent significant sensitization of 304L, the cooling rate of the canister wall should be at least 100°C/h in the range of 500° to 750°C .

During cooling below the glass transition temperature the walls of the canister are placed in a state of tensile stress. This is due to the fact that the glass contracts less as it cools than does the steel canister. Residual stresses have been measured at PNL at levels near the canister material yield strength of about 35,000 psi. Analyses and tests indicate that rapid cooling

FIGURE 4.5.72. Time-Temperature-Sensitization Curves for Stainless Steels with Various Carbon Contents

by water-quenching can redistribute the stresses, with the potential to reduce the canister stress to much lower levels. However, such quenching would be in conflict with the desire to minimize thermal-stress cracking in the glass. Section 4.5.2.4 discusses residual stresses in detail.

The cooldown operation may be performed in a specially designed rack in the primary cell. The canister may be cooled using forced air or conduction. The cooling rate will be controlled and recorded for use in quality verification. The rack will be able to cool several canisters individually, because the cooling time may exceed the glass-filling time. In addition, the rack will contain spall from the canister surface if it is present.

4.5.3.3 Closure

The final closure seals the glass inside the canister, and it must be a durable and reliable barrier to any interaction of the glass with the external environment. The criteria for a good closure weld are:

- a seal-weld must be made, and it must be sound and reproducible

- it must have adequate strength for the design loads
- it must be water-tight
- it must be inspectable by ultrasonic techniques in case such techniques are required.

The canister will be sealed after it has cooled to the appropriate temperature. The steps in the closure operation are weld-area preparation, welding, inspection, and repair.

Area Preparation

The welding area must be cleaned by removing any contaminants, and a proper fit-up of the parts must be made.

The entire ICM canister will have experienced the 1050°C processing temperature, so the weld area will be heavily oxidized. The degree of cleanliness required will be dictated by the welding process used. Some processes can tolerate more "residual contamination" than others.

In general, the weld area must be free of oxidation, oils, dirt, and, to the extent possible, radioactive contamination. The oxidized base material will be the most difficult to remove. It can be removed by grinding, machining, grit-blasting, or chemical treatment. Machining would require a device that could mount the canister and carefully position a grinding or cutting wheel. Grit-blasting would use conventional blasting techniques except for the particle material. Research is being conducted on using solid fluids (e.g., dry ice) as the blasting particles instead of sand. The advantage of solid fluids is that there is no cleanup needed except for a small volume of removed base material because the blasting material will melt or sublime. Chemicals could be used alone as with conventional descaling solutions or in conjunction with electric current. This latter technique is called electro-polishing and has become a proven metal-cleaning as well as a decontamination technique (Allen et al. 1978). Small, self-contained swabs have been shown to polish oxidized material with minimal release of electrolyte. A special coating could also be placed over the weld area during processing to prevent

oxidation. This coating would be designed to be easily removed after filling, leaving a clean surface. A reference cleaning process has not been selected.

Joint Fit-Up

A good fit-up of the lid and the canister is important in making remote welds that are consistently reproducible. The degree of accuracy required depends on the welding process and the condition of the canister. A more forgiving process, such as inertia-welding, does not require exacting fit-up, and the preparation of the parts to be welded need not be to high tolerances. Autogenous laser and gas tungsten-arc welding, on the other hand, require a tight-fitting joint--one in which there are not gaps between the parts to be welded. Even though gaps along the weld path can be successfully closed when welding with these processes, such joint discontinuities affect reproducibility by causing inconsistent penetration, head shape, and weld quality.

Fit-up will be controlled by the design of the closure. The design must be able to accommodate irregularities resulting from the cleaning process and from warpage of the canister due to processing. Careful control of the fit-up by design will also allow simplification in the design of the welder by removing the requirements that it accommodate irregularities in the joint.

Welding

Several welding processes have been considered for making the canister closure. Each process has advantages and disadvantages that must be evaluated. Before a final decision is made careful testing must be conducted, and an evaluation made on whether the process meets the following criteria:

- consistent, high-quality, reproducible welds
- remotely operated
- high reliability and easy maintenance in a remote environment
- minimization of necessary handling of the canister.

The processes currently being evaluated are gas tungsten-arc, plasma-arc, inertia, resistance, and laser. The gas tungsten-arc (GTA) process has been

selected at PNL for initial prototype development because it most closely meets the process requirements. The other processes can be used. GTA is the most common method in use today for welding nuclear equipment. It has been carefully studied and the techniques for making high-quality welds are well understood. This process has been used successfully in welding actual radioactive waste canisters (Mendel and McElroy 1972).

PNL has developed a prototype GTA welder for the twist-lock closure, (Figure 4.5.49) and has demonstrated it. The design includes all features necessary for radioactive use. The welding device uses the GTA process to make an autogenous fusion weld between the lid and the canister. The weld can range from 3 to 6 mm thick. Figure 4.5.73 shows the device placed on a prototypic canister top. The welding torch orbits the main body of the welder to make the weld. Welding is done on a vertical canister with the joint in a 2F position. The position of the electrode, relative to the weld joint, is set and locked before the device is placed in the cell. Positive location of the electrode is achieved by using an accurately machined positioning hole in the center of the lid. Tight tolerances are maintained on the welding surfaces of the lid, which eliminates the need for automatic tracking or voltage controls to position the electrode during welding.

The electrode can be moved in toward the center of the device by two 3-mm increments, which decreases the radial distance from the original welding position. This provision was made to allow a repair weld to be made if a portion of the first weld were removed by machining.

To make the weld, the device is moved by a powered arm or crane from its storage location in the cell and is set on the canister lid. The lid is tack-welded in four equal-spaced locations and then the automatic welding sequence is begun. The torch rotates around the central axis of the device in small steps. The current varies between a maximum and minimum value to make an even weld and to reduce heating of the torch. After about five minutes the weld is completed, the current decreases automatically, and the device stops.

The electrical cables are connected to the stationary body of the welder by special quick-disconnect couplings. The ground-current path is established

FIGURE 4.5.73. PNL Prototype Canister Closure Welder Using the GTA Welding Processes

through the legs of the welding device to the canister lid. The welding current passes to the tungsten electrode through gold plating on the rotating arm. No additional electrical connections are necessary.

The tungsten electrode holder assembly, or torch, is a finned tube with a small heat pipe inside. The heat pipe transfers heat from the electrode end of the torch to the finned area. This design allows adequate passive cooling of the electrode so water-cooling is not necessary. The purge gas also provides cooling of the electrode. The gas is piped through the inside of the rotating arm to the electrode end of the torch. The torch, held in the rotating arm by a special clamp, can be quickly and easily removed from the device for replacement or adjustment of the electrode.

Because the torch drive motor is potentially a high-maintenance item, it was designed to be easily replaced. The motor housing is keyed to be self-locating and is held in place by a simple latch.

The welding device has been tested on three prototypic waste canisters. The welds were examined through a helium-leak inspection to a level of about 5×10^{-9} atm-cm³/s. Many tests were also conducted on mockups of the lid/canister assembly. The welds were destructively examined and were shown to be of high quality.

Inspection

After the closure weld has cooled it will be inspected to assure that it is sound and leak-tight. It is not anticipated that the entire canister will need to be inspected for integrity, such as other welds, since the canister will be carefully inspected before filling and the service life is not expected to be severe enough to require inspection. There are many routinely used techniques for inspecting a weld during normal fabrication operations. However, severe limitations exist in a remotely operated, highly radioactive cell. The two most widely used techniques for this service are ultrasonic inspection and leak-testing using helium.

Helium Leak-Test. For the canister to meet its design goals and to perform properly in subsequent operations, the closure weld must be "leak-tight."

A "leak" is defined as an imperfection in the canister that will allow gases, liquids, or solids to enter or leave the canister. Nothing is absolutely leak-tight. The quantity of the leak will be dependent upon environmental conditions. The units of a leak will be atmospheric cubic centimeters per second (atm cc/s) at room temperature. To date no criterion has been established as to the level of leak-tightness required during the life of a canister.

Criteria for leakage from packages containing nuclear materials are contained in a number of documents such as the Code of Federal Regulations, ANSI Standards and others. However, no specific mention is made of waste canisters. Leak-tightness, relating to packaging for radioactive materials, is 10^{-7} atm cc/s at standard conditions (Anon. 1974). It is interesting to note that leak paths this size are small and clog easily, so they are rarely found in practice (Anon. 1974).

In order to quantify the leakage rate, those materials subject to possible leakage were identified. Leakage of materials from inside the canister are of most concern because they are radioactive. Canisters contain only waste glass and some nonradioactive gases--primarily helium. In the ANSI draft guide (Anon. 1974) it states that it is conservative to assume that solids, powders, or slurries leak as water. Hence, a criteria of water-tightness would seem to suffice. The major concern of material leaking from outside into the canister is water. Water is an important part of several processing steps. Efforts should be made to keep water out of the canister primarily to prevent possible canister pressurization if the canister was ever heated during normal or accident conditions. From PNL studies it was determined that a helium leak rate of 10^{-4} atm cc/s would be a suitable value for leak-tightness for liquid water. This criteria is conservative when considering the leaking of solids.

Commercial helium leak-test equipment under ideal conditions have sensitivities up to 10^{-12} atm cc/s. However, as piping, filters, cold traps, and test cells are added for hot-cell operation, the sensitivity decreases. Commercial leak-detector vendors have indicated the best sensitivity that could

be hoped for in a remote hot cell operation would be about 10^{-7} atm cc/s. However, at this level the amount of contamination in the hot cell may be large enough to create a significant helium background from reactions. This background may make the level of 10^{-7} atm cc/s meaningless, because a leak would not be detectable over the background reading. Based on PNL investigation it was concluded that a leak rate in the range of 10^{-5} to 10^{-6} atm cc/s would be practical and reliable to obtain under the expected operating conditions and still provide a conservative measure of leak-tightness.

Leak-testing of radioactive packages is a known technology. In fact, even high-level waste canisters have been checked by this method (Mendel and McElroy 1972). The leak test can be performed with commercial equipment. Performing the test remotely in a hot cell complicates the technique but is still within the state of the art.

A concept for the leak test is shown in Figure 4.5.74. Helium will be placed inside the canister before welding. After welding, a bell jar will be placed on the top of the canister and evacuated. The leak detector will then check for helium and measure the rate of leakage if there is any. The procedure does not require any handling of the canister.

There are several methods for putting helium inside the canister. The method will be selected for ease of operation and on the measure of assurance that sufficient helium is present for proper inspection. One method is to place a helium source inside and then make the closure weld. The helium would be slowly released until some fraction of the gas inside was helium. This could be done by 1) using a helium-saturated sintered-metal block; 2) using a pressurized cylinder with a slow, calibrated release; or 3) flowing helium in while welding. All three techniques would be easy to perform. However, it is difficult to consistently assure that there is helium present during the inspection. There is an uncertainty that the slow release had stopped or that all the helium went out through a gross leak. A more certain method is to place the helium inside through a small hole after welding. To do this the air inside the canister would be evacuated and replaced by helium at a known

FIGURE 4.5.74. Schematic Diagram of the Equipment for Helium Leak-Checking a Canister

pressure. The weld would then be checked, and if it was acceptable the hole would be sealed. The hole would also be tested. This technique has been used with success on nuclear components such as fuel pins. Also, a pressurized cylinder with a low-melting-temperature plug could be used. This fusion plug would be melted after the weld was made to release the helium.

Ultrasonic Inspection. There may be internal defects in the weld that may increase in size as a result of cyclic loads on the lid. Therefore, the closure should also be designed so that it can be inspected by ultrasonic techniques. Ultrasonic tests have been routinely used for inspection of in-service nuclear components.

The twist-lock closure was designed to ensure that the geometry was optimum for ultrasound. PNL has conducted analyses on the structural integrity of the weld to determine the defect size that the inspection must detect (Section 4.5.2.4). In general, the analyses show a defect one-half the thickness of the weld or larger must be detected. This is well within the range of most ultrasonic equipment.

The equipment to demonstrate this technique is still under development. The ultrasonic test could use an immersion/through-transmission technique that relies on loss of signal for flaw detection and sizing. Two transducers in the configuration shown in Figure 4.5.75 will be rotated around the weld. Any flaws will be detected and recorded on a permanent file in a conventional c-scan format. The coolant for the transducers will be water. The canister will either be in water, if it contains high-heat waste, or water will be injected under the transducers. Before each inspection the equipment will be calibrated on a standard weld with known defects.

Weld Repair

With nearly any welding process there will be some defective welds; thus, there must be provisions for repairing the weld. The methods used to repair a defective weld are dependent upon the type and severity of the defect. There are three repair methods available: 1) reweld over the defective area, 2) remove the weld and reweld, or 3) weld on another lid over the first one.

Rewelding over the defective weld would be the easiest method of repair. This procedure would be effective in eliminating minor defects such as porosity, surface cracks, and small wormhole leaks. Rewelding is an acceptable means of repair based on standard welding practice, but could only be done for those welding processes that use point heating, such as GTA, plasma, or laser.

For more serious defects, the weld, at least around the defect, would have to be removed. The weld would be removed in such a manner that the new joint would have the same geometry as the original joint. This would allow the same welder to make the repair weld with a slight adjustment. In the case of the twist-lock design a device would be mounted on the lid that would machine the weld off, leaving a squared-off edge on the lid. The torch on the welder would be indexed into the new radius and the repair would be made. Conceptual designs have been developed for this device. Free-hand welding to repair defective welds has been demonstrated (Mendel and McElroy 1972). In the case of solid-state welds, the entire lid would be removed and the joint would be machined to necessary tolerances for rewelding.

FIGURE 4.5.75. Schematic Diagram Showing Transducers and Instrumentation of Ultrasonic Inspection

Instead of removing the defective lid it may be simpler to put on another lid over the top of the old one. This technique is most applicable to the solid-state processes of inertia- or resistance-welding. This method requires that the canister top be designed for two different lids, that if the first lid was defective a second could be put on above it. This repair technique is simple to perform but requires a more complex closure design. In addition, some techniques would have to be developed to repair the second weld if it were also defective.

4.5.3.4 Decontamination

Canister decontamination will probably be necessary to reduce the surface radionuclide contamination of the canister. No firm criteria have been established, but some preliminary restrictive criteria have been proposed (Section 4.5.2.1) based on shipping-container contamination limits that may not be applicable for a HLLW canister. If the decontamination procedure is performed in stages, precautions need to be taken to avoid recontaminating the canister.

The first method of reducing contamination is preventing it in the first place. Radioactive contamination of the canister occurs principally as a result of contact with the solidification processes. This is either direct contact, such as calcine spillage, or by contact with contaminated surfaces.

Decontamination techniques have been investigated for a wide variety of nuclear applications. The procedures applicable to cleaning canisters are considered modifications of scrubbing, soaking, and spraying. The procedure used depends on the type of contamination.

Contamination loosely adsorbed to the canister surface can be removed by washing or scrubbing with a detergent or organic solvent. Contamination diffused into an oxide layer that may fall off cannot be washed or leached out. The only method to remove the contamination is to remove the oxide film from the metal surface. Radionuclides that have diffused into the metal may only be removed by removing a thin layer of the metal.

To facilitate decontamination the canister has been designed with smooth surfaces and rounded corners. Electrolytic prepolishing has been considered because it has been shown to assist in later efforts to decontaminate. Consideration must also be given in the canister design to the effect of decontamination on its quality. These effects are considered in the descriptions of the procedures.

Scrubbing

Scrubbing is the mechanical removal of the contamination from the base surface. This is typically done with a cloth, brush, or abrasive in conjunction with a detergent or solvent. This procedure can be adapted for remote operation, although it is typically used in a hands-on operation.

Scrubbing has the advantage that all the physical and chemical force can be applied to a specific area that is contaminated. It will also tend to remove contamination that adheres to the surface. A modified form of scrubbing incorporates an electrochemical feature (Allen et al. 1978). A special cleaning swab acts as a cathode and the canister is the anode with the

solvent acting as the electrolyte. Scrubbing will probably be used for removing small areas of contamination. Using it over the entire exterior surface would probably require complex equipment. The effect on the canister and glass should be minimal. However, if an abrasive is used it could not contain any materials that would degrade the corrosion performance of the canister if left on the canister surface.

Spraying

Canister decontamination using a spray system has been demonstrated on actual radioactive canisters at PNL. The canisters were raised vertically through a toroidal spray ring that was 2 in. from the canister wall. This canister was alternately sprayed with 100-psig steam and 75-psig water. Smearable contamination levels ranging from 8×10^3 to 8×10^4 dpm/cm² were reduced to 40 to 200 dpm/cm².

One concept is to have the canister rotate in a fixed position in front of a perforated pipe. Figure 4.5.76 is a flow diagram of the design. The spray would cover the entire exterior surface of the canister. The assembly would be enclosed to contain the water and removed material.

This procedure would produce secondary waste liquids. Efforts would be made to keep the amount of these materials to a minimum. The spent liquids that are produced would be combined with other liquid wastes for treatment.

There would be no harmful effects from this procedure on the canister. The canister would have to be designed so that all exterior surfaces could be sprayed. Thermal shock of the glass would have to be avoided. Therefore the glass should be cooled to a steady state with the canister-wall temperature equal to the water-spray temperature.

Soaking

Soaking is a widely used method for decontamination. The procedure is to place the contaminated part in a tank of solvent. The removal of contaminants is principally by chemical action. The part is then flushed with clean water. Physical cleaning forces such as agitation and spraying can be added to improve the removal process.

FIGURE 4.5.76. Flow Diagram for Spray Decontamination

At PNL an important modification of soaking, called electropolishing, has been developed (Allen et al. 1978). The object to be decontaminated serves as an anode in an electrolytic cell. The passage of current results in the anodic dissolution of the metal surface; under proper operating conditions a smoothing of the surface results. Any radioactive contamination on the surface or entrapped within the surface imperfections or oxide layer is removed and released to the electrolyte during this process. The amount of metal removed from the component surface to effect decontamination is usually 0.002 in. This material is removed uniformly and there is no preferential attack of grain boundaries or other microstructural features.

Tests have shown this technique to be very effective. Objects that have been severely corroded in a contaminated environment have been cleaned to releasable levels. Initial tests have shown that even the heavy oxide layer on an ICM canister can be removed.

A diagram of a canister electropolishing station is shown in Figure 4.5.77. The electrolyte, usually phosphoric acid, is held in a stainless steel tank. Capabilities for heating, cooling, and agitating the solutions are included. The process is simple; the canister is lowered into the tank and electropolished. While the electrolyte is rinsed off with hot water the canister is slowly removed. An additional rinse may be performed in another tank.

No harmful effects to the canister have been identified. In fact, the process could improve the corrosion resistance of the canister. The metal will tend to be passivated and the polishing action will remove any crevices that might contain contamination and be crack-initiation sites.

The amount of secondary waste should not be excessive. The electrolyte will still decontaminate even though it is highly contaminated itself. When the activity is too high the electrolyte can be reclaimed by fractionation,

FIGURE 4.5.77. Diagram of Canister Decontamination by Electropolishing

acid absorption, or solvent extraction, and then reused. The small amount of residual radioactive material will be combined with other liquid wastes for treatment.

Methods to measure smearable contamination after decontamination have been developed in industry and at PNL. These methods of random swiping may be adequate, although they are crude and subject to inaccuracies.

4.5.3.5 Quality Verification

Once each canister has been filled and sealed, the quality of the canister and glass waste form must be evaluated to determine conformance to performance, acceptance, and any other requirements. Quality verification refers to the tests or documentation needed to determine that the filled canisters of waste glass meets the associated requirements. Definition of the filled-canister requirements are still evolving; nevertheless, it is possible to discuss the necessary product quality assurance in general terms.

The quality assurance (QA) applied to the waste canister differs in important ways from that applied to the waste glass. Quality-assurance techniques applied to the canister are the standard procedures that have evolved over many years for the fabrication of metal vessels or containers. Hands-on inspection of each canister prior to filling, with the rejection of off-standard canisters, is possible.

In contrast to the canisters, waste glass is a more recently developed, highly radioactive substance for which QA techniques are still evolving. Hands-on inspection is, of course, impossible, and once the glass is in the canister the types of remote measurements that can be made to corroborate quality are somewhat limited. Therefore, process control becomes an important part of waste glass QA.

Process Control

By properly controlling the waste glass process, it is possible to produce waste glass within certain specifications. Process-control parameters of particular importance are listed below:

- Analysis of the liquid waste being fed to the vitrification facility: Both chemical and radioisotopic content of the incoming waste must be known. The former affects the composition of the product glass; the latter determines self-heating and radiation effects in the glass and the radiation dose rate from the canisters.
- Glass-additive composition: Glass-making additives can be added to the waste in a feed tank prior to processing or they can be metered into the process continually. Both methods have proven satisfactory.
- Input stream-flow ratios: Only two streams are involved--the liquid waste and the glass-forming additives. They must be mixed in a predetermined ratio to form the desired glass. Tests have shown that while it is possible to control the ratio closely, fluctuations of 20% on the high side for the waste and 20% on the low side for the glass-forming additives are permissible without changing waste-glass properties significantly. Fluctuations on the low side for the waste and on the high side for the glass additives are usually even less significant; the main effect is the production of a more dilute waste-loading in the glass.
- Processing temperature: Waste glasses are formulated to be melted at a certain temperature for a certain length of time (somewhere between 950⁰ and 1150⁰C, usually for at least 2 h). If these nominal conditions are not met, the product may contain waste oxides that are incompletely dissolved in the glassy matrix.
- Topping-off of filled canisters: Canisters are usually 80% to 90% filled with glass. In the processes by which waste glass is formed in the canister, precautions should be taken that no residue of unmelted waste calcine remains on top of the last glass melted in the canister. These precautions could involve the addition of some glass additives without waste, followed by holding the top of the canister at the processing temperature for an additional 2 to 3 h.
- Cooldown of canisters: The temperature regime used for cooling down canisters of waste glass is designed to minimize sensitization of the

canister walls and devitrification of the glass. Thus, after the canister is removed from the furnace, a rapid cooldown (greater than $50^{\circ}\text{C}/\text{h}$) to a temperature of approximately 500°C is desirable.

Standard reliable techniques can be used for most of the waste glass process-control requirements listed above.

~ Measurements on Product Glass and Filled Canisters

As described in the previous section, process control can be used to regulate waste-glass compositions and verify the quality of the final glass/canister package. The efficiency of process control, however, will be corroborated by certain measurements, made either routinely or as spot checks, on the product. These checks may include some, or perhaps all of the following measurements:

- Analysis of waste glass: Quality assurance usually includes periodic analyses of the product to determine if certain desired properties are within specifications. As described earlier, specifications have not been established for waste glass. The most probable analysis that would be performed on waste glass samples is a leach test. The leach rate of the glass would probably be determined after a prescribed thermal treatment designed to produce the maximum temperature effects anticipated in the waste glass. Several sampling techniques are available. The first involves taking an aliquot of waste calcine and melting it with the requisite amount of glass-forming additive. Secondly, it is even possible to core-drill samples from a filled canister and reseal the hole in the canister wall, as performed in the WSEP program. Analyses made on waste glass samples will probably be too time-consuming to be used as a control on each canister. More likely, a sample(s) will be used to certify the quality of all of the canisters in a given run period made from a batch of similar waste solution.
- Physical inspection: Each canister could be weighed and checked for dimensional stability during post-fill handling--i.e., changes in diameter, roundness, or longitudinal warpage that could conceivably result

from filling the canister with glass. The bulk density of the product glass will be calculated from weight and volume. In addition, each canister will be checked visually for obvious defects.

Furthermore, quality controls on the fabrication of the canister and design of the canister to sustain loadings during processing would ensure to a high confidence level that the canisters will survive processing and interim storage. Records could be reviewed to determine if adverse time-temperature exposures have been encountered, such as might result in material sensitization or other degrading effects on material properties.

- Radiation field: Measurements of the magnitude and uniformity of the gamma and neutron fields associated with waste glass canisters would help to: 1) corroborate the radiochemical analysis of the liquid waste fed to the process, 2) define transportation shielding requirements, and 3) determine the homogeneity of the waste glass.
- Heat generation: Measurement of the heat-generation rate of waste canisters would also help to corroborate the radiochemical analysis of the liquid waste fed to the process. Knowledge of the heat-generation rate of each waste-glass canister is required at the geologic repository, since there would be a maximum integrated heat-load limitation at each repository. Various types of calorimeters can be used to measure the heat-generation rate of individual canisters. Alternatively, the heat-generation rate can be calculated if the surface temperature of the canister and the emissivity of the canister surface is known (Mendel and McElroy 1972).
- Nondestructive testing: The nondestructive testing technique that has been most commonly applied to waste-glass canisters is ultrasonic scanning--particularly when checking for gross corrosion of the canister wall. It has been suggested that ultrasonic techniques may have application in measuring the amount of fracturing in canisterized waste glass, but no successful tests have been made.

4.5.3.6 Overpack and Recycle

The quality verification procedure would establish whether the glass and canister meet the necessary requirements for storage, transportation, and disposal. If the canister or glass is judged not to be acceptable, then some remedial action must be taken. If the quality of the glass is poor, then steps would have to be taken to modify it or recycle it into the solidification system. If the canister is defective it would need to be repaired or overpacked.

No detailed studies of remedial actions for low-quality glass have been made at PNL. These studies are planned as part of the canister development program. The nature of the remedies depends on the type of problem. Simple problems such as devitrification or excessive cracking due to improper cool-down can be corrected by simply reheating the canister and cooling again. The reheat operation should not have a significant detrimental effect on the canister. If the heat generation is too high, special storage provisions will have to be made. If there are major compositional problems the glass will probably have to be recycled. The operations to do this have not been investigated.

If a canister is defective, it may have to be repaired or overpacked. A repair operation, for example, might be spot decontamination of localized contamination. Many defects could be handled by overpacking.

Because there is a definite chance that some canisters will fail acceptance criteria, overpacks must be designed. One possible design is illustrated in Figure 4.5.78. In general, overpacks should be designed so that minimal additional facilities will be required to handle them. For example, the closure could be designed to use equipment similar to that for the canister closure. The overpack would preferably be emplaced in the second hot cell, where only minor decontamination would be necessary. A more detailed discussion of overpacks is contained in Simonen and Slate (1979).

4.5.3.7 Interim Storage

The canister will be placed in interim storage after all processing operations are completed. An interim storage period is needed for two main

FIGURE 4.5.78. Drawing of a Canister in an Overpack

reasons. The first is to provide for lag storage of canisters prior to transportation to the disposal site. Lag storage is needed to prevent hold-ups in shipping or disposal from delaying solidification. The second reason is to provide time for the heat-producing fission products to decay. This is done to reduce the power level in the canister before disposal. At the repository there will be strict limits on the power output of each canister, so the delay makes it possible to use fewer of the larger canisters than would be possible if they were shipped immediately after filling.

The period of time in interim storage will depend on a variety of factors such as facility design and disposal costs. The exact nature of interim storage will not be established until a waste facility has been designed. The reason is that the size and type of storage is dependent on the entire waste management system and its attendant development schedule and economics. However, some of the basic storage concepts and their impacts on the canisters can be described.

The two major types of interim storage are pool storage and air storage with natural or forced cooling. These and other types of interim storage were described by the Energy Research and Development Administration (ERDA) (ERDA 1976).

Water Storage

Canisters containing high-heat-generating wastes will usually be placed in water-pool storage. Water provides an efficient, reliable method of cooling and shielding. Cooling of the canisters is necessary to minimize the temperatures the glass experiences. Typical high-heat-generating glasses must be maintained below 500°C during the years of storage to prevent devitrification of the glass (Turcotte and Wald 1978). The limiting temperature is the centerline glass temperature, which is established by heat-generation rate, thermal properties, internal fin design, and wall temperature. Storage in water provides the lowest practical wall temperature, which means larger-diameter canisters can be used than in a comparable air-storage facility. Wall temperatures in water are expected to be no higher than 60°C , whereas they may exceed 300°C in air.

Pool designs for waste storage will be very similar to pools used for nuclear fuel storage. The water will be continuously recycled for cooling and deionization. The controls on the pool operation and conditions are expected to be closely maintained.

The major impact on the canister during pool storage is corrosion. If low-carbon or low-alloy steels are used, special measures will have to be taken to prevent oxidation (rusting). Rusting is undesirable primarily from a pool operation standpoint--causing visibility and filtration problems.

At PNL a survey of methods to prevent rusting was conducted. The methods included metallic and organic coatings, impressed voltages, and inhibitors. It was concluded that some type of inhibitor such as chromate would work quite well. The performance of carbon-steel in contact with chromate solution is known to be very good and has been demonstrated using mild-steel canisters with radioactive waste at PNL.

If stainless steels are used, rust is no longer a problem. The major concern is with SCC. The canisters will be susceptible to SCC because they have high residual-surface tensile stresses and may be sensitized. This problem is primarily associated with the austenitic stainless steel, but does occur in other stainless alloys. PNL has studied the SCC performance of several stainless alloys (Section 4.5.2.2). From this work it was concluded that SCC of 304L under expected pool conditions can be prevented by maintaining proper water quality and by controlling processing temperatures to minimize sensitization.

With any material there will be a certain percentage of failures. The actual number of failures and their ramifications are unclear. The number of failures should be quite small. The consequences from a failure will probably be minor. The amount of radioactivity released from a cracked canister is expected to be low. In fact, if failed fuel is stored in the same pool as the canisters, the increase in pool activity from a cracked canister may not be detectable. Data on releases from a cracked canister containing radioactive waste glass are discussed by Bradley (1977).

Air Storage

Air storage will be principally used in storage of low-heat-generating wastes. The cooling requirements, even for large-diameter canisters, will be minor in order to maintain the waste and canister at the appropriate temperatures. In this situation no degradation of the canister is expected, except for what might occur during normal handling. Because of this, air storage places few material requirements on the canister, allowing greater flexibility in meeting the material requirements of other operations such as glass-filling.

Air storage may also be used for storage of high-heat-generating wastes. The facility would be designed to be adequately cooled by natural convection, but for conservatism, cooling by forced convection would be available. The temperature of the canister is dependent on its heating rate and on the facility design. Normally the canister temperature would be less than 200°C. Even for low-alloy steels this would not be hot enough for serious oxidation to take place. Air storage of HLLW canisters is currently being done in France (Bonniaud, Jouan and Sombret 1980).

4.5.3.8 Transportation to Disposal

The canister will be transferred to a federal repository for disposal after interim storage. In this section the preparation of the canister for shipment is briefly discussed, as well as the shipping phase itself.

Upon removal from interim storage the canister will be inspected for corrosion or structural damage. For corrosion, the main concern is for canisters that might have suffered SCC. General corrosion should not be a problem. Structural damage may occur during handling by such events as dropping. The canister may be overpacked if damage is severe. The canister will then be decontaminated if necessary. The degree of decontamination will be in accord with the requirements of the shipping casks and the repository.

The canister will be shipped in a Type-B shipping cask, similar to those used for shipping spent fuel. These casks will of course be licensed according to all federal regulations. As in shipping spent fuel, the primary reliance for protecting the public health and safety is placed on the shipping cask. No containment requirements are anticipated on the canister during shipping. However, the presence of the canister as an impediment to activity release should be considered in evaluating design-basis and incredible accidents.

Shipping casks uniquely designed to transport waste canisters have not yet been developed, although the technology for doing so is available from experience with shipping fuel. Conceptual designs have been published by Oak Ridge National Laboratory (Perona and Blomeke 1972) and PNL (Rhoads and Peterson 1978). Figure 4.5.79 shows a conceptual drawing of the PNL

FIGURE 4.5.79. Conceptual Drawing of a Shipping Cask for Waste Canisters

design. The design provides for multiple canisters within a single cask. The close packing around the canisters makes it necessary that attention is given to making sure the canisters are compatible with the cask and all handling operations associated with it. In radionuclide shipping the regulations require that the shipping container provide total containment of the package being shipped.

4.5.3.9 Final Disposal

Specific performance criteria have not been developed for final disposal of the primary canister. During the course of PNL's canister development studies, guidelines from 10 CFR 50, Appendix F (Code of Federal Regulations, Title 10, 1978) were used, which required canister to maintain its integrity for only 90 days after receipt at the federal repository for disposal.

The proposed 10 CFR 60 criteria require that an engineered-barrier system must isolate the waste from the geology for a period of up to 1000 years. This new disposal philosophy may impact the design of the primary canister, because the barrier system may or may not take credit for protection provided by the canister. Also, the canister design must be compatible with the barrier system. This protection will depend upon which of two design philosophies are used.

The first philosophy has a canister being designed specifically for processing, interim storage, and transportation. Based on PNL work this should be possible without additional major development work. The barrier system would be designed to provide all of the required waste containment exclusive of the canister. This philosophy has the benefit of allowing the canister and barrier system to be designed for its own specific use without the necessary compromises that could accompany a "universal" canister. Also, the canister could be disposed of at any repository without the potential problems of qualifying its barrier value in a different environment.

The second philosophy would provide a canister designed to act as a major barrier during disposal. This would require that the canister be made of sophisticated materials and that its quality be carefully verified during all process steps. This approach may allow a cost reduction by eliminating an

additional barrier. It is also possible that processing operations could be simplified with the use of some alloy. However these operations could be complicated by the use of a fragile material such as a ceramic. Extensive development of this universal canister might be necessary in order to qualify it for use.

The decision on which design philosophy to use must be made based on an overall analysis of the waste management system. The first option can be considered for immediate use. Work on the second option may await more definitive criteria on the overall system.

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4.6 RADIOACTIVE WASTE GLASS

J. E. Mendel

Radioactive waste glasses are formulated by combining a selected mixture of glass formers, modifiers, and intermediates (called the glass-making additives) with the waste. The glass-making additive combination selected depends on the composition of waste being vitrified and on the properties desired in the waste glass. The glass-making additives usually comprise 65 to 85 wt% of the product waste glass. The composition selected for a given radioactive waste glass is governed by three factors:

- the constituents of the radioactive waste to be immobilized
- the vitrification process to be used for the immobilization
- the properties desired for the immobilized waste product--i.e., the physical and chemical characteristics desired for the waste glass that is transported away from the processing plants to be placed in geologic disposal.

Melt homogeneity is the critical requirement in waste glass formulation. All glass components should be in solution at the melter operating temperature. The SC/ICM process operates at what, for the commercial glass industry, is a very low temperature--1000⁰ to 1100⁰C. The viscosity of the glass melt is formulated to be less than 200 poise at the operating temperature. Viscosity is important, since it affects diffusion and mixing in the glass. The processes can impose additional constraints on the glass related to factors such as high-temperature volatility and corrosion.

4.6.1 GLASS FORMULATION

Glass formulation is the process in which suitable additives are selected to be added to the radioactive waste in the vitrification process, so that the resulting glass will have properties compatible with both processing and ultimate solidified product requirements.

4.6.1.1 Elements That Must Be Incorporated in Radioactive Waste Glasses

High-level liquid waste usually contains over 99.9% of the nonvolatile fission products and actinides except uranium and plutonium, which are recovered during reprocessing. Due to processing waste losses, about 0.05% to 1% of the uranium and plutonium in the initial fuel ends up in the HLLW. As shown in Figure 4.6.1, HLLW also contains other constituents in addition to fission products and actinides. These constituents, often referred to as the inerts, account for the diversity in HLLW compositions. They include corrosion products, process additives, and possible other waste streams added to the HLLW, because it is a convenient disposal route for wastes containing radioactivity. The inerts usually make up less than 50 wt% of the nuclear-power HLLW constituents; they may make up more than 99 wt% of defense HLLW

IA																		INERT GASES																
H	IIA																	IIIA					IVA	VA	VIA	VIIA	He							
Li	Be																	B	C	N	O	F	Ne											
Na	Mg	IIIB	IVB	VB	VIB	VII B	VIII				IB	IIB	Al	Si	P	S	Cl	Ar																
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr																	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe																	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn																	
Fr	Ra	Ac																																
LANTHANIDE SERIES																		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu			
ACTINIDE SERIES																		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw
PRINCIPAL FISSION PRODUCTS, ACTINIDES AND DAUGHTERS
POTENTIAL REPROCESSING CHEMICALS (INERTS)																

FIGURE 4.6.1. Elements in Commercial High-Level Waste

constituents. This is one reason defense HLLW has a much lower heat-generation rate than does nuclear-power HLLW. The relative amounts of the types of elements contained in HLLW investigated for incorporation into waste glass is shown in Figure 4.6.2.

4.6.1.2 Waste-Loading Considerations

The variable that exerts the most control over the properties of waste glass is waste-loading. Waste-loading, expressed as wt%, is the weight proportion of the glass that is waste components, as oxides, versus the overall weight of the glass, which includes the glass formers and modifiers added to produce desired properties in the product material.

FIGURE 4.6.2. Ternary Diagram of Nuclear Waste Compositions (mol%)

Factors that contribute to definition of the upper waste-loading limit include:

- maximum solubility of waste components in the glass
- viscosity increase of the molten glass due to excess waste-loading
- leach rate increase in the product glass due to excess waste-loading
- excessive glass centerline temperatures during waste canister storage due to the presence of too much heat-generating waste
- excessive canister wall temperatures during waste storage due to the presence of too much heat-generating waste.

When these factors are all taken into account the maximum waste-loading in low-melting waste glasses (processing temperature of 950° to 1100°C) is in the range of 25 to 45 wt%. As stated above, the specified waste-loading is typically maintained in the range of 15 to 35 wt% to allow processing flexibility.

Contrary to what might be expected, low-melting glasses permit higher waste-loadings than do higher-melting glasses. Higher-melting (above 1300°C) glasses, including about 95% of commercial glass, and the long-lasting natural rhyolitic obsidians and tektites, contain over 70 wt% SiO_2 . This immediately limits waste-loading to less than 30 wt%. The limits are actually much lower because of the poor solubility of many waste components in SiO_2 .

4.6.1.3 Structure of Radioactive Waste Glass

Glass is defined as, ". . . an inorganic product of fusion which has been cooled to a rigid condition without crystallizing" (ASTM 1955). Radioactive waste glass fits this definition quite well. There are usually a few scattered crystals (about 5 vol%) present in most waste glasses. As a glass material is cooled it gradually becomes more viscous. At a viscosity of about 10^{13} poise the change from a supercooled liquid to glass occurs. The temperature at which this occurs is known as the glass transition temperature (T_g). Above T_g the glass is plastic; below T_g the glass is brittle. The exact value of T_g depends

on the rate of cooling, being lower for a slower rate of cooling. Thus, in Figure 4.6.3, $(T_g)_1$ would result from a slower rate of cooling than $(T_g)_2$. Slower rates of cooling in the range of the glass transition temperature are said to "stabilize" the glass, and, as shown in Figure 4.6.3, result in a denser glass. Glass is always less dense than a crystalline material of the same composition because in glass the atoms are arranged in a random fashion rather than being locked in a symmetrical array as they are in crystalline materials.

Glasses are metastable. That is, at certain temperatures formation of crystals of fixed stoichiometry can occur spontaneously. This spontaneous crystallization, called devitrification, occurs most rapidly at temperatures 100° to 300°C above the glass transition point. At lower temperatures the

FIGURE 4.6.3. Volume-Temperature Relationships for Glasses, Liquids, Supercooled Liquids, and Crystals

kinetics of devitrification become very sluggish; thus, natural materials in the glassy state, although not in their most thermodynamically stable state, have survived for many millions of years on earth.

Glasses are nonstoichiometric (oxide components not in fixed ratio as in crystal) materials, which is a distinct advantage when they are being used to immobilize wastes of indefinite and variable compositions.

It is empirically observed that different elements have different effects when incorporated in glass. One theory is that the variation in effects is due to bond strength. According to this theory, the elements can be divided into glass-formers, intermediates, and modifiers based on their bond strengths. Table 4.6.1 lists the bond strengths of some of the oxides found in radioactive waste, plus others (Sun 1947). The glass-formers alone can form a three-dimensional, random network. The oxides of silicon, boron, and phosphorus are the principal inorganic glass-formers. Random networks established by these glass-formers are the "backbone" of glasses. The network structures tend to be covalently bonded. Modifiers (Table 4.6.1) tend to bond ionically to the anions in the glassy network. They are used to alter properties, e.g., the addition of modifiers can decrease viscosity and increase both electrical conductivity and thermal expansion coefficients. An intermediate, although not usually capable of forming a glass, can enter in a glass-forming position and/or a modifying position and thus can help stabilize the glass while also changing its properties. From Figure 4.6.1 and Table 4.6.1 it can be seen that almost all radioactive waste constituents can have a place in the glass structure as a modifier, an intermediate, or a glass-former.

Thus, the structure of glass permits the individual atoms of the radioactive waste to become a coherent part of the glassy structure. The waste is not just encapsulated in glass; each waste atom is separately bound in the glass structure by a chemical bond. (There are certain minor exceptions to this statement, e.g., ruthenium and palladium remain as discrete particles encapsulated in the glassy matrix.) Also, while there are certain guidelines that can be used in glass formation (Rawson 1967; Bacola, Donato and Sgalambro

TABLE 4.6.1. Bond Strength of Oxides

<u>Constituents</u>	<u>M in MO</u>	<u>Valence</u>	<u>Coordination Number</u>	<u>Single-Bond Strength, kcal/mol</u>
Glass-Formers	B	3	3	119
	Si	4	4	106
	Al	3	4	101-79
	B	3	4	89
	P	5	4	111-88
	Sb	5	4	85-68
	Zr	4	6	81
Intermediates	Ti	4	6	73
	Zn	2	2	72
	Pb	2	2	73
	Al	3	6	67-53
	Th	4	8	64
	Zr	4	8	61
	Cd	2	2	60
Modifiers	La	3	7	58
	Y	3	8	50
	Sn	4	6	46
	Th	4	12	43
	Pb	4	6	39
	Mg	2	6	37
	Li	1	4	36
	Pb	2	4	36
	Zn	2	4	36
	Ba	2	8	33
	Ca	2	8	32
	Sr	2	8	32
	Cd	2	4	30
	Na	1	6	20
	Cd	2	6	20
	K	1	9	13
	Rb	1	10	12
	Cs	1	12	10

1973; Heimerl et al. 1971; Grover and Chidley 1960), it is basically an empirical process because of the nonstoichiometric character of glass. It is even possible to make glasses that are deficient in glass formers.

4.6.1.4 Types of Radioactive Waste Glass

Waste glasses are most conveniently categorized according to the preponderant glass-forming oxide used in the formulation. Silica is the most commonly used glass-former in industry and also in waste glasses. Table 4.6.2 lists typical compositional ranges for components in most waste glass types considered most for use.

Throughout the world, most of the radioactive waste glasses that are developed to the point of process application are borosilicate formulations (IAEA 1976, IAEA 1977), which have been the bases for the SC/ICM process development. Borosilicate glass has long been used industrially and commercially. Pyrex (82% SiO_2 , 12% B_2O_3 , 4% Na_2O) is a borosilicate glass, although,

TABLE 4.6.2. Typical Waste Glass Compositions

Oxide	Glass Composition, wt%			
	Borosilicate	Silicate	Alumina-Ceramic	Glass-Phosphate
SiO_2	25-50	33-40	32-60	0-6
B_2O_3	9-22		1-11	
P_2O_5	0-2			30-55
Alkali metal oxides	8-19	18-22	0-13	5-25
Alkaline earth oxides	0-6	13-16	2-33	
Fe_2O_3 , Cr_2O_3 , NiO	1-20			0-30
Al_2O_3	0-10	26-30	10-24	0-35
TiO_2	0-3		0-3	
ZnO	0-22		0-13	
CuO	0-3			
PbO	0-50			0-30
Gd_2O_3	0-12			
Fission products	30	~5	~20	~30
Actinides	10	1	7	10

as can be seen by comparison with Table 4.6.2, it has quite a different composition from typical borosilicate waste glasses. Boron serves two major and desirable purposes in borosilicate waste glasses: 1) it lowers viscosity and, hence, the processing temperature; and 2) it increases the solubility of many waste constituents in silica-based glass. For these reasons most waste glasses, as shown in Table 4.6.2, contain from 5 to 15 wt% B_2O_3 .

There are few potential problems in using boron in waste glass and they are relatively insignificant. In some processes, it is desirable to mix the glass-making additives with the liquid waste before vitrification. When this is done, a flocculent precipitate of boric acid may evolve that is highly volatile at glass-melter operating temperatures. Care must be taken to assure that boron is homogeneously distributed in the feed to the vitrification process and added in a form that will not increase its volatilization. Liquid-liquid phase separation occurs in borosilicate glasses of certain compositions. This phase separation can affect waste glass properties; for example, waste glass leachability will be increased if the separation is significant. Generalized waste glass compositions investigated for HLLW immobilization are shown in Figure 4.6.4.

4.6.2 EFFECTS OF PROCESSING CONDITIONS

Even though chemical composition is the factor most controlling glass properties, the properties will also be affected significantly by processing parameters. Therefore, any consideration of glass properties must include information on how the glass was made or processed. Significant process parameters include:

- degree of mixing of constituents before melting
- processing temperature
- degree of melt agitation
- time at processing temperature
- materials of construction for melt containment

FIGURE 4.6.4. Ternary Diagram of Waste Glass Composition Region (mol%)

- rate of cooling from processing temperature to storage temperature
- reduction-oxidation conditions.

4.6.2.1 Elements of the Waste-Glass Process

The process brings the calcined HLLW and glass-making additives together with heat to form molten glass in the canister.

4.6.2.2 Feed Preparation (Premixing and Calcination)

In the SC/ICM process the HLLW is converted to an oxide powder in the calciner, after which it is combined with dry glass-making additives in the calciner bottom and fed to the melter as a dry mixture. Experience shows that intimate mixing of the calcine and glass-formers is not necessary in the process to achieve high-quality glass, but reasonable mixing is needed or a non-homogeneous glass will be formed. The degree of required mixing intimacy has not been defined and would vary with process conditions and the glass formulation.

4.6.2.3 Melting

Melting is the crucial processing step. Several factors must be considered in selecting the melting conditions to use in waste glass processing.

Processing Temperature and Melter Residence Time

The liquidus temperature is defined as the maximum temperature at which equilibrium exists between the molten glass and its primary crystalline phase, i.e., at temperatures above the liquidus temperature the primary crystalline phase is completely soluble in the melt. Waste glasses are usually raised to a temperature of 100°C or more above the liquidus temperature. In a composition as complex as that of waste glasses there may be minor crystalline phases whose liquidus temperatures are not exceeded at the operating temperature. Examples of crystalline phases that may exist in minor concentrations (total less than 5 vol%) at the melting temperature are RuO_2 (or ruthenium metal), palladium metal, spinel and CeO_2 . These are all inert crystalline phases and do not affect the quality of the solidified waste glass. Raising the

operating temperature as much as 300° to 400°C does not dissolve any of these phases except CeO_2 , which is usually completely dissolved in waste glasses melted above 1200°C , and spinel, which dissolves above 1100°C to its solubility limit.

Waste vitrification processes emphasize low melting temperatures to increase operating reliability. By melting in the range of 950° to 1150°C , corrosion is reduced and volatilization from the molten glass is decreased.

Waste glasses, because of their relatively low ratio of network formers to intermediates and modifiers, have relatively low viscosities (5 to 200 poise) at the operating temperature. The low viscosity assists in establishing equilibrium conditions quickly. Experience has shown that a residence time of 2 to 4 h at the operating temperature is sufficient to produce good-quality waste glass.

Volatility During Melting

Although volatility is minimized by the low melting temperatures used in waste vitrification, some waste constituents do have a significant vapor pressure in the melter. This means that some constituents of HLLW will not be incorporated in the waste glass but will go with the off gas. In particular, volatiles that could later cause pressurization of the canisters containing the product glass are removed. The product glass contains less than 0.001 wt% nitrate and less than 0.2 wt% H_2O .

Another significant constituent that is volatilized is the long-lived fission product ^{129}I . It will all be volatilized during vitrification. The volatilized ^{129}I will be scrubbed from the off gas and disposed of separately. Most chloride present in the HLLW will also volatilize during vitrification. Fluoride exhibits a lower volatility and can be incorporated in waste glass; a small fraction may volatilize, but it can be recycled.

Radioactive waste constituents that are partially volatile can also be recycled back to the glass process to achieve almost total incorporation in the glass. Recycling is usually done by returning a concentrated off-gas

condensate stream to the HLLW. HLLW constituents having radioactive isotopes and which exhibit a minor volatility that will be recycled include cesium, ruthenium, technetium, antimony, and tellurium. Solid adsorbents have also been used to collect volatile ruthenium, which can be recycled directly to the melter (Elliot et al. 1963).

Corrosion During Melting

Waste glass is melted in the canister, which forms the crucible for the melting process. The corrosion rate of metallic melters, other than platinum melters, may, however, result in minor and apparently inconsequential effects in the solidified glass. Continuous metallic melters are designed to have lifetimes of 3 to 6 months, and typically are made of high-nickel alloys such as Inconel[®]-601 or Inconel-690. The corrosion-product concentration in the melt is inconsequential because of the very low corrosion rate of the special alloys. Batch metallic melters, however, such as those used in the ICM process are typically made of stainless steel. Spalling of oxide from the stainless steel surfaces above the melt was observed when the process was shut down during an ICM fill and then the canister was heated up again to complete the fill. The spall collects as inclusions in the glass towards the bottom of the melter, but does not affect the durability of the glass (Mendel et al. 1977). Canister corrosion rates beneath the melt surface are less than 0.01 mm/h.

Corrosion creates a reducing potential at the stainless steel/melt interface, which on a microscale has been observed to change glass properties. For instance, CeO_2 , which is partially insoluble at the melting temperature, is not observed near the stainless steel surface because the cerium is reduced to Ce^{+3} , which is more soluble in the glass (Turcotte and Wald 1978).

Oxidation-Reduction During Melting

The example cited above is one effect that changing the oxygen potential in waste glass can have. Normally waste glass is in a highly oxidized state

[®] Inconel is a registered trademark of the International Nickel Co., Huntington Alloys, Inc., Huntington, West Virginia.

because of the nitrate in HLLW. In some situations it may be desirable to reduce the oxidation potential in waste glass. For instance, at high fission-product loading, liquid-liquid phase separation of a mixed alkali-alkaline earth-molybdate salt can occur in borosilicate waste glasses. Reducing the molybdenum to a tetravalent or lower state, or to the metal, prevents phase separation of the water-soluble molybdate salt. It has been demonstrated that silicon metal added to the melt batch can affect the desired reduction of molybdenum (Ross 1978b). Some other constituents of the waste glass melt may also be reduced to the metal when silicon is added. The reduced metal then appears as globules, usually less than 2 mm in dia, suspended in the solidified glass. The metal globules are alloys, often rich in tellurium, which do not affect the overall properties of the waste glass (Ross 1978b). It has also been observed that maintaining reducing conditions in the melter by procedures such as adding Si metal organic additives or coal reduces the foaming tendencies of HLLW that is inclined to foam during glass-forming.

Glass properties can be significantly affected by canister heat treatment and handling; they are discussed below and in Section 4.5.3.2.

4.6.3 PROPERTIES OF RADIOACTIVE WASTE IN CANISTERS

The properties of canisterized glass are examined in this section. The probable behavior of the canisters and the glass in the subsequent situations to which they may be exposed are not within the scope of this document and are discussed elsewhere (Mendel 1978).

Waste glass, although it resembles commercial glass and enamels, is a relatively new material. Therefore, an emphasis has been placed on a detailed characterization of waste glass properties. Detailed characterization has been done on laboratory-prepared specimens. Many tests have been performed on waste glass prepared in engineering-scale equipment--both nonradioactive and radioactive--as shown in Figure 4.6.5 which corroborate the laboratory-scale results.

Core Drilling to Obtain Waste Glass Samples for Characterization From Canisters Produced in Nonradioactive Pilot Plant

View Through Lead-Glass Window of 8-Year-Old Canister of Borosilicate Waste Glass Which Contained 1,400,000 Ci When Prepared. (Note Plugged Core-Drill Holes From Which Samples of Radioactive Glass Were Removed for Characterization.)

FIGURE 4.6.5. Waste Glass Canisters Prepared in Nonradioactive and Radioactive Pilot Plants at PNL

4.6.3.1 Physical and Mechanical Properties of Waste Glass

The physical and mechanical properties of radioactive waste glass are innate properties which may be treated generically. They are relatively independent of composition and are of much the same magnitude for most waste glasses.

Viscosity and Softening Point

Most waste glasses are generally formulated to have a viscosity of 5 to 200 poise at the processing (melting) temperature, which is usually within the range of 950° to 1150°C . The viscosity of waste glasses is contrasted with that of commercial glasses in Figure 4.6.6.

Some important properties of waste glass can be related to viscosity. The softening temperature (Littleton softening temperature) of glasses is defined as the temperature at which the viscosity is $10^{7.6}$ poise. Above this softening temperature, the glass cannot support its own weight and begins to slump. Cracks in the glass will heal rapidly at the softening temperature, which is about 575° to 650°C for most waste glasses. The glass transition temperature is the temperature at which the viscosity is about 10^{13} poise. For waste glasses this transition temperature is usually in the range of 500° to

FIGURE 4.6.6. Viscosity of Typical Waste Glass

550°C. As described earlier, glass is plastic above the glass transition temperature and thus is not susceptible to fracture.

Density

The density of glass is an additive function of the constituents (Elliot 1945). Within limits, the density of a glass can be predicted from empirically derived density factors for each constituent. The density factors are related to atomic weight. Thus, waste glasses containing high loadings of fission products, which have higher atomic weights than most usual glass constituents, will be more dense than those with low loadings of fission products. Certain special glass constituents, such as zinc or lead, also markedly increase density.

Common commercial soda-lime-silica glass has a density of about 2.5 g/cc. Depending on waste composition and waste loading, radioactive waste glass densities are usually in the range of 2.5 to 3.3 g/cc. Zinc-borosilicate waste glasses may have a density of 3.7 g/cc or higher and the density of a lead-borosilicate waste glass may exceed 4.8 g/cc. Radiation over long periods of time can cause changes in waste glass density; maximum change equals approximately 1%.

For a given glass composition, the density of the final product may vary over 0.1 g/cc depending on the time-temperature curve of its cooling through the transformation range (Figure 4.6.3). Thus, bulk density cannot serve as a precise quality control check on glass composition. It can, however, be a convenient quality control check for gross porosity or voids in the canister.

Friability

Friability refers to the fracture behavior of waste glass. Fractures increase the surface area, and the amount of activity released in a leaching situation is proportional to the exposed surface area. Also, the fractures may produce a small fraction of less than 10- μ m-dia particles, which are respirable. Friability becomes a factor in safety analyses only when the canister is breached. Canister-breaching requires either very high-energy

accidental impacts, which are improbable, or corrosion through the canister wall, which should not occur until well after the waste glass is in a geological repository.

Friability of waste glass is usually measured by impact tests of various kinds, in which either weights are dropped on a glass specimen, or the glass specimen itself is dropped onto an unyielding surface. Some of the PNL impact tests on waste glass have been described by Smith and Ross (1975). In these tests, the glass was cast in stainless steel canisters either 2 in. in dia by 4 in. long or 6.6 in. in dia by 52 in. long. The large canisters were dropped onto a concrete pad from heights of up to 30 ft (maximum impact velocity equalled 44 ft/s). The smaller canisters were released in the path of a 75-lb granite block mounted on a rotating arm. Impact velocities up to 117 ft/s (80 mph) were achieved in this apparatus. None of the large canisters failed in the impact tests; some of the small canisters had small cracks after impacts at 76 and 117 ft/s, but weight loss measurements showed that no glass escaped through the cracks. After the tests each of the canisters was opened and the particle size of the contained glass was determined. Figure 4.6.7 shows the amount of sub-10- μ m particles formed as a function of impact velocity. It should be noted that both vitreous and devitrified specimens of the same glass composition were included in these tests and no difference in fracture behavior was observed. Therefore, the curve shown in Figure 4.6.7 is based on data from both vitreous and devitrified glass.

Friability is also a function of internal stresses. These are difficult to define but include residual thermally induced stresses and, over the long term, radiation-induced stresses. Radiation can cause slow changes in density. In devitrified glass or crystalline materials, particularly, differing radiation-induced density changes in adjoining phases could lead to localized stresses.

Friability is relatively independent of glass composition. Impact tests comparing waste glasses and commercial soda-lime-silica glasses yielded similar results (Bunnell 1977).

FIGURE 4.6.7. Effect of Impact Velocity on Fraction of Respirable Particles Formed

Thermal Conductivity

Thermal conductivity is another physical property of waste glass that is relatively independent of glass composition. The thermal conductivity of most waste glasses falls within the limits shown in Figure 4.6.8. The thermal conductivity increases gradually with temperature until the softening point of the glasses is reached. Above the softening point, the increase in the thermal conductivity as a function of temperature is more rapid.

The importance of thermal conductivity is that it determines the temperature profile between the glass at the center of the canister and the glass at the canister wall. Higher thermal conductivities give less steep temperature profiles.

Thermal-Expansion Coefficient

The thermal-expansion coefficient of waste glasses is similar to that of commercial soda-lime-silica glasses. Representative thermal-expansion

FIGURE 4.6.8. Thermal Conductivity of Waste Glasses

coefficients of waste glass are shown in Table 4.6.3. The thermal-expansion coefficients are relatively independent of composition. Sodium probably has the greatest effect on thermal expansion of any of the waste constituents. Decreasing sodium content usually decreases the thermal-expansion coefficient. (Commercial low-expansion glasses, such as Pyrex, have very low sodium contents.)

A low thermal-expansion coefficient gives increased thermal shock resistance and decreases the time required to anneal a block of glass, and thus would appear to be a desirable characteristic. On the other hand, a low thermal-expansion coefficient will further increase the mismatch in thermal-expansion coefficient between the waste glass and its canister, and thus will increase the stress in the canister wall. The thermal-expansion coefficients of waste glass, as shown in Table 4.6.3, represent a good compromise between the opposing requirements. In any event, effecting significant changes in the thermal-expansion coefficient would probably be very difficult. Sodium, for instance, is almost always present in waste glasses in relatively high concentrations, either because it is an unavoidable constituent of the waste or because it is needed for viscosity control.

TABLE 4.6.3. Typical Thermal Expansion Coefficients of Waste Glass(a)

Waste Glass Type	Thermal Expansion Coefficient (25-400°C), $10^{-7}/^{\circ}\text{C}$
Borosilicate	80-100 ^(b)
Glass-ceramic	100-120 ^(c)
Phosphate	90-110 ^(d)

(a) For comparison, the values for soda-lime-silica bottle glass and Pyrex are 90×10^{-7} and 30×10^{-7} , respectively.

(b) (Ross 1978a)

(c) (De et al. 1976)

(d) (Thompson, Mendel and Kleinpetz 1970)

4.6.3.2 Thermal Effects and Devitrification

The facilities for waste vitrification and handling of the canisters of waste glass are designed to avoid deleterious temperatures. Thus, design limits based on known glass and canister properties are placed on the maximum temperatures allowed during waste glass manufacture and storage. For accident analyses, it is necessary to know what will occur when the design temperatures are exceeded.

Volatility

After manufacture, volatility from waste glass is a factor only in accident analyses. Waste glass manufacturing temperatures are several hundred degrees above the maximum design storage temperatures, which assures that any volatiles that might pressurize the canisters during storage have been removed. However, accidents involving external heat sources or clusters of uncooled waste canisters can be postulated in which the temperature rises far above normal storage or handling temperatures. Volatility data are available for analysis of these postulated accidents. An example of such data is shown in Figure 4.6.9. The data demonstrate that volatility is very temperature

FIGURE 4.6.9. Volatility of Waste Constituents (Gray 1976)

dependent. Analysis of postulated accident scenarios is continuing, but accidents in which waste glass could be exposed to temperatures as high as those shown in Figure 4.6.9 will be extremely rare.

Volatility experiments with waste glasses show that cesium is the most volatile radioisotope. Although ruthenium often exhibits significant volatility in radioactive processes, its volatility from waste glasses is less than that of cesium.

Devitrification and Phase Separation

Major thermal effects on waste glass are devitrification and phase separation. Both phenomena are very dependent on glass composition, but some effects are common to most compositions.

Devitrification. Devitrification is the formation of crystals caused by the rearrangement of certain atoms in the glassy matrix. Crystals form because their ordered structure has a lower free energy. The ordered structure is more thermodynamically stable than is the random network of the glass. The amount and identity of the crystals formed depends on the initial composition of the glassy matrix. The rate of crystal formation is time- and temperature-dependent. Measurable devitrification of waste glasses generally occurs only from 950° to 500°C . Above 950°C , the crystals redissolve.^(a) Below 500°C , the viscosity of the glassy matrix is so high that crystallization is diffusion-limited to extremely low rates. The maximum rate of formation of most crystalline species occurs somewhere between 800° and 850°C , but the equilibrium yield of crystals is low. At lower temperatures the rate of formation decreases but the equilibrium yield of crystals increases. It is possible to define approximate equilibrium yields at 700°C in experimentally practical times (1 year). At lower temperatures the experiments cannot be completed in practical times. But the temperature effect above 700°C exhibits Arrhenius behavior and can be extrapolated to lower temperatures. Extrapolation shows that the kinetics are extremely slow at geologic storage temperatures. Below approximately 200°C , measurable crystallization (anhydrous) would require millions of years

(a) There are some exceptions to this statement. Fission product ruthenium and palladium are insoluble in waste glass at all temperatures. The fission product oxide CeO_2 does not completely dissolve in waste glass until a temperature of about 1200°C is reached. Spinel, having the general formula A_2BO_4 , where A can be Fe or Cr and B can be Ni, Zn, Fe(II), etc., apparently may even exhibit a retrograde solubility above 950°C in certain waste-glass compositions. Regardless of their high-temperature behavior, the effects of these species are indistinguishable from the other devitrification species at the handling and storage temperatures concerned here.

(Turcotte and Wald 1978). The existence of natural glasses that are millions of years old is an indication that the extrapolation is justified.

It is important to understand what devitrification does to waste glass. Figure 4.6.10 shows photomicrographs of a typical waste glass before and after devitrification. It is only on the microscopic scale that the effects are truly apparent. Even totally devitrified waste glass usually includes only 30 to 40 vol% crystals, as compared to greater than 95 vol% in commercial glass-ceramics. To the naked eye the devitrified waste glass is unchanged, except that its luster is dulled and the color may be altered.

Changes in friability due to devitrification are slight--usually within experimental error. Devitrification should not be equated with disintegration. Properly formulated waste glass retains its coherence and strength when devitrified.

VITREOUS

DEVITRIFIED

FIGURE 4.6.10. Photomicrographs of Vitreous and Devitrified Waste Glass

Devitrification usually increases the overall leach rate of waste glasses. The increase may occur in the residual glass phase (due to depletion of silica) or in one of the crystalline phases that is formed, like strontium molybdate (Malow and Schiewer 1972). The increase in leaching of borosilicate waste glasses after devitrification is usually no more than a factor of 2 to 5, although in some instances an increase up to a factor of 10 has been observed in waste glass after maximum devitrification at 750°C as shown in Figure 4.6.11. Figure 4.6.11 also demonstrates that there can be considerable variation in the leach rate of nondevitrified waste glass.

Because the amount and identity of the crystalline species formed during devitrification are so dependent on composition, a large amount of work has been done to identify the various species that may form in specific waste glasses. A review of that work is beyond the scope of this report; however, some general observations may be made:

FIGURE 4.6.11. Leach Behavior as a Function of Devitrification for Two Representative Borosilicate Waste Glasses

- The species formed on devitrification of borosilicate waste glasses are often crystalline silicates; boron always remains in the glassy matrix. The end result is a boron-rich residual glassy phase, which has a somewhat higher leach rate than does the initial glass due to its higher boron content.
- A larger proportion of the high-valence, high-atomic-weight cationic constituents tend to appear in the crystalline silicate species. Sodium, potassium, and calcium, etc., are relatively absent from the crystalline silicate devitrification species. In general, however, other anions that may be present in the glass, such as molybdate, phosphate, or fluoride, exhibit a strong tendency to form crystalline devitrification species which, in contrast to the silicates, usually preferentially contain alkalis and alkaline earths. The identities of the exact crystalline compounds that will form from a given glass composition cannot yet be predicted with confidence; they must be determined empirically.
- Secondary devitrification reactions have also been observed in which a rapidly formed crystalline species is slowly converted into another crystalline species.
- At optimum devitrification conditions, crystals several hundred micrometers in the longest dimension may be formed. Microcracking in the surrounding glass matrix may occur, due to mismatching thermal-expansion coefficients.

It is apparent that devitrification of waste glasses is a complex phenomenon. Devitrification can be prevented by cooling the glass quickly and subsequently maintaining the glass at temperatures below approximately 500°C. However, the primary concern is: Need devitrification of waste glass be avoided? And the answer seems to be no, based on all available data. The only significant devitrification effect is on leach rate, and the magnitude of this effect can be defined for any given glass with a few simple tests. To date, these tests have always shown no more than a factor of 10 increase in the leach rate of cesium, the radioisotope whose leach rate is most sensitive to devitrification effects. It should be emphasized that if the decision is made to "accept

devitrification," only a limited central region (perhaps 20 vol%) of the waste glass in the canister would be affected. The waste glass at the canister wall would remain vitreous because the maximum allowable wall temperature during handling is significantly below 500°C.

A large amount of work is continuing on the devitrification of waste glass. Two areas in particular are receiving attention. More needs to be learned about the location of the actinides in devitrified waste glass. The effects of the nonuniform radiation pattern caused by the possible concentration of some actinides in certain crystalline species are now being measured. Hydrothermal alteration, as opposed to the thermal devitrification discussed so far, is also being studied. Based on analogies with naturally occurring glasses, the possible increase of crystallization by water at geologic storage temperatures is being examined.

Phase Separation. Phase separation is another time-temperature-dependent phenomenon involving atomic rearrangement. It is a liquid-liquid phase separation. Borosilicate glasses are particularly susceptible to phase separation, forming a boron-rich and a silica-rich phase (Doremus 1973). There is evidence that some borosilicate waste glasses are phase-separated as formed.

Phase separation studies done on waste glasses and sponsored by PNL indicate that borosilicate waste glasses generally phase-separate to some extent, as seen in Figure 4.6.12. It is inferred from laboratory etching studies on the phase-separated glass that the discontinuous phase is silica-rich. It is postulated that substantial phase separation may lead to increased waste glass leachability, but this has not been confirmed in the laboratory. These laboratory studies have also indicated that glass formation under reducing conditions decreases the amount of phase separation.

Molybdenum and sulfate also exhibit phase separation in borosilicate waste glasses. A molybdenum-rich salt phase that also contains sodium, cesium, and strontium separates. As is typical of phase-separation phenomena, the

500 nm

Melting Temperature: 1050°C
Time at Melting Temperature: 3 h
Air-Quenched Glass 76-68

150 nm

Melting Temperature: 1150°C
Time at Melting Temperature: 1 h
Air-Quenched Glass TDS/211

FIGURE 4.6.12. Transmission Electron Micrograph of Phase-Separated Waste Glass

molybdenum-rich phase is completely miscible in waste glasses above about 1150°C. At lower temperatures the phase separation is composition-dependent. If the concentration of molybdenum and sodium is high enough in borosilicate waste glasses, the molybdenum-rich phase will separate out on a macroscale and float to the surface of the molten glass. Reducing conditions can be used to avoid the separation of the molybdenum salt phase.

As in the case of molybdenum, sulfate tends to separate as a sodium salt phase, which may also contain other alkali metals, alkaline earths, and chromates. Immiscibility of Na_2SO_4 becomes apparent when the SO_4 content of borosilicate waste glass exceeds 1.2% (DPST 1976). If the sulfate content is expected to be higher than this, the presence of soluble Na_2SO_4 in the product glass can be prevented by adding reducing agents, such as carbon, to the melt. Sulfate will then be reduced to gaseous SO_2 at glass melt temperatures. Lead-borosilicate glass compositions have also been described for the immobilization of sulfate-containing radioactive waste (Shukla, Vaswani and Sunder Rajan 1977).

4.6.3.3 Leaching

The known chemical durability of the ancient man-made glasses of the Mesopotamians, Egyptians, Greeks, and Romans for 2000 to 4000 years, even during immersion in seawater for over 2000 years in the case of Greek and Roman glasses, was one of the original incentives for developing waste glasses. Following this lead, measurements of leach rate have been key factors in the selection of waste-glass compositions.

Table 4.6.4 shows the factors that can significantly affect the value obtained in a given leach rate. Some of these factors are intrinsic, related only to the waste glass itself and its condition. Others are extrinsic; they are external factors that can vary independently of the waste glass. The factors in Table 4.6.5 are interrelated. Understanding the leaching of waste glass rests on knowing the type of influence each factor has in relation to the others.

Mechanisms

Many commercial glass and PNL waste glass studies have advanced the understanding of chemical durability (resistance to leaching). However, the basic mechanisms of glass-leaching are not well known. Also a quantitative understanding of the various factors as applied to specific situations is still lacking in many cases.

A primary leaching mechanism is a diffusion-controlled ion exchange in which hydrogen or hydronium ions exchange for cations in the glass lattice. The overall result of this reaction is a depletion of cations from the glass

TABLE 4.6.4. Factors Affecting Leach Rate Measurements

<u>Intrinsic</u>	<u>Extrinsic</u>
Glass composition	Temperature
Thermal history	Pressure
Radiation effects	Composition of leachant (including pH and Eh)
Physical form	
Surface character	Flow rate of leachant

TABLE 4.6.5. Compositions of Glasses in Figure 4.6.13

Oxide Constituent	Glass Designation and Mol% Composition									
	1	2	3	4	5	6	7	8	9	10
SiO ₂	73.0	68.2	43.5	55.0	44.7	42.9	71.3	77.8	56.5	54.4
B ₂ O ₃	7.7	---	11.8	6.0	11.4	12.4	---	---	12.0	6.3
Al ₂ O ₃	5.7	10.6	14.5	14.6	14.8	14.4	---	---	---	---
TiO ₂	0.4	0.6	5.1	3.0	---	---	---	0.4	7.0	7.1
Cr ₂ O ₃	---	---	3.1	---	2.7	---	---	---	3.1	3.0
Fe ₂ O ₃	0.1	0.1	---	---	2.5	---	---	---	---	---
NiO	---	---	2.7	2.7	---	---	---	---	---	---
ZnO	---	---	6.0	---	---	6.0	---	3.2	6.1	---
MgO	---	5.4	3.1	7.5	7.7	---	5.6	---	---	---
CaO	3.0	0.6	---	---	1.2	13.8	8.8	7.8	---	13.8
BaO	---	---	---	---	---	---	---	0.9	---	---
Na ₂ O	10.1	14.5	10.2	11.1	15.0	10.5	14.3	9.9	15.3	15.4

surface leaving a hydrous silica layer, which also contains some slow-diffusing multivalent cations. As this silica-rich surface film develops, it may function as an increasingly protective barrier that progressively slows down the rate of leaching. The rate of leaching can be slowed until another mechanism assumes the rate-controlling function.

Another mechanism is surface chemical reaction. In this surface reaction the silica-rich film may be attacked by hydroxyl ions from solution or water which breaks up the glass-forming silica matrix. This reaction layer sloughs off in some cases, exposing additional glass surface for reaction. The ion-exchanged silica-rich layer and reacted surface layer can provide a protective layer to inhibit further glass leaching. At temperatures above about 80°C, surface reaction is the controlling mechanism in some glasses (Zager and Schillmoeller 1960).

Static leach tests (Figure 4.6.13) of waste glasses (Table 4.6.5) in deionized water at PNL, indicate that the leach solution may become basic or acidic. This basic solution results from the dominance of the ion-exchange

FIGURE 4.6.13. Silicon Released Versus Resulting pH of Solution

mechanism ($H^+ \rightleftharpoons Na^+$ exchange) over the OH^- or water attack. The dominance OH^- attack results in the leach solution becoming acidic in pH. The more durable waste glasses developed appear to be attacked primarily by the OH^- mechanism. High amounts of Al_2O_3 and low CaO increase glass durability; it is speculated that the Al combines with the OH^- to form a protective oxide layer which hinders ion exchange.

The following expression is often used to express the leach rate of silicate glasses (Paul 1977):

$$Q = at^{1/2} + bt, \quad (4.29)$$

where

Q = the quantity of a specific cation that has been removed from the glass

t = the time glass has been in contact with leachant

a, b = constants.

The first term represents the contribution due to diffusion and the second term--that due to surface corrosion.

The foregoing explanation of the mechanisms involved in leaching is based mainly on studies of simple alkali silicate glasses that have leach rates which are high enough to be measured conveniently. Commercial glasses contain constituents added specifically to increase leach resistance, such as alkaline earth and aluminum oxides. Overall, the results indicate that the basic mechanisms inferred from the simple glasses are useful guidelines for interpretation of the data--especially for extrapolation to longer-time behavior--but other factors are also involved. A principal factor is composition of the leachant. In actual leaching situations the water in contact with waste glass will be impure because: 1) natural waters contain dissolved ions, and 2) unless the water is moving very rapidly, dissolved ions from the glass will concentrate at the surface. These ions can participate in complex back reactions which usually, but not always, slow the leach rate of the glass (Adams and Lunney 1970).

The ultimate conclusion is: In order to evaluate a glass for a specific use, the test program should duplicate as closely as possible the conditions of that use (Bacon 1968). This is even more true for radioactive waste glasses than for commercial glasses, because of the complexity of the waste-glass compositions and their applications.

Figure 4.6.14 shows the typical range of leach rates obtained for waste glasses when leached according to the IAEA proposed standard leach test (or procedures that have basic resemblances to the IAEA test). An indication is also given of the usually observed relationships in the leach behavior of important radioisotopes. Leach rate is quite dependent on glass composition, but the leach behavior of most waste glasses lies somewhere within the range shown in Figure 4.6.14. As Figure 4.6.15 shows, the same leach data can be plotted as cumulative penetration, which is sometimes thought to give a more graphic interpretation of what the leach rates mean.

FIGURE 4.6.14. Typical Waste Glass Leach Rates

Effect of Flow Rate and Potential For Back Reactions

Various situations can be hypothesized in which waste glass could come in contact with water. The flow rate of water past the waste glass can vary widely in the hypothesized situations, ranging from the rate of a river running past particles of waste glass to zero flow rate in a repository containing water that never moves. The short-term effect of flow rate is that the leach rate decreases as the flow rate decreases. This is because of "back reactions," including formation of a saturated hydrous film on the surface and even the possible formation of precipitates that protect the surface from further reaction. Such short-term effects are well known in waste-glass leaching. Figure 4.6.16 shows an example of this effect.

At slower flow rates the pH of the solution in contact with the glass surface was observed to rise because hydrogen ions were used up in the leaching reaction. The rate of attack on glass increased significantly when the pH increased above 8.5 to 9.0 (Adams 1972). An equilibrium pH is observed in commercial glass bottles holding static water that may be as high as 9.5

FIGURE 4.6.15. Typical Waste Glass Leach Rate Data Expressed as Cumulative Penetration

(Budd 1961). Similar equilibrium pHs are observed with some waste glasses. Waste glass is being further tested, but present indications are that even though the pH may be quite high, steady-state stagnant systems exhibit very low leach rates.

Effect of Temperature and Pressure

The effect of temperature on leach rate must be considered because the waste glasses may be self-heating to various degrees. The leach rates of

FIGURE 4.6.16. Effect of Leachant Flow on Leach Rate

commercial glasses increase with temperature, usually by a factor of 10 to 100 for each 100°C increase in temperature (Adams and Lunney 1970). Similar increases are observed for waste glasses--i.e., about a factor of 10 for each 100°C increase in temperature (Mendel, McElroy and Platt 1976). However, subsequent studies have shown that this leachability dependence on temperature may increase or decrease, depending on the temperature range and experimental conditions.

In autoclave tests, reactions that can be characterized as hydrothermal alteration have been observed with waste glasses above about 150°C. In these reactions, crystalline species are formed at the surface of the glass. The reactions are probably a combination of atomic rearrangement in the leached portions of the glass matrix and deposition of precipitates formed from leached ions. Potential for the amount and number of latter reactions is greatly increased when the waste glass is in contact with a geologic medium.

Hydrothermal experiments involving waste glass and candidate geologic hosts--in particular, salt--have been under way at PNL for about 2 years.

Most of these tests have been conducted at 250⁰ to 350⁰C to obtain steady-state conditions rapidly (one to three weeks) at the extreme high end of the potential temperature range. As stated above, the design temperatures for the repository have not been fixed; data obtained in the hydrothermal experiments, and at lower temperatures, will serve as one input factor to the decision on what the design temperature should be. A recent topical report by Westsik and Turcotte (1978) describes the initial PNL hydrothermal tests. Data in the report demonstrate the following:

- The reaction rate of waste glass and aqueous solutions is a strong function of temperature. This is shown in Figure 4.6.17.
- Other "stable" materials, including candidate geologic media, react at rates similar to waste glass in the hydrothermal tests, as Figure 4.6.18 illustrates.
- The reaction mechanisms predominant in salt brine are different from those which predominate in pure water.

Figure 4.6.19 shows that reaction with the glass is slower in salt brine than in water, perhaps because of decreased H⁺ activity in salt brine. However, the ions that are released from the glass tend to stay in solution in salt brine because of chloride complexing, whereas in pure water they tend to recombine to form new crystalline compounds. Identification of the new crystalline compounds is just beginning.

The preliminary conclusion is that until the hydrothermal reactions are understood in more detail, they should be minimized, since both the geologic host rocks and the waste glass can be significantly altered.^(a) The reactions can be minimized if only small amounts of water are present while the repository is hot, or if the repository temperature never exceeds a certain

(a) The discussion has disregarded the presence of the canister. This is a conservatism, since it is probable that canisters of present design will provide a significant barrier. (See comparative corrosion rates in Figure 4.6.18). If the canisters were designed especially for this service, different materials of construction would probably be used, such as titanium.

FIGURE 4.6.17. Effect of Temperature on HLLW Glass Leach Rates in Salt Brine and Deionized Water

predetermined limit, or if a multiple-barrier system is used which prevents water from contacting the waste for several hundred years.

Effect of Leaching Media

Leaching media that need to be considered in evaluating the leach resistance of waste glass fall into three major classifications, as shown in Table 4.6.6.

Even though the variations possible in classifications 2 and 3 are very large, prohibiting experimental testing of all the possibilities, it is important to note that in the tests performed to date with various waste glasses, the leach rates measured in deionized water have always been equal to or

FIGURE 4.6.18. Comparative Leach Rates of Several Materials in Salt Brine at 250°C

higher than those measured in classification 2 or 3 media.^(a) This is apparently due to back reactions. It may be concluded that the leach rates measured with the Soxhlet test and the proposed IAEA standard test, using deionized water, yield conservative results. They represent probable maximum leach rates. This conclusion is borne out by the results of Canadian tests (Merritt 1977), which are the only experience to date with the in situ contact of waste glass with natural water.

In the Canadian tests, waste glass was buried approximately 10 to 12 ft underground in a swampy portion of the Chalk River nuclear reservation in 1960. The flow rate of groundwater past the buried waste glass waste was measured to be 200 ft/yr by a tritium inoculation technique. The groundwater downstream of the waste glass has been monitored for ⁹⁰Sr since the burial.

(a) An exception may be very low-pH natural waters, known to occur, but which have not yet been tested as leachants for waste glass.

Salt Brine Sample

Deionized Water Sample

FIGURE 4.6.19. Cross Sections of Waste Glass After Exposure to Salt Brine and Deionized Water for 1 week at 350°C

TABLE 4.6.6. Potential Leaching Media for Waste Glasses

<u>Classification</u>	<u>Potential Method of Encountering Media</u>	<u>Possible Variations in Media</u>
1. Deionized water	Canister leak in water basin	Minor
2. Nonsaline natural water	Canister failure during a transportation accident. Disposal in a nonsalt geologic repository. ^(a)	Large major variables are pH, Eh, carbonate-bicarbonate, sulfate, calcium, and chloride (minor concentrations of chloride are ubiquitous in nature)
3. Saline natural water	Disposal in a salt repository or in seabed ^(a)	Large major variables are pH, Eh, sodium, magnesium, and sulfate

(a) Canister failure by corrosion is assumed to occur within a finite time.

The leach rate calculated from the groundwater samples had decreased to 5×10^{-11} g glass/cm²-d by 1968 and has remained at that low rate. This leach rate is a factor of 10^3 to 10^6 lower than that measured on waste glasses in dynamic laboratory leach tests, such as the proposed IAEA standard test. In fact, the initial leach rate of the Canadian glass, as measured in the laboratory, was approximately 1×10^{-5} g glass/cm²-d (Merritt 1977). It appears that in the actual geologic exposure system, a relatively stagnant layer of naturally occurring and leached ions exists around the glass blocks, which is inhibiting further leaching to a very low rate.

Effect of pH

Most natural waters have a pH value of between 4 and 9. The pH of the solution in contact with waste glass is frequently increased by the leaching reaction to approximately pH 9, the highest pH extreme observed in nature. Therefore, high-pH natural waters are not a concern, since they do not appreciably change the conditions that would normally arise at the surface of waste glass being leached. In extreme cases, acidic natural waters can potentially have a significant effect. At pH 4, the leach rate of most waste glasses is

increased only slightly over that at pH 7, but at pH 3 the increases can be a factor of 2 to 10, or even more, depending on the glass formulation (Ross 1978b).

Effect of Salt Brine

Deep salt deposits which underlie extensive areas in many parts of the world are leading candidates for the location of final disposal sites for nuclear waste. They are obviously free of moving water--otherwise the salt would have migrated away as saline water long ago. Salt deposits do contain small amounts of stagnant waters as saturated salt brine. The total water content is usually less than 0.5% by weight. Most of the brine is in small "bubbles" occluded in the salt crystals. The brine bubbles will migrate toward heat sources because the crystalline salt is more soluble on the warm side of the bubble than on the colder side. Thus, canisters of waste buried in salt formations may partially, at least, contact brine solution. It has been estimated that a maximum of 30 L of brine could migrate to any given canister (Jenks 1972). (Significant amounts of this brine may evaporate when the repository is ventilated during filling.)

More tests are being made, but the tests made thus far indicate that the leach rate of waste glass at 25°C in salt brine, or in more dilute salt water, such as seawater, is up to a factor of 10 less than the leach rate of the same glass in deionized water. Leach rates at elevated temperatures may be more pertinent, since some exposure of the waste glass to salt brine is expected to occur while the repository is still at an elevated temperature. This is because rapid SCC that will fully penetrate the walls of the canisters is expected to occur only a few months after waste burial if appropriate engineered barriers are not employed. Autoclave experiments are being carried out at elevated temperatures to evaluate the behavior in these circumstances (Westsik and Turcotte 1978).

Effect of Nonsaline Geologic Waters

Other potential geologies being considered for disposal of nuclear waste include granite, basalt, and shale formations. These differ from salt

formations because the chemical and physical makeup of the geology is more complex and larger amounts of water can conceptually be present. Examination of the potential interactions between waste glass and these geologies is less advanced than it is with salt; only limited data has been reported (McCarthy 1978). However, based on available data, it is expected the leach rates of waste glass in these natural waters will be lower than the leach rate of the same waste glass in deionized water. Thus, the results obtained with deionized water yield conservative results when applied to the analysis of nonsaline geologic repositories. Hydrothermal reactions between waste glass and nonsaline repository materials are also being studied (McCarthy 1978).

Extrapolation of Leach Data--Fitting to Models

It is not practical to run leach tests for longer than a few months, or perhaps a few years (tests for process control purposes should not take more than a few days), yet leaching behavior over much longer periods should be understood. The periods of concern correspond to the lifetimes of the radioisotopes in the waste. Therefore, mathematical models based on postulated mechanisms and observed behavior, are being developed to extrapolate expected leach behavior to times beyond which it can be experimentally verified.

Factors that should be treated in leaching models are represented graphically in Figure 4.6.20. The location and shape of line AB is determined by the leaching mechanism, and represents leaching from a semi-infinite medium. The location and shape of line AB is very dependent on temperature and leaching media. It is important to realize that even though line AB cannot be totally verified, it is possible to verify the portion AA' within experimentally practical times, and thus establish the major behavior pattern with good confidence. Line AC represents leaching from a finite medium. Models should be able to predict releases from different sizes (and configurations) of initial waste forms. In addition, models should factor in radioactive decay, as represented by line AD. A final refinement would factor in the effect of leachant velocity. Leaching is suppressed by a low leachant flow. The low-flow situation, probably most representative of a geologic repository, would be represented by line AE.

FIGURE 4.6.20. Considerations in Modeling Long-Term Leaching

Several models have been proposed for extrapolating the leach behavior of solidified radioactive waste forms, including glass. Most include the effects of radioactive decay and specimen size. None include the refinement of factoring in the effect of flow rate. This may be very difficult. Efforts to do it for minerals being leached by groundwater have not been successful (Paces 1973).

A review of the various proposed leaching models is beyond the scope of this report. The interested reader is directed to the following list of references:

- Griffing 1974
- Cohen et al. 1977
- Moore, Godbee and Kibbey 1977

Godbee and Joy 1974

Logan and Berbane 1977

Kottwitz 1974

Anders, Bartel and Altschuler 1978

Ewest and Levi 1976.

4.6.3.4 Radiation Effects

Perhaps the most unique feature of waste glass is the high levels of contained radioactivity potentially possible. Depending on the type and amount of radioactivity incorporated in waste glass, the total beta-gamma dose to the glass may reach 10^{12} rads in the first 1000 years; the alpha events due to decay of the contained actinides, many of which have long half-lives, may exceed $10^{19}/\text{cm}^3$ of glass in 250,000 years.

Will self-radiation for thousands of years change the properties of waste glass in any way, making the assumptions concerning the glass used in various long-term behavior analyses invalid? It must be proven that, once the thermal and hydrothermal devitrification effects are defined, the glass will no longer change, and that long-term radiation effects can be discounted. With some reservations, described in the following sections, all evidence indicates that it is indeed legitimate to discount radiation effects. The evidence shows waste glass to be very radiation-resistant material.

Radiation can potentially cause:

- stored energy buildup
- bulk or localized density changes
- changes in rates of devitrification
- amorphization of crystalline species (metamictization)
- changes in mechanical strength
- changes in leach rate
- helium buildup (from alpha decay).

The effects can be due to the energetics of the decay event itself or, in some cases, to the fact that the alpha and beta decays transmute one element into another that may have a different valence, ionic radius, and chemical behavior.

Although the list of possible radiation effects is long, the tests performed to date have revealed no effects that would jeopardize the use of glass for the long-term immobilization of up to at least 1×10^5 Ci of fission products per liter of glass and 1×10^3 Ci of actinides per liter of glass.

Most radiation effects are temperature sensitive; most of the effects diminish as temperature increases. This means that there is an inverse time relationship between the thermal effects and the radiation effects. Whereas the potential for thermal effects is only in the early life of the waste glass, the potential for radiation effects reaches a maximum in the later life of the waste glass, when it is completely cool.

Comparison of Types of Radiation and Experimental Techniques

Waste glass will be subjected to a mixture of gamma, beta, neutron, and alpha radiation. Except for the associated heat generation, the effects of gamma and beta radiation on waste glass are minimal. This is according to theory and was demonstrated in the WSEP Program. The WSEP waste glasses received doses up to 5×10^{11} R with little effect. The contained isotope responsible for the major portion of the doses received by the WSEP waste glasses was $^{144}\text{Ce-Pr}$, a combined beta-gamma emitter. Neutrons also contribute little to the potential radiation damage mechanisms for waste glass, because the neutron flux associated with α -n reactions and spontaneous fission is comparatively low (Newman 1973). The alpha particles from decay of the actinides, and particularly the recoil particles associated with alpha decay, have the major potential for creating radiation effects in waste glass (Jenks and Bopp 1973). Therefore, it is the effects of actinides in waste glass that are receiving emphasis in studies being conducted at several sites in the U.S. and elsewhere.

The actinide content of waste glass is made up of a mixture of uranium, neptunium, plutonium, americium, and curium isotopes, plus their decay products. The relative amounts of the actinides in a waste glass depends on the source of the radioactive waste incorporated in the waste glass. In all

cases, however, the actinide alpha-decay effects will continue for long times. Table 4.6.7 lists the alpha-decays during the first million years for one representative waste glass.

It is apparent that the effects of the actinides cannot be studied when glasses are simply prepared with representative actinide concentrations. The doses achieved in practical experimental times would be relatively insignificant in terms of the overall dose, so techniques to accelerate the effects must be used.

Two basic accelerating techniques are available: external bombardment and internal bombardment. External bombardment with protons, alpha particles, or heavier particles can yield a very high dose rapidly, but since the effects are concentrated in a surface layer less than 100 μm deep, they are difficult to interpret. Fast neutron bombardment can give "knock on" particles with effects somewhat analogous to alpha-recoil particles, but quantification of the effects is difficult because of the assumptions that must be made. Slow neutron bombardment can be used to give high-energy fission fragments internally, but again somewhat tenuous assumptions have to be made to interpret the results. The conclusion is that the most realistic simulation of the actual situation is accomplished by internal bombardment using alpha decay. This is the approach that has been used in most waste glass studies.

Alpha effects are accelerated experimentally by preparing waste glasses containing actinide isotopes with short half lives. Isotopes that have been used include ^{238}Pu ($t_{1/2} = 87$ years), ^{242}Cm ($t_{1/2} = 162$ days), and

TABLE 4.6.7. Time Distribution of Alpha Decay in a Representative Waste Glass

<u>Time of Vitrification</u>	<u>Alpha Events, Percent of Total</u>
First 100 years	3.4
100 to 1,000 years	3.4
1,000 to 10,000 years	6.8
10,000 to 100,000 years	16.7
100,000 to 1,000,000 years	69.7

^{244}Cm ($t_{1/2} = 18$ years). The question then arises: What total dose is required in the accelerated experiments? The answer is simplified, because radiation effects tend to reach an equilibrium or saturation value, which changes very little with additional radiation doses. Thus for many of the effects, the goal can be simply to define the saturation values. The saturation doses can then be related to the doses expected in waste glass.

Representative doses have been calculated and reported (Mendel et al. 1977). The cumulative alpha dose in glasses containing once-through LWR fuel cycle waste and full-recycle LWR fuel cycle waste will be about 3×10^{18} and 3×10^{19} α/g , respectively, after 100,000 years. Experiments have shown that most of the radiation effects reach an equilibrium, or saturation value, which is relatively independent of waste glass composition (Ross 1978a). However, the dose required to saturate different property effects does vary. For instance, density change saturates at less than 2×10^{18} α/g , whereas stored energy does not saturate until the cumulative dose is about 4×10^{18} α/g . It has been calculated that a cumulative dose of 1.26×10^{19} α/g is required to achieve saturation radiation effects, i.e., full metamictization, of naturally occurring zircon (Bursill and McLaren 1966). Cumulative dose rates exceeding 1×10^{19} α/g of glass have been achieved in a waste glass at PNL that contains 8 wt% ^{244}Cm (Ross 1978a). Other specimens have been prepared containing 1 wt% and 3 wt% ^{244}Cm so that dose rate correlations can be made. No dose rate effects have been found, giving confidence that the results obtained in the accelerated tests are valid and can be used to predict the radiation effects on waste glasses many years into the future.

The radiation effects described in the upcoming sections were all determined using internal bombardment techniques, i.e., actinide doping. They are considered valid with one reservation. In the tests to date, the actinides have been fairly uniformly distributed in the glass matrix. In devitrified waste glass, particularly, it is conceptually possible that the actinides could become concentrated to form localized areas with higher dose rates than the surrounding glass. It has already been determined that this does not occur with curium. The behavior of other actinides in devitrified glass is still being evaluated.

Stored Energy

Stored energy is latent energy stored in a substance by radiation-induced displacement of atoms from their normal lattice position. The latent energy is released as heat when the temperature of the substance is raised sufficiently. The specific heat of waste glasses is usually about $0.2 \text{ cal/}^{\circ}\text{C-g}$. The maximum stored energies in waste glasses are in the range of 30 to 60 cal/g, thus under adiabatic conditions, the maximum additional temperature rise that could occur due to rapid release of the stored energy is only 150° to 300°C . It may be concluded that the stored energy levels in waste glass are not a hazard.

Stored-energy buildup is an inverse function of temperature, as shown in Figure 4.6.21. Figure 4.6.21 shows that the release of stored energy is fairly uniform over a temperature range from 150°C up to the softening point of the glass, at which temperature all of the stored energy has been released. The formation of stored energy reaches an equilibrium value at 25°C after an integrated dose of less than $4 \times 10^{18} \alpha/\text{g}$ of glass, as shown in Figure 4.6.21.

The data shown in Figure 4.6.21 were obtained on a specific zinc-boro-silicate waste glass composition using 1- and 8-wt% ^{244}Cm . Stored-energy measurements on other waste glasses have yielded similar results within a factor of 2 to 3 (Ross et al. 1978, Scheffler et al. 1977). The differences are attributed to compositional effects.

Density Change

Density change is a commonly observed radiation effect in ceramic substances. The density changes observed in waste glasses, which are a maximum of about 1%, are much smaller than those observed in some very stable ceramic materials. Density changes of 14% occur in irradiated crystalline silica (Le11, Kreidl and Hensler 1966) and 8% in irradiated alumina (Clinard, Bunch and Ranken 1975).

The density change in waste glass reaches an equilibrium value after about $2 \times 10^{18} \alpha/\text{g}$. Only minor density fluctuations occur with further increases in radiation dose.

a. EFFECT OF STORAGE TEMPERATURE

b. STORED ENERGY RELEASE RATES

EFFECT OF ALPHA DOSE

FIGURE 4.6.21. Stored Energy in Waste Glass (Stored Energy Release in Waste Glass Heated 20°C/min)

As shown in Figure 4.6.22, density change in waste glass can be positive or negative; the glasses can either shrink or swell. The direction of the density change is apparently a function of composition. Conceptually, it may be possible to formulate waste glasses that exhibit no density change.

Two potential effects of radiation-induced density change need to be evaluated: 1) possible canister strain, and 2) possible stresses in the glass that will cause some spontaneous fracturing. Tests indicate that neither effect is likely to cause problems. Increased canister strain results only with glass formulations where density decreases with radiation. At the maximum density decrease² observed of 1%, the circumference of a 12-in.-dia canister would be increased about 1/4 in., a strain readily accommodated by the canister metal. The potential for spontaneous fracturing is greatest in devitrified glass. No radiation-induced cracking has been observed in devitrified ²⁴⁴Cm-doped waste glasses.

Radiation Effects on Devitrification and Metamictization

Radiation seems to have little effect on thermal devitrification of waste glasses. Neither the species of devitrification crystals formed nor their rate of formation is believed to be significantly altered. Specimens of four different PNL glass compositions have been prepared with full levels of radioactivity. Similar specimens, but with nonradioactive isotopes of the fission products and chemical stand-ins (rare earths) for the actinide, have also been prepared. The nonradioactive and radioactive specimens have been subjected to the same thermal devitrification conditions. Preliminary results confirm expectations; devitrification behavior is similar. Radiation would not be expected to affect thermal devitrification, since radiation effects are annealed out at the temperatures where the devitrification rate is significant (above 500°C).

Over the long term, however, radiation can potentially be expected to affect some crystals in thermally devitrified glass. This conclusion is based on evidence from the metamict minerals. Metamict minerals are naturally occurring minerals which, when examined by x-ray diffraction, are found to be amorphous (Pabst 1952). When heated they release stored energy and become

FIGURE 4.6.22. Radiation-Induced Density Change in Waste Glass

crystalline. The metamict minerals were probably originally crystalline and became amorphous over many millions of years due to radiation effects from small amounts of contained uranium and/or thorium. This is why over the long term, the contained radioactivity in waste glass may tend to reverse devitrification by converting some crystalline phases back to an amorphous, glass-like state.

Radiation Effects on Leach Rates

Leach tests made on waste glasses containing up to 9×10^4 Ci/L of fission products are not more than a factor of two higher than those made on non-radioactive simulated waste glasses of the same general chemical composition (Mendel and McElroy 1972; Mendel 1973). This difference is within the normal experimental deviation of leach test data. Similarly, the leach rate of a ^{244}Cm -spiked waste glass was not significantly different from the leach rate of a comparable nonradioactive glass after a cumulative dose over 3×10^{17}

disintegrations/g (Mendel et al. 1977). Thus radiation does not affect the leach rate of waste glasses, and leach data obtained on nonradioactive simulated waste glass can be used to predict the leaching behavior of fully radioactive waste glass. Tests are producing more data that confirm this conclusion.

In some instances, the internal surfaces of glass vessels containing highly alpha-active solutions have become crazed and have even begun to slough off flakes of surface material (Tuck 1964). In those cases, the actinide concentrations in solution have been high (greater than 3×10^{-4} Ci/mL), probably higher than would exist in any solution likely to contact waste glass, even after prolonged static contact. This is an area that needs further investigation, although the effect is not thought to have an important impact even if it occurs. For instance, Scheffler et al. (1977) studied waste glasses having an abnormally high plutonium content (2 wt%) and observed a periodic sloughing-off of a hydrous silica-rich surface layer. Even so, the leach rate was low--less than 1×10^{-7} g of glass/cm²-d at 25°C. The small amount of plutonium leached could be filtered; it was evidently tightly bonded to hydrous silica particles.

Helium Behavior

Helium atoms are generated wherever alpha-decay events occur in waste glass. Each alpha particle captures two electrons to become a helium atom. Helium is slightly soluble in glass; helium also diffuses through glass quite readily. The diffusion is retarded as the glass composition increases in complexity; thus, helium diffusion in waste glass is lower than in quartz glass or commercial soda-lime-silica glass (Turcotte 1976). Figure 4.6.23 shows that the diffusion of a portion of the helium produced by alpha-decay is also further inhibited, when compared to that of helium implanted in the glass by solubility at high temperatures. The inhibition is attributed to trapping of some of the alpha-produced helium at point defects. Expressions for both untrapped (D_u) and trapped (D_t) helium-diffusion coefficients have been experimentally derived (Turcotte 1976):

FIGURE 4.6.23. Isothermal Helium Release From Glass

$$D_u = 2.1 \times 10^{-3} \exp(-15,000/RT) \text{ cm}^2/\text{s},$$

$$D_t = 1.7 \times 10^{-4} \exp(-15,000/RT) \text{ cm}^2/\text{s},$$

where R is the gas constant and T is the absolute temperature. Using these diffusion coefficients, canister pressurization was estimated at two temperatures (25° and 300°C) as a function of time for waste glass containing LWR once-through and full-recycle wastes. The estimated pressures are plotted in Figure 4.6.24. The solid lines represent no trapped helium; the shaded portion below the lines represents the potential effect of trapped helium. A 10-vol% plenum in the canister and 30-wt% waste loading in the glass was assumed.

Defense waste glasses are not shown in the figure, since their helium-generation rates are orders of magnitude below those of the LWR fuel cycle

a. Once-Through

b. Full Recycle

FIGURE 4.6.24. Potential Helium Pressure in Waste Glass Canisters

waste glasses. The important point is that helium pressurization is negligible even in LWR waste glass canisters; only in the unlikely event that the full-recycle waste glass canisters will still be at 300°C after 100 years, could the pressure reach 150 psig.

Transmutation

Radioactive decay results in the transmutation of the decaying isotope, often to atoms of significantly different valence and ionic radius. Some of the transmutations that occur in waste glass are shown in Table 4.6.8. Intra-lanthanide and intra-actinide transmutations are not shown because the resultant changes are insignificant. The actual number of transmutations that will occur in a given waste glass depends on the fission-product loading and the age of the waste when the glass is made. Even in glasses with a high waste loading, the total number of nonoxygen atoms undergoing transmutations will not exceed 2%. Because of the nonstoichiometric nature of the glass, it is expected that the transmutations can be accommodated without effect. The exception may be severely devitrified glass, because the effect of transmutation on the stability of crystals could be more severe.

TABLE 4.6.8. Radioactive Decay Transmutations That Occur in Waste Glass^(a)

<u>Initial Ion</u>	<u>Transmuted Ion</u>
Cs ⁺¹	Ba ⁺²
Tc ⁺⁷	Ru ⁺⁴
Sr ⁺²	Zr ⁺⁴
Zr ⁺⁴	Nb ⁺⁵
Ru ⁺⁴	Pd ⁺²
Pd ⁺⁰	Ag ⁺⁰

(a) Actinide and lanthanide transmutations are not shown because resulting effects are small.

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4.7 TECHNOLOGY DEVELOPMENT

D. E. Larson

The base technology for the conversion of HLLW waste to borosilicate glass and the associated equipment has been developed. Additional development will be required for application of this technology to specific circumstances, since the technology was developed generically. Also, it is expected that additional development work will be needed to assure compliance with associated future regulations. It is also desirable to perform additional development to optimize the process and equipment for operability, maintainability, and economics for a particular application. Areas in which additional process and equipment development effort are needed are subsequently outlined.

4.7.1 PLANT APPLICATION

The following development efforts should be performed before the SC/ICM process is applied to a specific facility:

- Perform glass formulation and characterization (nonradioactive and with actual wastes) to assure meeting product requirements/criteria.
- Determine effects of nonstandard formulation and process conditions on product quality.
- Establish proper process operating conditions such as temperatures, vibrator operation, nozzle operation, and time cycle, for the specific wastes.
- Determine waste behavior in process operations: determine if waste-foaming occurs; determine that there is no product phase separation or component precipitation (homogeneous glass); study calcine coating of calciner chamber and calcine removal; study calcine/frit pluggage at canister top and plug removal; and determine how equipment pluggage and settling of feed solids affects product quality.

- Determine equipment problems such as excessive corrosion/erosion to equipment (particularly the spray nozzle and sintered-metal filters) and/or equipment operating problems caused by particular operating conditions or feed characteristics.
- Review equipment and perhaps perform additional equipment development for plant application based upon specific plant design, operating and maintenance philosophy if necessary.
- Characterize POG for plant off-gas system design and determine specific off-gas treatment component performance.
- Determine techniques to handle characteristic secondary-process wastes such POG condensate.

4.7.2 FUTURE REGULATORY REQUIREMENTS

Federal regulatory requirements and specific waste-management facility criteria for the HLLW product and the associated package are currently not available. At this time the EPA, NRC, DOE, various standards organizations, and specific interest groups are developing proposed regulations. Proposed regulations and criteria vary widely in intent, content, and application. It would be highly speculative to anticipate what the final working regulations and criteria will contain and require in the way of additional development. It is not considered within the scope of this manual to speculate on the regulations content. However, it can be expected that future regulations will require specific product performance and product quality. It is indeterminant if the existing product quality or verification techniques are adequate.

4.7.3 OPTIMIZATION

The basic product, process, and equipment technologies have been developed. However, additional work could result in potential reduction of cost and risk with improved performance and utility to prospective users. Areas in which additional effort could result in significant benefits include the following:

- canister-connecting section (prevent pluggage and calcine buildup; improve mechanical reliability)

- ICM level detection (weighing and gamma-scanning to supplement canister thermocouples, mass balance, and ICM power consumption)
- off-standard glass rework
- off-standard canister repair
- methods to decrease change in canister properties, decrease canister residual stress, and decrease canister strain
- QA methods to reliably determine how applicable standards and regulations (when available) can be met
- equipment component reliability improvement--frit-feeder air lock, nozzle
- zone cooling of melter for some wastes
- spall generation suppression and removal
- eliminate use of in-cell manipulators
- calcine-frit mixing
- eliminate unfixed spall inside top of canister
- calcine/frit bridge-detection in canister
- contamination control during canister changeout
- canister design features--bottom support.

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SPRAY CALCINER/IN-CAN MELTER CONCEPTUAL DESIGN

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5.0 SPRAY CALCINER/IN-CAN MELTER CONCEPTUAL DESIGN

A conceptual design developed for an industrial-sized SC/ICM system is presented in subsequent sections. The purpose of the design is to relate the PNL equipment development experience and demonstrate how the equipment concepts may be adapted to plant application. The conceptual design concentrates on the SC, ICM, and the associated connecting section units. Also, description is provided for an associated cell, off-gas system, equipment feed system, and associated services to consider the whole system in perspective. This conceptual design and the technology summary are meant to provide a potential user or architect-engineer with a technical basis for adapting the process to a specific application. Since the SC/ICM system conceptual design has not been fully developed for design life and specific plant/process conditions, the design and analyses are regarded as the initial iteration to provide an appropriate plant design. Also, the associated facility and equipment descriptions should not be regarded as PNL-recommended designs, since the descriptions are only complementary (have been reviewed for compatibility) to the SC/ICM design and have not been developed for specific or general application.

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5.1 BASES

D. E. Larson

The following study bases are used for vitrification equipment design and studies.

- Flowsheet and equipment considerations were made for processing two types of HLLW (Section 5.2). One waste is characteristic of that generated by reprocessing spent nuclear power-reactor fuels (acidic HLLW). The other is characteristic of waste that has been neutralized and stored after being generated by the reprocessing of low-exposure nuclear fuels, such as defense wastes (neutralized HLLW).
- The vitrification facility would be designed to meet NRC requirements for licensed facility construction and operation at a generic site.
- The vitrification cells and equipment would be a part of a larger processing facility that would provide utilities and services. The larger facility could either be a fuels reprocessing plant or a waste-treatment complex handling existing stored HLLW.
- The process equipment and facility would be designed for totally remote operations and maintenance.
- Cells would be designed to have leak-tight liners and to facilitate cell clean-up and decontamination.
- The design operating life of the waste-vitrification facility would be 15 years. It is to the discretion of the designer to determine the economic life of the equipment.
- The vitrification system would have the capacity to process feed at a rate of 300 L/h.
- Equipment operations and maintenance would minimize manipulator use.
- No provisions would be made in the process or equipment for facility expansion.

- The facilities, with which the waste vitrification system is associated, would provide the capability for final low-level waste effluent decontamination before release to the environment.

Prior to actual plant implementation of the SC/ICM, process testing is needed to develop appropriate process operating conditions. Also, a product-development program would be needed to assure that an appropriate glass formulation is available that is compatible with the process and has the required performance properties. Also, it may be prudent to mock-up the vitrification equipment or specific systems to assure the operability and maintainability of the adapted design.

5.2 DESIGN-BASES FLOWSHEETS

D. E. Larson

The SC/ICM process converts HLLW to a glass in a canister that is subsequently sealed for delivery to a federal repository. The only current federal requirements (Code of Federal Regulations, Title 10, 1978) on the solidified waste product is that it be a "dry solid" which is "chemically, thermally and radiolytically stable to the extent that the equilibrium pressure in the sealed container will not exceed the safe operating pressure during the period from canning through a minimum of 90 days after receipt (transfer of receipt) at the federal repository." It is likely that these waste-product requirements will be modified in the near future to ensure low waste mobility and high waste integrity.

Two flowsheets will be adopted for use in this manual. One will be the vitrification of neutralized HLLW generated from low-burnup defense fuel. For the neutralized waste flowsheet the feed composition is shown in Table 5.2.1. The composition of the calcine and glass resulting from the vitrification flowsheet are shown in Tables 5.2.2 and 5.2.3, respectively. The vitrification flow diagram is illustrated in Figure 5.2.1, and the material balance is included in Table 5.2.4. The second flowsheet is the vitrification of concentrated, acidic HLLW which is mixed with intermediate-level liquid waste (ILLW) and generated from high-burnup commercial fuel. The acidic waste the feed composition is shown in Table 5.2.5. The composition of the calcine and glass resulting from the vitrification flowsheet are shown in Tables 5.2.6 and 5.2.7, respectively. The flow diagram is illustrated in Figure 5.2.2, and the material balance is indicated in Table 5.2.8. These flowsheets were derived from preliminary Savannah River Laboratory material (Landon 1978) for neutralized waste and Allied General Nuclear Services material (Hall 1977) for acid waste, but the flowsheets were modified to reflect PNL experience in the areas of SC/ICM and off-gas treatment.

After feed preparation, the steps involved include feeding the waste to the calciner followed by waste calcination and then vitrification in the canister. The glass-forming material (frit) is added to the calcine at the bottom

TABLE 5.2.1. Neutralized Waste Feed Slurry Characterization

<u>INERT SOLUBLES</u>	<u>g/L</u>
NaNO ₃	0.213
NaNO ₂	0.0693
NaAlO ₂	0.0374
NaOH	0.0315
Na ₂ CO ₃	38.3
Na ₂ SO ₄	0.0389
Na ₂ C ₂ O ₄	0.0158
Alk EDTA	9.79-4 ^(a)
NaBO ₂	3.85-6
Cl ⁻	8.62-4
F ⁻	4.03-5
H ₂ O	961
<u>INERT INSOLUBLES</u>	
Fe(OH) ₃	23.5
UO ₂ (OH) ₂	3.60
CaCO ₃	3.18
Ni(OH) ₂	1.59
Hg(OH) ₂	1.42
C	2.43
MnO ₂	5.70
Al ₂ O ₃	0.0247
NiO	1.31-3
SiO ₂	1.34
Insoluble Cl	0.795
Insoluble F	0.0419
Other	4.69 Incl. F.P. ^(b) + Actinides
<u>FISSION PRODUCTS</u>	
Ba	Included Above
Ce	in
Cs	"Other" Inert Insolubles
La	
Mo	
Nd	
Pd	
Pr	

TABLE 5.2.1. (contd)

<u>FISSION PRODUCTS (contd)</u>	<u>g/L</u>
Rb	Included Above
Rh	in
Ru	"Other" Inert Solubles
Sm	
Sr	
Tc	
Te	
Y	
Zr	
Other	
Total	

ACTINIDES (Excluding U)

Np	
Pu	Included Above
Am	in
Cm	"Other" Inert Insolubles
Total	

<u>RACIONUCLIDES-Ci/L</u>	<u>Fresh Wastes</u>	<u>Aged Wastes</u>
¹³⁷ Cs	26.0	23.1
⁹⁰ Sr	30.2	26.7
¹⁰⁶ Ru	30.4	0.98
¹²⁹ I	Negligible	Negligible
¹⁴⁴ Ce	555	6.05
Other	2688	83.2
Total	3330	140

PHYSICAL PROPERTIES

SpG	---	1.087
Watts/L	---	0.12
Age @ solid, yr	---	5 yr
Temp., °C	---	38

FLOW RATES

L/h	---	300
kg/h	---	326

- (a) Abbreviations 9.79-4 = 9.79×10^{-4}
 (b) F.P. = Fission Products

TABLE 5.2.2. Neutralized Waste Calcine Characterization
(Basis: 1 Liter Feed Slurry)

<u>INERTS</u>	Assume Complete Calcination
	<u>g/L Feed</u>
Na ₂ O	0.155
(Na ₂ CO ₃) → Na ₂ O	(38.3) → 22.4
(Na ₂ SO ₄) → Na ₂ O	(0.0389) → 0.0170 (or 0.04 g/L feed as SO ₄)
Al ₂ O ₃	25.7
B ₂ O ₃	2.05-6
Fe ₂ O ₃	17.6
U ₃ O ₈	3.22
(CaCO ₃) → CaO	(3.18) → 1.78
NiO	1.28
MnO ₂	5.70
SiO ₂	1.34
Other	3.7 ^(a)
Total	83

FISSION PRODUCTS

BaO	
CeO ₂	
Cs ₂ O	
La ₂ O ₃	
MoO ₃	
Nd ₂ O ₃	Included Above
PdO	in
Pr ₆ O ₁₁	"Other" Inerts
Rb ₂ O	
Rh ₂ O ₃	
RuO ₂	
Sm ₂ O ₃	
SrO	
Tc ₂ O ₇	
TeO ₂	
Y ₂ O ₃	
ZrO ₂	

TABLE 5.2.2. (contd)

FISSION PRODUCTS (contd)		Assume Complete Calcination
		g/L Feed
OF _P 2O ₃		
Total		
ACTINIDES - Excluding U		
NpO ₂		
Pu ₂ O ₃		Included Above
Am ₂ O ₃		in
Cm ₂ O ₃		"Other" Inerts
Total		
RADIONUCLIDES		Ci/L Feed--Aged Waste
137Cs		23.1
90Sr		26.7
106Ru		0.98
129I		Negligible
144Ce		6.05
Other		83.2
Total		140
PHYSICAL PROPERTIES		
SpG		1.0 Bulk Tapped
Watt/L		1.44
Age at solid, yr		5.5
Temp., °C		Variable
FLOW RATES		
L/h		24.9
kg/h		24.9
(a)	Feed	→ Calcine
	Insoluble Cl	0.795
	Other	4.69
		5.53
		→ 3.37
	Assume Average MW = 120	→ 80

TABLE 5.2.3. Neutralized Waste Glass Characterization

	Glass Composition		
	Calcine, g/L	Frit, g/L	Glass, g/L
<u>Chemical</u>			
<u>Calcine</u>	1000		
Inerts	1000		
Fission products	Negligible		
Actinides	Negligible		
<u>Frit</u>		1600	
SiO ₂		974	
Na ₂ O		80	
TiO ₂		188	
B ₂ O ₃		189	
CaO		94	
Li ₂ O		75	
<u>Glass</u>			2600
Calcine			1000
Frit			1600
<u>Radionuclides</u>			
	Ci/L	Ci/L	Ci/L
137Cs	277 (a)	0	277
90Sr	320	0	320
106Ru	11.8	0	11.8
129I	72.6	0	0
144Ce	---	0	72.6
Other	988	0	988
Total	1670	0	1680
<u>Physical Properties</u>			
SpG	~0.55 bulk ~1 bulk tapped	~1.6	2.6
W/L		0	1.44
Mesh	---	-20/+80	

(a) Calcine bulk tapped density = 1.

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FIGURE 5.2.1. High-Level Neutralized Waste Spray Calcliner/In-Can Melter Flow Diagram

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TABLE 5.2.4. High-Level Neutralized Waste Spray Calclner/In-Can Melter Process Flowsheet

Character- istics and Units	1 Calclner Feed	2 Atomizing Air	3 Air(a) In-Leakage	4 Air Blowback	5 Frit	6 Calclne	7 Glass	8 Calclner Off Gas	9 Ejector Off Gas	10 Cyclone Off Gas	11 Condenser Off Gas	12 Ru Heater Off Gas	13 Ru Sorber Off Gas	14 I Heater Off Gas	15 I Sorber Off Gas	16 Cooler Off Gas	17 Filter Off Gas	18 Scrubber TK Soln
CHEMICALS-kg/h																		
Feed (Total) 5 yr old	325							0	0	0	0	0	0	0	0	0	0	0
Frit					39.8			0	0	0	0	0	0	0	0	0	0	0
Calclne						24.9		See solids	See solids	See solids	See solids	See solids	See solids	See solids	See solids	See solids	See Solids	See solids
Glass							64.7	0	0	0	0	0	0	0	0	0	0	0
HNO ₃								0	0	0	0	0	0	0	0	0	0	≤0.03
H ₂ SO ₃								0	0	0	0	0	0	0	0	0	0	Trace
Cl								<0.239	Trace	Trace	0	0	0	0	0	0	0	≤0.239
F								<0.0126	Trace	Trace	0	0	0	0	0	0	0	≤0.0126
H ₂ O		Negligible	Negligible	Negligible				292.6	88.7	42.9	1.03	1.03	1.03	1.03	1.03	1.03	1.03	292
N ₂		50.4	16.8	1.46				68.7	68.7	68.7	68.7	6.87	6.87	6.87	6.87	6.87	6.87	0
O ₂		15.2	5.07	0.44				20.7	20.7	20.7	20.7	20.7	20.7	20.7	20.7	20.7	20.7	0
NO _x								≤0.048	≤0.04	≤0.04	≤0.01	≤0.01	≤0.01	≤0.01	~0	~0	~0	0
Hg†								<0.364	Trace	Trace	0	0	0	0	0	0	0	≤0.364
NaBO ₂ †								Trace	Trace	0	0	0	0	0	0	0	0	Trace
CO ₂								7.87	7.87	7.87	7.87	7.87	7.87	7.87	7.87	7.87	7.87	0
H ₂								--	--	--	--	--	--	--	--	--	--	0
Solids (Incl. in Inerts)								0.025	2.5-3	2.5-4	2.5-6	2.5-6	2.5-7	2.5-7	2.5-7	2.5-7	2.5-12	0.025
SO ₂								Trace	Trace	Trace	0	0	0	0	0	0	0	0
RADIONUCLIDES - Ci/h																		
137Cs	6,930	0	0	0	0	6,923	6,916	V 7(b) P 7(b)	P 7-1									14
90Sr	8,070	0	0	0	0	8,062	8,054	P 8	P 8-1	7-2	7-4	7-4	7-5	7-5	7-5	7-5	7-10	8
106Ru	294	0	0	0	0	294	293	V 0.3 P 0.3	V 3-2 P 3-2	P 8-2	8-4	8-4	8-5	8-5	8-5	8-5	8-10	0.6
129I	Negligible	0	0	0	0	0	0	Negligible	0	V 3-3 P 3-3	V 3-4 P 3-5	3-4 3-5	3-7 3-6	3-7 3-6	3-7 3-6	3-7 3-6	3-11	Negligible
144Ce	1,815	0	0	0	0	1,815	1,813	P 2	P 2-1	0	0	0	0	0	0	0	0	2
Other	24,960	0	0	0	0	24,935	24,935	P 25	P 2-5	2-2	2-4	2-4	2-5	2-5	2-5	2-5	2-10	25
TOTAL	42,000	0	0	0	0	42,000	42,000	V 7 P 42	V 3-2 P 4-2	2.5-1 V 3-3 P 4.2-1	2.5-3 V 3-4 P 4.2-3	2.5-3 V 3-4 P 4.2-3	2.5-4 V 3-7 P 4.2-4	2.5-4 V 3-7 P 4.2-4	2.5-4 V 3-7 P 4.2-4	2.5-4 3-7 4.2-4	2.5-9 3-7 4.2-9	49
PHYSICAL																		
SpG at T	1.085	2.9-3	1.2-3	4.7-3	~1.6	~1 Bulk Tapped	2.6 Warm	3.7-4	7.3-4	6.7-4	9.1-4	7.1-4	≥6.11-4	5.04-4	4.8-4	6.1-4	≤6.1-4	1.0
W/L	0.12	0	0	0	0	1.44	1.44	Negligible	0	0	0	0	0	0	0	0	0	0
Temp., °C	<50	Ambient	Ambient	Ambient	Ambient	~350	Ambient to 1,100	250-350	85	70	10	80	<80	150	150	55	55	≤40
Press. Atm	2.7	3.4	1	4	1	0.975	0.975 to 1	0.95	0.95	0.730	0.713	0.705	0.602	0.594	0.572	0.560	0.555	≤1
FLOWRATES																		
L/h	300	2.23x10 ⁴	1.86x10 ⁴	403	24.9	24.9	24.9	1.05+6	2.54+5	2.18+5	1.09+5	1.37+5	<1.61+5	1.95+5	2.06+5	1.60+5	1.62+5	292
kg/h	325	65.6	21.9	1.90	39.8	24.9	64.7	390	186	140.2	98.3	98.3	98.3	98.3	98.3	98.3	98.3	292
Frequency	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous	As designed
L/batch	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	As designed

(a) Excludes any air inleakage during canister changeout.
(b) V = Volatile; P = Particulate; if prefix is excluded, radionuclide is particulate.

TABLE 5.2.5. Acid Waste Calciner Feed Solution Characterization

Chemical	Composition, g/L			
	HLLW	ILLW	Recycle	Total
<u>INERTS</u>				
H ⁺	4-7	2.5	7	5.61
Na	--	17.64		5.45
K	--	0.36		0.11
Cr	0.0817	0.0323		0.0604
Ni	0.043	0.017	<0.07	0.0318
Fe	0.305	0.121		0.226
Gd	42.77	--		26.4
Mn	--	0.5		0.15
NO ₃ Max	574	217	434	453
PO ₄	0.03	23.0	--	7.12
SO ₄	--	0.11	--	0.0340
Cl	0.035	0.32	--	0.130
Shear Fines	0.44	--	--	0.27
H ₂ O	610	844	736	700
TOTAL	1234	1105	1177	1199
<u>FISSION PRODUCTS</u>				
Ba	2.33	Neglibl	Neglibl	1.44
Ce	3.85	Neglibl	Neglibl	2.38
Cs	4.06	Neglibl	Neglibl	2.51
La	1.97	Neglibl	Neglibl	1.22
Nd	6.38	Neglibl	Neglibl	3.94
Pd	2.13	Neglibl	Neglibl	1.32
Pr	1.86	Neglibl	Neglibl	1.15
Rb	0.52	Neglibl	Neglibl	0.324
Rh	0.60	Neglibl	Neglibl	0.37
Ru	3.40	Neglibl	Neglibl	2.10
Sm	1.45	Neglibl	Neglibl	0.896
Sr	1.36	Neglibl	Neglibl	0.837
Tc	1.30	Neglibl	Neglibl	0.807
Te	0.88	Neglibl	Neglibl	0.543
Y	0.726	Neglibl	Neglibl	0.448
Zr	5.72	Neglibl	Neglibl	3.53
Other	0.9	Neglibl	Neglibl	0.5
I (0.5%)	0.0022	0.0043	0.0773	0.0084
TOTAL	45.07	--	--	27.8

TABLE 5.2.5. (contd)

Chemical	Composition, g/L			
	HLLW	ILLW	Recycle	Total
<u>ACTINIDES</u>				
U (0.5%)	8.45	16.91	Negligible	10.408
Np	0.709	--	Negligible	0.438
Pu (0.5%)	0.076	0.152	Negligible	0.094
Am	0.43	--	Negligible	0.266
Cm	0.035	--	Negligible	0.0217
TOTAL	9.70	17.07	Negligible	11.3
<u>INSOLUBLE SOLIDS</u>				
(constituents included above)	9.7	2.0	--	6.6
<u>RADIONUCLIDES -</u>				
Ci/L				
¹³⁷ Cs	147	Negligible	Negligible	90.8
⁹⁰ Sr	105	Negligible	Negligible	64.9
¹⁰⁶ Ru	16.3	Negligible	Negligible	10.1
¹²⁹ I	6.1-9	1.2-8	2.14-7	2.33-8
¹⁴⁴ Ce	10.8	Negligible	Negligible	6.65
Other	380	Negligible	Negligible	235
TOTAL	660	Negligible	Negligible	407
<u>PHYSICAL PROPERTIES</u>				
SpG	1.296	1.124	1.179	1.245
W/L	2.51	0.012	Negligible	1.55
1/MTHM	567	284	67	918
Age @ solid-yr	5.7	5.7	--	5.7
<u>FLOW RATES</u>				
L/h	118	59	14	191
MTHM/d	5	5	5	5

TABLE 5.2.6. Acid Waste Calcine Characterization

Assume Complete Calcination		
Chemical	g/L feed	kg/MTHM
<u>INERTS</u>		
Na ₂ O	7.35	6.75
K ₂ O	0.13	0.119
Cr ₂ O ₃	0.0883	0.081
NiO	0.0405	0.037
Fe ₂ O ₃	0.323	0.296
Gd ₂ O ₃	30.4	27.9
MnO ₂	0.24	0.22
P ₂ O ₅	5.32	4.88
SO ₄	0.034	0.031
Shear Fines (Zr)	0.36	0.33
ZrO ₂	--	--
TOTAL	44.3	40.64

FISSION PRODUCTS

BaO	1.61
CeO ₂	2.92
Cs ₂ O	2.66
La ₂ O ₃	1.43
MoO ₃	5.00
Nd ₂ O ₃	4.60
PdO	1.51
Pr ₆ O ₁₁	1.39
Rb ₂ O	0.354
RH ₂ O ₃	0.46
RuO ₂	2.77
Sm ₂ O ₃	1.04
SrO	0.99
Tc ₂ O ₇	1.26
TeO ₂	0.68
Y ₂ O ₃	0.569
ZrO ₂	4.77

TABLE 5.2.6. (contd)

<u>Assume Complete Calcination</u>		
<u>Chemical</u>	<u>g/L feed</u>	<u>kg/MTHM</u>
<u>FISSION PRODUCTS (contd)</u>		
OP _P 2 ₃ O ₃	0.66	
--	--	
TOTAL	34.82	
 <u>ACTINIDES</u>		
U ₃ O ₈	12.3	
NpO ₂	0.497	
PuO ₂	0.106	
Am ₂ O ₃	0.292	
Cm ₂ O ₃	0.0238	
TOTAL	13.21	
 <u>RADIONUCLIDES-Ci/L Calcine</u>		
¹³⁷ Cs	908	
⁹⁰ Sr	649	
¹⁰⁶ Ru	101	
¹²⁹ I	23.3-8	
¹⁴⁴ Ce	66.5	
Other	235	
TOTAL	407	
 <u>PHYSICAL PROPERTIES</u>		
SpG	~0.8 Bulk	
	~1.0 Tapped	
W/L	13.4 Bulk	
L/MTHM	106 Bulk	
Age @ solid-yr	5.7	
 <u>FLOW RATES</u>		
L/h	34.8 Bulk	
MTHM/d	5	

TABLE 5.2.7. Acid Waste Glass Characterization

Chemical Oxides	Calcine (PW-7C-3 or -4 Excluding Fe)		Frit (76-199 77-296)		Glass (77-260)	
	g/L	kg/MTHM	g/L Glass	kg/MTHM	g/L glass	kg/MTHM
Calcine	1000	84.7				
Inerts	480	40.6				
Fission products	377	32.0				
Actinides	143	12.1				
Frit			2000	169.3		
Na ₂ O			240	20.3		
K ₂ O			60	5.1		
SiO ₂			1060	89.8		
B ₂ O ₃			280	23.7		
TiO ₂			180	15.2		
CaO			60	5.1		
CuO			90	7.6		
Al ₂ O ₃			30	2.5		
Glass					3000	254.0
Calcine					1000	84.7
Frit					2000	169.3
Radionuclides	Ci/L	Ci/MTHM			Ci/L	Ci/MTHM
¹³⁷ Cs	984	8.34 + 4	None		984	8.34 + 4
⁹⁰ Sr	703	5.96 + 4			703	5.96 + 4
¹⁰⁶ Ru	109	9.27 + 3			109	9.27 + 3
¹²⁹ I		---				---
¹⁴⁴ Ce	72	6.10 + 3			72	6.10 + 3
Other	2250	2.16 + 5			2550	2.16 + 5
Total	4418	3.74 + 5			4418	3.74 + 5
Physical Properties						
SpG - Variable						
(Bulk-0.8-1.2)	Use 1.0		~1.6		3.0	
W/L	16.8		0		16.8	
L/MTHM	84.7		106		84.7

FIGURE 5.2.2. High-Level Acid Waste Spray Calciner/In-Can Melter Flow Diagram

TABLE 5.2.8. High-Level Acid Waste Spray Calclner/In-Can Melter Process Flowsheet

Character- istics and Units	1 HLLW	2 ILLW	3 Recycle	4 Calclner Feed	5 Atomizing Air	6 Air (c) In-Leakage	7 Filter Blowback	8 Calclne(d)	9 Frit	10 Glass	11 Calclner(e) Off Gas	12 Quench Tower Off Gas	13 Cyclone Off Gas	14 Mist-Elim. Off Gas	15 Filter Off Gas	16 Ru Sorber Off Gas	17 I Sorber Off Gas	18 Filter Off Gas	19 Ammonia	20 NO _x Reactor Off Gas (f)	21 Calclner Condensate
CHEMICALS—kg/h																					
Feed (Total)	242	105	26	373							0	0	0	0	0	0	0	0	0	0	0
Frit									55.7		0	0	0	0	0	0	0	0		0	0
Calclne								27.8			See Solids	See Solids	See Solids	See Solids	See Solids	See Solids	See Solids	See Solids		See Solids	See Solids
Glass										83.5	0	0	0	0	0	0	0	0		0	0
HNO ₃	82(a)	14.6(a)	9.9(a)	106(a)							0	0	0	0	0	0	0	0		0	85.5
H ₂ SO ₄											0	0	0	0	0	0	0	0		0	Trace
Cl											0.039	Trace	Trace	0	0	0	0	0		0	0.039
H ₂ O	114(a)	78.6(a)	16.3(a)	210(a)	Negligible	Negligible	Negligible				225	152	68.0	9.09	9.09	9.09	9.09	9.09		39.1	203.8
N ₂					50.4	16.8	1.46				68.7	68.7	68.7	68.7	68.7	68.7	68.7	68.7		95.9	---
O ₂					15.2	5.07	0.44				73.3	58	48.7	40.7	40.7	40.7	40.7	40.7		27.4	---
NO _x											65.7	46	35	25	25	25	25	25		<0.5	See HNO ₃
SO ₂											Trace	0	0	0	0	0	0	0		0	See H ₂ SO ₄
CO ₂											0	0	0	0	0	0	0	0		0	---
NH ₃											0	0	0	0	0	0	0	0	18.9	Trace	---
H	1.30(a)	0.232(a)	0.158(a)	1.69(a)							Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace		Trace	---
Solids (Incl. in Inerts)	1.80(a)	0.186(a)	0.0379(a)	2.02(a)	0	0	0				0.028	2.8-3	2.8-4	2.8-6	2.8-9	2.8-10	2.8-10	2.8-14		2.8-14	0.028
Organics					0	0	0				0	0	0	0	0	0	0	0		0	0
RADIONUCLIDES—Ci/h																					
¹³⁷ Cs	2.73+4	Negligible	Negligible	2.73+4				2.73+4		2.73+4	V 27.3(b) P 27.3(b)	V 0 P 2.73	0.273	2.73-3	2.73-6	2.73-7	2.73-7	2.73-11		2.73-11	54.6
⁹⁰ Sr	1.96+4	Negligible	Negligible	1.96+4				1.96+4		1.96+4	P 19.6	1.96	0.196	1.96-3	1.96-6	1.96-7	1.96-7	1.96-11		1.96-11	19.6
¹⁰⁶ Ru	3.03+3	Negligible	Negligible	3.03+3				3.03+3		3.03+3	V 3.03 P 3.03	V 0.303 P 0.303	V 0.0303 P 0.0303	V 3.03-3 P 3.03-4	3.03-3 3.03-7	3.03-6 3.03-8	V 6.1-7 P 3.03-8	V 6.1-7 P 3.03-12		V 6.1-7 P 3.03-12	6.06
¹²⁹ I	3.68-8	Negligible	Negligible	3.68-8				0		0	P ≤3.68-8	P ≤3.68-8	P ≤3.68-8	≤3.68-8	≤3.68-8	≤3.68-8	≤7.3-11	Negligible		Negligible	≤3.68-8
¹⁴⁴ Ce	2.01+3	Negligible	Negligible	2.01+3				2.01+3		2.01+3	P 2.01	0.201	0.0201	2.01-4	2.01-7	2.01-8	2.01-8	2.01-12		2.01-12	2.01
Other	7.07+4	Negligible	Negligible	7.07+4				7.07+4		7.07+4	P 70.7	P 7.07	0.707	7.07-3	7.07-6	7.07-7	7.07-7	7.07-11		7.07-11	70.7
Total	1.23+5	Negligible	Negligible	1.23+5	0	0	0	1.23+5	0	1.23+5	V 30.3 P 123	V 0.303 P 12.3	V 0.0303 P 1.23	V 3.03-3 P 0.0123	V 3.03-3 P 1.23-5	V 3.03-6 P 1.23-5	V 6.1-7 P 1.23-6	V 6.1-7 P 1.23-10	0	V 6.1-7 P 1.23-10	153
PHYSICAL																					
Sp6 at T	1.29	1.12	1.18	1.245	2.9-3	1.2-3	4.7-3	~0.8 Bulk ~1.0 Tapped	1.6	3.0 Ambient	4.14-4	7.37-4	6.14-4	7.51-4	6.55-4	6.16-4	5.77-4	5.67-4	8.34-4	5.06-4	1.11
W/L	2.51	Negligible	Negligible	1.55	0	0	0	13.4 Bulk	0	16.7	0	0	0	0	0	0	0	0	0	0	Negligible
L/THM	567	284	67	918	--	--	--	106 Bulk	106	85	--	--	--	--	--	--	--	--	--	--	--
Temp., °C	60	25	80	≤50	Ambient	Ambient	Ambient	~350	Ambient	Ambient to 1100	250-350	85	70	40	80	80	80	80	-25	350	40
Press., Atm	~1	~1	~1	2.7	3.4	1	4	≤0.975	1	≤0.975	0.95	0.95	0.70	0.68	0.67	0.57	0.53	0.52	1.07	1.03	1
FLOWRATES																					
L/h at T	Batch	Batch	Batch	300	2.23+4	1.86+4	403	34.8 Bulk 27.8 Tapped	34.8	27.8	1.046+6	4.40+5	3.60+5	1.91+5	2.19+5	2.58+5	2.77+5	2.82+5	2.26+4	3.21+5	263
kg/h	--	--	--	373	65.6	21.9	1.90	27.8	55.7	83.5	432.8	324.4	221.2	143.5	143.5	143.5	143.5	143.5	18.9	162.4	289.3
Frequency	1.5/d	1.5/d	1.5/d	Continuous	Continuous	Continuous	Intermit.	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous	As-designed
L/batch	2,835	1,417	342	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--

(a) Amounts in Feed (total).
 (b) V = Volatile; P = Particulate; if prefix is excluded, radionuclide is particulate.
 (c) Excludes any air in-leakage during canister changeout.
 (d) Absorber + Calclner reactions.

(e) Assume all NO_x = NO.
 (f) 4 NH₃ + 3 NO₂ + 7/2 N₂ + 6 H₂O + heat.

of the calciner. The filled canister is removed from the melter after lid placement, then the canister lid is seal-welded and the canister integrity is tested prior to decontamination for storage, disposal, or overpacking. Process effluents are treated for NO_x , H_2O , iodine, volatile ruthenium, SO_2 , and particulate removal, which may be recycled to other processes in the associated facility for further treatment. The treated effluent is released to the facility ventilation system for final filtering and release to the atmosphere. The technology for these process steps is described below.

5.2.1 NEUTRALIZED HIGH-LEVEL LIQUID WASTE VITRIFICATION FLOWSHEET

The neutralized HLLW vitrification flowsheet, used as an equipment design bases, is described here. This flowsheet was selected because it is characteristic of those being considered for the stored wastes at Hanford and Savannah River Plant (SRP) (Landon 1978). The feed composition and stream characteristics used are only indicative, since they will fluctuate during processing due to composition variations between tanks, variations within a tank, processing effects, and changes in flowsheets. Final process design would need to accommodate these flowsheet variations.

5.2.1.1 Flowsheet Bases

For over 25 years, the Hanford Works and the SRP have produced special nuclear materials for defense puposes. High-level radioactive waste is generated in the chemical processing of fuel and target elements after irradiation in nuclear reactors. This waste is stored in large underground tanks as an alkaline liquid with a precipitated sludge until the decay-heating has abated appreciably. Then the supernate liquid is evaporated and returned to the tanks to form a salt cake to reduce volume and mobility. The presence of the soluble salts (NaNO_3 , Na_2CO_3 , etc.) could present significant difficulties if these salts had to be incorporated into a high-integrity form such as glass or concrete. A process for segregating the soluble salts from the radionuclides was developed to avoid these difficulties and reduce program costs.

The stored HLLW is reconstituted with water and blended. Soluble salts and insoluble sludges are separated by centrifugation, washing, gravity-settling, and filtration. Cesium and plutonium are removed from the salt solution using an ion-exchange resin. The cesium and plutonium are eluted from the resin and blended with the washed sludge. The elutriant is recovered and reused. Strontium is also removed from the salt solution by ion exchange and recycled to the primary centrifuge. The salt solution is concentrated for evaporation of water and storage of solid salt cake. In the SC/ICM process, the sludge is calcined and then melted with additives to form a borosilicate glass in stainless steel canisters, where it hardens as it cools. Lids are welded on the canisters. The canister is placed and welded in a steel storage container. The storage containers are inspected, leak-checked, and shipped to a federal repository. See Figure 5.2.3 for the process flow diagram.

The following assumptions have been made in the flowsheet:

1. The radioactive borosilicate glass will be contained in a 2-ft-dia, 10-ft-long stainless steel canister.
2. The effective age of the waste from defense fuel to be processed will be at least 5 years.
3. The vitrification plant is designed for an instantaneous calciner feed rate of 300 L/h.
4. Selection of materials of construction, particularly for items that would be difficult to replace (such as imbedded piping, cell liners, etc.) should assume the facility will be eventually decontaminated with nitric acid.

5.2.1.2 Process Description

The steps for the SC/ICM process are described here (Landon 1978).

Feed Preparation and Spray Calcination

The spray calcination step converts the sludge slurry from the sludge washing operation into a dry powder suitable for feed to the glass-melter.

FIGURE 5.2.3. Defense Waste Processing Flow Diagram

The inclusion of the spray calcining step simplifies sludge handling and avoids the addition of water to the melter.

The flow diagram and material balance for the spray calcination system is shown in Figure 5.2.1 and Table 5.2.4, respectively. In the waste solidification process, the washed sludge cake is slurried with the cesium carbonate solution from ion exchange and additional water in the slurry storage tank to produce a Na_2CO_3 slurry containing about 9 wt% total solids. The slurry is sampled for sludge content and subsequently transferred to the calciner feed tank. This slurry is then fed at a controlled rate to the calciner at a

pressure of 2 to 3 atm. The slurry is pneumatically atomized in an internal-mix nozzle and sprayed into the top center of a cylindrical calcination chamber. The mass ratio of atomizing air to slurry feed is controlled at greater than 0.2. The atomized slurry in the form of 70- to 100- μ m MVD (mean volume diameter) droplets is sequentially evaporated, dried, and partially calcined as it falls through the calcination chamber.

The calciner walls are heated to a temperature of between 700°C and 800°C. The radial temperature gradient in the calciner varies from the wall temperature to about 300°C at the centerline. Inside, the chamber heat is transferred to the droplets by a combination of radiation, convection, and conduction to produce a dry calcine powder containing less than 2 wt% moisture. Fouling of the calcination chamber heat-transfer surface is minimized by the periodic operation of wall-mounted vibrators. The calciner off gases, which consist primarily of superheated steam and air, entrain 15% to 50% of the calcine particles. The entrained calcine is removed by passing the off gas through sintered-metal filters. Less than 0.1% of the calcine penetrates the filters. The de-entrained off gas exits the filters at between 250° and 300°C and is routed to an off-gas system for radionuclide abatement and mercury recovery. The calcine collected on the filters is periodically removed by a pulse of blowback air. The quantity of blowback air is estimated to be roughly 1 SCFM for a filter unit of the size used in the full-scale SC at PNL. The dry powder (filter cake) from the filters drops into the cone below the calciner along with the calcine that falls directly from the calcination chamber and is combined with glass-forming frit. The calcine powder in the cone is at a temperature between 300° and 400°C. The frit is fed into the cone to provide a 38:62 ratio by weight of calcine to glass frit. The frit-addition rate is set based on a determination of the sludge content of the waste slurry and the calciner feed rate. No special care is provided to mechanically ensure good mixing of the calcine and frit. However, the frit particles should be as small as possible--consistent with reliable transport to the calciner cone. The calcine and frit are then discharged to the ICM by gravity flow.

The primary "reaction" assumed to occur in the calciner is loss of free water. However, the following reactions also are assumed to occur:

Gases that are expected to evolve from the calciner include H_2O , CO_2 , I, N_2 , O_2 , Hg vapor, and oxides of ruthenium and cesium. Steam forms when hydroxides and hydrated oxides are calcined to give anhydrous oxides. Carbon dioxide results from the decomposition of sodium oxalate, the oxidation of coal, and the decomposition of EDTA. Mercury volatilizes from the calciner as Hg vapor (Peyches 1978). Oxygen and nitrogen arise from air used to atomize the sludge slurry and blow back the filters, as well as from in-leakage. Ru and Cs form a small amount of volatile oxides in the oxidizing atmosphere expected in the calcination chamber. Halides, especially fluorides, volatilize to some extent as the halogen or as the hydrogen halide.

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 liner 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 liner wall. This cools it

and the canister to reduce crystalline phase settling and to prevent excessive system temperatures from waste self-heating. The small volume of gas generated during the melting is routed to the calciner.

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

The filled canister is disconnected from the calciner and the filled canister is then removed from the furnace; the lid is placed on the canister, seal-welded, and inspected.

For the reference flowsheet, calcine and borosilicate glass frit will be fed to the glass melter in an approximate weight ratio of 38:62, respectively. Frit components (in wt%) in reference flowsheet molten glass are: SiO_2 @ 38.1 (includes SiO_2 in calcine), Na_2O @ 13.4 (includes Na_2O from salts), B_2O_3 @ 7.25, TiO_2 @ 7.25, CaO @ 3.6 (excludes CaO from CaCO_3 in calcine), and Li_2O @ 2.9. This mixture is melted in canisters at the rate of 1.5 tonnes/d. Filled canisters will be moved for inspection, decontamination, and possibly encapsulation in a storage container before shipment to a federal repository. The canister fill time cycle is shown in Table 5.2.9.

The following major reactions are assumed to occur in the melter (these reactions may also occur to some extent in the calciner):

Also, the sodium sulfate decomposes to a large extent, and there is significant volatilization of sulfur dioxide. A small percentage of NaBO_2 will volatilize.

TABLE 5.2.9. Neutralized Waste Canister Fill Time Cycle

PROCESS PARAMETERS

Glass Generation Rate = 24.9 L/h = 0.88 ft³/h

Canister (23 in. ID x 10 ft high) = 26 ft³

Content (90% Equivalent Fill)

$$\begin{aligned} \text{Time To Fill Canister} &= \left(\frac{26 \text{ ft}^3}{\text{canister}} \right) / \left(\frac{0.88 \text{ ft}^3}{\text{h}} \right) \\ &= 29.6 \text{ h/canister.} \end{aligned}$$

$$\begin{aligned} \text{Heat Load in Canister} &= \frac{(1.44 \text{ W/L})(26 \text{ ft}^3/\text{canister})}{(0.0353 \text{ ft}^3/\text{L})(1000 \text{ W/kW})} \\ &= 1.06 \text{ kW/canister.} \end{aligned}$$

CANISTER OPERATING TIME CYCLE

<u>Operations</u>	<u>Time, h</u>
Place in Melter	0.5
Make Remote Connection	0.25
Heat Empty Canister	3.5
Fill Empty Canister	29.5
Top and Allow Bubble Release	3.5
Cool to 700°C	2.5
Disconnect	0.25
Remove from Melter	0.5
<u>Time Lags</u>	<u>18.5</u>
Total Cycle	59.0

It is expected that less than 1% of the Ru and a smaller amount of the cesium will volatilize, as may trace quantities of other radionuclides. Also, most of the halides present are volatilized.

Off-Gas Treatment

During spray calcination and vitrification of neutralized wastes, a vapor stream is evolved that contains both radioactive and nonradioactive contaminants. The vapor stream is composed mostly of steam, air, and NO_x with ruthenium and cesium as the principal volatile radioactive contaminants. Corrosive species such as alkali borates, halides, and sulfur compounds are also present. Mercury vapor could be present in a significant quantity. Adequate abatement systems must be provided such that the discharges of these various contaminants to the atmosphere will meet existing state and federal regulations.

A flow diagram of the proposed SC/ICM off-gas treatment system is shown in Figure 5.2.1. The vapor stream leaving the calciner is expected to range in temperature from 250° to 300°C and be composed primarily of air and water vapor. The vapor enters an ejector-venturi gas scrubber, where it concurrently contacts a cooled, circulating liquid stream. The vapor and liquid discharge into the scrubber tank, where liquids condensation, solids formation and coalescing takes place. The vapor stream exits the tank at about 85°C .

Exiting from the tank, the vapor stream is drawn through a venturi scrubber and a cyclone separator to achieve separation of liquid and particulate from the vapor. The cyclone drains into the scrubber tank. It is expected that most of the mercury vapor will condense in the scrubber and subsequent Hg condenser and collect in the scrubber-tank.

The vapor stream exits the cyclone separator and is then cooled to about 10°C in a shell and tube heat exchanger that employs a refrigerated cooling medium. Additional mercury and water vapor will condense and drain to the scrubber tank.

Exiting from the mercury condenser, the vapor stream is heated above its dew point and then drawn through two silica-gel beds in series to adsorb the volatile species of ruthenium. The adsorbed ruthenium may be desorbed with hot water and recycled back to the recycle evaporator. It is expected that an additional DF for particulates occurs across silica-gel adsorber beds.

A final cleanup of mercury vapor and also I is attained by drawing the vapor stream exiting the ruthenium adsorbent beds through a bed of silver-nitrate-exchange zeolite. It is expected that most of the mercury vapor entering the bed will be adsorbed.

Before discharging the vapor stream to the vessel vent system, it is drawn through HEPA filters arranged in series for additional particulate removal.

The reference material decontamination factors across the off-gas treatment system for neutralized waste processing are shown in Table 5.2.10.

The bases for preparing the material balance are as follows:

- The decontamination factors for the various contaminants across the individual subsystems are tabulated in Table 5.2.10.
- All of the vaporized Cl, F, Cs₂O, NaBO₂ and soluble salts become completely soluble across the wet-scrubbing system.

5.2.2 ACIDIC HIGH-LEVEL LIQUID WASTE VITRIFICATION FLOWSHEET

The acidic HLLW vitrification flowsheet described in this section is for the equipment conceptual design bases in this manual. This flowsheet was selected because it is representative of power-fuel waste, and it is

TABLE 5.2.10. Off-Gas System Decontamination Factors for Neutralized Waste Processing

Off-Gas Equipment	Decontamination Factors					
	Insoluble Solids	Soluble Solids	Hg Vapor	H ₂ O Vapor	Volatilized Ru	Volatilized Cs
Venturi, Cyclone	100	{ ∞	{ 40	7	100	∞
Hg Condenser	100			40	10	
Ru Sorption Beds	10		1	1	10 ³	
I (Hg) Sorption Bed	1		10 ³	1	1	
HEPA	10 ⁵		1	1	1	
TOTAL DF	10 ¹⁰	∞	4 x 10 ⁴	280	10 ⁶	∞

documented for potential application (Hall 1977). Other power-fuel reprocessing schemes incorporate some flowsheet variations and the vitrification of more concentrated and less aged waste.

5.2.2.1 Flowsheet Bases

The process requirements for the vitrification facility described by Hall (1977) are based on anticipated liquid waste compositions and volumes resulting from the reprocessing of spent LWR fuels having the following characteristics:

Burnup:	29,000 MWd/MTU
Specific Power:	32 MW/MTU
Initial Enrichment:	2.8% ^{235}U
Reactor Operating Factor:	80%
Age at Solidification:	5.7 years.

These fuel characteristics approximate the weighted average values of the equilibrium fuels reported in the "Fuel Trac" data. The assumption of 3-year "aged" fuel was precipitated by a series of technical evaluations that identified 1) a sufficient supply of old fuel through the foreseeable future, 2) economic advantages, and 3) reductions in population dose commitments as a result of this age restriction. The isotopic content of the spent fuel was determined by the "ORIGEN" code.

The capacity of the vitrification facility would be compatible with the capacity of the separations facility, and it would solidify 5 MTU equivalents of HLLW and ILLW per day of operation, for an estimated 300 operating days per year.

The concentration of the HLLW is expected to be solubility-limited when reprocessing 3-year "aged" fuel, and will range from 100 gal/MTU to 150 gal/MTU. The ILLW concentration will be approximately 75 gal/MTU. For these operating constraints, the composition of the HLLW and ILLW at the time of solidification are shown in Table 5.2.5.

Five-tenths of one percent (0.5%) of the uranium, plutonium and iodine isotopes are assumed to be associated with each of the liquid waste streams. To be consistent with previous studies and to avoid duplication of reported population dose commitments, all of the tritium (100%) is assumed to be released during reprocessing (Mays and Schwab 1975).

For simplicity, all of the fission products in the liquid waste effluents except iodine are assumed to be associated with the HLLW. The corrosion product concentrations in the wastes at the time of solidification are time-integrated average values for the combined separations and storage conditions.

The soluble poison concentration in the HLLW is based on a weighted average initial enrichment of 3.1% uranium-235 to reflect conservative requirements for criticality control during dissolution of the spent fuels (Final Safety Analysis Report 1973).

Undissolved solids removed by the feed-clarification centrifuge before solvent extraction are assumed to be routed to the HLLW storage tanks even though these constituents could be removed as solid wastes. The undissolved solids include shear fines and noble-metal alloys. Laboratory analyses indicate that a significant fraction (approximately 50%) of the ruthenium could be associated with these noble-metal alloys (Savannah River 1976). This conceptual study, however, conservatively assumes that all of the ruthenium is associated with and is soluble in the HLLW.

The vitrification facility is designed for the continuous processing of 5-MTU equivalents of HLLW and ILLW per operating day at the volumetric flow rates shown in Table 5.2.8. A process flow diagram and material balance based on this processing capacity is shown in Figure 5.2.2 and Table 5.2.8, respectively. Normal operating conditions and flow rates are also indicated. The maximum nitric-acid concentration in the waste (7 M) was assumed so as to reflect conservatively high requirements for process chemical additions and off-gas capacity. Ammonia requirements are based on the assumption that all of the nitrates are decomposed to NO_2 .

5.2.2.2 Process Description

The steps for the SC/ICM process are described below.

Feed Preparation

High- and intermediate-level liquid wastes are batch-transferred as required to the surge tanks. Appropriate volumes of HLLW and ILLW (based on surge-tank sample analyses) are subsequently batch-transferred to a feed tank and thoroughly mixed with a small volume of bottoms recycle from the HAW concentrator. The blended feed is sampled, chemically adjusted as required, and pumped at a controlled rate to the spray calciner. In order to sustain continuous operation of the calciner, two blended feed tanks are utilized alternately for feed preparation and for feed transfer.

Chemical adjustment of the blended feed could include the addition of formic acid to improve the suppression of volatile ruthenium, the addition of nitric acid and/or caustic for acid adjustment, and the addition of inert nitrate solutions for attaining the desired chemical composition, density and/or other characteristics of the vitrified waste. Minimal chemical adjustment of the feed is anticipated.

Calcination/Vitrification

Calciner and In-Can Melter flowsheets/operations for the acid flowsheet is similar to that for the neutralized waste (Section 5.2.1.2) with minor exceptions. The blended feed is metered to the spray calciner nozzle at 300 L/h and may be internally mixed in the spray nozzle with formic acid for denitration (volatile ruthenium suppression). Glass-forming reagent (frit) is introduced at a controlled rate (about 2 parts frit to 1 part calcine by weight) into the calciner's conical transition section to mix with the calcine for vitrification at about 1050°C in the canister, which is contained in the ICM. At a predetermined set point on the canister load cell (approximately 80% to 90% of canister capacity), the diverter valve is actuated to divert the frit and calcine flow into a preheated empty canister in the alternate melter furnace to initiate the next filling cycle. The estimated chemical compositions of the calcine, frit and vitrified waste (glass) are presented in Tables 5.2.6 and 5.2.7.

The fill cycle is immediately followed by a controlled canister/melter cooldown cycle. This is accomplished by blowing air from the operating gallery through the heating chamber of the annular furnace. The hot air from the furnace is cooled by a heat exchanger, filtered, and discharged to the main stack. Heat from the waste canister is removed by radiant heat transfer to the cooler wall of the melter furnace. The purpose of this controlled cooldown cycle is three-fold: 1) to solidify the molten vitrified waste, 2) to minimize thermal stressing of the glass and canister, and 3) to prevent the rapid discharge of heat to the solidification cell. The canister fill time cycle is shown in Table 5.2.11; it assumes a canister fill rate that is somewhat higher than has been demonstrated but one that is felt to be achievable.

The cooled canister is removed from the furnace and seal-welded using a remotely operated, programmable welding unit; leak-tested employing a helium mass spectrometer; and decontaminated in a series of chemically treated high-pressure sprays and/or ultrasonic baths. The clean canisters are smear-tested for surface contamination and transferred to the canister-storage pool.

Off-Gas Treatment

Condensable and noncondensable off-gas products introduced or formed during calcination/vitrification of the liquid wastes are vented through internal sintered-metal filters to remove most of the entrained calcine particles. The hot off-gas products exiting the calciner are cooled in a quench tower to remove process heat and to condense water vapor and volatile fission products. The cooled, noncondensable POG exiting the quench tower is further treated for the removal of particulates and aerosols by the combined effects of a venturi scrubber/wet cyclone. A water-cooled condenser is provided for further dehumidification of the noncondensable stream and for condensation and removal of residual ruthenium vapors.

Condensed vapor droplets in the condenser off gas are then removed with a deentrainer. The humid, noncondensable off gas exiting the deentrainer is heated to above the dew point prior to entering the secondary off-gas

TABLE 5.2.11. Acid Waste Canister Fill Time Cycle

PROCESS PARAMETERS

Glass Generation Rate = 27.8 L/h = 0.98 ft³/h

Canister (17.25 in. ID x 10 ft high) = 12.96 ft³

Content (80% Equivalent Fill) - Allow 10% fill for fins

$$\text{Equivalent MTHM in Canister} = \frac{(12.96 \text{ ft}^3/\text{canister})}{(3.06 \text{ ft}^3/\text{MTHM})}$$

$$= 4.24 \text{ MTHM/canister.}$$

$$\text{Time to Fill Canister} = \left(\frac{12.96 \text{ ft}^3}{\text{canister}} \right) \bigg/ \left(\frac{0.98 \text{ ft}^3}{\text{h}} \right)$$

$$= 13.2 \text{ h/canister.}$$

$$\text{Heat Load in Canister} = \frac{(16.7 \text{ W/L})(12.96 \text{ ft}^3/\text{canister})}{(1000 \text{ W/kW})(0.0353 \text{ ft}^3/\text{L})}$$

$$= 6.13 \text{ kW/canister.}$$

CANISTER OPERATING TIME CYCLE

<u>Operations</u>	<u>Time, h</u>
Place in Melter	0.5
Make Remote Connection	0.25
Heat Empty Canister	3.5
Fill Empty Canister	13.25
Top and Allow Bubble Release	2.0
Cool to 700°C	2.5
Disconnect	0.25
Remove from Melter	0.5
<u>Time Lags</u>	<u>3.75</u>
Total Cycle	26.5

treatment system. Final cleanup of the noncondensable off gas may be provided by a primary roughing/HEPA filtration unit, silica-gel ruthenium absorber, silver-zeolite iodine adsorber, and a final HEPA filtration unit.

Oxides of nitrogen associated with the noncondensable effluent are reduced to innocuous nitrogen and water vapor by reacting with ammonia gas over a zeolite catalyst bed at about 400°C. The hot gases from the NO_x destructor are passed through heat exchangers to preheat the inlet gases and to cool the effluent before discharge via the main stack.

The primary source of process liquid is from the condensation of water vapor associated with the primary off gas from the calciner. Scrubber solution is pumped from the scrubber recycle tank to the quench tower and venturi scrubber. The scrubber solution and condensate from the primary off-gas treatment system are returned to the scrubber recycle tank. These moderately contaminated waste accumulations are decontaminated for release to the environment.

5.3 FACILITY DESCRIPTION

D. H. Siemens, D. N. Berger

This generic facility description provides a framework for conceptual equipment design and a basis for equipment adaption to a production plant. No attempt is made to perform a facility design, since an actual vitrification facility would have to be designed to accommodate the balance of the plant and its unique design and maintenance philosophy. This description points out facility requirements, utilities, services, and other features that must be considered in an actual plant design. Specific facility features and configurations that must be provided to make this reference SC/ICM equipment operable and maintainable are indicated in this and subsequent sections.

5.3.1 VITRIFICATION CELL LAYOUT AND DESCRIPTION

The High-Level Waste Vitrification Cell (HLWVC) and associated operating galleries and control room are assumed to be an integral part of a waste treatment facility that is designed and constructed to Safety Class 1 requirements. It is also assumed that all normal services, cell and process ventilation, decontamination facilities, etc. are available as part of the associated facility.

The cell arrangement for the SC/ICM equipment is shown in Figures 5.3.1 through 5.3.4. Inside dimensions of the cell are 16 ft x 24 ft x 51.5 ft high. Shielding is equivalent to approximately 5 ft of reinforced concrete. Higher-density materials (high-density concrete, metal castings, etc.) are used where thinner walls are required.

The cell floor and walls, up to the crane rails, are lined with 1/4-in.-thick stainless steel for ease of decontamination and decommissioning. The balance of the cell interior is coated with epoxy paint. A spray/fog type decontamination system is provided to aid in decontamination of the cell and the installed equipment exteriors. This system consists of fixed spray heads and portable wands that can be operated with the master-slave manipulators. Where desired, decontamination sprays may also be provided in the process

5.40

FIGURE 5.3.1. Vitrification Cell and Associated Equipment Layout

FIGURE 5.3.2. Vitrification Cell and Associated Equipment Elevation

FIGURE 5.3.3. Spray Calclner/In-Can Melter Elevation

FIGURE 5.3.4. Spray Calciner/In-Can Melter--Side View

equipment. The floor of the cell is sloped to a sump. The sump liquid level is constantly monitored and recorded. A remote steam jet is used to transfer accumulated liquid from the sump to a storage tank.

Shielded cubicles are provided for making service connections to the ICM furnaces, the SC filter blowback air control valves and the frit-addition system air lock. In addition to shielding, the cubicles also serve as gloved hoods to aid in contamination control when performing contact maintenance. The cubicles are operated at a slightly less negative pressure than the cell. The exhaust air from the cubicle is routed through an absolute filter and then into the cell. The main purpose of the filter is to prevent back flow of contamination into the cubicle in event that cell ventilation is lost.

Two 12-ton-capacity, remote-operated, DC-powered bridge cranes are available in the cell for installation of equipment and for handling waste canisters. The cranes are moved to an adjacent shielded area for decontamination and repair.

Oil-filled, lead-glass shielding windows are provided at all locations where routine viewing is required. Through-wall periscopes are provided at the weld station for undistorted viewing of the canister welds and at locations where nonroutine viewing is required.

Master-slave manipulators are provided at locations where remote hands-on operation or maintenance is required. Manipulator use is not required for frequent and routine operations.

Cell illumination is provided by through-wall, shielded light fixtures. The fixtures can be maintained from outside the cell.

When arranging the equipment, consideration was given to operations, remote maintenance, solid flow, system hydraulics and connecting piping routings.

The major operational considerations in arranging the equipment were 1) providing convenient flow paths for the canisters, 2) assuring adequate viewing, and 3) providing sufficient in-cell crane and manipulator coverage.

Industrial facilities may have operating/maintenance philosophies and functional requirements that differ from those indicated here. Thus, an industrial facility need factor these items into the facility design. This operational description only covers in a general way those facility features needed for the operation, maintenance and safety assessment of the SC/ICM.

Considerations for remote maintenance are similar to those for operations. Major equipment pieces are arranged for direct overhead crane access to allow remote removal and installation. To facilitate remote maintenance, lifting lugs for cell crane handling are provided on the process equipment. Alignment dowels and fixed mounting trunnions are utilized to assure exact positioning of the various equipment and component parts. Hanford-type piping and electrical connectors are used for most service and process connections. Hanford-type remote tank flanges are also used where appropriate. VEE flanges and other quick-connective devices are used where appropriate.

In addition to the SC and the two ICMs, capabilities for canister cooling, seal-welding, leak-checking, inspection and possibly preliminary decontamination are also provided in the cell.

A canal that connects to the filled-canister storage basin is located in one corner of the cell. A swing-arm transfer device is located in the canal for transferring filled canisters to basin storage. The canal is designed to provide a ventilation seal between the storage basin and the cell. Water flow in the canal is toward the cell. (The intake for the water cleanup system is also in this location.)

All process piping is sloped to assure free drainage either to or from its point of origin. This is done to assist in decontamination of the piping interior 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. Radiation bends are provided in the piping as required to maintain shielding integrity.

Removable jumpers are used to make all in-cell process and service connections to the processing equipment. High-level waste transfer lines are not embedded in the concrete, where they could not be maintained or where secondary containment could not be easily provided for. An attempt was made to optimize the equipment arrangement so that favorable jumper geometry could be used, so that the jumpers would not unduly restrict replacement of equipment in the cell, and so that most of the jumpers could be removed without removing adjacent jumpers.

The HLWVC is constructed primarily of concrete. The vitrification equipment is constructed of steel and other nonflammable materials. Thus, the fire potential is very low. However, to provide complete fire protection, the following provisions are made:

- The facility is protected with heat and smoke detectors and manually activated fire alarm boxes.
- The cell is protected by a smother-gas fire extinguishing system.
- The ventilation system is equipped with devices to mitigate the spread of a fire or its agents (heat, smoke, combustion products) through the system.

The cell spray/fog decontamination system could also be used to extinguish a fire if required.

The cell is maintained at a negative pressure in respect to the surrounding galleries. Sufficient air flow is maintained through the cell to keep the cell air exhaust temperature at less than 50°C when all processing equipment is operating. Both the cell inlet and outlet ventilation ducts are equipped with HEPA filters and protected by backflow dampers. The inlet filters are located outside the cell. The exhaust filters are located in the cell and can be replaced remotely. The exhaust filters and associated ducts are divided into banks with appropriate dampers to allow for filter replacement without adverse affect on the cell ventilation. The exhaust filters should be protected so that they will not be damaged by the environment and activities in the cell.

Failed equipment is partially decontaminated in place before removal. This is accomplished by internal flushing with installed sprays and/or flooding and with the cell spray/fog decontamination system. The failed equipment is then removed from the cell.

5.3.2 AUXILIARY SUPPORTING SYSTEMS

Numerous auxiliaries are required to support the vitrification cell and equipment. Although these requirements may vary with plant design, operating philosophy and geographic location most of them are generic and will be required.

5.3.2.1 Analytical Laboratory

Analysis of the waste feed and various effluent streams are required for process control. In addition, analytical verification analysis of the glass additive (frit) and other chemical additives may be required to assure product quality.

5.3.2.2 Aqueous Chemical Makeup Facilities

No aqueous chemical makeups are required for routine operation of the vitrification equipment. However, they are required for the SC feed adjustment and off-gas treatment systems and may be required for equipment decontamination. Space for storage of dry chemicals and tankage for acid and caustic will also be required.

5.3.2.3 Operating Galleries

Operating galleries are required adjacent to the vitrification cell walls where manipulators and viewing windows are used. The gallery design must consider contamination control, manipulator operation, and have a low radiation background.

5.3.2.4 Process Control Room

A process room is required to accommodate control instrumentation, alarms, etc., associated with the SC/ICM. In all probabilities this room, for the SC/ICM instrumentation, would be part of a central control room servicing the entire waste-processing facility.

5.3.2.5 Radiation Detection Systems

A radiation detection system, capable of detecting low-level beta-gamma activity, will be required in all areas adjacent to the process cells. The primary function of the system is to provide early warning to personnel of any harmful level of radiation that may occur. In addition, continuous air monitoring is required to detect airborne radioactive contamination. Criticality monitors for the vitrification galleries could be an overall plant requirement.

5.3.2.6 Effluent Monitoring

All effluents, including cooling water, will require continuous monitoring for radioactivity prior to movement from the cell or release to the environment.

5.3.2.7 Cell Crane Maintenance

A shielded room, adjacent to the vitrification cell, will be required for maintaining the cell crane. The room should contain facilities for remote decontamination of both the crane and the room. After decontamination, the crane could be contact-maintained.

5.3.2.8 Manipulator Repair Station

A manipulator repair station is required close to the vitrification cell. Master-slave manipulators are provided in the vitrification cell at locations where hands-on remote work is required. Even rugged-duty manipulators are comparatively fragile and as a consequence may require frequent removal from the cell wall for repair.

The repair station should include facilities for decontaminating the manipulator and provisions for "hot side/cold side" repair.

5.3.2.9 Control Zone Change Rooms

Normal access to the galleries around the process cell should be through change rooms. The change rooms should be equipped with necessary personnel survey equipment and any protective clothing that may be required for working in a radiation zone.

5.3.2.10 Cell Ventilation

The vitrification cell should be operated at a negative pressure with respect to the surrounding galleries and the atmosphere. A sufficient air flow should be maintained through the cell to maintain the cell temperature below 50°C. The cell ventilation should be designed as a "pull-through" system to prevent cell pressurization due to a failed exhaust blower. Primary HEPA filtration is provided on the inlet and outlet cell-ventilation ducts. Additional filtration and monitoring should be provided as required by overall plant design.

5.3.2.11 Spray Calciner Feed and Off-Gas Treatment Systems

These systems are described in Section 4.0, Process Technology.

5.3.2.12 Canister Closure Welding, Leak Test/Non-Destructive Testing and Decontamination

After the canisters have been filled with glass in the ICM furnace, it will be necessary to seal them with a welded closure. Space has been provided in the vitrification cell to perform this function. Space is also provided for leak-testing and/or other nondestructive tests that may be required and for decontamination of the canisters. These steps would be performed before transferring the canisters to on-site storage.

5.3.2.13 Canister Storage

It is assumed that it will be necessary to store the canisters on-site for a period of time before shipping them to a federal repository. To accommodate this requirement, a wet-storage basin is shown adjacent to the vitrification cell. Regulations may require that the canisters be overpacked before being shipped to the repository. If so, facilities would be required to perform the overpack function.

5.3.2.14 Failed Equipment, Dry Waste

It is recommended that a cell or area be provided in which failed equipment can either be decontaminated for contact repair, repaired remotely, or remotely dismantled and packaged for disposal. This cell could also be used for packaging dry waste from the processing cells for disposal.

5.3.2.15 Vitrification Cell Integration into Plant Structure

The vitrification cell is connected to an airlock through which the vitrification equipment is brought into the cell. The cell must also be adjacent to an operating gallery on two sides to provide master-slave manipulator access to the calciner connecting sections, the tops of the ICMs and canister-sealing equipment. The cell must also provide access to a storage pool to dispatch canisters after filling and sealing. The location of the vitrification cell within the entire processing facility is a matter of overall economy and efficiency. This is also true of various cell-monitoring and control equipment and instrumentation when the decision is made to locate it either locally or in the control room.

5.3.2.16 Special Utility and Service Requirements

The vitrification equipment requires some special services in addition to the normal services required by a standard power plant. This process requires a unique power system for the SC/ICM system. The cell requires a distinctive ventilation system. The process requires a unique frit-addition system as well as specialized instrumentation for process control. A specialized ICM zone-cooling system may be used for canister cooling in addition to an inert gas-blanketing system in the melter to inhibit canister spalling. The specialized services and utilities will be provided locally as part of the vitrification facility. The following normal services will be provided by the primary facility with which the vitrification facility is associated: process, sanitary, and raw water; electricity; steam; instrument air; vessel ventilation air and treatment; plant emergency services.

5.4 SPRAY CALCINER/IN-CAN MELTER SYSTEM DESIGN

D. N. Berger

5.4.1. CONCEPTUAL DESIGN

This section provides a SC/ICM system conceptual design utilizing concepts developed at PNL and in the nuclear industry. The conceptual design demonstrates the potential application of this information for industrial use and documents PNL equipment-development technology. Design concepts and suggestions made in the conceptual design section provide a base technology for plant application. This technology may have to be modified for conformance to an individual plant operating/maintenance philosophy, design practices and regulatory requirements.

5.4.2 GENERAL DESIGN PHILOSOPHY

The SC/ICM system described here is designed for remote operations and maintenance in a canyon-type operation with the following particular features.

- Retractable and removable wall plugs provide service connections to some remotely installed/replaceable equipment located within the hot cell.
- Manipulator use is required for some service and maintenance operations at the vitrification and welding station.
- Cell operations are monitored directly through windows with little or no aid from TV cameras.
- Processes are controlled to the maximum extent from a central control room.

A general concern in the conceptual design of this vitrification system is the use of manipulators for equipment operations and maintenance. The majority of the equipment in the conceptual vitrification system is designed to be installed, operated and maintained in a canyon-type operation--i.e., the equipment would be handled with an in-cell crane and installed/removed with impact wrenches suspended from the in-cell crane. There are a few non-routine operations that require manipulators. Anticipated manipulator operations are indicated below:

- Guide the impact wrench for engagement with the VEE clamp bolts to install the diverter and the connecting sections (Section 5.4.4).
- Make up the thermocouple connection at the liner (Section 5.4.5).
- Install and connect the three load cells that weigh the ICM furnace (Section 5.4.5).
- Make up the air connections associated with the connecting section (Section 5.4.4), and
- Make intricate adjustments on the remote welder at the welding station.

For the manipulator operations, the Central Research System 50 manipulator or the equivalent appears appropriate. This sealed manipulator has a 50-lb capacity and does not require the use of boots within the cell. If maintenance is required on the slave end it can be disconnected at the cell wall with a cell crane, decontaminated, and removed from the cell for further decontamination and repair.

5.4.3 SPRAY CALCINER

The spray calciner shown in Figure 5.4.1 converts the liquid feed to a solid, provides containment for the processed materials, and provides for filtration of the POG.

The spray calciner material and heat balance for the reference acidic HLLW flowsheet is shown in Figure 5.4.2. The following bases and assumptions are used to develop the material balance:

- liquid feed and atomizing air temperatures are 50° and 25°C, respectively;
- outlet temperature for off gas and calcine is 250°C;
- enthalpy changes in chemical decompositions are assumed to be negligible, except for HNO_3 ;
- calcine heat capacity is assumed to be 0.20 BTU/lb-°F (representative of most oxides);

FIGURE 5.4.1. Spray Calciner Arrangement

- frit is assumed to collect a negligible amount of heat in the calciner;
- half of the HNO_3 is assumed to go to NO and half to NO_2 .

Figure 5.4.3 shows the instrumentation required for the SC. There are no internal thermocouples in the SC spray chamber. The thermocouples shown in the heating section area are part of the heating section. Instrumentation (except for sensing elements) is located outside of the cell to avoid damage

	1	2	3	4	5	6	7	8	9	10
NEUTRALIZED WASTE										
Kg/h	325	65.6	-	24.9	390	-	1.90	21.9	39.8	39.8
KW	0*	0*	60	1.2	230	291	0*	0*	0	0
°C	50	25		250	250		25	25	25	100
ACID WASTE										
Kg/h	373	65.6	-	27.8	432.8	-	1.90	21.9	55.7	55.7
KW	0*	0*	60	1.3	228	289	0*	0*	0	0
°C	50	25		250	250		25	25	25	100

NOTES

ASSUMPTIONS LISTED IN TEXT

* INLET FEED & AIR CONDITIONS ARE USED AS A ZERO REFERENCE

FIGURE 5.4.2. Spray Calciner Material and Heat Balance

FIGURE 5.4.3. Spray Calclner Instrument and Engineering Diagram

and the cell atmosphere, and to facilitate operations/maintenance. Thermocouples are located within the cell but have the remote cannon or equivalent connections shown in Figure 5.4.4.

Figure 5.4.5 shows the power control circuit for the 3-phase, 480-V Kanthal IA resistance-heating elements. There are four zones with 150 kW per zone. Normal operating temperatures at the spray chamber wall is 700° to 800°C. There are two thermocouples per zone; one of them must be on line to provide feedback for the controllers. The other thermocouple may be used to independently record the temperature and act as an installed spare for power control.

The SC arrangement (Figure 5.4.1) consists of numerous components that are discussed in the following areas: functions, materials, design features, installation, and operation/maintenance. The calciner components are listed below.

- support frame
- spray chamber, cone and filter chamber
- heater assembly
- feed nozzle
- vibrator
- filters.

5.4.3.1 Spray Calciner Support Arrangement

The SC support frame is constructed of 304L SS channel and angled to meet normal and accident structural loads. The support frame, shown in Figures 5.4.6 and 5.4.7, is remotely installed and replaceable. The heavy-duty structural support frame dictates the 7-ft width of the vitrification cell access door. The frame is brought in with a remotely removable adaptor and positioned over the dowels on its four support pads. The trunnion pins are located above the wall trunnions. When all the pins are engaged the frame is lowered down over the studs, which raises the nuts up out of the nut cups. The nuts, now resting on top of the studs, are engaged with an impact wrench suspended from a crane. The upper 3-in.-dia pins located within the trunnion blocks provide lateral support and seismic stability.

FIGURE 5.4.4. Spray Calciner Heater Assembly

FIGURE 5.4.5. Spray Calciner Power and Control Engineering Diagram

FIGURE 5.4.6. Spray Calciner Support Arrangement

FIGURE 5.4.7. Spray Calciner Support Frame

5.4.3.2 Spray Calciner Chamber, Cone and Filter Chamber

This unit performs and contains the spray calcining process. The entire spray calciner assembly shown in Figure 5.4.8 is one unit. The three segments, SC chamber, cone and filter chamber are all welded to the 1-1/4-in.-thick support plate, which in turn is bolted to the support frame as shown in Figure 5.4.6 when assembled.

The SC chamber dimensions are 3 ft in ID by 10-1/2 ft long with a 3/8-in.-thick wall. These dimensions are based on a similar-dimension SC chamber at PNL that has satisfactorily operated at greater than 300 L/h. It is expected that a chamber this size would perform satisfactorily at up to 400 L/h. Inconel-601 was selected for use as the SC chamber material over the 310 SS, with which PNL has had experience, due to expected improved high-temperature strength and oxidation-resistance properties. A 3/8-in.-thick chamber of Inconel-601 should prevent chamber warpage or failure under operating conditions for several years, but may require additional thickness to accommodate corrosion and other non-normal conditions. Other materials such as nickel alloys and perhaps thick stainless steels would perform adequately. In the full-scale SC there has been deformation of approximately 1-1/2 in. of the 310 SS, 1/4-in.-thick wall, yet there has been no deformation of the 3/8-in.-thick wall of the pilot-scale SC, which has encountered a much longer service life. The cone section, filter chamber and flange are made out of 304L SS because of its availability, low cost and corrosion resistance.

The inside of these segments should have at least a 63 γ finish with no walls, etc. less than a 60 $^{\circ}$ slope from horizontal to avoid calcine buildup. The vertical corners of the cone section should not be square because this reduces the overall vertical slope. The corners should be rounded to the extent possible, which increases the slope and decreases the potential for powder buildup.

A thermocouple on the outside of the cone section can be used for early detection of powder buildup. Preliminary studies indicate a more sensitive powder-buildup detection system would be a gamma scanner.

FIGURE 5.4.8. Spray Calciner Assembly

The vibrator contact plate centroid must line up with the vibrator arm. This plate is integral with the calciner wall and tapers from the thickest point of 3/4 in., where the vibrator arm comes in contact, down to the 3/8-in. wall thickness--a distance of 10 in.

Two 3-in. penetrations or ports are required in the calciner chamber support plate--one for the frit feed-addition system and one for the pressure-relief port. These penetrations must be located so as not to interfere with the installation of the heating sections nor the insulation around the filter chamber.

With the calcine chamber walls reaching temperatures of about 800°C, 2 in. of vertical-chamber thermal expansion is anticipated. Thus, there should be a 2-1/2-in. clearance above the calcine chamber and the bottom of the cover. A flexible feed jumper is therefore required. The entire SC assembly is bolted down to the support frame in six places with 1-1/4-in.-dia bolts.

The cone section terminates with a 4 in. conoseal flat-face flange 59-1/2 in. below the bottom of the support plate.

The filter chamber is made out of 1/4-in.-thick plate and is insulated with 2 in. of a low-thermal-conductivity blanket, which in turn is enclosed in a 1/8-in.-thick SS shell and seal-welded, except for a 1/4-in.-dia weep hole at the bottom of the filter chamber just above the support plate for moisture drainage within the jacket. This insulation maintains this section of the calciner at a sufficiently high temperature to prevent moisture condensation that would result in filter pluggage.

The cone section also has 2 in. of insulation and is totally enclosed in an 11-gage SS sheetmetal. The insulation stops 1-1/2 in. above the conoseal flange face to allow room for the conoseal clamp. There are also a couple of 0.25-in.-dia weep holes at the bottom of the insulation in the 11-gage SS sheet. This insulation reduces cell cooling requirements, prevents substantial heat loss that would have to be made up by the furnace and melter, and helps remove the condensation potential that would result in calcine cake buildup within the cone.

5.4.3.3 Spray Calciner Heater Assembly

The spray calciner heater consists of four individual zones. Each zone is capable of a 150-kW output. Each zone is individually installed with a heater section handling device, as shown in Figure 5.4.9. Each section is lowered over the calciner chamber with the use of a wall guide. This guide controls the heater sections both laterally and radially to protect the exposed heater elements within the sections. The four units stack on top of each other. This stackup and handling device determines the height of the upper crane.

Final alignment of the first heating section is made in the last 3 in., (while it is being lowered) by an additional guide plate on the SC support frame. The top of each heating section also has a guide plate, which will guide the subsequent sections into precise position. Then a cover (Figure 5.4.10) is installed over all four units. The cover also makes use of the wall guide for the installation and stability, but the cover has two lateral braces which have 2-in.-dia pins on the underside that engage in two wall trunnions for seismic bracing. The cover engages with guides on the unit below to provide stability to the assembly. Without this seismic bracing, a chamber support plate several inches thick would be necessary to prevent calciner damage from vibration in case of a design-basis earthquake. Each resistance-heater zone consists of a shell that is made out of 1/4-in.-thick, 300-series stainless steel. The shell has stiffeners on the outside in four locations. The shell comes part way in on the top and bottom of each zone to house the insulation and heating elements.

The thermocouple and electrical connector is a modified Cannon Connector that is made to receive a bayonet-type plug which is part of a retractable wall plug (Figure 5.4.4). This connector was recommended for use by a Bechtel study (Bechtel Inc. 1977a), but it has not been used by PNL. An alternate connector is a Hanford electrical connector (Figure 5.4.11), which has experienced considerable related service. Additional review and (perhaps) development is needed to determine the most suitable connector for power and thermocouple use.

FIGURE 5.4.9. Spray Calciner Heater Installation or Removal

FIGURE 5.4.10. Spray Calciner Heater Cover

FIGURE 5.4.11. Typical Purex Thermocouple and Electrical Jumper

If the connecting pins on electrical and thermocouple connectors were gold-plated, good contact could be assured in the adverse conditions of the vitrification cells.

PNL has used Kanthal A1 for resistance-heating elements for many years with favorable experience and still has some in operation after many years of cycling. There have been several occasions when the heating wire was warped out of its position within the firebrick, but this was felt to be a heater design problem.

The heater section handling tool is bolted to a heating section for installation or removal. Two guide pins (one taller than the other) guide the handling tool over two studs. The handling tool contains a nut cup and a nut so that when the handling tool is all the way down on the guide pin and stud, the nut in the cup has come to rest on the top of the stud that is partially thread-released at the top. At this point an impact wrench engages the nuts on the stud, and the section is ready for installation or removal. The handling tool is free-standing, so the crane can be used to position the impact wrench.

Visibility of this operation is accomplished by the use of the viewing windows on either side of the SC/ICM. All four heating sections are the same except for the holes in one section required for the vibrator arm that comes in contact with the calciner chamber.

5.4.3.4 Spray Calciner Feed Nozzle

The spray nozzle recommended for the 300-L/h flowsheets is shown in Figures 5.4.12 and 5.4.13. The tip of the spray nozzle should extend 2 in. below the inside wall of the spray calciner to achieve the desired air turbulence above the nozzle to prevent calcine buildup around the nozzle. Also, the metal fittings of the assembled nozzle should be tack-welded together to prevent disassembly that could be caused by the vibrators.

Spraying System Company's Setup Number 82 or the equivalent spray nozzle is appropriate for the reference flowsheets. Setup Number 82 has been

FIGURE 5.4.12. Spray Calciner Feed Nozzle

If the connecting pins on electrical and thermocouple connectors were gold-plated, good contact could be assured in the adverse conditions of the vitrification cells.

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FIGURE 5.4.12. Spray Calciner Feed Nozzle

FIGURE 5.4.13. Spray Nozzle Detail

modified per Figure 5.4.13. The modifications include turning down the hex on the fluid connection #6251000 to 0.010 in. under the ID of the 1-1/2-in. OD tubing for welding. A ceramic insert is fabricated to take the place of the stainless steel insert. The inside dimensions are the same, except that a 0.030-in. clearance is required between the inside of the ceramic insert and the outside diameter of the fluid connection (Figure 5.4.13); since the metal will expand more than the ceramic, a new 304L SS retainer cap with a wall thickness of 0.095 in. is required to contain the ceramic insert. Threads on the retainer cap are to match the fluid cap.

5.4.3.5 Vibrator

Vibrating the calciner chamber becomes necessary when calcine begins to build up on the walls. When the calciner is operating properly, the vibrators are not required. But as a precaution the vibrators are operated in a pre-established automatic mode.

The best location for two vibrators would be 180° apart, half way up the calciner chamber, but the vibrators are located 140° apart for the following reasons: 1) if the vibrators were located 180° apart, access to the ICM below with the crane would be blocked; and 2) support mechanisms from the wall would have to be much larger. The support cannot come from the heater sections because the vibration would cause cracking of the furnace insulation in a short time. The heating sections should not contact the vibrator arm, yet the hole provided should be minimal to reduce heat loss. Also, external adjusting of the vibrator arm can be accomplished more easily through a series of U-joints (Figure 5.4.14). The vibrators are adjusted until the highest noise level is attained between the vibrator arm and the calciner chamber wall. At this point the vibrators are locked in position. Adjustment in the cell with an impact wrench is difficult.

The vibrator used for this design is a Cleveland[®] Model number 1300 AC Vibramight or the equivalent. This vibrator has been used extensively in radioactive and in nonradioactive service and its service has been reliable.

The vibrator and its support is one pre-assembled unit that is retro-fitted in the full-scale mock-up before installation. The unit is placed in the respective trunnions provided for the vibrator support. At this point a wall plug is still further engaged until the gears on the locking hand-crank shaft engage with the gears on the vibrator adjustment shaft. Adjustment is made through the use of two universal joints; this adjustment allows movement of the slide tray, which is bolted/welded to the vibrator.

A flexible service jumper is installed to provide air at 40 psig to operate the vibrator in an automatic mode. The proper impact position is

[®]Cleveland Vibrator Co., 2828 Clinton Ave., Cleveland, Ohio

FIGURE 5.4.14. Spray Calciner Vibrator Plan and Partial Elevation

determined by listening via a cell microphone and adjusting until the loudest impact noise is obtained. The external hand wheel is then locked to maintain the desired position of the vibrator shaft for operation. This vibrator adjustment concept appears attractive but has not been tested at PNL.

The vibrator operation is controlled by an automatic timer and by controls attached to the air supply. The cycle use varies substantially, depending on the tendency of the feed to stick to the calciner walls. For acid feed, each vibrator would typically operate for two seconds every hour. For caustic waste, a characteristic vibration cycle might be two seconds every 30 min for each vibrator, 15 min out of phase.

5.4.3.6 Filters

During calcination, the referenced system should be maintained at a negative pressure of 8 to 12 in. of H_2O . This is maintained through the use of an air-tight system and sintered Inconel-690 filters as shown in Figure 5.4.15. Inconel-690 was selected over the 316 SS used at PNL as the material of filter construction because it is expected that the Inconel would be more resistant to corrosion of some species such as Cl, F, and SO_x and would be more resistant to high-temperature oxidation that may be inadvertently encountered in calciner operation.

During calciner operation, a layer of powder filtered from the off gas builds on the filter surface until either the calciner has insufficient vacuum or the desired filter pressure drop of 15 to 20 in. is exceeded. Before this occurs, a 0.25-s pulse of high-pressure air is directed to counter the off-gas stream through a venturi and into the filters as shown in Figure 5.4.16. To prevent pressurization of the calciner during blow-back, only about one-twelfth of the 64 filters are cleaned at one time on equal intervals. Static pressures of 40 psig to 100 psig have been successfully used.

Thermocouples in the filter area are required to monitor the temperature during periods of shutdown when it is possible for the filters to heat up and cause some low-melting powder to stick. Thermocouples are also monitored to ensure the gasses exiting through the filters are well above the dewpoint of each component, since condensation can blind the filters.

The sintered filters are very fragile and require special hardware to protect them--especially during installation in the remote facility. A guard all the way around the filters is provided and cross-bracing on the bottoms of

FIGURE 5.4.15. Spray Calciner Filter Arrangement

FIGURE 5.4.16. Filter Detail

all the filters (see Figure 5.4.15, Section A-A) is also provided for their longevity, should vibration or shock become unavoidable. Some of the filter parameters for this referenced flowsheet can be found in Figure 5.4.16.

The filter life is not known at this time. Eventually the filters will plug and need to be repeatedly blown back while the calciner is at a minimum negative pressure and/or flushed with water or nitric acid to extend the filter life temporarily as discussed in Section 4.2.3. Eventual remote replacement will be required. The filters may be susceptible to an increased corrosion rate because of the large surface area.

5.4.4 CONNECTING SECTION

There are two connecting sections attached to the bottom of the diverter, as shown in Figures 5.4.17 and 5.4.18, so that a filled canister in one ICM can be cooled and removed while the other ICM is vitrifying waste.

The left side of Figure 5.4.18 shows the cone valve, spout and weight in the retracted position--pivoted to one side for canister installation or removal. Air motors operated from the cell exterior raise and swing the connecting sections back and forth for canister access.

The right side of Figure 5.4.18 shows the connecting section in the lowered position ready to receive the calcine-frit mixture from the calciner.

The primary functions of these connecting sections are to transfer the calcine and frit from the calciner to the canister below in the ICMs and vent off gas from the canisters to the calciner. The design is complicated by the following requirements:

- the system diverts the calcine-frit mixture from one connecting section to the other;
- each connecting section below the diverter swings to one side of the ICM for canister removal;
- each connection section flexes as the bottom-supported canister expands vertically when heated to operating temperature;

FIGURE 5.4.17. Connecting Section Arrangement

FIGURE 5.4.18. Connecting Section Operating Plan and Elevations

- the spout extends down into the ICM furnace and makes a seal with the canister and need be capable of being retracted above the ICM so the assembly can swing out of the way during canister exchange;
- the cone, retracted to seal the spout during side-swinging maneuvers, extends down into the canister to deflect the frit-feed mixture and then retracts back up to seal the spout upon canister exchange;
- the entire connecting section should have minimal air in-leakage so that a vacuum can be maintained on the canister and spray calciner;
- each connecting section need be remotely replaceable and operated;
- a slope of 60° should be maintained to prevent the calcine-frit mixture from plugging its delivery tube;
- the entire connecting section should be capable of accurate alignment with the canister top to incorporate the seal;
- the connecting section should not interfere with the ICM weight-monitoring system, if used.

This connecting section has been designed and constructed at PNL to determine its applicability to a remotely operated industrial facility; however, the equipment had not been adequately tested and developed to ascertain its application.

The following functions and/or equipment assemblies will be discussed in terms of: requirements, materials, design features, installation, and operation and maintenance:

- diverter
- swivel joints
- cone valve
- containment
- alignment
- installation, operation and maintenance.

5.4.4.1 Diverter

Since there is one SC and two ICMs, a diverter is needed to change the path of the calcine-frit mixture from one connecting section to another, depending on which ICM is receiving feed.

The diverter is a funnel, enclosed in a housing, which is motivated by an external air cylinder operated from the operating gallery.

The shaft on the diverter should maintain a tight air seal. Using a packing gland is one approach. A good packing gland material is Grafoil,[®] due to its ability to withstand radiation and maintain a seal.

The air cylinder seals should not contain any organic material that will deteriorate in a high radiation field, and a dry lubricant is required. An alternative approach is to make the air cylinder easily replaceable by remote means.

The diverter is a separate, remotely replaceable unit utilizing the remote features of Nucoseal Vee flanges, gaskets and clamps.

5.4.4.2 Swivel Joint

A swivel joint just below the diverter and a set of bearings on the support arm in line with the swivel joint allow the connecting section to swing to one side of the canister, provided that the cone valve has raised the spout up above the surface of the ICM. The entire raised connecting section is driven to one side or the other of the canister by an externally operated air motor through the use of worm gears.

5.4.4.3 Cone Valve

The cone, when raised, acts as a valve and seals off the end of the spout, which prevents calcine from falling out of the connecting section when the spout is up during canister exchange. A small amount of frit/calcine sticks to the bottom of the cone valve. The cone, when raised up against the

[®] Union Carbide Corporation, Carbon Products Division, 270 Park Avenue, New York, New York

end of the spout, also helps to maintain a vacuum required on the entire system. The diverter does not seal off the other delivery tube when switching from side to side.

The cone valve deflects the calcine-frit mixture away from the center of the canister, where the mixture could build up on the fins and plug up the canister opening.

The cone valve must be cooled to 300°C to prevent the calcine-frit mixture from sticking to it. To monitor the temperatures of the cone valve, thermocouples are required in duplicate--one as a back up to the other.

5.4.4.4 Containment

Metal bellows are installed where flexing joints are required to contain the calcine-frit mixture. Sliding seals make use of Grafoil material for gaskets. Metal-to-metal surfaces make use of metal E- or C-rings to reduce air in-leakage and to increase product containment.

5.4.4.5 Alignment

Accurate alignment of the vertical connecting section and the horizontal surface of the canister is made possible through the use of a gimbal where the vertical portion of the connecting section is supported. This upper flexibility allows the spout to seal against the metal E-ring that is seated in the canister opening. The weighted spout provides the force necessary to make the seal. Proper alignment also prevents the binding that interferes with the weighing.

5.4.4.6 Installation, Operation and Maintenance

Figure 5.4.19 shows the connecting section in the removable position. After the vee-flange coupling is fully opened and the bellows retracted, the cell crane raises the unit 1 in., at which time the connecting section disconnects from the support bracket shown in the middle of the figure. Now the unit can be horizontally moved away and be repaired or replaced. The vee flange at the bottom of the diverter is removed with a crane-supported impact wrench positioned by a manipulator, since the flange clamp is located under the SC.

FIGURE 5.4.19. Connecting Section Installation and Removal

When the flange is free it will drop down (air to flange clamp air cylinders has been shut off), compressing the bellows (provided there is no appreciable calcine-frit mixture buildup within the bellows). One inch of clearance is required between the top of the vee-flange clamp and the bottom of the upper vee-flange because the entire unit is then raised 1 in. with the crane and horizontally moved out of the sockets in the support bracket.

The pivot arm support bracket shown in Figure 5.4.17 is remotely replaceable, as it only rests in a tight-tolerance square hole in the building structure. It has two roller-bearing sockets for the pivot arm to engage with for each connecting section. An air motor drives the worm gear, which swings the pivot arm into the desired position.

Figure 5.4.20 shows the instrumentation diagram. Connections to the air cylinders, air motors and thermocouples are made up with manipulators.

Jumpers to the air motor on the vertical portion of the connecting section cannot be hard-piped, so a flexible jumper made of neoprene with Hansen quick-disconnects are used. These jumpers must be periodically replaced because of eventual radiation damage to the neoprene. Stainless steel flex jumpers have been tested in hot cells, and they fatigue and crack sooner or later. The life of these is, of course, dependent upon the amount of flexing each is required to do and upon its internal pressure. Double-braided neoprene hoses are preferred by many in various applications in the PNL hot cells.

Routine operations are performed by installed air motors such as those in impact wrenches. These motors are controlled from the operating gallery.

5.4.5 IN-CAN MELTER

The ICM produces the heat required to melt a calcine-frit mixture (Figure 5.4.21). Vitrification is performed in a canister that is up to 60 cm in dia by 300 cm long (24 in. by 10 ft) and which is contained in the liner of the melter furnace. Once the calcine-frit mixture in a zone has melted at 1050°C, heating in that zone is terminated and cooling air may be blown to the

FIGURE 5.4.20. Connecting Section Instrument and Engineering Flow Diagram

FIGURE 5.4.21. In-Can Melter Arrangement

zone on the outer liner wall until the canister wall has cooled down to about 700°C. This cooling may be done in five segments because of the five separately controlled heating/cooling zones of the melter. The cooling air is cooled after it leaves the melter by circulating it through a cooler before having it enter the cell atmosphere. After the canister is cooled to 700°C, it is then removed to the cooling station, where the melter cover is removed and the canister lid is twisted into position; the canister, after cooling to an appropriate temperature, is moved to the welding station and the lid is seal-welded to the canister.

Figure 5.4.22 shows the material balance for both of the references flowsheets.

5.4.5.1 Design Requirements

Following is a list of ten design requirements imposed upon the ICM:

1. Heat the canister to an operating temperature of 1050°C (maximum capability to be 1200°C).
2. Establish individual-zone temperature control--both heating and cooling--and limit heat-exchange interactions between zones.
3. Have cover interface with connecting section and be integral with canister for handling and minimizing heat loss during vitrification.
4. Provide bottom support for canister during vitrification.
5. Monitor temperatures of each furnace zone and canister wall temperatures in each zone.
6. Collect and dispose of spall.
7. Provide backup containment to a canister.
8. Weigh the amount of calcine and frit in the canister during vitrification.
9. Provide structural support.
10. Utilize remotely replaceable components and remote connections.

The following components of the ICM will be discussed in terms of special features, materials, functions, installation, and operations/maintenance:

SPALL 2.5 TO 3kg / 24-INCH-DIA CANISTER
1.8 TO 2.2kg / 18-INCH-DIA CANISTER

NEUTRALIZED WASTE	
IN	OUT
26.92 kg/h calcine	2.02 kg/h offgas
39.8 kg/h frit	64.7 kg/h vitrified waste
<hr/> 66.72 kg/h total	<hr/> 66.72 kg/h total

ACID WASTE	
IN	OUT
31.8 kg/h calcine	4.02 kg/h offgas
55.7 kg/h frit	83.5 kg/h glass
<hr/> 87.5 kg/h total	<hr/> 87.5 kg/h total

FIGURE 5.4.22. In-Can Melter Material Balance

- furnace
- heat exchanger
- canister
- liner
- structural support
- load cells
- service connections
- frit feed system.

5.4.5.2 Furnace

A calcine-frit mixture flows into the canister contained in the liner of the five-zone melter furnace. This mixture is melted into a glass at about 1050°C. Once a zone is filled and the temperature brought up to 1050°C, heating to that zone is terminated and it is cooled.

The optimum heating length for a 10-ft-long canister is 10 ft, 10 in. To assure complete vitrification in both the top and bottom of the canister, there should be 6 in. of the heating zone above the canister top and 4 in. of the heating zone below the bottom of the canister. This establishes a melter furnace with five zones at 26 in. per zone. Twenty-six inches is about the maximum zone length to be controlled by heating and cooling to reduce crystalline phase-settling and control temperatures from waste self-heating.

Each zone is rated at 150 kW, which is more than twice the required power. Hanford connectors and jumpers are indicated to transmit power to the ICM furnace sections. However, additional consideration need be given as to what type of connector to use, since it is felt that the Hanford connector's demonstrated performance is marginal for the planned load application. Refer to Figure 5.4.23 for the power and control diagram. The ICM instrument and engineering diagram is shown in Figure 5.4.24.

The cover is an important piece of equipment to the overall operation. The cover is twisted into an empty canister on the canister storage rack and both are lifted and inserted into the melter. The cover must then allow the spout of the connecting section to pass through and engage with the seal at

FIGURE 5.4.23. In-Can Melter Power and Control Engineering Diagram

FIGURE 5.4.24. In-Can Melter Instrument and Engineering Diagram

the canister opening. The cover must allow the liner to expand as it is heated, yet maintain a seal. Then, as the canister comes up to process temperature the cover will be lifted as the canister expands, yet a seal must be maintained between the cover and furnace to minimize heat loss.

The space between a 24-in.-dia canister and the liner is recommended to be 2 in., and the distance from the liner to the resistance-heated Kanthal A-1 wound heating elements is also 2 in.

Figure 5.4.25 shows the heater section being lowered inside of the furnace support frame, which is suspended by a trunnion and two support columns.

5.4.5.3 Heat Exchanger

It is necessary to cool the filled canisters down to 700°C in about 2.5 h so that it can be removed from the melter furnace. A stainless steel canister may distort if handled at temperatures above this point. Cooling is also necessary on an individual zone basis to control crystalline phase-settling and waste that is self-heating.

Cooling individual zones requires the use of baffles between each zone to restrict the flow of air up past the zone above that is still being heated to 1050°C. A complete seal between zones would be difficult to obtain, since the liner is removable.

Air is introduced at the bottom of each zone through a circumferential exterior ring that has many horizontal tubes extending towards the canister, which allows air to be exhausted directly on the liner.

The heated air is allowed to leave the zone at the top through larger horizontal tubes that connect to a circumferential ring, which in turn connects to the cooler. The down-draft cooler has dividers to prevent the connection of other zones and possible inadvertent cooling. The cooling tubes on the bottom of each zone are part of the baffle for the zone above and are integrated with the tubes. The baffles and tubes are made out of Inconel-601 or other nickel alloys that exhibit high-temperature oxidation resistance.

FIGURE 5.4.25. Heater Section Installation

5.4.5.4 Canisters

Two different-sized canisters are used for the referenced flowsheets. An 18-in.-dia by 10-ft-long canister is used for the acid waste flowsheet and a 24-in.-dia by 10-ft-long canister is used for the neutralized waste flowsheet, as shown in Figure 5.4.26.

For general handling, the canister is suspended by the twist-lock cover-canister connection, but during vitrification the canister is bottom-supported. During canister installation and removal, the ICM furnace cover is installed and used for canister movement. The filled stainless steel canister is handled by its top only after the thermocouples on the liner indicates the safe handling temperature of 700°C.

A stainless steel canister will oxidize significantly at the temperatures required to vitrify waste. Therefore, a spall collector on the bottom of the liner need be provided to collect spall for a removal and disposal as necessary. This spall container makes contact with the liner side wall only when it is in its lowest position. This collector must also support the canister during vitrification. If stainless steel canisters are not allowed to cool below 700°C in the furnace after oxidizing at 1050°C, the spall in the furnace should be minimized, since it does not occur until about 500°C.

To reduce the amount of spalling, a cover gas could be introduced into the liner through the ICM cover. On occasion, PNL experimented with argon at 5 ft³/min. It would be possible to use a cover gas other than argon, such as nitrogen, although this could possibly cause nitriding of the stainless steel. PNL used argon at 5 ft³/min and did not attempt to reduce this rate and check the effects on the canister. If a canister material other than stainless steel were used, such as Inconel, spalling would not be a problem, but the canister price would increase. Removing the liner and dumping the spall should be avoided if economically feasible. Cell activity should always be kept at a minimum. Stainless steel canister pretreatment should be considered. A result of this would be to provide a clean surface upon which to weld the canister lid, which eliminates a preparation step for welding.

FIGURE 5.4.26. Canisters

The canister must be supported with at least 75% of the canister bottom in contact with its support to prevent warpage during filling. The spall container is periodically removed by lowering a shaft (suspended by a crane) down through a hole in the center of the spall container. Engagement is made when a manipulator releases a rod in the center of the shaft that forces the ball detents out, securing the container.

Releasing the spall container after it has been emptied is done when a manipulator cams an arm of the inner rod, forcing the rod up, releasing the ball detents and the spall collector.

5.4.5.5 Liner

Temperature measurement of the furnace zones and relative canister areas is achieved by placing Type-K thermocouples in the center of each zone on the liner, which is remotely replaceable. The connector is located above the furnace and out to one side, but still needs to be air-purged for cooling.

This liner provides a secondary containment in the event of a canister failure during vitrification. It also protects the furnace interior from the possibility of collecting or being hit by spall, which may cause damage.

The thermocouples run through protective tubes/pipes that are attached to the liner and terminate on the centerline of the zones intended for monitoring (see Figure 5.4.21, Detail 1). There may be up to three thermocouples per zone on the inside of the liner to monitor the canister, and there may be up to three thermocouples per zone on the outside of the liner to monitor the furnace temperatures.

The tubes have an opening near the end of the tube that allows the radiant heat to be detected by the end of the thermocouple. The back side of the last 3 in. of the thermocouple is shielded by a ceramic insert and heat is given off by the 1/4-in., Inconel-690 liner. Other oxidation-resistant alloys that can withstand high temperatures (such as Inconel and Hastelloy) may be considered for use as liner material. The end of each tube/pipe is capped to contain and orient the ceramic insert.

5.4.5.6 Structural Support

Support for the five heating sections and the insulated section at the bottom is provided for by a triangular cage, as shown in Figures 5.4.21 and 5.4.27. This cage is supported from the top in three locations by a trunnion and two columns (see installation in Figure 5.4.28.) The trunnion is wall-imbedded and is located under the SC. The two support columns are bolted to the cell floor and rise to the same height as the top of the trunnion.

The top of this trunnion and both columns is where the load cells are positioned before installation of the triangular cage. The load cells are placed in a shallow cup on the trunnion and columns. The cage also has a shallow cup on the bottom of the plate that is going to support the entire ICM. The cage straddles the trunnion and columns on two sides, virtually confining the trunnion and upper end of the column.

5.4.5.7 Load Cells

Control of the ICM-temperature and the calcine-frit mixture ratio is required for product control. Many attempts at various methods have been made to weigh this calcine-frit mixture in the canister. A method developed for controlling the calcine-frit feed ratio (in combination with weighing the frit feed rate) is weighing the entire ICM assembly and a portion of the connecting section.

The load cells mentioned earlier give the process control computer the total weight of the calcine and frit fed into the canister to control the right ratio when integrated with the frit feed rate. Weighing the entire unit will also provide detection of changes to the ICM input, which may indicate a powder buildup in the calciner or connecting section and problems with the frit feed system. However, weighing will not detect bridging in the canister or provide melt-level detection, though other methods such as gamma emission techniques will.

Load cells have been tested for weight measurement, but their application in a remote, hot-cell environment needs to be further assessed.

FIGURE 5.4.27. Furnace Support Frame

FIGURE 5.4.28. Furnace Support Frame Installation

5.4.5.8 Service Connections

If the entire ICM is being weighed, flexible ICM service connections will be required. Each heating section requires cooling air in, exhaust air, and an electrical supply jumper. These jumpers must have a flexible stainless steel section between the rigid connections at either end.

The cooling air and the electrical jumper utilize the standard Purex connections that have been proven in remote facilities for many years.

The exhaust-air jumper to the cooler utilizes a ground ball and socket joint with a short tube extension on the end of the ball. This extension stabilizes the jumper in a vertical position, and the extension weight seals the joints adequately and does not require any additional clamping force.

The flex jumpers need to have a rigid bar installed between connections for installation and removal. The bar needs to be removed when the jumpers are in service.

The frit feeder is located outside the cell in a dust-tight system. The frit is added to a hopper, metered by a gravimetric feeder and then allowed to drop down to a pair of isolation valves. When it passes through the valves, it falls through a sloped pipe to the cell and enters the spray calciner at the support plate at the top of the cone section. At this point it begins mixing with the calcine and falls to the ICM below.

A computer regulates the gravimetric feeder, since the frit must be added in definite proportions to the amount of calcine generated by the SC to make a quality glass product. This gravimetric feeder is located in a potentially contaminated area even though two air vents in the system protect the potential air flow reversal.

The timed, computer-controlled, sequencing isolation valves that are operated by air cylinders are located within a cubicle on the back side of a cell wall. The cubicle is sealed with the exception of the two filter ports and is always under a negative pressure in relation to the operating gallery and a positive one in relation to the cell. Because of the air flow to the

cell, an absolute filter is needed before the air enters the cubicle, and one must be located in the cubicle before the air enters the cell.

Due to the abrasive characteristics of the frit, the valve ends have been made of neoprene and tend to mold themselves around an obstruction. Eventually these neoprene stoppers attached to the end of the air cylinder shaft will require replacement.

After the frit leaves the valves it passes through a 3-in.-dia pipe that has a radiation offset in the center of the cell wall. (Every section of the frit feed system below the gravimetric feeder is vertical or has a minimum slope of 45° to prevent the frit from getting stuck. It is anticipated that the frit will flow in a pipe at an angle of less than 60° to horizontal and greater than or equal to 45° based on limited testing, but this needs further verification.) Just inside the cell this 3-in. pipe terminates in a 3-in. Purex male nozzle.

A slightly non-standard Purex jumper (non-standard because of the angles involved) is then remotely installed between the wall connector and the spray calciner (see Figure 5.4.29). This jumper must also be sloped at 45° or more to prevent frit from building up. This frit feed jumper must also be strategically located so as not to interfere with the vibrator, which is also located in the same vicinity. This jumper must be insulated or purged to prevent steam condensation from the calciner.

In the event an isolation valve fails and plugs up the system, a dual valving system is recommended for continuing operation or the system has to be shut down while repairs are made.

The system as shown in Figure 5.4.30 has been developed by PNL and used for hot-cell operations. A current problem with this system is that the silicon-metal dust that may be a component of the frit boils out of the vacuum break within the cubicle and soon plugs up the absolute filter within the cubicle. The frit feed system using the spherical valves (see Section 4.3.4) shows promise and should be considered for use.

FIGURE 5.4.29. Frit Feed Jumper

FIGURE 5.4.30. Frit Feed System

5.4.6 SUPPORT EQUIPMENT

5.4.6.1 Gamma-Level Detection System

The Gamma-Level Detection System shown in Figure 5.4.31 can be used to determine the level of the vitrified waste in the canister at any given time and shows any calcine buildup within the system.

The cell wall penetrations at the levels shown in the ICM allow readouts on fixed detectors. The SC and connecting section penetrations are monitored by a moveable detector that routinely monitors the system during operation.

5.4.6.2 In-Cell Pipe and Electrical Jumpers

Figures 5.4.32 and 5.4.11 show typical Purex piping jumper and electrical jumpers, respectively. These types of jumpers have been in use for many years in various parts of the United States and their continued use is recommended in this reference manual, except in those areas specified.

FIGURE 5.4.31. Gamma-Level Detection System

FIGURE 5.4.32. Typical Purex Piping Jumper

Blank

5.120

5.5 DESCRIPTION OF ASSOCIATED PROCESS EQUIPMENT

K. H. Oma

Major auxiliary process support equipment requirements for the SC/ICM process is described in this chapter. Table 5.5.1 lists the equipment, and Figures 5.5.1 through 5.5.20 present equipment schematics, operating conditions and design parameters. The off-gas systems for the neutralized and acid flowsheets are based upon solidification facility conceptual flowsheets at Savannah River (Landon 1978 and 1979) and at Barnwell (Hall 1977), respectively, as well as upon vitrification process development experience at PNL (Bonner, Blair and Romero 1976; Larson and Bonner 1976; Larson et al. 1978). Operating conditions given with the equipment schematics are standard flow-sheet conditions from Tables 5.2.4 and 5.2.8. Design parameters shown for the HEPA filters are based on specifications of a commercially available filter. Design capacities for all other associated equipment were derived by assuming a 50% over-design, while design temperatures and pressures are values that could conceivably be obtained during extreme process conditions or equipment malfunction.

This section addresses the description and operation of individual pieces of equipment that can be incorporated into the reference flowsheet process design and does not represent an integrated system design nor necessarily state PNL recommendations. In an integrated system, the capability to obtain and analyze off-gas samples at various points would be helpful for diagnosing off-standard conditions; some differential pressure indicators/recorders, referenced to the cell, would complement individual pressure-drop instruments; also, individual cooling water and condensate streams should be monitored for leak detection. Information on the equipment description sheets should be regarded as representative of the reference processes and not necessarily as design recommendations for site-specific applications.

Corrosion-resistant materials of construction are suggested for equipment exposed to frit, calcine, or off gas because of corrosive Cl, F, S, and NO_x present from the liquid waste of both neutralized and acid flowsheets. The

TABLE 5.5.1. List of SC/ICM Associated Process Equipment

Process Equipment	Figure(a)	
	Neutralized Waste Flowsheet	Acid Waste Flowsheet
Cell Filters	5.5.1	5.5.1
Off-Gas Ejector Venturi	5.5.2	
Off-Gas Venturi Scrubber	5.5.3	
Off-Gas Cyclone	5.5.4	
Off-Gas Mercury Condenser	5.5.5	
Off-Gas Heaters	5.5.6	5.5.6
Off-Gas Ruthenium Sorber	5.5.7	5.5.16
Off-Gas Iodine Sorber	5.5.8	5.5.17
Off-Gas Cooler	5.5.9	
Off-Gas HEPA Filter	5.5.10	5.5.18
Off-Gas Quench Tower		5.5.11
Off-Gas Venturi Scrubber/Cyclone Separator		5.5.12
Off-Gas Condenser		5.5.13
Off-Gas Mist Eliminator		5.5.14
Off-Gas HEPA Filter		5.5.15
Off-Gas Heat Exchanger		5.5.19
Off-Gas NO _x Destructor		5.5.20

(a) Legend is given in Table 5.5.2.

acid waste flowsheet has the highest NO_x concentrations, while the neutralized waste flowsheet has the highest Cl, F and S concentrations.

Table 5.5.2 supplies a legend for interpretation of the equipment data sheets.

OPERATING CONDITIONS

CAPACITY: $113 \text{ m}^3/\text{min}$ (4000 cfm) OF CELL AIR

TEMPERATURE: $\sim 65^\circ\text{C}$

PRESSURE: $\sim 1 \text{ atm}$

HUMIDITY: $\leq 30\%$ RELATIVE

DESIGN PARAMETERS

TYPE: CUSTOM FILTER ASSEMBLY

CAPACITY: $170 \text{ m}^3/\text{min}$ (6000 cfm) OF CELL AIR

TEMPERATURE (CELL AIR): $\leq 100^\circ\text{C}$

PRESSURE DIFFERENTIAL: $\leq 1.8 \text{ psi}$ (SHOCK OVER-PRESSURIZATION)

FILTERS (HEPA AND ROUGHING)

CAPACITY: $28 \text{ m}^3/\text{min}$ (1000 cfm) OF CELL AIR EACH

DIMENSIONS $0.61 \text{ m} \times 0.61 \text{ m} \times 0.29 \text{ m}$ (24 in. x 24 in. x 11.5 in.)

FRAME: FIRE-RETARDANT WOOD

HOUSING MATERIAL: 304L STAINLESS STEEL

FILTER ASSEMBLY: 2 ASSEMBLIES REQUIRED, EACH HOLDING 3 HEPA FILTERS AND 3 PREFILTERS

FIGURE 5.5.1. Cell Filters (Both Flowsheets)

OPERATING CONDITIONS

CAPACITY: 7290 std L/min (257 SCFM) OF CALCINER OFF GAS [TABLE 5.2.4(8)
CALCINER OFF GAS] AT 350°C COOLED TO 85°C

TEMPERATURE (OFF GAS): INLET-350°C, EXIT-85°C

PRESSURE (OFF GAS): 0.95 atm

MOTIVE FLUID: CALCINER CONDENSATE SOLUTION

PRESSURE (SOLUTION): 5 atm (60 psig)

FLOW (SOLUTION): 273 Lpm (72 gpm)

DESIGN PARAMETERS

TYPE: EJECTOR VENTURI

CAPACITY: 10930 std L/min (386 SCFM) OF CALCINER OFF GAS [TABLE 5.2.4(8)
CALCINER OFF-GAS] AT 350°C COOLED TO 110°C

TEMPERATURE (OFF GAS): 0-400°C

PRESSURE (OFF GAS): 0.5-1.2 atm

MATERIAL: INCONEL-625 OR HASTELLOY B

NOTE: THE FOLLOWING EJECTOR VENTURI SYSTEM, EQUIVALENT, OR BETTER CAN BE
CONSIDERED FOR DESIGN PURPOSES.

S+K TYPE 7010, EJECTOR VENTURI SCRUBBER, 25.4 cm (10 in.). THE
SCRUBBER WILL HAVE A 3.2-cm (1-1/4-in.) (EXTRA LARGE) SPRAY NOZZLE.

THE EJECTOR VENTURI MAY BE CHANGED TO A HIGH-ENERGY VENTURI TO ACHIEVE A MORE
EFFICIENT SCRUBBING SYSTEM.

FIGURE 5.5.2. Off-Gas Ejector Venturi (Neutralized Waste Flowsheet)

OPERATING CONDITIONS

CAPACITY: 3070 std L/min (108 SCFM) VENTURI EJECTOR OFF GAS [TABLE 5.2.4(9)]

TEMPERATURE (OFF GAS): INLET-85°C, EXIT-70°C

PRESSURE (OFF GAS): 0.95 atm

DESIGN PARAMETERS

TYPE: VENTURI SCRUBBER

CAPACITY: 4600 std L/min (162 SCFM) VENTURI EJECTOR OFF-GAS [TABLE 5.2.4(9)]

TEMPERATURE (OFF GAS): 0-200°C

PRESSURE (OFF GAS): 0.5-1.5 atm

MATERIAL: INCONEL-625 OR HASTELLOY B

LIQUID FLOW RATE: 6.8 Lpm (1.8 gpm)

FIGURE 5.5.3. Off-Gas Venturi Scrubber (Neutralized Waste Flowsheet)

OPERATING CONDITIONS

CAPACITY: 3000 L/min (106 ACFM) VENTURI SCRUBBER OFF GAS

TEMPERATURE (OFF GAS): 70°C

PRESSURE (OFF GAS): 0.730 atm

DESIGN PARAMETERS

CAPACITY: 4500 L/min (159 ACFM) VENTURI SCRUBBER OFF GAS

TEMPERATURE (OFF GAS): 0-150°C

PRESSURE (OFF GAS): 0.5-1.5 atm

MATERIAL: INCONEL-625 OR HASTELLOY B

FIGURE 5.5.4. Off-Gas Cyclone (Neutralized Waste Flowsheet)

OPERATING CONDITIONS

CAPACITY: 3000 L/min (106 ACFM) OFF GAS [TABLE 5.2.4(10) CYCLONE OFF GAS] IS COOLED FROM 70°C to 10°C and 0.4 kg H₂O/min CONDENSES

TEMPERATURE (OFF GAS): INLET=70°C, EXIT=10°C

PRESSURE (OFF GAS): 0.713 atm

DESIGN PARAMETERS

TYPE: VERTICAL SHELL-TUBE, SINGLE-PASS, BAFFLED, FLOATING-HEAD, AIR ON TUBE SIDE, WATER ON SHELL SIDE

CAPACITY: 4500 L/min (159 ACFM) OF WATER-SATURATED CYCLONE OFF GAS IS COOLED FROM 70°C to 10°C

TEMPERATURE (OFF GAS): 0-150°C

PRESSURE (OFF GAS): 0.5-1.5 atm

HEAT-TRANSFER AREA: 12.3 m² (130 ft²)

HEAT LOAD: 0-18 kW (0-62,000 BTU/h)

MATERIAL: 304L STAINLESS STEEL

FIGURE 5.5.5. Off-Gas Mercury Condenser (Neutralized Waste Flowsheet)

OPERATING CONDITIONS

CAPACITY: 1890 std L/min (66.8 SCFM) OF CALCINER OFF GAS

TEMPERATURE (OFF GAS):	INLET	EXIT
• CAUSTIC FLOWSHEET		
Ru HEATER -	10°C	80°C
I HEATER -	80°C	150°C
• ACID FLOWSHEET		
Ru HEATER -	40°C	80°C
RE HEATER -	≤ 80°C	80°C

PRESSURE (OFFGAS):

• CAUSTIC FLOWSHEET	
Ru HEATER -	0.705 atm
I HEATER -	0.602 atm
• ACID FLOWSHEET	
Ru HEATER -	0.68 atm
RE HEATER -	0.59 atm

DESIGN PARAMETERS

TYPE: ELECTRICAL RESISTANCE

CAPACITY: 2840 std L/min (100 SCFM) OF CALCINER OFF GAS

TEMPERATURE: 0-250°C

PRESSURE: 0.5-1.5 atm

HEAT LOAD: 0-4.3 kW (14,650 BTU/h)

MATERIAL: 304L STAINLESS STEEL EXCEPT FOR HEATING
ELEMENTS AND INSULATION AND OTHER ITEMS
AS MAY BE APPROPRIATE

NOTE: FOR PRELIMINARY DESIGN ASSUME ~0.65 m² (~7 ft²) OF HEAT-
TRANSFER AREA IS NEEDED AND THIS IS SUPPLIED BY 5-cm (2-in.)-
DIAMETER PIPE THAT IS 4.2 m (14 ft) LONG. THE HEATING ELEMENT
SUPPORT STRUCTURE AND INSULATION ARE PLACED IN A 15-cm (6-in.)
PIPE.

FIGURE 5.5.6. Off-Gas Heaters (Both Flowsheets)

OPERATING CONDITIONS

CAPACITY: 1250 std L/min (44.0 SCFM) OF HEATER OFF GAS [TABLE 5.2.4(12)]

TEMPERATURE (OFF GAS): $\leq 80^{\circ}\text{C}$

PRESSURE (OFF GAS): 0.602-0.705 atm

DESIGN PARAMETERS

TYPE: PACKED SILICA-GEL BED

CAPACITY: 1870 std L/min (66.0 SCFM) OF HEATER OFF GAS [TABLE 5.2.4(12)]

TEMPERATURE (OFF GAS): $0-150^{\circ}\text{C}$

PRESSURE (OFF GAS): 0.5-1.5 atm

MATERIALS: VESSEL -304L SS
BED -12-40 MESH
SILICA GEL

VESSEL DETAIL:

SIZE: 64 cm (25.2 in.) ID,
1.8 m (70 in.) HEIGHT

THICKNESS: 0.64 cm (0.25 in.)

BED SUPPORT: 0.48-cm (3/16-in.) 304L SS PLATE
DRILLED FULL OF 0.64-cm (0.25-in.)
HOLES SUPPORTING A 304L SS HEAVY SCREEN
WHICH IS ≤ 80 MESH

HEADS: STANDARD DISHED

BED: DAVIDSON GRADE-40 SILICA GEL OR EQUIVALENT

SIZE: 77.2-cm (30.4-in.) dia
66-cm (27-in.) DEPTH

PARTICLE SIZE: 12-40 MESH

JETS (TYPE-STEAM): ~ 100 L/min (25 gpm)

FIGURE 5.5.7. Off-Gas Ruthenium Sorbers (Neutralized Waste Flowsheet)

OPERATING CONDITIONS

CAPACITY: 1250 std L/min (44.0 SCFM) OF HEATER OFF GAS [TABLE 5.2.4(14)]

TEMPERATURE (OFF GAS): 150°C

PRESSURE (OFF GAS): 0.594 atm

DESIGN PARAMETERS

TYPE: CUSTOM ANNULAR SORBER BED

CAPACITY: 1870 std L/min (66 SCFM) OF HEATER OFF GAS [TABLE 5.2.4(14)]

TEMPERATURE (OFF GAS): 0-250°C

PRESSURE (OFF GAS): 0.5-1.5 atm

MATERIALS: VESSEL - 304L SS
BED - 12-14 MESH SILVER-EXCHANGED MORTINITE

VESSEL: CONCENTRIC ANNULI CONSTRUCTION

SIZE: 40.6 cm ϕ x 1.78 m (16 in. ϕ x 7.0 ft)
END PLATE: 0.64 cm (0.25 in.) (BED AND VESSELS)
SCREEN: HEAVY, 30 MESH

BED: LINDE 13X ZEOLITE IN AG FORM

ANNULUS BED DIMENSIONS

ID = 11.4 cm (4.5 in.)
OD = 34.8 cm (13.7 in.)
DEPTH = 1.98 m (6.5 ft)
MESH = 12-14

FIGURE 5.5.8. Off-Gas Iodine Adsorber (Neutralized Waste Flowsheet)

OPERATING CONDITIONS

CAPACITY: 1250 std L/min (44.0 SCFM) I SORBER
OFF GAS [TABLE 5.2.4(15)] IS COOLED FROM
150°C to 55°C

TEMPERATURE (OFF GAS): INLET - 150°C, EXIT - 55°C

PRESSURE (OFF GAS): 0.560 atm

DESIGN PARAMETERS

TYPE: SHELL-TUBE, SINGLE-PASS, BAFFLED, FLOATING-HEAD,
AIR ON TUBE SIDE, WATER ON SHELL SIDE

CAPACITY: 1870 std L/min (66 SCFM) Hg VAPOR SORBER
OFF GAS [TABLE 5.2.4(15)] IS COOLED FROM
150°C to 55°C

TEMPERATURE (OFF GAS): 0-250°C

PRESSURE (OFF GAS): 0-1.5 atm

HEAT LOAD: 0-4.0 kW (0-13,500 BTU/h)

MATERIAL: 304L STAINLESS STEEL

FIGURE 5.5.9. Off-Gas Cooler (Neutralized Waste Flowsheet)

OPERATING CONDITIONS

CAPACITY: 1250 std L/min (44.0 SCFM) of Ru SORBER
OFF GAS [TABLE 5.2.4(15)] Ru SORBER OFF GAS

TEMPERATURE (OFF GAS): 55°C

PRESSURE (OFF GAS): 0.555 atm

DESIGN PARAMETERS

TYPE: CUSTOM FILTER ASSEMBLY

CAPACITY: 3580 std L/min (125 SCFM)

TEMPERATURE (OFF GAS): 0-150°C

PRESSURE (OFF GAS): 0.555 atm

MATERIALS: FILTER CASE: 304L SS AND FLANGES

GASKETS: ASBESTOS OR SILICONE

FILTERS: STANDARD FIRE-RESISTANT HEPA AND
PREFILTERS WITH FIRE-RESISTANT CASE

DIMENSIONS: ~35 cm x 35 cm x 1.5 m
(~14 in. x 14 in. x 60 in.)

FIGURE 5.5.10. Off-Gas HEPA Filters (Neutralized Waste Flowsheet)

OPERATING CONDITIONS

CAPACITY: 7260 std L/min (256 SCFM) OF CALCINER OFF GAS
[TABLE 5.2.8(11)]

TEMPERATURE (OFF GAS): INLET - 350°C
EXIT - 85°C

PRESSURE (OFF GAS): 0.95 atm

DESIGN PARAMETERS

TYPE: SPRAY QUENCH TOWER

CAPACITY: 10,890 std L/min (384 SCFM) OF CALCINER OFF GAS
[TABLE 5.2.8(11)]

TEMPERATURE (OFF GAS): 0-400°C

PRESSURE (OFF GAS): 0.5-1.5 atm

MATERIAL: INCONEL-625 OR HASTELLOY B

FIGURE 5.5.11. Off-Gas Quench Tower (Acid Waste Flowsheet)

OPERATING CONDITIONS

CAPACITY: 5310 std L/min (188 SCFM) OF QUENCH TOWER
OFF GAS [TABLE 5.2.8(12)]

TEMPERATURE (OFF GAS): INLET - 85°C
OUTLET - 70°C

PRESSURE (OFF GAS): 0.95 atm (INLET)

DESIGN PARAMETERS

TYPE: VENTURI SCRUBBER/CYCLONE SEPARATOR

CAPACITY: 7970 std L/min (281 SCFM) OF QUENCH TOWER
OFF GAS [TABLE 5.2.8(12)]

TEMPERATURE (OFF GAS): 0-200°C

PRESSURE (OFF GAS): 0.5-1.5 atm

MATERIAL: INCONEL-625 OR HASTELLOY B

FIGURE 5.5.12. Off-Gas Venturi Scrubber/Cyclone Separator
(Acid Waste Flowsheet)

OPERATING CONDITIONS

CAPACITY: 3350 std L/min (118 SCFM) OF CYCLONE OFF GAS
[TABLE 5.2.8(13)] IS COOLED FROM 70°C TO 40°C

TEMPERATURE (OFF GAS): INLET - 70°C, EXIT - 40°C

PRESSURE (OFF GAS): 0.70 atm

DESIGN PARAMETERS

TYPE: VERTICAL SHELL-TUBE, SINGLE-PASS, BAFFLED, FLOATING-HEAD,
AIR ON TUBE SIDE, WATER ON SHELL SIDE.

CAPACITY: 5020 std L/min (177 SCFM) OF CYCLONE OFF GAS
[TABLE 5.2.8(13)] IS COOLED FROM 70°C to 40°C

TEMPERATURE (OFF GAS): 0-150°C

PRESSURE (OFF GAS): 0.5-1.5 atm

HEAT-TRANSFER AREA: ~16 m² (~170 ft²)

HEAT LOAD: ~30 kW (~103,000 Btu/h)

MATERIAL: 304L STAINLESS STEEL

FIGURE 5.5.13. Off-Gas Condenser (Acid Waste Flowsheet)

OPERATING CONDITIONS

CAPACITY: 1890 std L/min (66.8 SCFM) OF CONDENSER OFF GAS

TEMPERATURE (OFF GAS): 40°C

PRESSURE (OFF GAS): 0.68 atm

DESIGN PARAMETERS

TYPE: BRINK® PACKED-FIBER OR YORK MESH DEENTRAINER IN PIPE OR EQUIVALENT

CAPACITY: 2840 std L/min (100 SCFM) OF VAPOR SATURATED OFF GAS AT 40°C.
ENTRAINED LIQUID ~2.2 M HNO₃ AND OFF GAS WILL CONTAIN SOME
NO_x. ≥99.9% COLLECTION EFFICIENCY ON PARTICLES LARGER THAN 3
µm.

TEMPERATURE (OFF GAS): 0-150°C

PRESSURE (OFF GAS): 0.5-1.5 atm

MATERIAL: 304L STAINLESS STEEL HOUSING, GLASS FIBER DEENTRAINER

NOTE:

DEMISTER: TYPICAL YORK DESIGN AT 4780 L/min (169 ACFM) at ≤540°C LINEAR
FLOW RATE ≤4.5 m/sec (15 ft/sec)

10-cm (4-in.)-THICK YORK MESH DEMISTER

EFFECTIVE AREA = 174 cm² (0.1876 ft² = 27.0 in.²)

EFFECTIVE DIAMETER = 14.9 cm (5.9 in.)

PIPE ID = 15 cm (6 in.)

PIPE THICKNESS = ~0.64 cm (1/4 in.)

MESH SUPPORT - WELDED IN ANNULAR PLATES

TOTAL HEIGHT ≤30 cm (1 ft) (EXCL. CONNECTOR HEADS)

MESH ΔP ≤0.02 atm (8 in. H₂O)

FIGURE 5.5.14. Off-Gas Mist Eliminator (Acid Waste Flowsheet)

® Brink is a trademark of Monsanto Enviro-Chem Systems, Inc., St. Louis, MO.

® York is a trademark of Otto H. Co., Inc., Fairfield, NJ.

OPERATING CONDITIONS

CAPACITY: 1890 std L/min (66.8 SCFM) of Ru SORBER OFF GAS
[ABOUT SAME CONDITIONS AS IN TABLE 5.2.8(15)]

TEMPERATURE (OFF GAS): $\leq 80^{\circ}\text{C}$

PRESSURE (OFF GAS): 0.67 atm

DESIGN PARAMETERS

TYPE: CUSTOM FILTER ASSEMBLY

CAPACITY: 3580 std L/min (125 SCFM)

TEMPERATURE (OFF GAS): $0-150^{\circ}\text{C}$

PRESSURE (OFF GAS): ~ 0.67 atm

MATERIALS:

FILTER CASE: 304L SS AND FLANGES

GASKETS: ASBESTOS OR SILICONE

FILTERS: STANDARD PREFILTER AND HEPA FILTERS
WITH FIRE-RESISTANT CASE

DIMENSIONS: ~ 35 cm x 35 cm x 1.3 m
(~ 14 in. x 14 in. x 50 in.)

FIGURE 5.5.15. Off-Gas and HEPA Filter (Acid Waste Flowsheet)

OPERATING CONDITIONS

CAPACITY: 1890 std L/min (66.8 SCFM) OF FILTER OFF GAS
[TABLE 5.2.8(15)]

TEMPERATURE (OFF GAS): 80°C

PRESSURE (OFF GAS): 0.67 atm

DESIGN PARAMETERS

TYPE: PACKED SILICA-GEL BED

CAPACITY: 2840 std L/min (100 SCFM) OF FILTER OFF GAS
[TABLE 5.2.8(15)]

TEMPERATURE (OFF GAS): 0-150°C

PRESSURE (OFF GAS): 0.5-1.5 atm

MATERIALS: VESSEL - 304L SS
BED - 12-40 MESH
SILICA GEL

VESSEL DETAIL:

SIZE: 97.5-cm (38.4-in.) ID
2.3-m (92-in.) HEIGHT

THICKNESS: 0.64 cm (0.25 in.)

BED SUPPORT: 0.48-cm (3/16-in.) 304L SS PLATE DRILLED FULL OF
0.64-cm (0.25-in.) HOLES SUPPORTING A 304L SS
HEAVY SCREEN WHICH IS ≤ 80 MESH

HEADS: STANDARD DISHED

BED: DAVIDSON GRADE-40 SILICA GEL OR EQUIVALENT

SIZE: 97.5-cm (38.4-in.) dia
132-cm (52-in.) DEPTH

PARTICLE SIZE: 12-40 MESH

JETS (TYPE-STEAM): ~ 100 L/min (25 gpm)

FIGURE 5.5.16. Off-Gas Ruthenium Sorber (Acid Waste Flowsheet)

OPERATING CONDITIONS

CAPACITY: 1890 std L/min (66.8 SCFM) OF RU SORBER OFF GAS
[TABLE 5.2.8(16)]

TEMPERATURE (OFF GAS): 80°C

PRESSURE (OFF GAS): 0.63 atm

DESIGN PARAMETERS

TYPE: CUSTOM ANNULAR SORBER BED

CAPACITY: 2840 std L/min (100 SCFM) OF FILTERED OFF GAS
[TABLE 5.2.8(16)]

TEMPERATURE (OFF GAS): 0-200°C

PRESSURE (OFF GAS): 0.5-1.5 atm

MATERIALS: VESSEL: 304L SS
BED: 12-14 MESH SILVER ZEOLITE GRANULES

VESSEL: CONCENTRIC ANNULI CONSTRUCTION
SIZE: 40.6 cm ϕ x 2.59 m (16 in. ϕ x 8.5 ft)
END PLATES: 0.64 cm (0.25 in.) (BED AND VESSELS)
SCREEN: HEAVY, 30 MESH

BED: LINDE 13X ZEOLITE IN AG FORM

ANNULUS BED DIMENSIONS

ID = 11.4 cm (4.5 in.)
OD = 34.8 cm (13.7 in.)
DEPTH = 2.44 m (8.0 ft)
MESH = 12-14

FIGURE 5.5.17. Off-Gas Iodine Sorber (Acid Waste Flowsheet)

OPERATING CONDITIONS

CAPACITY: 1890 std L/min (66.8 SCFM) OF I SORBER OFF GAS
[TABLE 5.2.8(17)]

TEMPERATURE (OFF GAS): $\leq 80^{\circ}\text{C}$

PRESSURE (OFF GAS): 0.63 atm

DESIGN PARAMETERS

TYPE: CUSTOM FILTER ASSEMBLY

CAPACITY: 3580 std L/min (125 SCFM)

TEMPERATURE (OFF GAS): $0-125^{\circ}\text{C}$

PRESSURE (OFF GAS): 0.63 atm ($\Delta P \pm 2.0$ psi)

MATERIALS:

FILTER CASE: 304L SS AND FLANGES

GASKETS: ASBESTOS OR SILICONE

FILTERS: STANDARD FIRE-RESISTANT HEPA AND PREFILTERS
MADE FROM GLASS FIBERS WITH FIRE-RESISTANT CASE

DIMENSIONS: ~ 35 cm x 35 cm x 1.3 m
(~ 14 in. x 14 in. x 50 in.)

FIGURE 5.5.18. Off-Gas HEPA Filters (Acid Waste Flowsheet)

OPERATING CONDITIONS

CAPACITY: 1890 std L/min (66.8 SCFM) OFF GAS FROM BLOWER ON TUBE SIDE [HAVING COMPOSITION SHOWN IN TABLE 5.2.8(18)] IS HEATED FROM $\leq 80^{\circ}\text{C}$ TO $\geq 200^{\circ}\text{C}$. 2420 std L/min (85.3 SCFM) OFF GAS FROM NO_x DESTRUCTOR [TABLE 5.2.8(20)] ON SHELL SIDE IS COOLED FROM $\sim 400^{\circ}\text{C}$ TO $\leq 300^{\circ}\text{C}$.

TEMPERATURE:	INLET	EXIT
OFF GAS	$\leq 80^{\circ}\text{C}$	200°C
OFF GAS FROM BLOWER	$\sim 400^{\circ}\text{C}$	$< 300^{\circ}\text{C}$

PRESSURE (OFF GAS):	
TUBE SIDE	1.07 atm
SHELL SIDE	1.03 atm

DESIGN PARAMETERS

TYPE: SHELL-TUBE, SINGLE- OR MULTIPLE-PASS, BAFFLED, FLOATING-HEAD, GAS ON BOTH SIDES, HOT GAS ON SHELL SIDE

CAPACITY: 2840 std L/min (100 SCFM) OFF GAS ON TUBE SIDE AND 3610 std L/min (128 SCFM) OFF GAS ON SHELL SIDE

TEMPERATURE (OFF GAS): $0\text{--}750^{\circ}\text{C}$

PRESSURE (OFF GAS): $0.5\text{--}1.5$ atm SHELL AND TUBE SIDES

MATERIAL: 304L STAINLESS STEEL

HEAT LOAD: 8 kW (27,000 BTU/h)

FIGURE 5.5.19. Off-Gas Heat Exchanger (Acid Waste Flowsheet)

OPERATING CONDITIONS

CAPACITY: 2410 std L/min (85.1 SCFM) OF REACTION OFF GAS [REACTION PRODUCT OF FILTER OFF GAS AND AMMONIA - TABLE 5.2.8(18) and (19)] APPROXIMATELY 25 kg NO_x/h CONVERTED TO N₂ and H₂O.

TEMPERATURE (OFF GAS): INLET ~200°C, EXIT ~400°C.

PRESSURE (OFF GAS): 1.05 atm

DESIGN PARAMETERS

TYPE: CUSTOM DESIGN CYLINDRICAL-BED REACTOR

CAPACITY: 3610 std L/min (128 SCFM) OF REACTION OFF GAS DESCRIBED ABOVE. APPROXIMATELY 37.5 kg NO_x/h CONVERTED TO N₂ and H₂O

TEMPERATURE: 0-750°C

PRESSURE: 1-2 atm

MATERIAL:

VESSEL: 304L SS, 0.64 cm (1/4 in.) THICK
BED: 0.16-cm (1/16-in.) ZEOLON-900 EXTRUDATE PELLETS

VESSEL: CYLINDRICAL WITH TAPER CONE ENDS

SIZE: 40.6 cm ϕ x 0.91 m (16 in. ϕ x 3 ft)

BED PARTICLE SIZE: 12-14 MESH EXTRUDATE ZEOLON-900

SIZE: 20 cm (8 in.) DEEP
40.6 cm (16 in.) IN DIAMETER

HEATER: 23-kW RESISTANCE HEATER USED FOR STARTUP
INSULATED OUTSIDE OF ELEMENTS
HEATER COVERED WITH 304L SHELL

FIGURE 5.5.20. Process Off-Gas NO_x Destructor (Acid Waste Flowsheet

TABLE 5.5.2. Legend for Equipment Data Sheets

Flow Element
Motor
Diaphragm-Operated Valve
Solenoid-Operated Valve
3-Way Solenoid Valve
Ball Valve
Needle Valve
Reverse-Flow Check Valve
Restricting-Flow Orifice
Jet Mixer
Process Service Lines
Pneumatic Instrument Lines
Primary Process Lines
Electronic Wires or Hidden Lines

AM	Ammeter	AHWA	High Weight Rate Change Alarm
AS	Air Supply	IAS	Instrument Air Supply
ATM	Atmosphere	IC	Ionization Chamber
CI	Circuit Interrupter	IS	Current Switch
DPA	Differential Pressure Alarm	IY	Relay
DPI	Differential Pressure Indicator	JR	Electrical Power Recorder
DPR	Differential Pressure Recorder	JS	Electrical Power Switch
DPT	Differential Pressure Transmitter	KJC	Timer
DR	Density or Specific Gravity Recorder	LC	Load Cell
ETM	Elapsed Time Meter	LLA	Liquid-Level Alarm
FA	Flow Alarm	LLI	Liquid-Level Indicator
FC	Flow Controller	LLR	Liquid-Level Recorder
FE	Flow-Sensing Element	ΔLWA	Low Weight Rate-Change Alarm
FI	Flow Indicator	PCV	Pressure Control Valve
FR	Flow Recorder	PE	Pressure-Sensing Element
FT	Flow Transmitter	PGM	Programmer
FY	Converter	PI	Pressure Indicator
HLA	High-Level Alarm	PR	Pressure Recorder
		ΔPR	Change-in-Pressure Recorder
		PS	Pressure Switch

TABLE 5.5.2. .(contd)

RC	Ratio Controller	TRC	Temperature Recorder
REF	Reference Pressure Header		Controller
RR	Radiation Recorder	TT	Temperature Transmitter
RW	Raw Water (Unsanitary)	VC	Valve Controller
SE	Sensing Element	VIB	Vibrator
SPL	Sample	Δ WA	Weight Rate Change Alarm
SS	Steam Supply	WC	Weight Controller
SUM	Summer	Δ WC	Weight Rate-Change Controller
SW	Selector Switch	Δ WI	Weight Rate-Change Indicator
TA	Temperature Alarm	$\Sigma\Delta$ WI	Weight Total and Rate-Change
TC	Temperature Controller		Indicator
TE	Temperature Element	WR	Weight Recorder
TI	Temperature Indicator	Δ WR	Weight Rate-Change Recorder
TR	Temperature Recorder	WS	Weight Supply

5.6 SPRAY CALCINER/IN-CAN MELTER STRUCTURAL ANALYSIS

J. A. Griffiths, R. J. Shippell, C. A. Williams

5.6.1 GENERAL INTRODUCTION

5.6.1.1 Purpose and Scope

This section describes selected SC/ICM system structural analyses to help assess the equipment service life and structural integrity. Specific structural analyses highlight key stress areas in the SC or ICM equipment. Stresses were estimated for loading situations covering normal, upset, and emergency conditions. Loading conditions selected for analyses are generic in nature.

Normal operating conditions consider deadweight loading (1-g vertical loading), stresses due to internal pressure or vacuum, vibratory dynamic loading, and thermal stresses due to normal operating temperatures. Upset conditions are those conditions that include additional loading due to equipment malfunction with a moderate frequency of occurrence. Emergency conditions are more severe additional loadings, which have a low probability of occurrence. Roughly speaking, these three types of loadings correspond to the ASME Boiler and Pressure Vessel Code (ASME 1977) Level A, B and Levels C and D combined service loadings, respectively. The ASME Code does not strictly apply to these structures. Table 5.6.1 provides the assumed loading conditions.

Three possible modes of structural failure are addressed: 1) excessive single-application stresses resulting in catastrophic structural failure or excessive deformation; 2) stresses exceeding cyclic-stress allowable limits, resulting in structural fatigue failure; and 3) stresses exceeding allowable creep stresses resulting in excessive deformation or creep-fatigue interaction failure.

Detailed designing and final design stresses are beyond the scope of this study. Basic design features are considered in the analysis. Some suggestions for detailing the final design configuration are provided later in this section based on normal design practices and experiences with operation of a prototype SC/ICM system.

TABLE 5.6.1. Assumed Loading Conditions for SC/ICM System

Component	Normal	Upset	Emergency
Calcliner Assembly: Calcliner Chamber, Cone, Filter Chamber	$\Delta p_{ext} = 2480 \text{ Pa (0.36 psi)}$ 1-g weight loading Periodic vibratory impact from 2 vibrators to remove calcine from walls Thermal stresses; maximum $T = 800^\circ\text{C}$	1) loss of furnace control-furnace power increases from 50-70 kW per zone to 150 kW per zone, maximum T increases to 900°C ; Δp_{ext} increases to 4960 Pa (0.72 psi) 2) loss of filter chamber blower control or blocked feed inlet, vacuum relief system operates; Δp_{ext} increases to 4960 Pa (0.72 psi) 3) blocked cone outlet, pressure relief system operates, maximum $\Delta p_{int} = 10,300 \text{ Pa (1.5 psi)}$ 4) Operating-Basis Earthquake (OBE)(a)	1) loss of filter chamber blower control or blocked feed inlet and loss of vacuum relief system; Δp_{ext} increases to $4.96 \times 10^{-2} \text{ MPa (7.2 psi)}$ 2) blocked cone outlet and loss of pressure relief system; maximum $\Delta p_{int} = 0.138 \text{ MPa (20 psi)}$ 3) tornado depressurizes off gas duct; maximum $\Delta p_{ext} = 20,600 \text{ Pa (3 psi)}$, drop at 13,800 Pa/sec (2 psi/s) 4) tornado depressurization of hot cell; maximum $\Delta p_{ext} = 20,600 \text{ Pa (3 psi)}$, drop at 13,800 Pa/sec (2 psi/s) 5) Safe-Shutdown Earthquake (SSE)(a)
Calcliner Assembly Support Structure	1-g weight loading	1) Operating-Basis Earthquake (OBE)(a)	1) Safe-Shutdown Earthquake (SSE)(a)
Piping/Jumpers	Internal pressure End displacements due to thermal expansion of calcliner assembly 1-g weight loading of piping/jumpers plus contents	1) Operating-Basis Earthquake (OBE)(a)	1) Safe-Shutdown Earthquake (SSE)(a)
In-Can Melters	Thermal stresses 1-g weight loading	1) Loss of furnace control 2) Operating-Basis Earthquake (OBE)(a)	1) Safe-Shutdown Earthquake (SSE)(a)

(a) Earthquake Loading - Two loading conditions were analyzed. First, pseudo-static loading was used with a maximum horizontal acceleration of 1.0 g and a vertical acceleration of 0.67 g. Second, a scaled El Centro-1940 earthquake response spectrum was used with a maximum horizontal ground velocity of 0.41 m/s (16 in./s), and a maximum vertical ground velocity of 0.27 m/s (10.7 in./sec). See text for details.

5.6.1.2 General Analytic Approach

Finite-element model methods were used extensively for the structural analyses of the SC/ICM system. Where simple geometry permitted, closed-form analytic models were also used.

ANSYS (Swanson 1978), the computer code used predominately in the study, is a general purpose code based on a wavefront solution technique. ANSYS has both linear and nonlinear material behavior capabilities. ANSYS has both static and dynamic analysis provisions. In dynamic analysis, either response spectrum techniques based on structural modal participation analysis or direct time integration of the motion equations are available.

5.6.2 STRUCTURAL ANALYSES OF THE SC ASSEMBLY

5.6.2.1 SC Assembly Model for Static and Seismic Loading Conditions

Introduction

A 3-D finite-element model of the SC assembly is used to predict structural vibration modes shapes, associated natural frequencies, and corresponding seismic response. Static load cases considered include dead-weight loading and pressurization/vacuum under various calciner operating conditions. This section contains detailed model descriptions, engineering assumptions, and finite-element study results.

General Assumptions

General assumptions used in formulating the spray calciner assembly model are presented here. Other more detailed assumptions are discussed where appropriate along with the model detailing.

An approximate temperature distribution is applied to the calciner assembly finite-element model. Although the thermal stresses are addressed by a separate analysis, a simplified temperature distribution was used in this analysis to assign the appropriate temperature-dependent material properties. The generic material properties are taken from the ASME High-Temperature Code Case N47 (ASME 1977) and the Aerospace Material Handbook (DOD 1978).

Effects of pipe lines and other connectors to the calciner and filter chamber were modeled as lumped masses. Inertia contributions were present while the added support from the connectors was neglected. Both assumptions are considered conservative with respect to the overall structural response. Insulation on the filter chamber and cone was ignored; it provides no stiffness and little additional mass.

Finite-Element Model

The SC system was modeled as an assemblage of 3-D elastic beam, shell, and generalized mass elements. The 3-D beam element is a uniaxial element with tension-compression, torsion, and bending characteristics. A 3-D shell element was the second type of element used in this analysis. This element is an elastic, flat, triangular element with both bending and membrane characteristics. The last element type used in this model was the generalized mass element, which is a point element having six degrees of freedom such as used for the above elements. A different mass and rotary inertia may be assigned to each coordinate direction or a mass matrix may be defined. The finite element model has 81 nodes and is made up of 62 beams, 84 plates, and 11 lumped masses.

The entire SC system is shown in Figure 5.6.1. The calciner frame, chamber, and filter chamber were represented by 3-D elastic beams. The frame is made up of 51 beam elements. The beam elements are "sized" to the appropriate geometry and material. General structural steel mechanical properties were taken from the ASME Code, Section VIII, Division II (ASME 1977). The calciner frame is connected to the foundation at the floor and wall. The frame was treated as a fixed connection at the floor (i.e., it was assumed that the floor bolts would restrict all translations and rotations). Results from subsequent analyses proved the validity of using this approach. The frame is connected to the wall via mechanical trunnions. Boundary conditions at the wall-frame interface allow vertical structural translation only. Model translations in the nodal x and y directions and rotations about the nodal x, y, and z axes were zeroed out. General vertical translation was allowed. This neglects the nonlinear gap effect of possibly bottoming the structure against the trunnion.

FIGURE 5.6.1. Finite-Element Idealization of Spray Calciner System - Normal Orthographic and Isometric

Offsets in support-assembly beam elastic axes were ignored in this model. This effect would tend to couple bending and torsional deformations of the various assembly elements. The final geometry of the support assembly connections is subject to equipment detailing, so this effect was ignored for this generic structural modeling.

Equivalent beam systems were used to model the SC chamber and filter chamber. The SC chamber and filter chamber were modeled using four and six beam elements, respectively. Actual inertia properties and densities were input to maintain proper mass distributions. The SC chamber was of circular cross section with an outer diameter of 0.91 m (36 in.) a height of 3.3 m (130 in.), and a wall thickness of 9.5 mm (0.375 in.). The filter chamber was of rectangular cross section with nominal measurements of 1.78 m x 0.91 m x 6.35 mm (70 in. x 36 in. x 0.25 in.). Material properties for the Inconel-601 SC chamber were taken from the Alloy Digest (1970). Due to the relatively rigid nature of the SC chamber's response to the loading conditions, a 310 stainless steel SC chamber would experience stresses similar to those the Inconel-601 chamber analyzed even though the two material properties differ somewhat. The filter chamber was a typical 304 stainless steel. These mechanical properties were taken from ASME (1977).

The interfaces of the SC chamber and filter chamber with the horizontal base plate were modeled using rigid regions approximating the actual geometry of the SC chamber and filter chamber. In this manner, the interface geometry with the base plate is realistic. This approach reduces modeling time at the cost of sacrificing chamber and filter chamber ovality mode deformation. Separate analyses (Bechtel, Inc. 1977b) have indicated that the frequencies of these ovality modes are beyond the seismic range (above 100 Hz); this assumption will therefore have little impact upon the overall structures' seismic response. The upper attached piping or braces to the SC chamber and filter chamber were assumed to be sufficiently stiff to prevent any end SC chamber or filter chamber translations except for vertical motion. Reaction forces in the braces proved to be sufficiently low to bear out this model. A worst-case study with free ends was also considered for seismic response.

The calciner base plate and cone section are represented by 3-D shell elements. The 2.54-cm (1-in.)-thick base plate model was comprised of 48 triangular shell elements. The plate used in the analyses was a 2.0 m x 1.2 m x 25.4 mm (80 in. x 48 in. x 1 in.) piece of 304 stainless steel. Mechanical properties for this material were taken from ASME (1977).

Two simplifying approximations were made in modeling the plate-frame interface. The first ignored the noncoincidence of the centroids of the shell and beam elements. This type of detailed study is most appropriately done following final structural detailing. The second approximation is matching the six degrees of freedom at the plate-frame junction. This approach simulates a welded interface while the actual structure should be bolted to permit thermal expansion of the baseplate relative to the colder frame. The number of bolts and bolting pattern can be chosen to limit edge rotation of the plate and approach the welded condition, thereby reducing the error involved in this assumption. This again must be determined at final structural detailing.

The cone section was modeled using thirty-six 6.35-mm (0.25-in.)-thick triangular shell elements. The model of the cone had an elliptical cross section with major and minor diameters of approximately 1.5 m (59 in.) and 0.86 m (34 in.). The sides of the cone taper to a point at the bottom. The cone section material was 304 stainless steel.

A conservative boundary condition was applied to the bottom of the cone section, i.e., that point was given full translation and rotational degrees of freedom. The diverter assembly bellows is considerably less stiff than the cone itself and therefore would afford no support of the cone section during an earthquake.

The furnace, filters, and external pipes were modeled as generalized mass elements. In all cases point masses were placed so as to produce near actual weight and mass distributions. An equivalent furnace mass was located around the perimeter of the chamber's rigid region. Due to the furnace "T" bar connection at the wall, furnace masses were constrained to have no lateral translation. Inherent in this model is the assumption that the relative motion

between the furnace and plate would not overcome static, restraining frictional forces. Similarly, equivalent pipe weights were specified at the top of the SC chamber assembly and the top of the filter chamber. The filter masses were distributed through the filter chamber and across the length of the filters in a linear fashion.

Load Conditions for Analysis

The SC assembly was analyzed for both static and dynamic loading conditions. The two static load conditions were gravity and pressure. Dynamic loads included seismic loading modeled by either the El Centro earthquake or any assumed pseudo-static loading. The following sections contain descriptions of various loading conditions and assumptions and idealizations for each. It is believed that the loading schemes selected result in a conservative estimate of the calciner's response. Refining the loading functions to reduce the uncertainties associated with the assumptions is not expected to substantially change the conclusions. Such refinement must be based on site-specific data.

Gravity Loads. Structural dead-weight gravity loads due to static body forces were computed from the mass density of the element materials and the element geometry. Lumped masses were used to account for attached equipment weights.

Pressure Loads. Pressure Loads postulated for calciner normal, upset and emergency operating conditions are described in Table 5.6.1. Normal operating pressure was 2480 Pa (0.36 psi) vacuum. Upset pressures or vacuums can be generated from several fault paths. An upset vacuum of 4960 Pa (0.72 psi) can result from loss of the filter chamber blower control or a blocked feed inlet with the vacuum relief system operational. An internal upset pressure of 10,300 Pa (1.5 psi) can be encountered if the cone section becomes blocked to a degree that would cause the pressure relief system to operate. An emergency condition is encountered with the loss of the vacuum relief system in conjunction with either the loss of the filter chamber blower control or the blockage of a feed inlet. Either double fault condition could produce a vacuum of

4.96×10^{-2} MPa (7.2 psi). If the cone section outlet becomes blocked and the pressure relief system is lost, an internal pressure of 0.138 MPa (20 psi) will result, causing an emergency operating condition.

In summary, the pressures under consideration were: a normal operating condition vacuum of 2480 Pa (0.36 psi); upset conditions of vacuum 4960 Pa (0.72 psi) and 10,300 Pa (1.5 psi) internal pressure; and emergency conditions of 4.96×10^{-2} MPa (7.2 psi) vacuum and 0.138 MPa (20 psi) internal pressure.

Seismic Loading. Two methods were used to simulate seismic motion. First, for the case where the SC chamber and filter chamber upper ends were considered constrained by attached piping and braces, lowest structural natural frequencies were sufficiently high to allow pseudo-static seismic loading. In this case a 1-g maximum horizontal acceleration was assumed for both horizontal directions and a 0.67-g maximum vertical acceleration was also supplied.

To check the sensitivity of the model to the SC chamber and filter chamber constraints at their upper ends, the model was also run with these degrees of freedom unconstrained. Due to the reduced structural natural frequencies, an earthquake response spectrum approach was used. The El Centro earthquake was chosen and its velocity response spectrum used (Harris and Crede 1976) in Figure 5.6.2. A maximum horizontal ground velocity of 0.27 m/s (16 in./s) was assumed. No floor-response filtering was assumed, since this is highly site-dependent. This roughly corresponds to a 0.33-g maximum horizontal acceleration. Again, the vertical component was assumed to be two-thirds of the horizontal components.

Thermal Loads. An approximate temperature distribution was applied to the finite-element model. These temperatures were used in assigning the appropriate temperature-dependent material properties. Thermal stresses were not calculated using this model. Detailed internal stresses are calculated using a separate model. Due to the design of the structure, any thermal stresses are highly localized phenomena.

FIGURE 5.6.2. El Centro Earthquake Nondimensional Response Spectrum
Taken from Harris and Crede (1976)

Results of Analyses

Study results are separated into a discussion of the static and dynamic analyses. The static load cases included dead-weight loading and dead-weight loading combined with system pressures of 2480 Pa, 4960 Pa and 4.96×10^{-2} MPa (0.36, 0.72 and 7.2 psi) vacuum and 10,300 Pa and 0.138 MPa (1.5 and 20 psi) internal pressure. Mode-shape predictions and seismic responses were studied under the dynamic section. Peak stresses and displacements for the various calciner components were noted for all load cases. Frame-foundation reaction forces were observed during the seismic study.

Static. Static load case results are summarized in Table 5.6.2. The maximum stresses and displacements were identified for each load case. The maximum system vacuum of 4.96×10^{-2} MPa (7.2 psi) occurs during upset operation. This condition would cause a system peak stress of approximately

TABLE 5.6.2. Results from Static Analysis: Maximum Displacements and Stresses Corresponding to Various Combinations of 1-g_z Loading With Different Calciner Operating Pressures

Maximum Stresses and Displacements	Static Load Cases (a)					
	Deadweight ($\approx 1 g_z$)	1 g _z + 2480 Pa ^{VAC} (1 g _z + 0.36 psi ^{VAC})	1 g _z + 4960 Pa ^{VAC} (1 g _z + 0.72 psi ^{VAC})	1 g _z + 10300 Pa ^{INT} (1 g _z + 1.5 psi ^{INT})	1 g _z + 4.96 x 10 ⁻² MPa ^{VAC} (1 g _z + 7.2 psi ^{VAC})	1 g _z + 0.138 MPa ^{INT} (1 g _z + 20 psi ^{INT})
Maximum x-displacement (b)	-0.20 (-0.77 x 10 ⁻²)	-0.24 (-0.95 x 10 ⁻²)	-0.51 (-0.20 x 10 ⁻¹)	1.09 (0.43 x 10 ⁻¹)	-5.08 (-0.20)	14.22 (0.50)
Location	SC Chamber	Cone	Cone	Cone	Cone	Cone
Maximum y-displacement	-0.08 (-0.31 x 10 ⁻²)	-0.10 (-0.40 x 10 ⁻²)	0.10 (0.40 x 10 ⁻²)	-0.30 (-0.12 x 10 ⁻¹)	1.27 (0.50 x 10 ⁻¹)	-3.56 (-0.14)
Location	Frame	Frame	Cone	Cone	Cone	Cone
Maximum z-displacement	-0.26 (-0.101 x 10 ⁻¹)	-0.20 (-0.80 x 10 ⁻²)	-0.20 (-0.80 x 10 ⁻²)	-0.69 (-0.27 x 10 ⁻¹)	2.31 (0.91 x 10 ⁻¹)	-7.11 (-0.28)
Location	Plate	SC Chamber	Cone	Cone	Cone	Cone
Maximum Frame Stress (c)	-9.00/-2.07 (-1300/-300)	-8.27/-2.55 (-1200/-370)	-8.27/-2.55 (-1200/-370)	-8.07/-2.48 (-1170/-360)	-8.72/-2.69 (-1265/-390)	-6.72/-2.07 (-975/-300)
Maximum SC Chamber Stress (c)	-0.31/-0.31 (-45/-45)	-0.41/-0.34 (-60/-50)	-0.45/-0.41 (-65/-60)	-0.10/-0.10 (-15/-15)	-1.48/-1.38 (-215/-200)	-2.90/-2.90 (-420/420)
Maximum Filter Chamber Stress (c)	-0.55/-0.52 (-80/-75)	-0.69/-0.59 (-100/-85)	-0.76/-0.62 (-110/-90)	-0.55/-0.41 (-80/-60)	-1.34/-1.24 (-195/-180)	1.93/1.90 (280/275)
Maximum Plate Stress	-8.55 (-1240)	-6.79 (-985)	-6.83 (-990)	-6.65 (-965)	7.48 (1085)	18.62 (2700)
Maximum Cone Stress	2.34 (340)	3.25 (-470)	-8.00 (-1160)	-18.00 (-2610)	83.43 (12100)	234 (33870)

(a) Positive stresses are tension; negative stresses are compression.

(b) All units mm or MPa except within parentheses, where units become in. and psi.

(c) (Maximum Inplane Stress/Maximum Axial Stress)

83 MPa (12,000 psi) to occur in the cone section. At this level of loading all members remain elastic. The maximum system pressure of 0.138 MPa (20 psi) occurs during a possible emergency operation condition. Peak stresses again were observed to appear in the cone. Elastic theory predicts a stress level of about 234 MPa (34,000 psi). This would result in a localized yielding and stress relief effect and is not expected to affect the overall integrity of the components analyzed. Such a plastic deformation would probably be acceptable for the emergency shutdown loading case.

A static elastic buckling external pressure has been calculated for the calciner cone based on analogy with an equivalent cylinder (Roark and Young 1975, Table 35, Number 23). Based on the major diameter of the cone and its maximum slant height, a buckling pressure of 0.34 MPa (49 psi) is predicted for cone-operating temperatures of about 260°C (500°F). The maximum emergency-condition vacuum is 4.96×10^{-2} MPa (7.2 psi), well below the critical buckling pressure. Thus, the cone should not buckle under emergency loading conditions.

Dynamic.

Mode Frequencies. Mode shapes and natural frequencies were predicted for two cases: a more realistic situation in which the tops of the SC chamber and filter chamber were assumed to be constrained laterally (due to stiff piping attachments or seismic bracing); and a worst-case study that freed all six degrees of freedom at the ends.

A summary of the mode-frequency analysis for both cases is presented in Table 5.6.3 below.

TABLE 5.6.3. Mode-Frequency Analysis for Fixed and Free Cases

SC Chamber and Filter Chamber End Conditions	Natural Frequencies, Hz				
	Mode 1	Mode 2	Mode 3	Mode 4	Mode 5
Fixed	36	47	54	56	61
Free	15	19	29	33	39

Typically, the cutoff frequency for seismic amplification effects is considered to be 33 Hz. The lowest natural frequency for the fixed-end condition is above this frequency. The free-end condition has four modes that can resonate to some extent during an earthquake.

The mode shapes for the first four modes of the free-end case are shown in Figures 5.6.3 through 5.6.6. The first mode shape indicated a y-z plane in phase rocking of the SC chamber and filter chamber. The second mode showed similar motion, but a change in the plane of action from y-z to the x-z plane was noticed. Out-of-phase x-z rocking was observed in the third mode. The fourth mode indicated similar effects, but the plane was shifted from the x-z to the y-z.

The first mode for the fixed-end case (which occurs outside the seismic range) was a frame oscillatory mode. Except for vertical translation, the SC chamber and filter chamber remains stationary for this mode, while the frame and legs move (Figure 5.6.7).

FIGURE 5.6.3. First Mode Shape at a Frequency of 15 Hz. (In-phase rocking of calciner chamber and filter chamber in y-z plane excited by El Centro Spectrum.)

FIGURE 5.6.4. Second Mode Shape at a Frequency of 19 Hz. (In-phase rocking of calciner chamber and filter chamber in x-z plane excited by El Centro Spectrum.)

FIGURE 5.6.5. Third Mode Shape at a Frequency of 29 Hz. (Out-of-phase rocking of calciner chamber and filter chamber in x-z plane excited by El Centro Spectrum.)

FIGURE 5.6.6. Fourth Mode Shape at a Frequency of 33 Hz. (Out-of-phase rocking of calciner chamber and filter chamber in y-z plane excited by El Centro Spectrum.)

FIGURE 5.6.7. First Mode Shape With Laterally Constrained Calciner Barrel and Filter Chamber Ends at a Frequency of 36 Hz. (Frame oscillatory mode excited by pseudo static spectrum technique.)

Seismic Response. Fixed-end and free-end conditions of the SC chamber and filter chamber required separate seismic studies. Since the fixed-end model's first mode was above the usual cutoff for spectrum analyses, a pseudo-static approach to the earthquake response was applied. Three static-load cases were studied: a 1-g loading in the global x direction, a 1-g loading in the global y direction, and a 2/3-g loading in the global z direction.

The outputs from the individual cases were summed using the Absolute Sum response-spectrum technique. The results from this procedure are summarized in the Tables 5.6.4, 5.6.5 and 5.6.6.

TABLE 5.6.4. Maximum SC Component Displacement for Seismic Response (Fixed End)

Maximum Displacement	mm (in.)		
	Maximum x Displacement	Maximum y Displacement	Maximum z Displacement
Magnitude	0.24 (0.93 x 10 ⁻²)	0.24 (0.96 x 10 ⁻²)	0.16 (0.64 x 10 ⁻²)
Location	Frame	Frame	Plate

TABLE 5.6.5. Maximum SC Component Stress for Seismic Response (Fixed End)

Maximum Stress	Maximum Component Stress, MPa (psi)				
Magnitude(a)	5.58/2.21 (810/320)	0.66/0.21 (95/30)	6.31/0.34 (915/50)	6.52 (945)	2.38 (345)
Location	Frame	SC Chamber	Filter Chamber	Plate	Cone

(a) Maximum inplane stress (maximum axial stress)

TABLE 5.6.6. Maximum SC Component Reaction Forces for Seismic Response (Fixed End)

Maximum Reaction Forces	Maximum Reaction Forces, kN (lbf)		
	F _x	F _y	F _z
Magnitude	32.5 (7315)	18.8 (4230)	14.5 (3250)
Location	Frame	Frame	Frame

This technique sums the results in a worst-case fashion. Examination of the results indicates a low (elastic) stress level in all components analyzed.

The free-end model had four modes that could possibly be excited by an earthquake. In this case, due to the lack of site-specific seismic data, a scaled El Centro earthquake velocity-response spectrum was applied to the structure. Two percent of critical damping was assumed.

The contributions of the various modes were summed using the Absolute Sum response spectrum technique. The results from this procedure are presented in Tables 5.6.7 through 5.6.9.

TABLE 5.6.7. Maximum SC Component Displacement for Seismic Response (Free End)

<u>Maximum Displacement</u>	<u>mm (in.)</u>		
	<u>Maximum x Displacement</u>	<u>Maximum y Displacement</u>	<u>Maximum z Displacement</u>
Magnitude	2.79 (0.11)	4.06 (0.16)	1.02 (0.4 x 10 ⁻¹)
Location	SC Chamber	SC Chamber	Plate

TABLE 5.6.8. Maximum SC Component Stress for Seismic Response (Free End)

<u>Maximum Stress</u>	<u>Maximum Component Stress, MPa (psi)</u>				
Magnitude ^(a)	16.38/9.38 (2375/1360)	8.90/0 (1300/0)	2455/0.21 (3500/30)	39.72 (5760)	11.86 (1720)
Location	Frame	SC Chamber	Filter Chamber	Plate	Cone

TABLE 5.6.9. Maximum SC Component Reaction Forces for Seismic Response (Free End)

<u>Maximum Reaction Forces</u>	<u>Maximum Reaction Forces, kN (lb_f)</u>		
	<u>F_x</u>	<u>F_y</u>	<u>F_z</u>
Magnitude	50.6 (11375)	23.4 (5270)	59.5 (13385)
Location	Frame	Frame	Frame

Although the displacements' stresses and reaction forces were increased by the free-end assumption, the level of excitation still appears to lie well within the elastic design region.

Conclusions

The overall structural response generally indicated low (elastic) stress levels for all load cases considered. Some localized plastic stresses, however, would be developed in the cone section during emergency operation. Such localized yielding effects are anticipated to be acceptable for emergency conditions. However, some form of external bracing (Bechtel, Inc. 1977b) might be used to alleviate plastic deformation under emergency conditions.

5.6.2.2 Thermal Stresses in the Calcliner Chamber/Base Plate Junction and Central Calcliner Chamber

Introduction

The calcliner chamber is heated up to a design temperature of 800⁰C. Actual operating temperatures may be less than this design temperature, depending on process conditions. The chamber is heated by a four-zone furnace, with the lowest several centimeters of the furnace having no active heating elements. In addition, most of the SC support frame and chamber base plate are not directly heated by the furnace. Thus, a large thermal gradient exists in the lower portion of the calcliner chamber. Expansion of the lower edge of the chamber is constrained by the relatively cooler base plate. The thermal stresses at the SC chamber/base plate junction are limiting stresses in the SC design. A separate ANSYS finite-element model was used to estimate these stresses. Thermal stresses in the central SC chamber due to radial thermal gradients are also significant and are discussed separately below. No other large thermal gradients exist in the assembly, so thermal stresses are not significant elsewhere.

Modeling Considerations

An axisymmetric model of the SC chamber/base plate junction was used. Although this is not strictly representative of the actual geometry, the local nature of the thermal stresses at the junction makes this a good approximation.

A total of 60 linear, elastic, 2-D, isoparametric, solid finite elements were used in the model. Figure 5.6.8 shows the model geometry. Stainless steel alloy 304 material properties based on ASME Code (ASME 1977) design values were used for the 304L base-plate elements. Inconel-601 alloy was used for

FIGURE 5.6.8. Model Geometry for SC Chamber/Base Plate Junction Thermal Stresses

the chamber. The Inconel-601 material properties were taken from Alloy Digest (1970) and the Aerospace Structural Metals Handbook (DOD 1978).

Due to limited material data, a classical bilinear stress-strain curve model was used for the Inconel-601 material with kinematic hardening. Temperature-dependent Young's Moduli were used. A more general, piecewise linear stress-strain curve was used for 304 stainless steel based on ASME Code Case N47 (ASME 1977) material hot tensile isochronous stress-strain curves.

The temperature distribution used for the analysis was based on actual SC chamber temperatures measured by a series of thermocouples located near the base of a prototype SC chamber during processing of nonradioactive, simulated waste. Temperatures for this run were somewhat lower than the design temperature. The actual high temperature in the lowest furnace zone for this run was 695°C . Of primary interest at the SC chamber/base plate junction is the axial thermal gradient along the SC chamber. The experimentally measured thermal gradient was linear over the lower 11.4 cm (4.5 in.) of the chamber. For analysis purposes, a linear axial thermal gradient was assumed with the base plate at 510°C and the upper chamber at 695°C . Stresses due to radial thermal gradients in the central chamber are discussed separately.

It was further assumed that the base plate was mounted on the support structure in a manner that allows free outward expansion of the plate for the base plate temperature rise from 20° to 510°C . This can be accomplished by bolting the plate to the support structure with oversized bolt holes to allow for thermal expansion. If the plate is welded to the frame, additional compressive stresses arise in the plate due to the restraint in "radial" thermal expansion.

The model was analyzed for a four-step process as follows:

- a) The initial structure is at ambient temperature (20°C) and is initially stress-free.
- b) The structure is heated to the 510°C to 695°C temperature range, described above, resulting in some plastic deformation of the lowest region of the chamber.

- c) The structure is then cooled to the ambient (20°C) condition and residual stresses are calculated.
- d) The structure is then reheated to the 510° to 695°C condition. The strain range between the last two steps was used in the fatigue analysis.

This multi-step model was used to account for initial elastic shakedown due to material work hardening.

Predicted Stresses and Deformations

Stresses and deformations were predicted for the series of load cases previously described. Figures 5.6.9 and 5.6.10 show the distorted geometry following the second (cooldown) and third (reheat) load steps, respectively.

Note that both figures show exaggerated distortions with different magnification factors for the displacements. Figure 5.6.19 shows the permanent set deformation due to plastic deformation in the lower SC chamber on initial heating. The local restraint in SC chamber expansion due to the cooler base plate is evident in Figure 5.6.10. The maximum radial displacement at the outer base plate edge is 0.56 cm (0.221 in.) at temperature.

Figures 5.6.11 through 5.6.14 show the normal stress components and the stress intensity distribution at temperature for the region nearest the SC chamber/base plate junction, where thermal stresses are the highest. The Inconel-601 chamber has been subjected to plastic deformation; the 304 stainless steel base plate remains elastic.

Figures 5.6.15 through 5.6.18 show the residual normal stress components and the stress intensity distribution when the junction is cooled. Residual stresses in the SC chamber are significantly higher than those in the plate, but all stresses remain elastic.

Creep-Fatigue Interaction Associated With Thermal Stresses

Two possible failure modes for the SC chamber/base plate junction are creep and fatigue damage. The ASME elevated temperature Code Case N47 (ASME 1977) provides rules for assessing the combined effects of creep and fatigue.

FIGURE 5.6.9. Distorted Geometry of SC Chamber/Base Plate Junction Following Cooldown

FIGURE 5.6.10. Distorted Geometry of SC Chamber/Base Plate Junction Following Reheating

A combined usage factor approach is used. Although the Code Case does not strictly apply to the SC assembly, this method of assessing cumulative damage is used in this analysis.

Limited information is available on Inconel-601 material fatigue properties at the service temperatures involved in the SC assembly. In particular,

FIGURE 5.6.11. Junction Radial Stress Distribution at Temperature

FIGURE 5.6.12. Junction Axial Stress Distribution at Temperature

FIGURE 5.6.13. Junction Hoop Stress Distribution at Temperature

FIGURE 5.6.14. Junction Stress Intensity Distribution at Temperature

FIGURE 5.6.15. Junction Residual Radial Stress Distribution Upon Cooling

fatigue data are highly dependent on test conditions such as specimen surface finish, mean stress level, and environmental conditions. However, to assess likely fatigue damage, three approaches were used. In light of the relatively low equivalent strain range calculated for the highly stressed regions of the junction, low fatigue damage is expected under normal operation.

The first method compares the expected strain range directly with the Inconel-601 material fatigue curves from the Aerospace Structural Metals Handbook (DOD 1978). Test data are available for hot-rolled rod (both annealed and solution-treated) and cold-rolled and annealed sheet. Figure 5.6.19 duplicates the test data. After correcting for test temperature differences,

FIGURE 5.6.16. Junction Residual Axial Stress Distribution Upon Cooling

FIGURE 5.6.17. Junction Residual Hoop Stress Distribution Upon Cooling

a worst-case service life of approximately 10^6 cycles is still predicted. This would indicate that expected fatigue damage to the junction is negligible under any reasonable service cycling.

A second approach is to use Manson's "Universal Slopes" low-temperature generalized fatigue equation (Bechtel, Inc. 1977b) to estimate fatigue life for a given strain range. Factors of 20 on the calculated number of allowable cycles and two on strain range are used as factors of safety to account for the use of this equation at a temperature of 510°C (950°F). For a calculated strain range of 0.00145, the fatigue life thus calculated is approximately 50,000 cycles. Fatigue damage due to startup/shutdown cyclic thermal stresses at the SC chamber/base plate junction is therefore expected to be negligible.

FIGURE 5.6.18. Junction Residual Stress Intensity Distribution Upon Cooling

The third approach is to compare the predicted strain range against all materials for which design fatigue data are available in the ASME Code for the service temperatures involved. These materials are 304 stainless steel; 316 stainless steel, and Inconel 800H. The two design curves are simultaneously shown as Figures 5.6.20. The predicted junction equivalent strain range is also shown. The minimum fatigue life thus predicted to 800 cycles based on Inconel 800H properties. This value will be used in service life predictions in order to be conservative.

FIGURE 5.6.19. Inconel-601 Fatigue Data Reproduced From Aerospace Structural Metals Handbook (DOD 1978)

Using the Aerospace Structural Metals Handbook (DOD 1978) creep data for Inconel-601 solution annealed material (Figure 5.6.21) a creep rupture time of 60,000 h is predicted based on the maximum Von-Mises equivalent stress of 228 MPa (33 ksi) in the junction of chamber and plate.

FIGURE 5.6.20. ASME Code Fatigue Data at 510°C (950°F) Using Figures T-1430-1A and -1C of Code Case N47

FIGURE 5.6.21. Creep Rupture Data for Inconel-601 Reproduced From Aerospace Structural Metals Handbook (DOD 1978)

Using the usage fraction approach, service lives are predicted for a weekly and monthly cycle of operation. The service lives are 4.7 years and 6.3 years are predicted, respectively, excluding shutdown time. If fatigue damage is neglected based on the Aerospace Structural Material Handbook Data, a service life of 6.8 years excluding down time is predicted for either case. From these analyses, the controlling factor in the SC chamber life is expected to be creep damage, as opposed to fatigue damage.

A junction thermal stress analysis was also conducted for a 310 stainless steel chamber using ASME Code (ASME 1977) Type 304/316 stainless steel design material property values. Type-304 stainless steel has a lower Young's modulus at temperature than Inconel-601 but a higher coefficient of thermal expansion. Thus, thermal strains are higher in the 300-series SC chamber than in an Inconel-601 SC chamber, but associated stresses are lower. The high-stress region is also somewhat more extensive in the 300-series chamber than in the Inconel chamber due to the lower Young's modulus of the stainless steel.

The maximum equivalent strain range predicted by finite-element analyses for the 300-series chamber is 1.63×10^{-3} . This corresponds to an allowable number of cycles for fatigue damage of 3000. The corresponding minimum time to stress rupture for the maximum predicted Von Mises equivalent stress of 132 MPa (19,200 psi) is 200,000 h. Using the piecewise-linear creep fatigue envelope (Figure 5.6.22) for 300-series stainless steels from ASME Code (ASME 1977), operating lives of 12 years and 19 years are predicted for weekly and monthly cyclic operation, respectively.

Central SC Chamber Thermal Stresses Due to Radial Thermal Gradient

The central SC chamber is essentially free to expand and has minimal axial thermal gradients. However, a radial thermal gradient exists due to the heat flux through the wall from the surrounding furnace. This radial gradient (assuming only radial heat flow in the chamber) is approximately 12°C (22°F) for the 70 kW per zone normal operating condition of the furnace and increases to 27°C (48°F) when, with loss of furnace control, the furnace section operates at its rated 150 kW per zone.

FIGURE 5.6.22. Creep Fatigue Interaction Envelope for 300-Series Stainless Steels Taken from the ASME Code (ASME 1977)

Using a linear elastic closed-form solution (Timoshenko and Goodier 1951), thermal gradient stresses are predicted as shown in Table 5.6.10.

These stresses are well within elastic limits. Creep rupture life at these stresses for solution-treated Inconel-601 is approximately 40,000 h or 4.6 years of continuous operation based on peak bending stresses in the chamber. This is a highly conservative figure, since it is an elastic analysis. In actual practice, stress relaxation would occur that would lessen creep damage; creep life would be significantly better.

Creep rupture at the inner surface of the SC chamber would likely initiate cracking of this surface. However, due to the net compressive membrane stresses in the section under normal operating conditions, it is unlikely that cracks so initiated would propagate through the chamber wall.

A similar analysis was conducted for a 310 SS chamber. Due to a higher thermal conductivity of 310 SS over Inconel-601, the radial gradient in this case is estimated to be approximately 10°C (18°F) for the 70 kW per furnace

TABLE 5.6.10. Central SC Chamber Thermal Stresses

<u>Stress</u>	<u>Normal Operating Conditions</u>	<u>Upset Conditions Loss of Furnace Control</u>
Inner surface hoop and axial stresses	24 MPa (3480 psi)	51.7 MPa (7500 psi)
Outer surface hoop and axial stresses	23 MPa (3340 psi)	49.6 MPa (7200 psi)

zone normal operation and increases to 22°C (39°F) under loss of furnace control. The maximum predicted normal operating stresses are the axial and hoop stresses at the inner chamber surface, which are 16.8 MPa (2400 psi). Using the ASME Code (ASME 1977) minimum time to creep rupture curves for 304 SS, a design operating life of 27,000 h is predicted (3.1 years). This is somewhat less than that previously predicted for the Inconel-601 chamber.

Creep Buckling of SC Chamber

Creep buckling of the SC chamber was briefly investigated. The elastic critical external pressure for buckling of a thin tube with closed ends is predicted using a closed form model (Roark and Young 1975, Table 35, Number 20). For the SC chamber the elastic buckling pressure is 1 MPa (144 psi) at 800°C. Using a model for creep buckling for cylindrical shells (Bargmann 1972), a critical time to complete creep collapse is predicted. A uniaxial steady creep power law with $n = 5$ is assumed for the Inconel-601 material (i.e., $\dot{\epsilon} = k\sigma^5$). An initial out-of-roundness of 1 cm for the chamber was assumed (equal to the wall thickness to account conservatively for initial imperfections). Using this model and a creep rate of 0.0001%/h at 800°C and 53 MPa (7600 psi) stress based on Aerospace Structural Metals Handbook (DOD 1978) data. A creep life in excess of 10^{10} years is predicted for the normal operating condition of 2480 MPa (0.36 psi) external pressure. Thus, the chamber is not likely to collapse due to creep buckling or elastic buckling under normal operating loads. A similar conclusion should be equally valid for a 310 SS chamber.

5.6.2.3 Vibratory Behavior of SC Chamber Under Dynamic-Impact Loading

Introduction

The purpose of this section is to identify the transient stresses caused by vibration of the calciner chamber for fatigue life evaluation. Two vibrators alternately impact the spray calciner at elevated temperatures. The dynamic analysis is performed at design operating conditons. This section describes the analysis approach, results of the analysis, and conclusions.

Method of Analysis

Loading Condition. The spray calciner was analyzed for static and dynamic loading at design operating temperatures (800°C). Dynamic loading is caused by two vibrators alternately striking the calciner chamber. The applied vibrator force function was taken from a previous Bechtel study of SC assembly response to vibratory loading (Bechtel, Inc. 1977b). Briefly, the force function was experimentally determined by pressurizing the vibrator and striking a target impact plate. From a displacement versus time chart and experimentally determined spring constant, the magnitude of the forces was calculated. Although geometry changes to the structure may modify the actual loading function, the assumed loading function represents the best model available.

Finite-Element Model. Design specifications were followed as closely as available information allowed. An ANSYS finite-element model comprising one quarter of the chamber represents the spray calciner chamber with a height of 3.2 m (10.5 ft), a diameter of 91.44 cm (36 in.), a chamber thickness of 0.953 cm (0.375 in.) and an impact plate thickness of 2.54 cm (1.0 in.). The model shown in Figure 5.6.23 is symmetric about a vertical plane through the vibrator impact points and a horizontal plane at mid-height. This models a condition of vibrator loading 180° apart. A localized stress distribution is to be reasonably expected from alternate vibrator loading at the design placement of 120° apart. Assumption of 180° loading points permitted use of an additional plane of symmetry in the model which considerably reduced modeling time and computer costs, but due to the local nature of the impact pad effects, this assumption should have little effect on predicted chamber stresses.

FIGURE 5.6.23. Finite-Element Model of Spray Calciner -- One Quarter Axisymmetric Model

The calciner is modeled using three-dimensional, rectangular and triangular shell elements with both bending and membrane characteristics. Both elements have 6 degrees of freedom at each node: three components of translation and three components of rotation about nodal axes. A relatively fine mesh is used to model the impact area where higher stresses are expected. A coarser mesh is used to model the rest of the cylinder where stresses are not expected to be significant. The model uses 100 elements and 106 nodes. The impact plate is modeled with an assumed corner radius of curvature of approximately 2 in. Figure 5.6.23, a plot of the model, shows the mesh refinement modeling the impact plate. Temperature-dependent material properties are input. The

model experiences a uniform temperature rise to the design operating temperature of 800°C (1472°F) and vibratory stresses are evaluated using appropriate material properties. Thermal discontinuity stresses were not calculated using this model. The generic material properties are taken from the ASME High-Temperature Code Case (ASME 1977) and the Aerospace Material Handbook (DOD 1978). Results are similar for both 310 SS and Inconel-601 chambers, since their respective Young's Moduli do not differ significantly at temperature.

The top of the SC chamber is restrained against all translation and rotation. Restraint is provided at the upper end of the chamber by the plate welded to the chamber and the spray nozzle acting as a shear pin tying the plate to the SC assembly seismic bracing. The lower end of the chamber is welded to the base plate. At the midplane of symmetry in the model, the calciner is allowed to expand radially but is prevented from translating vertically and circumferentially.

Two checks were performed to assure the reliability of the finite element model in representing the behavior of the spray calciner. The fundamental natural frequency was calculated by using the ANSYS model and then compared with Bechtel's results (Bechtel, Inc. 1977b) and a closed-form solution using Donnell's equations (Kraus 1967). Both checks showed good agreement with the finite-element model results.

Results

Mode Frequency Analysis. The first seven natural frequencies are listed in Table 5.6.11. The fundamental frequency computed by finite-element analysis is 106 cycles per second. It agrees very well with 111 cycles per second calculated using Donnell's equation. It is also in close agreement with Bechtel's results when scaled by appropriate factors for differing shell thickness and elastic modulus.

Figure 5.6.24 is a plot of the lowest natural frequencies as a function of the number of circumferential waves calculated with Donnell's equation. It predicts the lowest natural frequency corresponding to $n = 3$. Figures 5.6.25

TABLE 5.6.11. Natural Frequency of Spray Calclner Chamber

<u>Mode</u>	<u>Inconel-601 Chamber Frequency, cps</u>	<u>310 SS Chamber Frequency, cps</u>
1	106	98
2	137	126
3	149	138
4	156	144
5	167	154
6	184	169
7	195	180

and 5.6.26 are plots of the mode shape of the fundamental frequency. Figure 5.6.24 clearly shows that the lowest frequency occurs at $n = 3$. The mode shapes for modes two and three appear in Figures 5.6.27 through 5.6.30.

Dynamic-Response Analysis. A dynamic-response analysis determined the linear elastic transient stresses induced in an Inconel-601 chamber in the SC

FIGURE 5.6.24. Natural Frequencies of Spray Calclner

FIGURE 5.6.25. Mode Shape for Mode 1, $f = 106$ Hz

FIGURE 5.6.26. Mode Shape for Mode 1, $f = 106$ Hz

FIGURE 5.6.27. Mode Shape for Mode 2, $f = 137$ Hz

FIGURE 5.6.28. Mode Shape for Mode 2, $f = 137$ Hz

FIGURE 5.6.29. Mode Shape for Mode 3, $f = 149$ Hz

FIGURE 5.6.30. Mode Shape for Mode 3, $f = 149$ Hz

assembly by vibrator impact forces represented in Figure 5.6.31 (310 SS chamber stresses would be similar). Two vibrators are mounted per assembly, 120° apart. The two vibrators alternate operation every 3 min, with each vibrator being operated separately for a 3-s duration. Response to a single period of operation of one vibrator was analyzed. A previous Bechtel study (Bechtel, Inc. 1977b) found that the maximum SC chamber response to such loading occurred in the first 3 s of operation. [Bechtel analyzed a similar SC assembly, but with a 0.63-cm (1/4-in.) wall structure.] Therefore, the dynamic loading of Figure 5.6.31 was repeated for nine cycles to simulate the applied loading to the calciner for the 3-s forcing period. Direct numerical integration of the equations of motion were used with a time step of 0.0005 s. Twenty master degrees of freedom were used in a reduced analysis.

Figure 5.6.32 is a plot of the predicted radial displacement response at the point of vibratory hammer impact over 2.5 s. It indicates the periodicity of the response corresponding to the vibrator's impact force period of 0.32 s. Figure 5.6.33 is an enlarged view of the radial displacement response over one cycle of load. Figure 5.6.34 plots the Von Mises equivalent stress response for one cycle of the outer shell surface under the point of impact. The

FIGURE 5.6.31. One Cycle (0.32 s) of Vibratory Force Function (Bechtel, Inc. 1977b)

FIGURE 5.6.32. Radial Displacement Response of Cylinder to Vibratory Loading at the Shell Surface at the Impact Point

maximum Von Mises equivalent stress developed by the structure is approximately 3860 MPa (560 psi) at the point of impact. The corresponding displacement is 0.00546 cm (0.00215 in.).

A contour stress plot of the impact plate and adjoining area, Figure 5.6.35 shows two areas of stress concentration. As mentioned previously,

FIGURE 5.6.33. Radial Displacement Response for One Cycle of Vibratory Loading at the Shell Surface at the Impact Point

the peak stresses occur at the point of vibratory loading. The closely spaced stress contours at the impact point indicate this stressed area. The plot shows a second area of stress concentration at a lower magnitude. The corner of the impact plate, develops a stress of approximately 3380 MPa (490 psi). This is to be expected at the discontinuity in shell thickness.

FIGURE 5.6.34. Equivalent Stress Response for One Cycle of Vibratory Loading at the Shell Surface at the Impact Point

The Bechtel study (Bechtel, Inc. 1977b) predicted a maximum stress of 1330 psi at the weld around the impact plate for the thinner-walled SC chamber. Two differences in the model geometry may account for the variation in the maximum stresses predicted by Bechtel and the present one. First, the Bechtel model used a square-cornered impact plate. The square corner induces a further stress concentration beyond that inherent in the abrupt change in wall thickness at the edge of the impact plate. The present model uses an

FIGURE 5.6.35. Contour Equivalent Stress Plot Near Impact Plate Shows Peak Stresses Occur at the Impact Point and Corner of Weld Plate

arbitrarily chosen corner radius of approximately 5.08 cm (2 in.) for the impact plate. Second, a difference in shell thickness, 0.635 cm (0.25 in.) versus 0.953 cm (0.375 in.) contributes to the higher stresses in the Bechtel model.

Conclusions

Fatigue Life. The Manson "Universal Slopes" fatigue equation (Bechtel, Inc. 1977b) was again used to estimate fatigue life for the predicted stress level at 800°C (1472°F). Again, factors of 20 were used on the number of allowable cycles and two on strain range to account for uncertainties of using this equation in elevated temperature applications. Even so, a fatigue life

of 5×10^{12} cycles was predicted for the Inconel-601 chamber and 5×10^{13} cycles for the 310 stainless steel chamber for the equivalent strain range associated with the highest peak stress in the transient that occurs once every 0.32 s of vibratory operation. Fatigue damage, therefore, was negligible.

Low stresses are predicted for the vibratory transient response. The ASME strain range associated with these low stresses is well below strain ranges for which design fatigue data are available (ASME 1977) for materials covered by the ASME Code. Thus, distortion and fatigue failure does not appear to be a significant consideration.

5.6.2.4 Filter-Element Stress Analysis

A closed-form model of a cantilever beam with the other end hinged was used to predict bending stresses in the filter during vibratory loading. The lateral filter supports provide the hinged constraint at the lower filter end. The stiffness of the internal axial rod brace within the filter was not accounted for in the model.

Bending stresses equal to the Inconel-601 yield stress are reached for a solid filter (i.e., no porosity) under a 360-g static horizontal loading. This is well above vibratory or seismic loading conditions. Although, the model includes no microstructural effects on strength of the filter porosity, the high margin of safety inherent in the present calculation indicates the satisfactory design of the filters. In addition, porosity effects reduce filter mass (hence material loading) during vibration. This offsets to some extent the strength reduction due to porosity. It should be noted that no structural failures due to mechanical properties have occurred in the prototype SC assembly filters during operation at PNL to date. Failure of the filters is more likely to be controlled by corrosion or other phenomena.

A simple cantilevered filter without lower-end support would be subject to four times the stress at the attachment point than predicted above. Therefore, the lower supports for the filters may not be necessary, since acceptable stresses occur during vibration loading without them; however, they provide a further margin of safety for the design.

5.6.3 IN-CAN MELTER STRUCTURAL REVIEW

The following components and their loadings are considered to be the most significant with respect to the integrity of the ICM.

Canister Lid

This component is used to gain access to the canister as it is being filled in the melter, and it must be capable of sustaining the lifting load of the empty canister as it is placed into the melter. This load should be less than that occurring during the canister's removal when it is filled. Since the integrity of the twist-lock closure is discussed and established (Simonen and Slate 1979) for the greater load acting on the closure, it is assumed that this part of the lid can be similarly designed to be adequate. The remainder of the lid structure should present no structural integrity problems.

Liner

The most severe condition experienced by the liner is the thermal straining due to the effects of adjacent cooling and heating zones. The five zones can be controlled to be heated up to 1200°C (maximum) or cooled down to 700°C. The corresponding temperatures of the liner will fall within this range over some limited axial distance encompassing the boundary of two adjacent zones imposing the two temperature conditions.

An evaluation of the consequences of such a temperature distribution is described for the canister (Simonen and Slate 1979), which is also 6.35 mm (0.25 in.) thick. However, two different materials are involved: 304 stainless steel for the canister and Inconel-690 for the liner. The properties of the Inconel-600 series and 304 stainless steel (specifically, Young's modulus and the linear thermal expansion coefficient) are well within an order of magnitude in similarity as they change with temperature. It is estimated that the canister could experience a permanent radial deformation of 0.058 mm (0.0023 in.) for a change in axial temperature from 900°C to 1050°C. The conditions defined for the liner could be more severe, with a maximum possible temperature transition of 500°C. It is anticipated that the corresponding deformation (permanent) for one cycle of heat-up and cool-down could be an

order of magnitude greater than was concluded possible for the canister. After 10 such cycles the change in radius would accumulate to 0.23 in.

The maximum stress of the liner, due to its own weight, is 0.24 MN/m^2 (0.035 ksi). For the stability of the thin-walled tube to be impaired, thermal degradation of the modulus of elasticity would have to reduce it to a value of approximately 5,600 psi. Such a low value would not ever occur if the temperature were to approach the melting point of the material.

Furnace

The five furnace zones are not restrained from moving relative to one another other than by friction. Thus, they are not going to experience any stress due to differences in temperature.

Similarly, under seismic loading the various furnace zones are free to move laterally with respect to one another if the static friction between adjacent furnace zones is overcome by lateral seismic loading. Thus, the maximum seismic acceleration for which the furnace zones remain stationary with respect to one another is related to the coefficient of friction between the two furnace jacket surfaces.

Accounting for reduction in normal forces due to a vertical component of seismic acceleration, the maximum horizontal seismic acceleration without "walking" of the furnace zones can be calculated by:

$$\text{maximum horizontal seismic acceleration} = \frac{\mu}{1 + 0.67\mu} g \quad (5.1)$$

where a 0.67 factor is assumed for vertical seismic acceleration with respect to horizontal seismic acceleration, and μ is the indicated static coefficient of friction for the furnace liner metal. Using a typical range of values for μ for metal alloys (0.5 to 0.9), the associated seismic acceleration range is 0.37 g to 0.56 g which exceeds El Centro earthquake levels.

5.6.4 OVERALL CONCLUSIONS

The main stresses under both normal and upset or emergency loading conditions have been predicted. Stresses are generally low enough to provide reasonable assurance of proper operation.

Careful attention should be paid to final detailing of the assembly to prevent undesirable stress concentration effects. For example, a prototype SC chamber used for nonradioactive testing was fabricated of uniform wall thickness, and impact pads were then fillet-welded to the sides of the chamber. These welds subsequently failed by crack propagation due to local stress concentrations associated with this type of construction. Essentially, a large "circular" crack under the plate was manufactured into the structure. The prototype chamber was modified to use a one-piece impact-plate insert with taper to the nominal wall thickness. Such an insert is less subject to stress concentration effects.

Two key stresses with respect to limiting SC assembly service life are the radial thermal gradient thermal stresses in the central SC chamber and the axial thermal stresses at the SC chamber/base plate junction. Several steps can be taken to alleviate these stresses and extend chamber service life, if desired.

- a) The nominal chamber wall thickness can be reduced. For fixed heat flux, this reduces the radial wall thermal gradient, thereby reducing thermal stresses. Small reductions in stress at the elevated service temperatures can yield significant changes in time to creep rupture. However, care must be taken to ensure that vibratory stresses due to the impact hammers used to remove calcine are not increased to the extent that they become controlling.
- b) The calciner chamber can be increased in thickness near its lower junction with the base plate. This provides more material to accommodate the highly localized bending stresses there. A transition nozzle from 2.54 cm (1 in.) to the final central chamber wall thickness is suggested with no less than a 3:1 taper ratio. This option is even more necessary if option (a) above is also exercised.

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6.0

SAFETY AND ENVIRONMENTAL ASSESSMENT

6.0 SAFETY AND ENVIRONMENTAL ASSESSMENT

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6.0 SAFETY AND ENVIRONMENTAL ASSESSMENT

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This section summarizes the safety and environmental assessment of the SC/ICM system. The review includes the process equipment associated with the SC feed system, SC, ICM, canister-handling operations, the effluent treatment system, and the cell structure. The assessment was based on several independent safety studies of the system and extensive internal reviews (Larson and Bonner 1976; Barnes and Bendixsen 1977; Southern Sciences Applications, Inc. 1978).

The safety assessment is purposefully general and inclusive. As such, it serves as a design guideline. As the design of the facility is carried beyond the conceptual stage it will be possible to narrow the range of the safety assessment, make the accident analyses more quantitative, and decrease the conservatism in the assumptions underlying the accident groups. An aid to interpreting the severity of the radionuclide releases, calculated for the accident groupings, is provided by an estimated source term.

The environmental assessment only provides source terms and data from the SC/ICM system that may be used to perform environmental analyses and determine materials consumption. It is beyond the scope of this document to perform an environmental analysis.

6.1 ACCIDENT AND SAFETY ANALYSES

Facility accidents and off-standard operations were classified on the basis of increasing radionuclide release, consequence potential, and/or frequency:

- Off-Standard Conditions
- Minor Incidents
- Moderate Accidents
- Design-Basis Accidents
- Hypothetical Accidents

These off-standard operations and accident classifications are defined below.

6.1.1 OFF-STANDARD OPERATIONS

Off-Standard Operations are those events that do not release significant amounts of radionuclides from the primary confinement system over normal releases through the process off-gas systems. These incidents involve small deviations from normal operating conditions. They may result from a single failure of a plant component or system, or from an operational error. These incidents are anticipated in the normal operations of the plant.

6.1.2 MINOR INCIDENTS

Minor Incidents are those events that can release an incremental amount of radionuclides outside the primary confinement systems. Incidents in this category involve such occurrences as operational errors, single failures of a plant component or system equipment reaching end-of-life cycle (e.g., momentary venting of seals to the cell atmosphere, spills of process materials, and leaks from equipment). Plant personnel and population exposure from the radionuclide releases are well within the guidelines established by 10 CFR 20 (Code of Federal Regulations, Title 10 1978). These accidents are infrequent. Facilities and associated operations are designed to easily accommodate these accidents with minimum upset in plant operations. Generally there is no increase in population exposure from these accidents.

6.1.3 MODERATE ACCIDENTS

Moderate Accidents are defined as those unplanned occurrences that could result in releases of significant amounts of radioactive material to the environment. These accidents would result in population exposures that are only a small fraction of the guidelines set in 10 CFR 100 (Code of Federal Regulations, Title 10 1978). The plant is designed specifically to avoid such accidents. However, the possibility remains that one or more such accidents could occur during the plant lifetime. The accident could result in plant operations disruption and equipment damage. The increase in population exposure could generally be on the order of background radiation.

6.1.4 DESIGN-BASIS ACCIDENTS

Design-Basis Accidents are very low-probability events that are hypothesized as a challenge to the engineered safety systems. The engineered safety systems are those systems designed to prevent the release, or mitigate the potential effect of a release of radioactive materials to the environment. These engineered safety systems include: a) confinement structures; b) ventilation systems including ductwork, filters, blowers and backup power; and c) emergency cooling supply systems, including backup power. Radionuclide releases from this accident could be a major fraction of guidelines stated in 10 CFR 100. These accidents could result in major disruptions in plant operations and equipment damage.

6.1.5 HYPOTHETICAL ACCIDENTS

Hypothetical Accidents are those events that are potentially more severe than Design-Basis Accidents but have such a low probability of occurrence that there is no need to design the facility to withstand their effects.

6.1.6 ACCIDENT SCENARIOS

Over 96 accidents and off-standard operating scenarios were developed and examined in the accident analyses for the SC/ICM process. The scenarios selected provide a complete range of probable accidents. The cause for the event, safety systems to prevent the event from occurring, methods of

detection, required corrective action, and consequences for the event were reviewed for each accident. A summary of these off-standard operations and accidents appears in Tables 6.1.1 through 6.1.5.

TABLE 6.1.1. Off-Standard Operations

Event	Potential Causes	Safety/Prevention	Detection	Corrective Actions	Consequences
A. FEED SYSTEM					
1. Tank cooling coil fails	-Improper design and fabrication -Corrosion failure -Fatigue failure	-Coils designed and operated for the intended process -Coil cooling water leakage contained by feed tank -Contaminated cooling water radiation detection and retention	-Detect increase in liquid level in feed tank -Detect radionuclide contamination of cooling water -Detect change in cooling water cooling coil outlet temperature or pressures	-Reduce or stop coil water flow -Transfer tank contents -Replace failed coil and possibly tank	-Potential contamination of cooling water with feed solution
2. Feed pump fails	-Loss of power -Pump part failure -Solids cause pump to seize -Corrosion -Erosion	-Pump designed and modified for reliable service and so as not to cause missiles on failure -Failure leads to system shutdown assuming a safe standby status -Instrumentation indicates failure	-Instrumentation indicates no power consumption -Loss of calciner feed flow	-Replace pump	-Calciner feed shutdown -Solids settle in feed line between tank and calciner
3. Loss of cooling water flow to feed tank	-Failure of water source line -Cooling water pump failure -Cooling line plugged	-Emergency cooling water supply system -Feed heats up slowly (if at all) and boils to maintain temperature -Routes to empty tank or to another tank for cooling	-Increase in tank content temperature -Abnormal cooling water outlet temperature -Instrumentation detects cause of failure	-Initiate flow of emergency cooling water -Transfer tank contents to where it can be cooled	-Would probably cause calciner shutdown -Tank feed heatup
B. CALCINER					
1. Loss of atomizing air flow	-Feed nozzle pluggage -Loss of air pressure -Instrumentation failure	-Instrumentation indicates air flow and shuts off feed flow on air loss -Air flow system designed to operate reliably -Check valve prevents feed flow up the air supply line	-Air flow detector would detect loss of flow and cause alarm -There would be a pressure drop in the feed system	-Correct equipment failure or operating problem which caused air flow loss	-Calciner shutdown -Some possible calcine buildup on walls from damp calcine generated before feed pump cut-off. Some damp calcine may reach filters -Damp calcine in connecting section leads to plugged calcine line which leads to pressurized ICM -Potential for feed back-up into air line if check valve fails or feed not shut off

TABLE 6.1.1. (contd)

Event	Potential Causes	Safety/Prevention	Detection	Corrective Actions	Consequences
B. CALCINER (contd)					
2. Nozzle enlarges due to cracks or erosion	<ul style="list-style-type: none"> -Highly erosive feed -Extreme mechanical or thermal shock causes cracking of insert 	<ul style="list-style-type: none"> -Nozzle designed to operate reliably under operating conditions -Nozzle failure does not cause safety hazard 	<ul style="list-style-type: none"> -Increase in atomizing air flowrate for controller valve settling -Decrease in feed system operating pressure -Possible change in calciner power requirements for constant feed condition -Increase in pressure drop across metal filters -Calciner cone temperature decrease 	<ul style="list-style-type: none"> -Replace nozzle 	<ul style="list-style-type: none"> -Calciner shutdown -There may be some damp calcine buildup on the calciner walls and metal filters which should be removed -During nozzle replacement calcine may become airborne and reach cell filters -Wet calcine may plug connecting section causing ICM pressurization
3. Nozzle tip plugs	<ul style="list-style-type: none"> -Buildup of cohesive solids on tip -Solution dries on tip -Solid lump plugs tip 	<ul style="list-style-type: none"> -Nozzle designed to minimize plugging possibility -On encountering sufficient feed nozzle back pressure the feed system will shut down -Air supply check valve provided to prevent feed flow into air line -Air supply pressure higher than feed supply pressure 	<ul style="list-style-type: none"> -Feed supply decrease -Increase in feed system pressure -Feed supply valve would open above normal -Decrease in calciner power used due to reduced feed -Potential wet calcine could result in: ΔP increase in filters -reduced calcine feed rate to ICM 	<ul style="list-style-type: none"> -Flush out nozzle -Replace nozzle 	<ul style="list-style-type: none"> -Calciner shutdown -During nozzle replacement calcine may become airborne and reach cell filters -Wet calcine buildup in SC
4. Furnace elements burn out	<ul style="list-style-type: none"> -Elements reach end of service life -Faulty construction or installation -Operation at higher than anticipated temperature and excessive cycling -Physical abuse in operation -Furnace elements short to calciner wall 	<ul style="list-style-type: none"> -Furnace elements designed for reliable operation -Furnace element burnout would not cause an immediate safety problem -Current limiter on power supply -Calciner properly grounded 	<ul style="list-style-type: none"> -Power supply instrumentation would indicate discontinuity -Calciner temperature would decrease or power requirements in other zones would increase -Change in calciner temperature profile -Calciner temperatures significantly below the set point will cause an alarm -Furnace element burnout would set off an alarm 	<ul style="list-style-type: none"> -Replace failed furnace zone -Potentially need for calciner cleanout 	<ul style="list-style-type: none"> -Calciner shutdown -During equipment replacement calcine becomes airborne and reaches cell air filters -Possibly melt hole in calciner barrel -Potential wet calcine buildup in SC

TABLE 6.1.1. (contd)

Event	Potential Causes	Safety/Prevention	Detection	Corrective Actions	Consequences
B. CALCINER (contd)					
5. Vibrators inoperative	<ul style="list-style-type: none"> -Improper position adjustment -Component failure -Loss of air pressure or control instrumentation -Piston seizes from inadequate lubrication or corrosion 	<ul style="list-style-type: none"> -Vibrators designed to operate reliably -Vibrator failure would cause no immediate safety problem -Instrumentation is available to detect failure 	<ul style="list-style-type: none"> -Vibrator noise would cease or change -For some failure modes, instrumentation such as air supply or power continuity would slowly change 	<ul style="list-style-type: none"> -Correct cause of vibrator improper operation -Replace vibrator 	<ul style="list-style-type: none"> -Some calcine buildup on calciner walls
6. Failure of furnace control thermocouples	<ul style="list-style-type: none"> -Thermocouples reach end of service life -Thermocouples or connections damaged 	<ul style="list-style-type: none"> -Power automatically shuts down -Secondary thermocouple can be used for control 	<ul style="list-style-type: none"> -Alarm -Loss of power to zone 	<ul style="list-style-type: none"> -Switch to redundant thermocouple for control -Replace thermocouple 	<ul style="list-style-type: none"> -Calciner zone temporarily shut down
7. Diverter valve is inoperative	<ul style="list-style-type: none"> -Failure of valve mechanical linkage -Loss of activation air cylinder air supply -Failure of valve activation solenoid valve -Valve becomes jammed by calcine deposits 	<ul style="list-style-type: none"> -Valve and operating mechanism is conservatively designed for reliable operation 	<ul style="list-style-type: none"> -Position indicator on valve will indicate inoperability -Loss of activation system continuity should be indicated by instrumentation -Loss of air supply would be indicated 	<ul style="list-style-type: none"> -Correct equipment failure 	<ul style="list-style-type: none"> -Canister overflow -If the diverter valve is replaced there could be calcine released to the cell of which some would become airborne
8. Seals on diverter valve operator shaft leak	<ul style="list-style-type: none"> -Equipment erosion and corrosion 	<ul style="list-style-type: none"> -Seals are designed for a specific life -Seals are designed to minimize calcine buildup around them 	<ul style="list-style-type: none"> -Reduction of vacuum in calciner -Gradual increase in cell radioactivity -Irregularities noticed in valve operation and instrumentation 	<ul style="list-style-type: none"> -Change valve 	<ul style="list-style-type: none"> -There could be some calcine released to the cell in the valve replacement of which some would become airborne
9. Cone valve sticks closed	<ul style="list-style-type: none"> -Buildup of calcine around valve opening -Valve activator broken 	<ul style="list-style-type: none"> -Design to prevent occurrence -Operate calciner to prevent occurrence -Valve activator designed to overcome binding 	<ul style="list-style-type: none"> -Indicator shows valve closed -Instrumentation shows no feed to ICM canister 	<ul style="list-style-type: none"> -Replace cone valve -Or remove blockage by impacting valve -Or replace activator 	<ul style="list-style-type: none"> -If cone valve is replaced some calcine and frit mixture would be lost to cell (valve remains closed) of which some would become airborne
10. Seal pot (Attached to pressure relief port) loses water	<ul style="list-style-type: none"> -Calciner pressurization -Evaporation -Operator neglect 	<ul style="list-style-type: none"> -Seal pot water level detection -Periodically check seal pot operation to assure reliability -Calciner operates at vacuum to other systems except the off-gas 	<ul style="list-style-type: none"> -Instrumentation indicates water loss -Detection of vacuum loss in calciner 	<ul style="list-style-type: none"> -Fill seal pot with water 	<ul style="list-style-type: none"> -If seal pot loses water calcine may be lost to the associated tank

TABLE 6.1.1. (contd)

Event	Potential Causes	Safety/Prevention	Detection	Corrective Actions	Consequences
B. CALCINER (contd)					
11. Frit gravimetric feed device inoperative	<ul style="list-style-type: none"> -Mechanical failure -Instrumentation failure -Frit bin empty -Frit fines clog feed mechanism 	<ul style="list-style-type: none"> -Designed to prevent failure -Instrumentation operating to detect failure 	<ul style="list-style-type: none"> -Detection of frit flow loss to melter by weight change instrumentation -Instrumentation shows inoperability by power loss or readings -Alarm on belt drive tachometer 	<ul style="list-style-type: none"> -Correct instrument or mechanical failure -Fill frit bin 	<ul style="list-style-type: none"> -Off-standard frit/calcine ratio in canister which could cause off-specification glass
12. Pressure relief port fills with calcine	<ul style="list-style-type: none"> -Normal operation -Pressurization of calciner 	<ul style="list-style-type: none"> -Periodic routine flushing -Instrumentation to detect foreign materials buildup 	<ul style="list-style-type: none"> -Specific gravity and weight factor increase of seal pot water 	<ul style="list-style-type: none"> -Flush or dissolve out solids 	<ul style="list-style-type: none"> -If calciner pressurizes, equipment could be damaged and there may be some calcine released to the hot cell
13. Frit feed airlock inoperative	<ul style="list-style-type: none"> -Instrumentation failure -Valve, linkage, operator failure -Damp frit clogs line or jams valve -Lose air pressure 	<ul style="list-style-type: none"> -Instrumentation operating to detect failure 	<ul style="list-style-type: none"> -Detect loss of frit flow to the melter -Detect imprint of airlock operation on calciner pressure -Airlock instrumentation would show abnormal operation 	<ul style="list-style-type: none"> -Correct instrument or mechanical failure -Replace airlock components if necessary -Restore air supply 	<ul style="list-style-type: none"> -Extended outage of frit flow could cause making of out of specification glass
14. Frit feed line blocked	<ul style="list-style-type: none"> -Damp frit clogs line -Calciner moisture migrates back up through frit feed line -Inadequate line slope to make frit flow -Frit-calcine buildup at calcine entry opening -Line allowed to get too cool 	<ul style="list-style-type: none"> -Calciner operated at vacuum to line to inhibit moisture entry -Instrumentation to detect blockage -Line is insulated and/or heated 	<ul style="list-style-type: none"> -Loss of frit flow to the melter -Calciner vacuum history may be altered 	<ul style="list-style-type: none"> -Impact line to remove clog -Replace line if clog cannot be removed 	<ul style="list-style-type: none"> -Potential production of out-of-specification glass -Potential for calcine release during change-out
15. Blockage forms at diverter entry (bottom of calciner cone) or in connecting section	<ul style="list-style-type: none"> -Inadequate vibration by vibrators -Calcine damp and resists flowing down cone walls -Slow calcine buildup due to ledge or improper operation of diverter valve -Nozzle failure 	<ul style="list-style-type: none"> -Equipment designed to prevent accumulation (cone slope, no ledges, and vibrators) -Calciner operation designed to prevent accumulation (high temperature, vibration, and adequate calcine residence times) -Adequate atomization 	<ul style="list-style-type: none"> -Canister fill monitoring systems (weighing, thermocouple, and radiation detection systems) detect no or insufficient glass buildup in canister -Thermocouples in cone and connecting section indicate a temperature drop and a very stable temperature -Increased pressure drop across connecting section 	<ul style="list-style-type: none"> -Assess situation and shut down operations -Clear blockage by impact, vibration, or flushing -Decontaminate cell and equipment as necessary -Modify or replace any nonfunctional equipment as necessary 	<ul style="list-style-type: none"> -Calcine released to cell during calcine and frit removal operation and some calcine reaches cell filter system -Pressurization of the melter and connecting section results in venting of calciner/frit to the cell

TABLE 6.1.1. (contd)

Event	Potential Causes	Safety/Prevention	Detection	Corrective Actions	Consequences
C. MELTER					
1. Furnace elements open	<ul style="list-style-type: none"> -Elements reach end of service life -Faulty construction or installation -Operation at higher than anticipated temperature and excessive cycling -Physical abuse in operation -Furnace element shorts to liner -Duty cycle caused distortion of liner 	<ul style="list-style-type: none"> -Furnace element designed for reliable operation -Melter temperature significantly below set point will cause alarm -Furnace element burnout will cause an alarm -Furnace element burnout would not cause an immediate safety hazard 	<ul style="list-style-type: none"> -Power supply instrumentation would indicate discontinuity -ICM temperature would decrease or power requirements in other zones may change -Abnormal melter temperature -Abnormal temperature profile 	<ul style="list-style-type: none"> -Replace failed furnace zone -May need to replace retort if substantially warped 	<ul style="list-style-type: none"> -System would have to operate with only one melter or shut down -During equipment replacement calcine dust in cell becomes airborne and reaches filters -Complete canister processing in another furnace
2. Spout fails to seal	<ul style="list-style-type: none"> -Gasket missing -Poor alignment 	<ul style="list-style-type: none"> -Gasket designed to maintain position -Equipment designed for proper alignment 	<ul style="list-style-type: none"> -Detect excessive air in leakage when cone valve opened -Visual observance of alignment 	<ul style="list-style-type: none"> -Repeat coupling procedure -Replace gasket -Reposition canister in furnace 	<ul style="list-style-type: none"> -Release some calcine to cell -Delay canister filling cycle
3. Spout fails to completely retract	<ul style="list-style-type: none"> -Obstruction in top of canister -Obstruction in bellows -Drive mechanism failure 	<ul style="list-style-type: none"> -Designed to avoid this problem 	<ul style="list-style-type: none"> -Visual observation -No change in limit switch position 	<ul style="list-style-type: none"> -Remove obstruction causing jam -Correct mechanical failure causing jam 	<ul style="list-style-type: none"> -May cause spread of calcine in cell during corrective action -Delay canister fill time cycle
4. Connector rotation attempted when canister is attached to fill chute	<ul style="list-style-type: none"> -Activation of wrong leg of connecting section -Faulty disengagement of canister from spout -Operator inattention -Interlock failure 	<ul style="list-style-type: none"> -Interlock -Cell HEPA filters and APS -Visual observation -Connector would not rotate with spout attached to canister 	<ul style="list-style-type: none"> -Observe spout elevation -Cone valve instrumentation and readings disrupted -Loss of calciner vacuum -Increase in cell and cell filter radiation readings 	<ul style="list-style-type: none"> -Assess situation and shut down operations -Decontaminate cell and equipment as needed -Replace failed equipment and instrumentation as needed -Replace damaged equipment 	<ul style="list-style-type: none"> -None
5. Sintered calcine bridge in canister causes calcine backup into diverter	<ul style="list-style-type: none"> -Calcine bridge formed on canister fin top -Poor placement or design of fins in canisters -Excessive canister feed rate -No frit feed -No heat at canister top 	<ul style="list-style-type: none"> -System designed to prevent bridging 	<ul style="list-style-type: none"> -Detect abnormal weight buildup rate -Canister gamma monitoring detects abnormal fill rate -Increased ΔP across connecting section 	<ul style="list-style-type: none"> -Attempt to remove bridge by shutting down calciner and operating melter -Or shutdown calciner/melter -Close cone valve and replace canister (minimize calcine spread) 	<ul style="list-style-type: none"> -Delay canister fill cycle if bridge can be removed by melter operation -Or canister will be only partially filled -Some calcine spread to melter and cell, cone valve may have to be replaced -Pressurize ICM

TABLE 6.1.1. (contd)

Event	Potential Causes	Safety/Prevention	Detection	Corrective Actions	Consequences
<u>C. MELTER (contd)</u>					
6. Overheating canister	-Operator programs inappropriate cycle -Malfunction of furnace programmer -Malfunction of canister cooling system -Malfunction of thermocouples	-Operator training -Redundant temperature instrumentation to detect high temperatures -Interlocks and current limiters	-Alarm on incurrence of high temperatures -Observe inappropriate instrument settings	-Change instrument settings -Correct malfunctioning equipment operation	-None (evaluation would have to be made of canister to see if canister integrity is compromised)
7. Excessive canister feed rate causes canister overfilling	-Blockage occurs in canister -Low melter furnace power input -Excessive calcine or frit feed rate -Improper readout of solids levels in canister	-Redundant instrumentation for canister fill detection -Operators experienced to detect off-standard operating conditions from instrument readings	-Change in melter instrumentation from normal cycle readings -Operator observes inappropriate instrument settings -Instruments would show inappropriate level readings relative to weight	-Stop canister feed and melt excessive calcine and frit into canister -Clean up any frit/calcine overflow on canister change	-There may be some calcine/frit loss to the cell or melter on canister change (cone valve may get jammed and need replacement)
8. Loss of canister cooling in ICM immediately after filling	-Malfunction of valve -Loss of air header	-Instrumentation will allow early detection -Alternate air header in system as part of design criteria	-Furnace temperatures are monitored	-Remotely rig air jumper to ICM -Uncouple ICM and blow air into ICM from top	-With 17 w/L glass (acid HLLW) a preliminary calculation indicates the decay heat will be offset by heat loss through the furnace wall
<u>D. CANISTER HANDLING</u>					
1. Canister impacts cell or equipment during handling	-Operation mishandling -Crane failure	-Trained operators	-Visual observation	-Restore proper canister movement	-Canister has to be inspected for damage -Impacted equipment inspected for damage
2. Canister transfer interrupted and canister suspended by crane in cell	-Crane failure -Loss of crane power	-None	-Visual observation	-Stabilize canister with redundant hoist system -Restore power	-None, canister with 17 w/L glass can be adequately cooled in air. Centerline temperature is ~260°C. Wall temperature is ~150°C
3. Transfer of canister in an overpack interrupted and canister suspended by crane in cell	-Crane failure -Loss of crane power	-None	-Visual observation	-Stabilize canister with redundant hoist system -Restore power	-None, canister with overpack can be adequately cooled in air. For 17 w/L glass centerline temperature is ~360°C. Wall temperature is ~250°C

TABLE 6.1.1. (contd)

Event	Potential Causes	Safety/Prevention	Detection	Corrective Actions	Consequences
E. OFF-GAS SYSTEM					
1. Condensate return pump fails	-Loss of power -Pump component fails -Instrument failure	-Pump system designed for reliable service in process operations -Instrumentation installed to detect failure	-Loss of power consumption by pump motor and indication -Condensate flow rate indicator would indicate loss of flow -Detection of increased activity downstream of scrubber	-Replace pump or replace failed instrumentation	-Process will be shut down on pump failure. -Radioactivity downstream of scrubber will go up by factor of 10 to 100 until calciner shutdown -Activity release to cell on pump replacement
2. Condenser clogging leads to large pressure drop or partial pluggage	-Gradual calcine and solids buildup on heat transfer surfaces	-Periodic flushing -Low probability of substantial solids buildup	-Decrease in heat transfer efficiency (greater cooling water requirements) -Increased pressure drop in condenser or greater operating pressure detection	-Periodic flushing to remove crud deposits -Replace condenser if heat transfer capacity cannot be returned to adequate capacity	-System shutdown -Possible contamination of condenser cooling water -Possible low vacuum in calciner/melter or may be even some pressurization
3. Rupture of condenser tubes injects water into off-gas stream	-Excessive corrosion rate of condenser tubes -Faulty tube manufacture -Off-gas composition more corrosive than designed for	-Condenser designed to operate reliably over its intended life -Instrumentation designed to detect contamination in cooling water and cooling water in leakage to OG system -Condenser leak would not cause any immediate safety problem	-Excessive buildup rate of water in the condensate receiver detected -Increase in pressure drop across condenser and increased back pressure upstream of the condenser	-Replace condenser	-Possible contamination of condenser cooling water -System shutdown during repair -Potential flooding of condensate receiver tank
4. Off-gas equipment clogging leads to large pressure drop	-Buildup of calcine fines -Particulate bed degradation, breakup and fines deposition	-Off-gas system specifically designed to prevent pluggage -Instrumentation designed to detect pluggages and high pressure drops -System designed to relieve pressure and/or shutdown due to excessive pressure	-Instrumentation detects large pressure drop -Pressure increase upstream of the constriction	-Shut down system and attempt to flush out or remove cause of pluggage -Replace the piece of equipment causing pluggage if plug cannot be removed	-System shutdown if system needs repair -Possible low vacuum in calciner/melter or maybe even some pressurization
5. Condenser condensate removal drain blocks and backs up condensate	-Calcine or corrosion product solids gradually build up around drain	-Process off-gas system designed to prevent material which could plug drain from reaching it -Instrumentation available to detect pluggage	-Detection of condensate flow stoppage from the condenser -Off-gas system upstream of the condenser pressurizes	-Shut down system and chemically flush condenser -Replace condenser if plug cannot be removed	-System shutdown if equipment replaced

TABLE 6.1.1. (contd)

Event	Potential Causes	Safety/Prevention	Detection	Corrective Actions	Consequences
E. OFF-GAS SYSTEM (contd)					
6. Loss of NH ₃ feed to NO _x destructor	-NH ₃ feed control system malfunctions (loss of power, breakage) -No NH ₃ in feed system	-Feed control system designed for reliable operation -Instrumentation and alarm would indicate loss of flow -NH ₃ supply is periodically checked for adequacy	-Loss of flow would be detected on flow instrumentation -Bed and off-gas temperature and other instrumentation would show chemical reaction termination	-Correct flow controller operation or replace	-Higher than normal NO _x emission to atmosphere until NH ₃ flow corrected or system shut down
7. Excessive NH ₃ feed to NO _x destructor	-Process off-gas contains less than normal amount of NO _x and NH ₃ flow not changed to accommodate -NH ₃ flow control system malfunctions and NH ₃ flow is excessive	-Detect excess of NH ₃ in reactor off-gas -Excess of NH ₃ in off-gas causes no immediate safety hazard -Control system designed to control NH ₃ flow rate appropriately	-Detection of excessive NH ₃ concentration in the off-gas	-Correct NH ₃ flow controller operation or replace	-Higher than normal NH ₃ emission to atmosphere until NH ₃ flow corrected or system shut down
8. Loss of catalytic bed structure of NO _x destructor	-Due to extended use under operating conditions the bed deteriorates -Due to off-specification material or chemical reaction of bed with off-gas materials, bed deteriorates	-Process conditions controlled avoid bed degradation	-Detect change in differential pressure across bed in operation -Possible detection of particulate buildup on equipment or filters downstream of the reactor -Detection of reactants in off-gas stream	-Replace bed or reactor	-Increase in NO _x and NH ₃ emissions to atmosphere -System shutdown if equipment replaced
9. Loss of heat source on NO _x destructor	-Reaction terminates due to inadequate reactant (temporary loss of NH ₃ or off-gas flow) -Reactor falls below temperature to sustain operation -External heater fails	-Instrumentation to control and detect loss of temperature -Exterior heat supply available to keep temperature up	-Detect temperature decrease in reactor and off-gas -Detect unreacted components in off-gas -Instrumentation indicates no power to external heater	-Replace external heater if failed -Supply additional heat to reactor by external heater	-Higher than normal NO _x and NH ₃ emission to atmosphere until reaction reinitiated
10. Overheating of noncondensables in NO _x destructor	-Higher than normal reaction rate due to increased NO _x and NH ₃ concentration	-Process operations designed to prevent excessive temperature by NH ₃ reactant flow control -Instrumentation detects excessive system temperatures -Process automatically shuts down on occurrence of high temperatures	-Detection of high NO _x concentration in destructor off-gas or high bed temperature	-Adjust process operating conditions -Shut down process -Increase off-gas cooling -Cooling incoming reactor gases more	-Increased reactor off-gas temperature -Possibly increased reactor bed degradation rate

TABLE 6.1.1. (contd)

Event	Potential Causes	Safety/Prevention	Detection	Corrective Actions	Consequences
E. OFF-GAS SYSTEM (contd)					
11. Bed channeling or break-through in NO_x destructor	-Bed maldistributed on installation -Bed poisoned or coated	-Proper bed and equipment installation -Instrumentation to detect off standard equipment operating conditions	-Detect abnormally high NO_x and NH_3 concentration downstream of NO_x destructor -Detect abnormally low pressure drop across reactor for channeling	-Change bed	-Some process time will be lost changing bed -Higher than normal NO_x and NH_3 concentrations for short time in NO_x destructor off-gas
12. Malfunction in scrubber flow causes water vapor entrainment	-Excessive scrubber solution flow rate -Excessive off-gas flow rate	-Process operating conditions developed and monitored to prevent occurrence	-Detection of off normal operating conditions -Detect increase in condensate load from the demister and the condenser -Detect increased activity downstream of the scrubber	-Change operating conditions	-None
13. Ru sorber bed poisoning	-Off-normal flow of condensables -Deposition of organic materials -Sorption of other materials in the off-gas -Inadequate bed regeneration	-Bed designed and operated for reliable long-term performance -Instrumentation available to detect effects of bed poisoning	-Detect increase in activity downstream of Ru sorber	-Regenerate bed -Replace unit	-Some process downtime during bed change or regeneration if cannot be done during normal maintenance -Potential increased volatile Ru release in process off gas
14. Ru sorber granules entrained in gas stream	-Granule fines placed in bed -Bed deterioration caused by reaction with off-gas or mechanical stresses caused by operating life cycle	-Fines retained on off-gas system filters and beds -Granule fines removed before placement in equipment -Instrumentation may detect loss of fines	-Detect abnormal loading rate of downstream filters -Detect abnormal Ru activity buildup rate on downstream filters	-Change bed granules if detected leak rate excessive or bed about to lose utility	-Some process downtime if it is decided to change bed and this cannot be done during maintenance -Release of granular fines containing Ru downstream of bed
15. Ru sorber clogged by water	-Inadequate mist removal prior to Ru sorber -Inadequate temperature control in off-gas system causes condensation in the Ru sorber -Inadequate bed regeneration operation (bed not dried)	-Process procedures and operations designed to prevent occurrence -Instrumentation available to detect condition	-Detect high pressure drop across sorber -Other process indicators would show the cause is water	-Dry bed out -Correct process condition causing moisture condensation	-Some process downtime during bed dry out

TABLE 6.1.1. (contd)

Event	Potential Causes	Safety/Prevention	Detection	Corrective Actions	Consequences
E. OFF-GAS SYSTEM (contd)					
16. Ru sorber bed channeling or breakthrough	<ul style="list-style-type: none"> -Bed loaded to capacity -Bed maldistributed on installation -Bed poisoned or coated -Bed maldistribution of regeneration -Inadequate bed regeneration 	<ul style="list-style-type: none"> -Proper bed and equipment installation -Equipment designed to minimize bed maldistribution -Instrumentation available to detect effects of bed maldistribution 	<ul style="list-style-type: none"> -Detect abnormally high Ru activity downstream of Ru sorber -Detect abnormally low pressure drop across the Ru sorber 	<ul style="list-style-type: none"> -Change or redistribute bed 	<ul style="list-style-type: none"> -Some process time lost during bed redistribution or changing if necessary -There will be higher than normal Ru loss from the Ru sorber
17. Roughing and HEPA filters become wet or incur high loadings	<ul style="list-style-type: none"> -Greater than design mist concentrations reaches filters due to low upstream operating temperature or high system operating capacity -Failure of off-gas heater 	<ul style="list-style-type: none"> -Instrumentation available to detect filter pluggage 	<ul style="list-style-type: none"> -Detection of high differential pressure across filters 	<ul style="list-style-type: none"> -Shut down process and allow airflow to dry filters -Replace filters if there appears to be any damage 	<ul style="list-style-type: none"> -System may be down for a short time for filter changeout -There would be decrease in system vacuum and greater potential for some system pressurization -Increased potential for HEPA filters failure and particulate release to downstream system
18. HEPA filter develops leak	<ul style="list-style-type: none"> -Rough handling and faulty construction causes filter damage -Repeated abnormal operating conditions cause filter physical integrity deterioration 	<ul style="list-style-type: none"> -Filters are inspected and tested before installation -Instrumentation available to detect filter failure 	<ul style="list-style-type: none"> -Decrease in pressure differential change across filter -Increase in activity detected downstream of the filters 	<ul style="list-style-type: none"> -Change out filter 	<ul style="list-style-type: none"> -Some process downtime during filter change out -There would be higher than normal activity by-pass through the filter
19. De-entrainer becomes plugged	<ul style="list-style-type: none"> -Calcine solids buildup on mesh element -Excess spray reaching filter exceeds de-entrainer capacity 	<ul style="list-style-type: none"> -De-entrainer designed for reliable long-term operation -Instrumentation available to detect plugging 	<ul style="list-style-type: none"> -Detection of increased pressure drop across de-entrainer -Change in pressure indications upstream and downstream in the de-entrainer 	<ul style="list-style-type: none"> -Decrease system operating capacity -Shut down system and flush de-entrainer -Change de-entrainer 	<ul style="list-style-type: none"> -System capacity may be reduced for a short period -There would be a reduction in system vacuum and potential for system pressurization
F. CELL					
1. Major equipment removal or replacement	<ul style="list-style-type: none"> -Failed equipment replacement 	<ul style="list-style-type: none"> -Use procedures which have been developed using a QA and QC system 	<ul style="list-style-type: none"> -Observance of abnormal instrument readings which indicate failure -Visual observance that equipment has failed -Equipment leak detection 	<ul style="list-style-type: none"> -Replace failed equipment 	<ul style="list-style-type: none"> -During the equipment replacement calcine could become airborne and reach the cell filters

NOTE: Conditions for the I sorber bed could generally arise similar to those above for the Ru sorber bed.

TABLE 6.1.2. Minor Accidents

Event	Potential Causes	Safety/Prevention	Detection	Corrective Actions	Consequences
A. FEED SYSTEM					
1. Feed solution backup in atomizing air line	<ul style="list-style-type: none"> -Feed nozzle plug -Atomizing air check valve fails -Pump shutdown interlock fails -Low atomizing air pressure 	<ul style="list-style-type: none"> -Antibackflow check valve -Air supply pressure exceeds feed pressure -Multiple detection devices -Low atomizing air pressure interlock 	<ul style="list-style-type: none"> -Service gallery radiation alarms -Low atomizing air pressure alarm 	<ul style="list-style-type: none"> -Capability for remote flushing of contaminated line -Change check valve and make any other required equipment adjustments 	<ul style="list-style-type: none"> -High radiation field in service gallery from feed backing up in air supply and pressure sensor lines -Occupational exposure in cleanup
2. Feed line to spray calciner leaks	<ul style="list-style-type: none"> -Leakage in pressurized line at fitting or connection -Piping failure by corrosion or fatigue 	<ul style="list-style-type: none"> -Solution contained in floor sump -Primary welded connections -Cell HEPA filters and APS -Sump alarm permits early detection 	<ul style="list-style-type: none"> -Sump level alarm -Increased cell radiation -Feed system pressure decrease -Visual detection 	<ul style="list-style-type: none"> -Tighten connection or change equipment causing leak -Route HLLW in floor sump to tank -Decontaminate as necessary 	<ul style="list-style-type: none"> -Solution release to cell -Small amount of solution may become airborne as spray or steam if gets onto hot surface
3. Leak in feed tank	<ul style="list-style-type: none"> -Tank corrosion -Impact of tank by equipment -Faulty construction 	<ul style="list-style-type: none"> -Conservative design for operating conditions with QA and QC -Emergency empty out systems -Tank leak detection systems 	<ul style="list-style-type: none"> -Leak detection in cell sump -Liquid level in tank falls over a period of time 	<ul style="list-style-type: none"> -Remove leaking tank for repair or replacement 	<ul style="list-style-type: none"> -Solution release to cell floor -Small amount of solution becomes airborne -Tank removal and disposal required
4. Feed tank overfills and ventilation line overflows	<ul style="list-style-type: none"> -Operator neglect -Faulty function of fill jet controls -Instrumentation maloperation 	<ul style="list-style-type: none"> -Strict QC procedures for tank transfers -Tank high-level alarm systems 	<ul style="list-style-type: none"> -High-level alarm -Apparent decrease in tank vacuum -Possible increase in VOG radioactivity 	<ul style="list-style-type: none"> -Partially empty tank -Decontaminate instrument or other lines if nuisance contamination proves to be a problem 	<ul style="list-style-type: none"> -Possible increase of activity to VOG system
B. CALCINER					
1. Calciner damaged due to overheating	<ul style="list-style-type: none"> -Operator error -Furnace control malfunction -Instrumentation maloperation -Incorrect high temperature control setting 	<ul style="list-style-type: none"> -Multiple zone furnace with separate controls and alarms -Redundant temperature sensors on each zone -Designed to minimize need for replacement -Automatic high temperature shutdown -Cell HEPA and APS filters 	<ul style="list-style-type: none"> -Calciner temperature alarm sounds -High temperature detected and shutdown system shuts down calciner 	<ul style="list-style-type: none"> -Calciner decontamination in place -Replace damaged portions of calciner furnace or calciner 	<ul style="list-style-type: none"> -Calciner replacement and disposal required -Calcine leakage to cell during replacement, calcine may become airborne

TABLE 6.1.2. (contd)

Event	Potential Causes	Safety/Prevention	Detection	Corrective Actions	Consequences
B. CALCINER (contd)					
2. Sintered filters clog and produce large pressure drop which causes release through the pressure relief port	-Damp calcine clogs sintered stainless steel filters -Filter blowback inoperative	-Design to minimize occurrence -Operate to prevent occurrence -Calciner pressure relief system to prevent overpressure -Instrumentation to detect calciner pressure and filter differential pressure increase	-Detection of high pressure drop across filters -Detection of pressure increase in calciner -Reduction in off-gas flow from calciner -Seal pot may blow from calciner pressurization	-Cease calciner operation, dry cake, and blow off filter -Or remove cake by blowback with high pressure air -Or replace filters -Or backflush with stream or acid solution	-If seal pot blows, calcine is released through the seal pot to the feed tank -If filters are replaced calcine is released to the cell of which some becomes airborne
3. Frit feed line broken	-Mechanical impact -Fatigue -Erosion, corrosion	-Instrumentation operating to detect failure -Calciner operated at vacuum to cell -Cell filters and APS	-Visual observation -Loss of calciner vacuum -Loss of frit flow to melter	-Cease operations -Replace frit feed line	-Extended outage of frit flow could cause making nonspecification glass
4. Calcine spill during canister changeout	-Cone or spout warped by overheating -Cone valve fails to seal properly -Vibrator operation dislodges calcine from chute -Low vacuum on calciner -Calcine/frit accumulate on cone or inside spout	-Weight of spout on cone valve results in restricted leakage area -Cell HEPA filters and APS -Vacuum on spout at all times causes air flow to be into calciner	-Increase in cell and cell filter radiation readings -Low vacuum in calciner and alarm -Possible increased air leakage to calciner	-Assess situation and shut down operations -Cycle cone valve to see if operation can be restored -Decontaminate cell and equipment as necessary -Replace cone valve and/or sprout if necessary after flushing	-Calcine released to cell and some of calcine becomes airborne
5. Sintered metal filter failure	-Filter fatigue -Filter chamber stressed by equipment operations -Corrosion and overpressure -Excessive temperature	-Calciner operation automatically shuts down on no filter ΔP with major failure -Balance of COG designed for particulate removal -Calciner operation shutdown on detection of significant activity increase in scrub tank	-Low ΔP across filters and alarm for major failure -Increase in radionuclide activity downstream of filters and scrub tank -Increase in loading of calcine in off-gas equipment downstream of filters	-Assess situation and shut down operations -Change filters after preliminary decontamination	-Calcine activity downstream of filters increases by 10- to 100-fold before shutdown -Fractional dislodgement of residual filter calcine inventory during replacement -Increased calcine loading in downstream off-gas equipment

TABLE 6.1.2. (contd)

Event	Potential Causes	Safety/Prevention	Detection	Corrective Actions	Consequences
B. CALCINER (contd)					
6. Insulation of furnace supply cables burns	<ul style="list-style-type: none"> -Improper cable construction -Cable damage causes high cable temperature -Cable operation at higher currents than designed -Radiation damage -Corrosion of cable junctions could cause hot spots burning insulation 	<ul style="list-style-type: none"> -Probability of scenario causing incident very low -Fire would be detected so action could be initiated to extinguish it 	<ul style="list-style-type: none"> -Fire detector would detect and alarm fire -Cable insulation fire would cause abnormal power supply instrument readings and other lines in fire vicinity would be affected 	<ul style="list-style-type: none"> -Determine extent of damage -Replace failed cables and equipment 	<ul style="list-style-type: none"> -Entire system shut-down and evaluation -Some instrument and equipment fire damage -Cell filters could plug, need replacing -Fire causes calcine dust in cell to become airborne and reach cell filters
C. MELTER					
1. Forced air cooling by zones inoperative	<ul style="list-style-type: none"> -Failure of blower -Air lines to melter blocked or damaged -Instrumentation for blower fails 	<ul style="list-style-type: none"> -System conservatively designed to operate reliably -Ample instrumentation to detect such a failure -Redundant system blower 	<ul style="list-style-type: none"> -Blower motor instrumentation would indicate nonoperation -Canister thermal instrumentation would monitor lack of cooling -Air flow indicator and alarm would indicate no air flow 	<ul style="list-style-type: none"> -If required, melter furnaces will be shut down and the calciner operation will be shut down or output diverted -Correct equipment failure -Pull can out of furnace 	<ul style="list-style-type: none"> -Potential for canister failure due to excessive temperature -Possibility of some non-homogeneous materials in glass settling
2. Crane not over center of canister when canister is lifted out of furnace	<ul style="list-style-type: none"> -Incorrect crane positioning -Operator error 	<ul style="list-style-type: none"> -Crane centering system with interlocks -Visual references -Liner designed to protect furnace heaters 	<ul style="list-style-type: none"> -Visual -Audio 	<ul style="list-style-type: none"> -Inspect and repair interior of furnace 	<ul style="list-style-type: none"> -Damage to interior of ICM furnace
3. Furnace cable insulation burns	<ul style="list-style-type: none"> -Improper cable construction -Cable damage causes high cable temperature -Cable operation at higher currents than designed -Corrosion of cable junctions could cause hot spots burning insulation 	<ul style="list-style-type: none"> -Fire would be detected so action could be initiated to extinguish it 	<ul style="list-style-type: none"> -Fire detector would detect and alarm for fire -Cable insulation fire would cause abnormal power supply instrument readings and other lines in the fire vicinity would be affected 	<ul style="list-style-type: none"> -Determine extent of damage -Replace failed cables and equipment 	<ul style="list-style-type: none"> -Entire system shut-down and evaluation -Some instrument and equipment fire damage -Cell filters could plug and need replacing -Fire causes calcine dust to become airborne and reach cell filters

TABLE 6.1.2. (contd)

Event	Potential Causes	Safety/Prevention	Detection	Corrective Actions	Consequences
C. MELTER (contd)					
4. Furnace element shorts out due to canister spall buildup (Assume no liner between furnace and canister)	-Spallation from canister builds up in the bottom of the melter (or bridge between canister and furnace element)	-ICM design recognizes spallation problem -Power to furnace from an isolation transformer	-High current alarm -Burnout of furnace element	-Replace furnace element -Clean out spallation -Redesign as necessary to prevent reoccurrence	-Canister may require overpack due to shorting damage -Slight contamination release to cell as a result of removing canister before fully vitrified
D. CANISTER HANDLING					
1. Canister drop	-Lifting system failure -Operator error -Grapple failure	-Lifting system subject to QA procedures to minimize failure potential -Filled canister not lifted prior to vitrifying contents -Lid locked on canister before it is lifted -Cell HEPA filters and APS -Cell air balance	-Visual observation	-Inspect canister -Overpack if necessary (canister is not breached) -Inspect, test, and replace equipment as necessary that canister may have impacted	-No direct release of particulate material from canister -Deposited calcine dust in cell becomes airborne -Potential damage to other equipment or windows in cell which may cause release of radioactivity to cell
2. Canister cracks	-On canister cooling differential shrinking between glass and canister causes rupture -Canister impacts melter or blunt instrument on removal	-Canister designed considering off-standard operations and accidents	-Visual observation and inspection -High activity in canister decontamination solution -Detect high residual activity in furnace	-Decontaminate facilities as necessary -Overpack canister	-Some possible loss of glass to the cell or furnace -Some possible loss of calcine to the furnace
3. Canister failure during storage	-Corrosion -Excessive pressure buildup	-Container and storage basin water chemistry designed to minimize corrosion potential -Container heated to drive off volatile material before sealing -Water cleanup system permits removal of cations (Cs, Sr)	-Increase in radionuclide contamination of pool -Search of storage pool to isolate leaking canister	-Container retrieved and repaired or overpacked -Pool water decontaminated	-Cesium leached from calcine on upper surface of glass -Temporary increase in occupational exposure to plant personnel

TABLE 6.1.2. (contd)

Event	Potential Causes	Safety/Prevention	Detection	Corrective Actions	Consequences
E. OFF-GAS					
1. Off-gas blower failure	-Mechanical failure -Loss of electrical power	-In-line spare blower -Spare off-gas blower on emergency power system -Calcliner automatically shuts down on loss of vacuum -APS	-All differential pressure and pressure instrumentation indicates pressure loss	-Replace blower component -Restore power	-Possible pressurization of the calciner, melter, and off-gas system -Possible activity dispersed to the cell through any leaks -Possible activity back up through service connections
2. Ru adsorber failure	-Exhaustion or degradation of the sorbent -Channeling in the bed	-Substantial bed depth (30 in.) used to assure sorptive capacity and minimize channeling -RuO ₄ reduction to RuO ₂ in NO _x destructor -Two stages HEPA filtration -APS	-Increase in activity in off-gas downstream of the Ru sorber -Change in equipment operating pressure drop radiation readings	-Regenerate or change sorbent -Replace equipment if necessary	-Increase in activity downstream equipment 10- to 100-fold
3. Failure of process off-gas filters	-High moisture concentration in off-gas -Preheater failure	-Ru sorber bed at 80°C preceeding filters minimizes likelihood of moisture entering filters -APS	-Change in pressure drop across equipment pieces -Increase in off-gas activity downstream of the failed equipment	-Change failed equipment piece -Correct cause of failure	-Increase in activity carryover to APS
4. Venturi scrubber system failure	-Nozzle pluggage by solids -Scrub pump failure -Spray nozzle failure -Corrosion of internals	-System designed to minimize corrosion potential -Off-gas treatment equipment downstream -APS	-Change in operating pressure -Detect loss of scrub solution flow -Detect increased activity downstream of the scrubber	-Change venturi or failed equipment component -Remove solids pluggage	-10- to 100-fold increase in activity carryover to downstream equipment -<10-fold increase in activity from process off-gas to APS
5. Iodine Sorber failure	-Equipment failure due to corrosion -Bed poisoning -Bed channeling -I displacement by Cl or F	-Over design of bed used to assure adequate sorptive capacity and minimize channeling -Elevated discharge from APS	-Detection of abnormally high I concentrations in downstream off-gas -Changes in differential pressure across sorber	-Replace I sorber bed material or equipment piece	-Increase in activity carryover to APS
6. Blower pulls full vacuum on off-gas system	-Loss of calciner feed and air -Tight off-gas system seal and seal pots plugged and rupture disk does not rupture -Vacuum relief system fails	-Air in leakage -High-vacuum blower cut-off -Vacuum relief system -All equipment components designed to withstand maximum vacuum of blower used	-High vacuum detection and alarm	-Find restriction in off-gas system and correct -Replace any failed equipment	-Jumper connector gaskets or connections failure possibility

TABLE 6.1.2. (contd)

Event	Potential Causes	Safety/Prevention	Detection	Corrective Actions	Consequences
E. OFF-GAS (contd)					
7. Excessive calcine through sintered metal filter clogs scrubber solution line	-Major undetected filter failure and solid calcine buildup in elbow	-Filter system is designed for long-term reliable service -Scrubber system is designed to handle the calcine from a failed filter -Instrumentation is designed to detect filter failures and blockages in scrubber solution line	-Significant filter rupture detected by change in pressure drop across filters -Line plug detected by reduced solution flow rate and attempt of flow control system to increase flow rate -Detection of increased radioactivity downstream of the scrubber	-Shut down system and attempt to flush out pluggage -Replace line with pluggage	-Concurrent loss of filters and venturi scrubber operation would lead to an increase in process off-gas activity for only a very brief period during system shutdown
F. CELL					
1. Equipment drop during maintenance operations	-Lifting system failure -Operator error	-Qualified operators -Lifting system subject to QA procedures to minimize failure potential -Special procedures for maintenance operations to reduce error potential -Cell HEPA filters -APS	-Visual observation	-Pick up equipment -Perform any needed repairs to other equipment damaged	-Equipment damage with release of activity to cell -Deposited calcine dust becomes airborne
2. Cell viewing windows damaged (not broke through)	-Impact during in-cell equipment movements -Fire -External impact	-Qualified operators -Lifting system subject to procedures and design to minimize damage potential -Windows not protected in-cell by impact resistant glass -Fire prevention/suppression systems	-Gallery radiation detection instrumentation -Visual observation	-Shut down operations and inspect -Repair or replace window	-No direct release of activity -Potential for contamination spread and personnel exposure during window replacement -Loss of optical oil
3. Excessive activity transfer to personnel zone during manipulator removal	-Operation of manipulator with damaged boots -Operator error during manipulator removal	-Manipulator cleaning facilities designed to minimize spread and personnel exposure -Qualified operators -Constant survey during manipulator removal -Removal procedure designed to prevent release of contamination	-Detection of increased activity in personnel zone	-Decontaminate area as necessary -Provide interim shielding as required	-Contamination spread to occupied zone -Personnel exposure during cleanup

TABLE 6.1.3. Moderate Accidents

Event	Potential Causes	Safety/Prevention	Detection	Corrective Actions	Consequences
A. FEED SYSTEM					
1. Feed tank pressurizes due to explosion	<ul style="list-style-type: none"> -Extended undetected loss of air purge with hydrogen accumulation and ignition -Organic in feed tank ignited 	<ul style="list-style-type: none"> -Air purges with flow indicators -Designed to eliminate ignition sources -Operation under vacuum and air in leakage -Designed to eliminate organic from feed tank -Cell HEPA filters and APS -VOG treatment system -Heat sources limited to 138°C 	<ul style="list-style-type: none"> -Pressure spike detection in tank and alarm -Pressure surge detection in VOG and alarm -Possible permanent loss in tank vacuum -Other tank instrument readings disturbed 	<ul style="list-style-type: none"> -Access damage and shut down operation -Decontamination may be required -Replace any needed failed seals, instrumentation, and equipment 	<ul style="list-style-type: none"> -Seals to tank lines blown and possible overpressure damage to instrumentation transmitters -Pressure surge to VOG -Possible backflow of feed into instrument lines and service gallery -Feed solution released through leaks to cell and some reaches cell filters
2. Break in calciner feed recirculation line or significant leak	<ul style="list-style-type: none"> -Feed line impacted with piece of equipment -Improper feed piping installation -Piping corrosion -Connections work loose or gaskets deteriorate 	<ul style="list-style-type: none"> -Equipment not normally handled around feed system piping -Feed system checked for continuity and leaks after maintenance -Use of proven designs and operating methods to ensure integrity -Feed system automatically shut down on low back pressure 	<ul style="list-style-type: none"> -Low feed system pressure -Possible high cell and cell filter radiation readings -Cell sump filling and alarm -Material balance discrepancy 	<ul style="list-style-type: none"> -Assess damage and shut down operation -Decontaminate cell and equipment as required -Correct connection or replace piping 	<ul style="list-style-type: none"> -Calciner feed sprayed into cell of which some reaches cell filters
B. CALCINER					
1. Calcine spill due to backup in chute and cone valve stuck open on canister disconnection	<ul style="list-style-type: none"> -Calcine backup due to bridging in melter or partial plugging in chute -Gross failure in cone valve sealing -Loss of cone valve position indicator -Calcine buildup jams cone valve in open position 	<ul style="list-style-type: none"> -Cone valve position indicator and interlock -Canister gamma scanner -Canister weigh system -Vibrators on calciner to reduce holdup -Cell HEPA filters and APS 	<ul style="list-style-type: none"> -Cell and canister radiation detector change and possible alarm -Gamma scanner detects bridging and alarms -Decrease in rate of weight increase in canister -Change in temperature of connecting section -Increased ΔP in connecting section 	<ul style="list-style-type: none"> -Assess situation and shut down operation -Remove calcine/frit from chute -Decontaminate cell and equipment -Place vibrator on chute -Change chute or chute configuration 	<ul style="list-style-type: none"> -Calcine and frit fall on melter furnace, canister or floor and some calcine become airborne

TABLE 6.1.3. (contd)

Event	Potential Causes	Safety/Prevention	Detection	Corrective Actions	Consequences
B. CALCINER (contd)					
2. Calcine release due to calciner pressurization	<ul style="list-style-type: none"> -Undetected seal leakage at calcine discharge to canister -Pressurization due to high system dp, abnormal filter blowback, loss of vacuum supply, organic oxidation -Seal between spout and canister destroyed by calciner pressurization 	<ul style="list-style-type: none"> -Calcine largely contained within calciner/melter -Calclner system designed to handle pressurization (materials, seal pot, rupture disk) -Calciner feed and operation operated to prevent -Cell HEPA filters and APS -Air break in frit addition line to keep calcine from being ejected from isolated system 	<ul style="list-style-type: none"> -Low vacuum detection and alarm -COG instrumentation readings become non-characteristic or high-surge -Radiation increase on cell filters and alarm 	<ul style="list-style-type: none"> -Assess situation and shut down operation -Decontaminate cell and equipment as necessary -Replace failed seals and affected seals and equipment as necessary 	<ul style="list-style-type: none"> -Calcine released to cell -Calclner off-gas released to cell -Some equipment seals fail and some instrumentation may be affected -Closure area of canister contaminated -Calcine blown up frit addition line
3. Cone valve stuck in canister (sticks open)	<ul style="list-style-type: none"> -Loss of cone valve cooling -Material buildup on shaft prevents retraction -Shaft failure -Valve does not retract from canister due to mechanism failure -Melt on valve or canister opening 	<ul style="list-style-type: none"> -Systems oversized to minimize failure potential -Valve system subject to QA procedures to minimize failure potential -Cell HEPA filters and APS 	<ul style="list-style-type: none"> -Limit switch and detector indicates valve open -Valve and mechanisms designed to prevent this occurrence -Increase in cell filter radiation readings 	<ul style="list-style-type: none"> -Remove canister and melter from chute -Clean up any resulting contamination -Replace chute connecting section 	<ul style="list-style-type: none"> -Calcine and frit fall on melter furnace, canister or floor and some of calcine becomes airborne -Equipment dismantling required for recovery and cone valve damaged
4. Calciner vessel cracking due to vibration-induced fatigue	<ul style="list-style-type: none"> -Excessive vibrations beyond design -Operation of calciner to provide stresses and fatigue not accounted for in design 	<ul style="list-style-type: none"> -Calciner specifically designed with adequate safety factors to prevent occurrence 	<ul style="list-style-type: none"> -Loss of calciner vacuum and alarm -Crack may cause "ringing" of calciner instrumentation readings -Increase in cell filter radiation readings 	<ul style="list-style-type: none"> -Assess situation and shut down operations -Decontaminate cell and equipment as necessary -Replace failed equipment 	<ul style="list-style-type: none"> -Calcine released to cell through crack and some of calcine reaches filters -Calciner vessel requires replacement -Calclner off-gas released to cell
5. Calciner ruptured by equipment drop	<ul style="list-style-type: none"> -Operator error -Failed equipment handling system 	<ul style="list-style-type: none"> -Operator QA approved -Operator training and safety awareness 	<ul style="list-style-type: none"> -Visual observation -Disruption or nonroutine calciner instrumentation readings -Loss of calciner vacuum 	<ul style="list-style-type: none"> -Assess situation and shut down operations -Decontaminate cell and equipment as necessary 	<ul style="list-style-type: none"> -Calcine released to cell through breach and some calcine reaches filters -Calciner vessel requires replacement -Other equipment may require repair or replacement -Calclner off-gas released to cell

TABLE 6.1.3. (contd)

Event	Potential Causes	Safety/Prevention	Detection	Corrective Actions	Consequences
C. MELTER					
1. Canister spill due to overfilling, spout disconnection, and cone valve jammed open	<ul style="list-style-type: none"> -Calcine bridging -Low density material -Excessive feed due to operator error, weighing system failure, diverter drive failure -Cone valve fails to seat properly -Operator inattention and instrument failure -Load cell read improperly -Furnace failure so calcine/frit doesn't melt 	<ul style="list-style-type: none"> -Canister gamma scanner -Cell HEPA filters and APS -Redundant fill detection systems (canister weight, radiation monitoring, and thermocouples) and alarms 	<ul style="list-style-type: none"> -Detection by gamma scanner thermocouples, radiation level, or weigh system and alarm -Possible increase in cell and cell filter radiation readings 	<ul style="list-style-type: none"> -Assess situation and shut down operations -Decontaminate cell and equipment as necessary -Check equipment operation and correct if necessary 	<ul style="list-style-type: none"> -Calcine released during operation and fraction of calcine becomes airborne some of which reaches the cell filters -Calcine released to melter and cell when spout disconnected and some calcine becomes airborne; a fraction of which reaches cell filters
2. Canister overheats and ruptures	<ul style="list-style-type: none"> -Loss of furnace temperature control -Operator error -Loss of canister cooling 	<ul style="list-style-type: none"> -Redundant temperature sensors -High temperature alarms -Current limiters -Power monitors and alarms 	<ul style="list-style-type: none"> -Melter thermocouples show high canister temperatures and alarm -Power indicators show too much power use and alarm -Cooling air flow meters show low or no air flow and alarm -High cooling air flow effluent temperature 	<ul style="list-style-type: none"> -Assess situation and correct instrument settings -Repair instruments or equipment -Decontaminate equipment as necessary 	<ul style="list-style-type: none"> -Molten glass and possibly some calcine/frit in furnace liner -Release of some volatile species to cell
D. CANISTER HANDLING					
1. Canister top ruptured due to high temperature and/or pressure	<ul style="list-style-type: none"> -Due to procedure error all water not removed and/or nitrate decomposed before canister is sealed -Gases generated in canister after seal welding which itself may rupture canister -Canister experiences significant temperature increase 	<ul style="list-style-type: none"> -Canister designed for elevated temperatures and pressures -Outgassing procedure designed to prevent this incident -Canister and lid designed such that lid seal weld will fail first 	<ul style="list-style-type: none"> -Visual inspection 	<ul style="list-style-type: none"> -Inspect canister for cause of failure -Decontaminate equipment and cell if necessary -Overpack failed canister or repair seal weld -Or return canister to melter 	<ul style="list-style-type: none"> -Calcine may be released to cell and some of calcine reaches cell filters -Canister ruptured -Cell contamination -Some volatile species may be released

TABLE 6.1.3. (contd)

Event	Potential Causes	Safety/Prevention	Detection	Corrective Actions	Consequences
E. <u>OFF GAS</u>					
None					
F. <u>CELL</u>					
1. Failure of cell exhaust filters	<ul style="list-style-type: none"> -Not properly seated -Damaged during handling of filter or process equipment -Moisture buildup and pressure surge 	<ul style="list-style-type: none"> -Periodic test of filter efficiencies -APS -Filter changeout at high ΔP -Filter protection from missiles or impact -Series of one roughing and two HEPA filters 	<ul style="list-style-type: none"> -Increased activity to APS -Decrease in ΔP across filter bank 	<ul style="list-style-type: none"> -Shut down cell -Replace failed or questionable filters 	<ul style="list-style-type: none"> -Increase of dust and activity to APS

TABLE 6.1.4. Design-Basis Accidents

Event	Potential Causes	Safety/Prevention	Detection	Corrective Actions	Consequences
A. FEED SYSTEM					
1. Hydrogen or organic vapor explosion in feed tank and tank rupture	<ul style="list-style-type: none"> -Red oil ignition -Extended undetected loss of air purge, and hydrogen accumulation and ignition -Organic in feed tank (high feed temperature) 	<ul style="list-style-type: none"> -Air purges with flow indicators -Designed to eliminate ignition sources -Solution contained in cell floor pan -Cell HEPA filter and APS -VOG treatment system -Operation under vacuum and air in leakage 	<ul style="list-style-type: none"> -Pressure spike detection in tank and alarm -Pressure surge detection in COG and VOG and alarm -Change in cell radiation readings and alarm -Increase in sump level and alarm -Loss of tank vacuum or detection -Loss of liquid level or detection 	<ul style="list-style-type: none"> -Move HLLW from sump to tank -Decontaminate failed equipment in-place -Decontaminate cell -Assess damage -Replace failed equipment 	<ul style="list-style-type: none"> -Tank rupture -Solution spill to floor -Calcine dust airborne in cell -Flows up instrument lines into service gallery
B. CALCINER					
1. Calciner pressurized and ruptured	<ul style="list-style-type: none"> -Solvent buildup in feed tank and high concentration solvent feed to calciner -Excessive feed rate of formic acid to calciner -Red oil detonation -Pressure relief system restricted 	<ul style="list-style-type: none"> -Preceding process systems limit potential for solvent buildup -Feed system intake limits potential for concentrated solvent feed -Pressure relief designed to minimize potential for restriction -Cell HEPA filter -APS -Solvent will burn instead of detonate -Backflow dampers protect against reverse flow to galleries 	<ul style="list-style-type: none"> -Pressure spike on detector and alarm -Decrease in calciner vacuum and alarm -Pressure surge in cell, detection, and alarm -Personnel feeling of shock wave -Detect COG system pressure increase and alarm -Instrumentation reading disruption 	<ul style="list-style-type: none"> -Shut down or cut power to equipment operation -Evacuate people from contaminated operating areas -Decontaminate facility and equipment -Assess damage -Replace failed equipment 	<ul style="list-style-type: none"> -Major fraction of calciner inventory dispersed in cell air and some calcine transported to cell HEPA filter -COG system seals may be blown and some equipment may be damaged -Release of calcine, Ru on particulate, or I on particulate from COG system -Radioactive particulates and gases forced through instrument lines into service gallery
C. MELTER					
1. Canister and liner rupture at molten glass temperature	<ul style="list-style-type: none"> -Canister and liner experience thermal excursion and loss of mechanical integrity due to loss of temperature control caused by controller failure or operator error 	<ul style="list-style-type: none"> -Automatic high temperature alarm and power cutoff -Redundant equipment, high temperature sensors and alarms -Equipment designed to take temperatures significantly higher than normal without failure -Cell HEPA filters and APS -Current limiters -Multiple zone furnaces with independent controls 	<ul style="list-style-type: none"> -Abnormal canister fill readings -High canister temperature reading and alarms -High furnace temperature reading and alarm -Decrease in calciner vacuum and alarm -Instrument reading disruption -Abnormal power reading and alarm 	<ul style="list-style-type: none"> -Shut down operations -Decontaminate if warranted -Assess damage -Overpack failed canister -Remove solid waste from furnace and canister -Remove and dispose of melter components -Replace failed equipment 	<ul style="list-style-type: none"> -Glass released to melter shell and floor -Calcine released to melter shell of which some calcine reaches cell and cell filters -Canister and melter structure damaged -Cell contamination -Additional calcine airborne during cleanup

TABLE 6.1.4. (contd)

Event	Potential Causes	Safety/Prevention	Detection	Corrective Actions	Consequences
D. CANISTER HANDLING					
1. Canister drop	<ul style="list-style-type: none"> -Error in handling -Handling equipment failure 	<ul style="list-style-type: none"> -QA procedures and operator training for handling -Visual observation of lifting operation -Equipment periodic inspection -Equipment design 	<ul style="list-style-type: none"> -Visual observation -Perhaps some cell instrumentation disturbed and alarms set off 	<ul style="list-style-type: none"> -Pick up canister, inspect and repair if necessary -Observe to see if canister had done any equipment or cell damage -Repair any associated damage 	<ul style="list-style-type: none"> -Canister distorted, breached, and some glass breakage and loss from canister -Possibility of other equipment damage due to canister impact -Cell contamination from damaged equipment possible
E. OFF-GAS					
1. Off-gas explosion	<ul style="list-style-type: none"> -Presence of explosive (or flammable) concentration or mixture of hydrogen, methane, ammonia, or ammonium nitrate in off-gas system -Ignition source 	<ul style="list-style-type: none"> -Process designed and controlled to prevent explosive mixture in the off-gas -Ignition sources in off-gas system are minimized -Where remote potential of flammable mixture and ignition source, a pressure relief is provided 	<ul style="list-style-type: none"> -Detect pressure spike in system pressure instrumentation and alarm -Loss of COG system vacuum and alarm -Radiation detection in COG where not allowed and alarm -Visual equipment inspection -Possible instrumentation reading disruption 	<ul style="list-style-type: none"> -Shut down operations -Inspect for damage -Decontaminate as necessary -Replace failed equipment, gaskets, piping, and instrumentation 	<ul style="list-style-type: none"> -COG jumper and equipment seals fail -Possible COG equipment vessel failure -Rupture of HEPA filters, Ru bed retainer, or I bed retainer -Release of calcine, Ru on particulate or I on particulate some of which reaches cell filters
F. CELL					
1. Fire in cell	<ul style="list-style-type: none"> -Accumulation of combustible materials in cell (i.e., plastics, dust, solvent leak, some cloth, grease, organic film) and ignition -Cell window breaks and oil ignites 	<ul style="list-style-type: none"> -Limit combustible materials in cell -Limit ignition sources in cell -Fire detection and alarm systems -Fire suppression system in cell 	<ul style="list-style-type: none"> -Cell temperature detector and alarm -Equipment temperature detector and alarm -Visual detection -Instrument reading disruption 	<ul style="list-style-type: none"> -Shut down operations -Automatic fire suppression system puts out fire -Inspect for damage -Decontaminate as necessary -Replace failed or damaged equipment 	<ul style="list-style-type: none"> -Cell filters clogged -All plastics in cell lose integrity -Cell pressurizes and radioactive material disperses to operating and service areas -Calcine transported to cell filters

TABLE 6.1.4. (contd)

Event	Potential Causes	Safety/Prevention	Detection	Corrective Actions	Consequences
F. CELL (contd)					
2. Explosion in cell (pressure and projectile)	<ul style="list-style-type: none"> -Solvent vapor buildup in cell space -Hydrogen buildup in "dead" air space in cell because of cell ventilation failure -Red oil accumulation in sump or on floor -Ignition source 	<ul style="list-style-type: none"> -Exclusion of explosive materials from cell -Limit ignition sources in cell -Cell containment designed to limit consequences of overpressure -Backflow dampers protect against reverse flow to galleries 	<ul style="list-style-type: none"> -Instrumentation reading disruption -Cell high pressure detector and alarm -Detect shock wave in other cell instruments -Operator detection of shock wave -Visual observation of disruption of cell status -Possible area radiation detection alarm from radionuclide containment loss 	<ul style="list-style-type: none"> -Shut down operations -Inspect for damage -Decontaminate as required -Repair failed facilities and equipment 	<ul style="list-style-type: none"> -Equipment distorted -Plastic seals to cell blown -Cell filters ruptured -Loss of calcine to operating service areas -Loss of calcine from cell to VOG
3. Design basis earthquake	<ul style="list-style-type: none"> -Design basis earthquake 	<ul style="list-style-type: none"> -Facility and equipment designed for this occurrence 	<ul style="list-style-type: none"> -Motion detectors and alarm -Facility shaking motion 	<ul style="list-style-type: none"> -Shut down operations -Inspect for damage -Decontaminate as required -Replace any failed equipment 	<ul style="list-style-type: none"> -Some seals in equipment or facility may develop leaks or rupture -Some equipment may become slightly distorted -Calcine, Ru, and I lost from COG -Calcine lost from cell to VOG
4. Design basis tornado	<ul style="list-style-type: none"> -Eye of design bases tornado passes over plant stack 	<ul style="list-style-type: none"> -Facility and equipment designed for this occurrence 	<ul style="list-style-type: none"> -Cell low pressure alarm -Tornado alert and watch 	<ul style="list-style-type: none"> -Shut down operations -Inspect for damage -Decontaminate as required -Replace any failed equipment 	<ul style="list-style-type: none"> -Some seals in equipment or facility may develop leaks or rupture -Extremely remote possibility of cell filters, COG filters, or COG equipment particulate retainers rupturing -Calcine, Ru, and I lost from COG -Calcine lost from cell to VOG

TABLE 6.1.5. Hypothetical Accidents

Event	Potential Causes	Safety/Prevention	Detection	Corrective Actions	Consequences
A. <u>FEED SYSTEM</u>					
1. Criticality (see C.1)					
B. <u>CALCINER</u>					
None					
C. <u>MELTER</u>					
1. Criticality	<ul style="list-style-type: none"> -High Pu and/or U-235 content in calcine -Pu settles to bottom of canister -High Pu and/or U-235 content in HLLW -Solids containing high Pu content accumulate in feed tank 	<ul style="list-style-type: none"> -Fissile material and configuration in system does not approach that needed for a criticality -Fissile material content in HLLW controlled and measured -Feed system agitates feed to prevent solids build-up -Personnel are shielded from radiation should a criticality occur 	<ul style="list-style-type: none"> -Area gamma and/or neutron monitors would alarm 	<ul style="list-style-type: none"> -Dilute critical material to less than critical concentration -Transfer material into a critically safe configuration 	<ul style="list-style-type: none"> -Slightly higher than normal dose rate to operating personnel -May be some spread of contamination in facilities if canister or tank breached
D. <u>CANISTER HANDLING</u>					
None					
E. <u>OFF-GAS</u>					
None					
F. <u>CELL</u>					
1. Explosion in cell	<ul style="list-style-type: none"> -No air flow through the cell -Accumulation of hydrogen, organic vapor or methane -Ignition source 	<ul style="list-style-type: none"> -Emergency power available for ventilation fans -Backup ventilation available -Explosive gases and vapors contained in closed systems -Limited potential ignition sources 	<ul style="list-style-type: none"> -Cell pressure alarm -Area radiation alarm (cell) -Shock wave 	<ul style="list-style-type: none"> -Facility and local environment decontamination -Operating personnel decontamination and medical care -Facility repair or decommissioning 	<ul style="list-style-type: none"> -Cell structural integrity maintained -Window broken out by missile -Cell air filter system and nonsolid entries blown out -Calcliner, feed tank, and canister contents dispersed to cell -Particulates escape out cell filter duct -Particulates escape to operating gallery -Possibly operator physical injury by broken window

TABLE 6.1.5. (contd)

Event	Potential Causes	Safety/Prevention	Detection	Corrective Actions	Consequences
F. CELL (contd)					
2. Airplane or meteor crashes into cell	-A 747 engine or a meteor directly impact the hot cell roof	-Probability of occurrence is negligible	-Viewing and evaluating effects	-Facility and local environment decontamination -Operating and local population decontamination and medical care -Facility repair or decommissioning	-Cell structural integrity grossly breached -Barriers between cell, operating and service areas breached -Canister, feed tank, and canister contents released -Particulates released to environment and breached facility -Facility operators killed or injured by crash
3. Beyond safe shutdown earthquake	-Beyond safe shutdown earthquake occurs at the facility	-Probability of occurrence is negligible	-Motion and earthquake detectors	-Facility and local environment decontamination -Operating personnel decontamination and medical care -Facility repair or decommissioning	-Cell structure impaired by cracks in concrete which penetrate to environment and operating areas -Loss of all ventilation -Calcliner and feed tank breached releasing contents -Particulates migrate through crack to environment -Feed leaks through breach in cell liner and foundation to ground -Particulates released to operating areas -Operators injured
4. Military action or sabotage	-Nuclear device detonated in the vicinity of the cell	-Probability of military action is negligible -Plant security personnel -Plant security systems	-Viewing and evaluating effects	-Civil defense actions commensurate with nuclear weapon effects	-Facility demolished -Cell radionuclide content dispersed to the environment -All operating personnel and local population destroyed from blast effects

6.2 REFERENCE ACCIDENT CONSEQUENCE ANALYSES

Of the accidents examined, thirteen were selected as worst-case or representative of accident classes and are analyzed in greater depth in this section.

6.2.1 DESCRIPTION OF CONCEPTUAL PLANT FACILITY

A typical cell layout for the SC/ICM process is presented in Section 5.3, "Facility Description." The vitrification cell has a 16-ft by 24-ft floor and is 52 ft high. Adjacent to the vitrification cell is a 20-ft-high effluent and radioactive feed cell with about the same floor dimensions. The effluent and radioactive feed cell will contain the HLLW feed tanks and the majority of the off-gas equipment.

The cell ventilation requirements call for a single HEPA filter located outside the cells for all incoming air streams (in order to prevent facility contamination due to loss of ventilation or cell pressurization). A bank of HEPA filters is located within the cells for exhaust air filtration. The exhaust air is ducted to the plant atmospheric protection system, which performs further filtration. The bank of exhaust HEPA filters in both the vitrification cell and the effluent and radioactive feed cell consist of a prefilter plus double HEPA filters. Each HEPA filter is 0.61 m x 0.61 m x 0.29 m deep (24 in. x 24 in. x 11-1/2 in.).

The cell boundaries and the HEPA filters provide the Class I (high-integrity) safety boundary against the release of radioactive effluents to the environment. Although some of the accidents analyzed in this section are postulated to involve a rupture of this boundary, the final design is expected to reduce the probability of such a breach to a negligible consideration. There is additional containment and ventilation filtering by nature of the controlled ventilation building housing the cells and the plant atmospheric protection system. Figure 6.2.1 is a schematic of a conceptual plant ventilation system with assumed airflows shown.

FIGURE 6.2.1. Generic Waste Solidification Facility Ventilation Diagram

(a) Prefilters are used in the plant ventilation system as shown; however, for this safety analysis no credit is taken for their presence.

6.2.2 ASSUMPTIONS FOR ACCIDENT ANALYSES

The waste processing parameters used for evaluation of consequences from the accidents reviewed in depth is summarized in Table 6.2.1. These waste-processing parameters are based on the flowsheet for the solidification of power-reactor acid waste. Treatment of this waste is potentially more dangerous by virtue of its high radionuclide concentration as compared to defense-type wastes.

Inventories of radionuclides in the HLLW are based on computations made by the ORIGEN Code (Bell 1973). The reference fuel was typical LWR oxide fuel, with an initial enrichment of 2.8%, operated at a power level of 26 MW/MTU, to a total exposure of 29,000 MWd/MTU. It is assumed that 0.5% of the uranium and plutonium in the discharged fuel remained in the waste; 100% of the noble gases and 99% of the iodine is removed at separation. The radioactive inventories in the waste are based on 5.7 years' cooling after discharge from the reactor.

Decontamination factors for the filters depend on particulate size and operating conditions. A single particulate decontamination factor of 100 is assumed for the HEPA filters, and a decontamination factor of 5 is assumed for the prefilters (roughing filters). These values used in this safety analysis are conservative. There are some volatile species such as RuO_4 and I_2 for which HEPA filters offer only small decontamination factors. All filters are conservatively assumed to have a decontamination factor of 1 for volatile chemicals. Other radioisotopes such as Cs which may be volatilized at calcination and vitrification temperatures are assumed in accident calculations

TABLE 6.2.1. Waste Processing Parameters

<u>Parameter</u>	<u>Value and Units</u>
Spray Calciner Feed Rate	300 L/h
Spray Calciner Feed Concentration	918 L/MTU
Glass Production Rate	85 kg/h
Glass	254 kg/MTU
Calcine	84.7 kg/MTU

to condense as particulates in the cell atmosphere before penetrating the filters. Therefore, the decontamination factors for particulates apply.

Radionuclides and chemicals are generated as effluents from the process as the result of normal and abnormal process operations and accidents. These radionuclides and chemicals could provide a source of radioactive contaminants (source terms) to the environment. The consequence from each of thirteen selected representative accidents reviewed can be characterized as a source term release. This source term release is characterized as either a calcine, glass, HLLW, ruthenium or iodine release to the cell environs.

Of the 96 accidents summarized in Tables 6.1.1 through 6.1.5, 13 were chosen for more detailed review and are listed below:

Feed System

Explosion in the feed tank

Feed line break

Calciner

Calciner pressurized and ruptured

Ruptured by overhead crane

Melter

Canister and furnace liner melt

Canister Handling

Canister Drop

Off-Gas

NO_x destructor

Ruthenium-bed failure

Iodine-bed failure

Cell

Fire in cell

Explosion in cell

Earthquake

Tornado

The accident review includes the accident scenario, mitigating factors associated with the accident, corrective actions, and identification of source terms associated with the accident. In many cases, the source term for a particular accident was bounded by more severe accident. Source terms were therefore only evaluated for these most severe accidents.

6.2.3 ACCIDENT CONSEQUENCE ANALYSES

The nine design-basis accidents and four other accidents identified in Section 6.2.2 are analyzed here.

6.2.3.1 Feed System

Explosion in the Calciner Feed Tank.

Accident Scenario

The spray calciner feed tank is located in a cell adjacent to the vitrification cell. Any disruptive incidents associated with the spray calciner feed tank would not damage the vitrification equipment or associated effluent cleanup equipment.

The rupture of the spray calciner feed tank could occur from extreme pressures developed within the feed tank originating from an explosive source. The source of this disruptive energy could be:

1. explosion of hydrogen within the feed tank,
2. "red oil" explosion within the feed tank, and/or
3. a solvent explosion within the feed tank.

The consequences from the explosion of material within the feed tank are varied, depending upon the severity of explosion. A severe explosion would rupture the feed tank, spilling HLLW to the floor of the cell. Liquid waste could also be forced up the instrument lines into the service gallery. It is also probable that a pressure wave from the explosion would damage other equipment in the cell.

Detection of the feed tank rupture would be accomplished by several methods. Liquid waste accumulated at the cell sump would be detected by the

sump alarm activation. Liquid flow rate to the spray calciner would be interrupted, setting off flow alarms to the spray calciner. The liquid-level indicators for the feed tank would not behave properly. Actual behavior would depend upon the type of damage that the dip legs had received. A radiation alarm would sound if liquid waste were forced through the dip legs into the service gallery during pressurization. Constant pressurized air-purging of the lines and air-purge system design should prevent this from occurring. A visual inspection of the feed tank would help assess the severity of damage.

Mitigating Factors

The following events must occur concurrently for a hydrogen explosion to occur within the spray calciner feed tank.

1. air sparge to the feed tank must be inoperable,
2. hydrogen concentration in the vapor space must reach at least 4.1% by volume (Coward and Jones 1952),
3. an ignition source must be present at a temperature of at least 585°C (Coward and Jones 1952).

The feed tank will have alarms or detection methods to indicate inoperability of the sparging and venting system on the feed tank. No ignition sources are associated with the feed tank. Mixing of the HLLW will be accomplished by tank agitators. These agitators have the drive motor located outside the tank, eliminating this potential ignition source. Hydrogen generation rates are approximately 4.0 cc/W-h of absorbed decay heat based on acid waste [G value = 0.5, (Spinks and Woods 1964)]. It would conceptually take approximately 6 h for the hydrogen concentration to build up to 4.1 vol% in a 7000-L feed tank half full of HLLW--although air in-leakage would probably greatly extend the time needed to obtain this concentration.

Detonation of "red oil" in evaporators has occurred, causing extensive damage (Stoller and Richards 1961). Maintaining the temperature of the HLLW in the feed tank at a temperature below 135°C will prevent red oil detonation. The feed tank is equipped with cooling coils, temperature measurement

sensors and temperature alarms to prevent and indicate HLLW heatup as the result of fission product decay heat. The nominal temperature of the HLLW feed to the spray calciner will be less than 50°C, maintaining a safe margin in the temperature range.

The HLLW will contain several types of organic material originating from solvent-extraction, ion-exchange and other processing steps. Compounds such as EDTA, tributyl phosphate, dibutyl phosphate, coal, and thermally degraded organic compounds will be present. The deflagration of these materials can only occur in the gas phase with sufficient oxygen present to allow complete combustion. The vapor pressure and corresponding gas phase composition of these materials is low due to their high molecular weight. The spray calciner feed tank will be cooled to remove radionuclide decay heat. Keeping the tank cool will prevent excessive buildup of solvent vapors. In addition, with limited potential ignition sources present within the tank and an oxygen supply in the tank, chance for an extensive combustion or energetic explosion is low.

Corrective Actions

HLLW spilled to the floor will be removed through sump drainage to a storage vault or process tanks within the cell. Decontamination of the walls and equipment can be performed by a steam or water spray. Failed equipment will be decontaminated, removed from the process cell and replaced.

Source Term

The source term release for the explosion of the feed tank is judged to be bounded by a source term from a feed line break which generates an aerosol that is entrained in a ventilation flow path. HLLW released during a hypothesized tank rupture would accumulate on the cell floor and drain to the cell sump. Here the HLLW would be collected and returned to a tank for storage.

6.2.3.2 Feed Line Break

Accident Scenario

The feed line break is classified as a moderate accident because of the general industrial experience which indicates that a break in piping runs with

mechanical couplings is an event that may be expected in the life of a plant. It has been included with the analyses of Design-Basis Accidents because the leaking pipe can conceivably generate a larger source term than can the more improbable feed tank explosion scenarios. The pipe break, of course, results in much less equipment and cell damage.

A leak in the HLLW piping could be the result of many failure modes. These include corrosion, erosion, mechanical failure of a coupling, failed gasket, improper installation, and piping damage due to maintenance or operations movement of the overhead cranes.

The leak could vary from the complete rupture of a large recirculation feed line on the feed tank (approximately 240 L/m at 551 KPa) to a small crack that releases an aerosol spray.

The leak would be detected by many systems almost immediately. If it were a large leak in the feed line the spray calciner feed rate would alarm as well as a low-pressure alarm on the feed system. A large leak would also initiate a sump-level signal very rapidly. A small leak would probably first be detected as a high cell and ventilation radiation alarm.

The piping breaks are expected to have no significant effect on the cell equipment or the cell with the exception of the cell HEPA filters, which must be protected from direct impingement from a liquid and which must be protected from a high vapor loading to prevent a high pressure drop across the filter, which could cause its rupture.

In selecting representative source terms, some preliminary calculations indicated the liquid source term leading to the highest potential release was a small HLLW leak that was highly atomized. While larger leaks would result in much larger spills, the liquid would just be routed to a holding tank by the radioactive waste sump in the cell and very little airborne contamination would result. On the other hand, if a leak were to generate an aerosol it could be entrained in the ventilation flow and would have to be removed by the cell HEPA filter bank. As an upper bound the aerosol generation rate of the spray calciner was taken for the source term.

Mitigating Factors

Proper design, installation, and initial testing as part of a good quality-assurance program will be the primary defense against piping leaks. The corrosive and erosive properties of the HLLW are well known and the design will reflect appropriate conservatism in the piping specifications. After maintenance functions are completed, the piping involved in the maintenance can be tested as practical to discover leaking connections or gaskets prior to feeding the HLLW.

Corrective Action

Corrective action consists of suspending the feeding operation as soon as detection is made via one of the modes discussed above and initiating decontamination as soon as possible. The cell will be designed to facilitate decontamination and the resulting radioactive solutions will be collected in the sump of the cell, where it will be routed to holding tanks and ultimately be fed back into the HLLW system. The failed equipment will be repaired and the incident subjected to appropriate engineering review to predict and prevent future occurrences.

Source Term

For the purposes of calculating a source term the assumptions are made that maximize the source term while still retaining a physical basis. In the case of the HLLW piping leak, the leak was assumed to have the same capacity as the spray calciner atomization system, which is 300 L/h. The droplet size was assumed to be 70 to 100 μm . This degree of atomization is, in fact, difficult to achieve and requires approximately a 300:1 volume ratio of atomizing air through a special-purpose atomizing nozzle in the case of the spray calciner. The leak is assumed to persist for 10 min before being detected by the abnormal radiation alarms for the cell and the ventilation system. This would result in the atomization of 50 L of HLLW solution, which is equivalent to 0.054 metric tonne uranium waste equivalent (MTUWE).

Most of the aerosol would settle out as indicated by the following information. The density of this amount of liquid if totally dispersed in the

vitriification cell volume ($20,000 \text{ ft}^3$, 570 m^3) is 90 g/m^3 . This density is equivalent to that of a light rain and the liquid droplets would quickly agglomerate and precipitate out. The terminal settling velocity for $85\text{-}\mu\text{m}$ water droplets is 20 cm/s . Droplets with a diameter of $200 \mu\text{m}$ will settle out at 76 cm/s (Fig. 5.82, Perry and Chilton 1973). The average horizontal air flow through the vitriification cell is 1.7 cm/s , which is much less than the air flow necessary to support the assumed aerosol. For the purpose of this calculation it was assumed that only 90% of the aerosol settled out in the cell and the remainder ($5 \text{ L} = 0.0054 \text{ MTUWE}$) challenged the HEPA filter system of the vitriification cell.

There may arise a source term from volatilized Ru. If significant evaporation of HLLW takes place, up to about 1% of the Ru may become volatilized in high-molarity nitric acid solution (Christian and Pence 1977). The volatile Ru component would therefore be $5.4 \times 10^{-5} \text{ MTUWE}$ entrained in the ventilation flow.

The prefilter removes 80% ($\text{DF}=5$) of the remainder, which leaves 1.0 L of HLLW aerosol entering the HEPA filters. The HEPA filters are susceptible to clogging by heavy mists, which could raise the pressure drop to the point that they rupture. However, the 1.0 L of aerosol is not expected to result in failure of these filters. The combined particulate DF of the vitriification cell HEPA filters and the APS HEPA filters is 5×10^8 . Therefore the source term at the stack exit is $1.1 \times 10^{-11} \text{ MTUWE}$. The DF for volatile Ru is 1. Therefore, the source term at the stack is $5.4 \times 10^{-5} \text{ MTUWE}$.

6.2.3.3 Calclner

Calclner Pressurized and Ruptured.

Accident Scenario

Rapid oxidation of solvent, "red oil" and other organics, within the spray calclner can cause pressurization. Sufficient pressure can rupture the calclner at a prestressed point such as a weld along the spray calclner cone. Normally any pressurization of the spray calclner would be relieved through the seal pot and off-gas system.

If the rupture of the spray calciner did occur, a large majority of the calcine held up in the calciner could be released to the cell. This pressurization could produce a shock wave damaging the cell HEPA filters and cause structural damage to the cell.

Any slight pressurization of the calciner would be recorded or detected on instrumentation. The following events would occur, assuming pressurization of the calciner: 1) initially a pressure spike would be observed on the spray calciner vacuum recorder, followed by 2) a loss of vacuum observed in the ruptured spray calciner. Both of these incidents would be alarmed. In the event of calciner rupture or pressurization, calcine dust may be observed in the cell through cell windows. The spray calciner feed system would be equipped with a feed failsafe system such that if vacuum were lost in the spray calciner system, the HLLW flow to the calciner would be discontinued. This would minimize the amount of HLLW entering the open system. The effluent cleanup equipment for the calciner is located in an adjacent cell. Minimal equipment damage would occur to this system as the result of calciner pressurization.

Detection of significantly increased activity in the APS would indicate the radionuclide release that would occur as a result of the calciner pressurization and rupture.

Mitigating Factors

The mitigating factors associated with calciner pressurization, due to solvent oxidation, are discussed first. The initiating sequence required to produce pressurization and rupture of the spray calciner is complex. First, it is postulated that the fuel processing solvent extraction operations resulted in the accumulation of a significant quantity of solvent in the spray calciner feed tank. Second, it must be assumed that withdrawal of waste solution from the feed tanks occurs such that there is an abrupt change from aqueous to organic feed. Third, it would be necessary for the spontaneous ignition of the solvent stream to be delayed until the amount of solvent in the calciner was stoichiometrically equivalent to and intimately mixed with the oxygen in the spray calciner.

The dimensions of the reference spray calciner chamber are approximately 0.91 m in dia by 3.05 m in height. Considering the volume of the chamber, the volume of the cone section and the volume of the filter housing, the total number of moles of oxygen in the calciner at a temperature of 750°C is 5.0. This amount of oxygen, if assumed to react completely with a stoichiometrically equivalent amount of organic present would not produce sufficient pressures to cause other than a normal pressure fluctuation in the process. The calciner is not an accumulator of material. "Red oil" or other organics could not collect within the calciner and fail to burn.

Corrective Action

The possibility of equipment damage from this hypothetical accident is remote. All failed equipment will be replaced.

Source Term

The calcine hold-up in the spray calciner has been experimentally determined in nonradioactive tests. The sintered-metal filter area is assumed to be 15.6 m² (168 ft²). The lower cone (2 m²) may also have a thin coating of calcine. Experience has shown that the calcine thickness is nominally 2 mm on the filters and this is assumed for the lower cone section. This assumption results in the release of 35 kg of calcine. Therefore, 41% of a MTUWE is released to the cell atmosphere. Conservatively, assuming no settling-out in the cell, all of the release would be filtered by the set of cell HEPA filters (one pre-filter and two HEPA filters) and also the atmospheric protection system consisting of one pre-filter (no DF credit taken for pre-filter) and two HEPA filters. The total DF is then 5×10^8 .

6.2.3.4 Calciner Rupture by Overhead Crane

Accident Scenario

The lifting operations carried out during operations and maintenance have been identified as one of the few sources of significant potential disruptive energy in the process and vitrification cells. Calciner rupture by overhead crane has been identified as a moderate accident based on the perceived

probability of occurrence in an operating facility. The two potential causes have been identified as operator error and a malfunction in the equipment-handling system.

An examination of the spray calciner system shows the chamber and filter box to be both massive and rugged. The portion of the system that is predicted to be the most vulnerable is the calciner delivery system which consists of piping, bellows, special-purpose valves, rotating sections, and cooling systems. An accident is postulated wherein the crane hook or a piece of equipment being moved in the cell impacts or otherwise engages the delivery piping and ruptures either the piping connections or the connection to the bottom of the calciner delivery funnel.

This accident would release some fraction of the calcine hold-up in the calciner chamber and on the calciner filters. The potential magnitude of the release is judged to be less than that of the Design-Basis Accident, "Calciner Rupture Due to Explosion." Therefore, a source term is not calculated for this particular accident.

Detection of the accident is expected to be by visual observation, since some type of handling operation serves as the initiator of the accident. However, the accident will also be announced by the normal spray calciner instrumentation, especially the off-gas vacuum measurement, as a result of the air in-leakage.

Mitigating Factors

A QA program that requires operator training and thorough procedures for hoist and crane operations in the cell will be the first line of defense against this type of occurrence. The potential for this type of accident has been historically recognized and the design of the equipment will be tested against this potential occurrence. Although not specifically required by the current design specifications, it may be possible to improve the controls for the handling systems such that the probability of control system malfunctions is greatly reduced.

The spread of contamination due to this type of rupture is expected to be very small as a result of the off-gas vacuum in the spray calciner.

Corrective Action

The equipment and cell may require decontamination. The damaged equipment will be replaced. Although not identified as such at this stage in the design, it is very probable that the calcine delivery system can be replaced as a module, thereby minimizing the process disruption as a result of this occurrence.

Source Term

The source term for this accident is bounded by the "Calciner Rupture Due to Overpressurization or Explosion."

6.2.3.5 Melter

Rupture of Canister and Furnace Liner Due to Over-Temperature.

Accident Scenario

An accident is postulated wherein an over-temperature condition in the ICM furnace causes both the furnace liner and the canister to rupture. The potential causes of this accident have been identified as operator error or malfunction of the temperature controllers.

The consequences of this accident would be the release of molten glass at temperatures significantly higher than the normal 1050°C process temperature. The furnace insulation and shell are not engineered as a barrier. Therefore, the molten glass may run out onto the cell floor, where it will begin to cool, solidify and crack. Although there may be some cracking of the glass as it solidifies and cools it will not generate an airborne aerosol. The only projected path for radionuclide release into the atmosphere is due to the volatility principally of Cs and Ru. Data on volatilization rates of these elements is given by Gray (1976). Assuming the spilled glass is at 1200°C , Cs and Ru are volatilized at $0.005 \text{ g/cm}^2\text{-h}$, and $0.00015 \text{ g/cm}^2\text{-h}$, respectively. During normal operation these volatiles are drawn up through the spray calciner and either recycled into the glass by being absorbed on calcine or captured in the

off-gas system. Since the release of these volatiles is modeled as a surface-diffusion phenomena, it is necessary to hypothesize a model of the glass spill in order to calculate the absolute release amounts of the volatiles. This is done in the source term calculation below.

For this accident the only facility damage would be to the canister and the ICM furnace that failed. In addition to the contamination of the cell floor with the solid glass mass there would be some additional cell and associated equipment contamination by the condensation of the volatile radionuclides. There is also the possibility that the hot glass could cause some warping of the cell liner, and any combustible material or insulation would be damaged if contacted with the molten glass.

This accident would be detected by anomalies in the process instrumentation for the ICM system. Excessive air in-leakage, loss-of-weight indication, over-temperature alarms, loss of argon cover gas, and abnormal power consumption are some of the potential indicators.

Mitigating Factors

The basic assumption for this accident is that the ICM furnace is capable of heating the furnace liner and canister to the point that there is local melting or loss of structural integrity. Once a specific furnace design is realized, it will be possible to carry out a detailed heat-transfer analysis to disprove or substantiate this basic assumption. Engineering judgment based on the performance of developmental ICM furnaces in that the furnace will not be capable of sufficient output to cause this accident. Still another reason to judge that this accident is very improbable is the assumption that a malfunction in a furnace temperature controller could initiate the accident. In the developmental ICM furnaces there has been a separate controller for each zone of the furnace. Therefore, this mode of accident initiation would essentially be impossible if the same control scheme is used for the reference facility.

Other mitigating factors are the time it would take for the furnace temperature to reach the damaging level and the number of process indications to the operator that the process was not normal.

Corrective Action

The damaged furnace and canister will have to be decontaminated and removed from the cell. The solidified glass will require retrieval and recycling into a new canister for remelting. Since there is no additional radionuclide release once the spilled molten glass has solidified, there will be sufficient time to develop cleanup and recovery procedures that provide adequate contamination control for the cleanup operations.

Source Term

A source term is developed for this design basis accident, since the other accident involving a glass spill is the canister drop, in which case the glass temperature is so low that volatilization of Cs and Ru is negligible. In order to calculate the amount of material that is volatilized as a result of the overheating accident it is necessary to model the glass spill sufficiently to predict surface area and surface temperature. In keeping with the philosophy of this hazards analysis to maximize the source term within physical limitations, a relatively slow leak was assumed to occur over a 4-h period. The glass was assumed to leak from the furnace at 1200°C and expose 7.1 m² of surface area (3-m dia). At the end of the 4 h the total canister inventory of 540 kg would have formed a glass slab 2.55 cm thick. By postulating this slow leak the volatilization is maximized because new hot glass is continually being expelled over a large surface area. In reality the glass would run out onto the cell floor (a stainless steel liner) and solidify so rapidly that the amount of material volatilized would be orders of magnitude less than that calculated with the above assumptions.

Using the volatilization rates from Gray (1976), the above assumptions for a 7.1-m² pool of 1200°C temperature glass exposed for 4 h yields 1420 g of Cs (0.66 MTUWE) and 43 g of Ru (1.0×10^{-2} MTUWE). The total amounts of Cs and Ru in the glass are 4.9 kg and 4.2 kg, respectively.

The volatile species of the above elements includes both the metallic and the oxide forms. Both would tend to condense on any cool object the vapor contacts. Since the vapor will tend to agglomerate into particulates or plate out on the cell filters, the decontamination values given in the cell

ventilation layout are used to determine the stack release. For Cs the release is treated as particulates, for which the system has a decontamination factor of 5×10^8 . The Ru is assumed to be in the volatile form of RuO_4 with a DF of 1 by all HEPA filters. The resulting stack release rates are therefore 1.3×10^{-9} MTUWE for Cs and 1.0×10^{-2} MTUWE Ru, all for a period of 4 h.

6.2.3.6 Canister Handling

Canister Drop.

Accident Scenario

This accident analyzes the consequences of a dropped waste glass container filled with hot, radioactive glass. The potential causes of this accident include operator error, malfunction of the overhead crane hoisting system, mechanical failure of the cable or hook, mechanical failure of the lifting device or the canister flange, or loss of structural integrity of the canister itself.

The release of contamination could arise from two modes. First, there is the possibility that some contamination in the form of slag or very viscous glass could be released from a damaged canister. Secondly, the dropped canister could damage some other piece of process equipment and cause a release of the radioactive process material.

The canister surface is cooled to approximately 700°C in the ICM furnace before it is lifted out. At this time the glass temperature will range from 700° to 1000°C . Glass below 900°C will not flow readily, and the amount actually escaping to the cell floor will depend on the type of canister damage. The only radionuclides that may become airborne from the glass are the Cs and Ru isotopes as a result of the high vapor pressure of these elements. But at the temperature of the precooled glass, the volatility rates of even these elements are negligible. The volatility at 1000°C is 25 times less than at 1200°C (Gray 1976). A representative source term from spilled glass has been calculated for the hypothesized case where loss of furnace temperature control leads to melting of the canister and the furnace liner.

Consideration of the types of source terms that could arise as the result of equipment damage due to the canister drop indicates a HLLW feed line could be ruptured, the spray calciner system could be ruptured leading to calcine release, or a canister being filled and which contains molten glass could be ruptured leading to molten glass release. (It has been assumed that the off-gas system is not exposed to the potential of a canister drop as a result of its location.) In each case the potential source term is less than that of another Design-Basis Accident assumed to occur for that system. Therefore a source term unique to the canister-drop accident is not developed.

The potential damage to the process equipment as a result of this accident could require substantial repair time. If the stainless steel cell liner were ruptured as a result of the accident, it might be necessary to repair this rupture before wet decontamination of the cell could be carried out.

Detection of the canister drop would be visual, since it would occur during a handling operation. Depending on the damage done, the event may set off process alarms.

Mitigating Factors

The first line of defense against the canister-drop accident is a quality assurance program that requires thorough training and instruction of the proper procedures for an operator to carry out a canister transfer operation. An inservice inspection program will also ensure periodic inspection of the overhead crane and its components. Likewise, the QA program will specify appropriate inspection requirements for all of the canisters received at the site before they are used in the cell.

Corrective Action

As a result of this accident it may or may not be necessary to shut down operations, depending on the circumstances. A special grappling jig may be required to recover the dropped canister. An assessment of the damage will be carried out and decontamination and repair will be initiated. An engineering review of the incident will be carried out to determine if any changes to operating procedures or equipment design are required.

Source Term

As discussed, this accident could conceivably lead to the same source term as calculated for the spray calciner rupture or the HLLW feed line break. The glass spill source term would be negligible compared to the source term for the furnace liner and canister melt-through accident.

6.2.3.7 NO_x Destructor Explosion

Accident Scenario

An ammonium nitrate explosion in the NO_x destructor or the downstream piping is postulated. The NO_x destructor is located outside of the vitrification cell. An explosion in the NO_x destructor resulting from improper operation could damage the off-gas system, in addition to disrupting the normal flow of gaseous effluent to the building stack. Disrupting the vacuum source to the vitrification process would signal alarms, and the process operations would be discontinued.

Mitigating Factors

Ammonium nitrate can be formed in or downstream of the ammonia burner if the temperatures of operation are greater than 600°C and the reactants are present or downstream of the ammonia burner if the temperature is less than 350°C. Proper instrumentation and control will maintain the equipment reaction temperature within these limits.

Most investigators agree that when heat is applied to ammonium nitrate, the reactions shown in Table 6.2.2 are possible. Every reaction that forms ammonia requires energy, while reactions consuming ammonia are spontaneous. Thermodynamically, ammonia should be consumed in the atmosphere of the reactor, since reactions consuming ammonia proceed much more readily than do reactions producing ammonia. It is conceivable that steam might shift the equilibrium of reactions consuming ammonia to form ammonia; experiments indicate that this can happen. Large quantities of nitrogen dioxide present will counteract this shift of equilibrium.

TABLE 6.2.2. Probable Ammonium Nitrate Decomposition Reactions

Temperature, °C	Reaction	Heat Produced per mole NH_4NO_3 , kcal
180	$\text{NH}_4\text{NO}_3 \rightarrow \text{NH}_3 + \text{HNO}_3$	-40
180 to 200	$\text{NH}_4\text{NO}_3 \rightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O}$	+13
230	$3\text{NH}_4\text{NO}_3 \rightarrow \text{N}_2\text{O}_3 + 6\text{H}_2\text{O} + 2\text{N}_2$	+21
260 to 270	$4\text{NH}_4\text{NO}_3 \rightarrow 2\text{NH}_3 + 3\text{NO}_2 + \text{NO} + \text{N}_2 + 5\text{H}_2\text{O}$	-19.5
260 to 270	$2\text{NH}_4\text{NO}_3 \rightarrow 2\text{N}_2 + \text{O}_2 + 4\text{H}_2\text{O}$	+30
260 to 300	$8\text{NH}_4\text{NO}_3 \rightarrow 2\text{NO}_2 + 4\text{NO} + 5\text{N}_2 + 16\text{H}_2\text{O}$	--
>300	$4\text{NH}_4\text{NO}_3 \rightarrow 2\text{NO}_2 + 3\text{N}_2 + 8\text{H}_2\text{O}$	+30
>300	$2\text{NH}_4\text{NO}_3 \rightarrow 2\text{NO} + \text{N}_2 + 4\text{H}_2\text{O}$	+9

Corrective Action

Damaged equipment will be replaced. The cause of the accident will be determined and corrective actions administered.

Source Term

The radioactive source term release for an off-gas explosion will be bounded by other accidents reviewed in this section.

6.2.3.8 Ruthenium Bed Failure

Accident Scenario

The ruthenium adsorber bed of silica gel may contain up to 7.5×10^{-3} MTUWE (90 Ci) of ^{106}Ru at the end of a projected 300-day service life based on a process system DF of 2×10^5 to this point. Design-Basis Accident summaries for reprocessing plants have historically included a hypothesized release of a major fraction of the Ru on the adsorber bed. A review (Christian 1976) of Ru chemistry in waste processing plants indicates the complexity of trying to predict what a Ru-loaded silica-gel bed might do during postulated accident conditions.

However, it has been observed that heating a bed up to 600°C merely stabilized the Ru that was adsorbed. If the bed were actually exposed to an oxidizing flame, experiments indicate the Ru would be driven off in its volatile form [RuO₄(g) or RuO₃(g)]. Potential for Ru release resulting from physical damage to the bed has been considered. However, this event would not result in re-volatilization of the Ru and the cell HEPA filters would trap any small amounts of airborne particulates generated by the event. It is possible to elute the Ru from a silica-gel bed with hot water. The volatile species expected to be adsorbed on the bed is not well characterized, but is judged to be a nitrosyl ruthenium gas complex. Based on the above information (Christian 1976) the possibility of an over-temperature condition causing a release is considerably less than the possibility that water is somehow forced through the silica-gel bed. The water-loading in the off gas would be assumed to subsequently cause a failure of the process off gas HEPA filters immediately downstream of the iodine adsorption bed. This accident scenario would be detected by radiation alarms and possibly high equipment differential pressures in the off-gas system.

Mitigating Factors

The hypothesized water injection into the off-gas system would have to come from the venturi/wet cyclone in the high-level acid-waste off-gas system. The recycle drains on the cyclone, the condenser, and the mist eliminator would have to be blocked before the water could be drawn downstream. Alarms in the off-gas system would originate such a process upset in time to prevent significant Ru elution. Assuming a Ru-loaded solution were drawn downstream past the HEPA filters it would not all revolatilize upon evaporation. The amount that did volatilize could be expected to plate out in the steel ducting. Eventually the remaining volatile Ru would encounter the NO_x reactor system, which could be expected to provide a DF of 300 (Newby, Barnes and Thomas 1976). Some further plateout might be expected in the plant atmospheric protection system.

Corrective Action

The process would be shut down immediately upon detecting trouble in the off-gas system. The off-gas system would require correction of the initiating

events and replacement of the HEPA filters. Depending on the extent to which Ru contamination was carried downstream it may be necessary to carry out decontamination of the ducting downstream of the off-gas equipment.

Source Term

The source term arbitrarily assumes 50% of the Ru is eluted (3.8×10^{-3} MTUWE of ^{106}Ru) and the DF to be a factor of 100 provided by the NO_x destructor and a factor of 10 (total DF = 1000) provided by the plateout and APS. The source term from the stack is 3.8×10^{-6} MTUWE of ^{106}Ru . An accident time of 10 min is taken as a commonly accepted time for operator action.

6.2.3.9 Iodine Bed Failure

Accident Scenario

The removal of I_2 and CH_3I by a silver exchanged mordenite (AgZ) bed is a chemisorption process and is not easily reversed (Gal et al. 1974). The bed operates best at approximately 150°C (Burger and Burns 1979). The presence of H_2O and NO_2 in the off-gas stream improves the DF (Murphy, Staples and Thomas 1977). The suggested desorption process is the passing of dry H_2 at 400°C to 500°C through the bed.

Therefore, the iodine bed would appear immune to significant iodine desorption due to excessive water vapor or pre-heater over-temperature. No significant source of hydrogen has been identified in the off-gas stream.

No source term is calculated for this accident, since no mechanistic release mechanism is postulated. The potential for such an accident is analyzed because the bed represents a significant source of a difficult-to-trap radionuclide. Further safety analysis may be warranted when details of bed regeneration are developed in the design of an actual plant or if a significant source of hydrogen (possibly from radiolytic decomposition) is identified.

Mitigating Factors

Probable mechanisms for iodine desorption are absent.

Corrective Action

The process can be shut down and flow of off gas through the bed could be stopped until normal process parameters are re-established.

Source Term

None.

6.2.3.10 Cell Fire

Fire in Cell.

Accident Scenario

There are few combustibles in either the vitrification cell or the effluent and radioactive feed cell. The principal combustibles that are present are electric cabling insulation and oil in the shielding windows. There are no significant quantities of solvents or pyrophoric metals in the normal process operation.

Although a fire would not be expected to breach any of the process vessels, an arbitrary assumption is made that the fire is coincident with the molten glass spill or could be caused by the glass spill. Therefore, the source term calculated for the glass spill is assumed to apply for this case.

Mitigating Factors

As previously stated, there are very few combustibles located in the cells. The cells are designed with fire detectors and a smother-gas fire-extinguishing system. Perhaps the initiator with the greatest probability of occurrence is an electrical short.

Corrective Action

The fire would be extinguished, the processing operation halted, and decontamination and recovery would be carried out.

Source Term

As described in the melter accident, 1420 g of Cs and 42 g of Ru are volatilized. The source terms at the stack are the same as for the glass spill. The cesium is 1.3×10^{-9} MTUWE, and the ruthenium is 1.0×10^{-2} MTUWE.

6.2.3.11 Cell Explosion

Accident Scenario

An explosion in the cell is traditionally postulated on the assumption that a solvent, combustible dust, or hydrogen concentration will build up to the explosive level in a cell. While this may have some small probability of occurring in some types of process cells in a reprocessing plant, there are no significant sources of these explosive combustibles in the vitrification cells.

The accident scenario for rupture of the spray calciner has been presented. In that accident, calcine is released to the cell atmosphere as a result of a rupture in the calciner chamber. The source term assumes the cell HEPAs to be intact. The case of the cell HEPA filters being ruptured for this accident is considered in Section 6.2.4.

Mitigating Factors

Fire and explosion potential can be prevented by keeping the combustible vapor concentrations too low to support combustion. Continual ventilation of the cell (twelve times per hour) with proper ventilation paths should eliminate accumulation of vapor in the cell. The safety philosophy of keeping all initiators of combustion to a minimum will be maintained.

Corrective Actions

In the event of air explosion, all process equipment will be shut down. The facility will be inspected for damage, decontamination of operating areas will be provided, and repair of damaged equipment will be initiated.

Source Term

A separate source term has not been calculated for this accident, since it is bounded by the SC rupture accident.

6.2.3.12 Earthquake

Accident Scenario

The site-specific Safe-Shutdown Earthquake (SSE) is assumed to occur. As a result of the earthquake there may be minor damage to the process equipment.

Examples of the damage include leaks at gaskets and connections. Leakage of some HLLW and some calcine to the cell are assumed to occur. The process cell is the primary radionuclide boundary and would be designed to withstand the SSE.

Detection of the SSE would be due to the obvious plant movement and from earthquake alarm and recording instrumentation.

Mitigating Factors

Because of the nature of the vitrification process equipment and the expectation of limited service life of many of the components, it is not cost-effective to design the process equipment to survive the SSE with complete assurance that no damage would occur. However, there is a great deal of conservatism in the earthquake design standards and substantial no damage to the process equipment is anticipated even in the case of a SSE. A SSE analysis need be performed on the process equipment to the extent necessary to prove that a failure in the process equipment will not damage the integrity of the process cell.

Corrective Action

Upon detection of the earthquake the operators will shut the process equipment down according to procedures for this event until a thorough system checkout can be performed to verify the operability of the process equipment. Any contamination will be controlled and damaged equipment will be repaired or replaced.

Source Term

A source term unique to the SSE has not been calculated. Source terms have been calculated for both the HLLW leak and the calcine release which are expected to contain the source terms of this accident.

6.2.3.13 Tornado

Accident Scenario

The eye of the Design-Basis Tornado (DBT) passes over the plant. The generic site is assumed to be in a Region I tornado area as defined in the NRC

Regulatory Guide 1.76, April 1974. The depressurization characteristics of the tornado are a 3.0 psi depressurization at the rate of 2.0 psi/s, which lasts for 20 s. The tornado phenomenon affecting equipment design is depressurization. For this design, two design-basis cases are considered.

- Case 1: The vitrification cell is exposed directly to the depressurization, while the cell equipment is operating at maximum off-standard pressure and temperature conditions.
- Case 2: The vitrification equipment interior, through the vessel off-gas system, is exposed directly to the depressurization in addition to the maximum off-standard operating condition vacuum while operating at the maximum off-standard condition temperature. The vitrification cell is at atmospheric pressure.

The result of Case 1 is assumed to be a leak of calcine of 50 g (5.9×10^{-4} MTUWE) at the point where the spray calciner connects to the canister. The off-gas system can structurally withstand the imposed pressure differential. Therefore no release of any radionuclides held in the off-gas system is anticipated. No mechanism for liquid or molten glass release has been identified. The depressurization of the process cell is assumed to rupture the APS HEPA filters, but a more detailed analyses may show that their integrity can be maintained. No settling out of the calcine is assumed. The cell inlet HEPA filter may also be ruptured, in which case the operating area may become contaminated. Contamination alarms in this area would alert operators who would use air packs while dealing with the DBT.

The result of Case 2 is a rupture of the APS HEPA filters and the off-gas HEPA filters. Based on the activity balances presented in the high-level acid-waste flowsheets, the off-gas HEPA filter would have trapped 8.8×10^{-3} Ci of radionuclides during one year of operation. This amount of activity (2.4×10^{-8} of a MTHM) was assumed to be released as a result of the HEPA filter ruptures but is bounded by the Case 1 release.

Detection of the DBT would be due to direct observation by the operators as well as pressure imbalance alarms from the plant ventilation system.

Mitigating Factors

For the DBT the equipment located in the waste vitrification cell and associated vital (Class 1) service are protected from wind-generated forces and associated missiles by the building structure. Under the depressurization scenarios described as Case 1 and Case 2, the equipment will be designed such that it will maintain its structural integrity and be capable of resuming normal operation with only minor corrective action. Although pressure-equalizing devices are considered to be part of the design to protect the equipment and HEPA filters, these devices were assumed to be inoperative in calculating the consequences.

Corrective Action

The process will be shut down as soon as anomalies in the building air balance are detected. The procedures for recovery operations when a HEPA filter has been breached will be put into effect. HEPA filters will be replaced and decontamination of the cells and the operating areas will take place.

Source Term

The release of 50 g of calcine to the vitrification cell for Case 1 can be expressed as a release of 5.9×10^{-4} MTUWE. Since the cell pre- and HEPA filters are assumed to be intact during Case 1, the decontamination factor is 5×10^4 . The resulting release from the plant stack would be 1.2×10^{-8} MTUWE.

6.2.4 DISCUSSION OF SOURCE TERMS

Five source terms were defined as radioactive material release consequences from the 13 accidents reviewed. These source terms provide an inclusive envelope in which to consider the radionuclide releases from all accidents considered. No attempt is made to analyze the consequences of these releases, since this is site- and assumption-specific. However, these source terms, when used with appropriate assumptions, can be used as input to environmental and dose calculations. The source terms presented are very conservative (high) due to the assumptions used. Thus, the assumptions should be considered for

applicability in using these source terms. The source terms for the accidents reviewed are summarized in Table 6.2.3. The largest particle release is seen in the case of the DBT, when the assumption was made that the tornado ruptured the pre- and HEPA filters in the plant APS at the stack. A specific site design may be able to show this assumption is unnecessarily conservative.

The importance of the cell HEPA filters in preserving the integrity of the cell boundary to challenges from process release in the cell is demonstrated by the accidents reviewed. Many of the accidents could threaten the cell HEPA filters by such means as missile rupture due to explosions, excessive water loadings from liquid leaks or cell fire suppression sprays, heavy smoke loading from cell fires, or from heat damage from the fire. To illustrate the importance of a design that protects the cell HEPA filters from these challenges, the source terms at the stack for the case where the cell HEPA filter is ruptured is presented in Table 6.2.4.

TABLE 6.2.3. Source Term Release to the Stack, Cell HEPAs Intact

Accident	Source Term	Duration of Release, min	DF(a)	Source Term Release to Stack, MTUWE
HLLW Leak	Particulate	10	5×10^8	1.1×10^{-11}
	Ru (volatile)		1	5.4×10^{-5}
Calcine Release	Particulate	10	5×10^8	8×10^{-10}
Ruthenium Release	Ru (volatile)	10	10^3	3.8×10^{-6}
Glass Spill	Cs	240	5×10^8	1.3×10^{-9}
	Ru (volatile)		1	1.0×10^{-2}
Design-Basis Tornado	Particulate	10	5×10^4	1.2×10^{-8}

(a) DF = Decontamination Factor = $\frac{\text{Fraction of material in entering stream}}{\text{Fraction of material in exit stream}}$

TABLE 6.2.4. Source Term Release to the Stack, Cell HEPAs Ruptured

Accident	Source Term	Duration of Release, min	DF (a)	Source Term Release to Stack, MTUWE
HLLW Leak	Particulate	10	10^4	5.5×10^{-7}
	Ru (volatile)		1	5.4×10^{-5}
Calcine Release	Particulate	10	10^4	4.0×10^{-5}
Ruthenium Release	Ru (volatile)	10	10^3	3.8×10^{-6}
Glass Spill	Cs	240	10^4	6.5×10^{-5}
	Ru (volatile)		1	1.0×10^{-2}
Design-Basis Tornado	Particulate	10	1	5.9×10^{-4}

(a) DF = Decontamination Factor = $\frac{\text{Fraction of material in entering stream}}{\text{Fraction of material in exit stream}}$

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6.3 MATERIALS-USE ASSESSMENT

D. E. Larson

The materials-use assessment for the reference SC/ICM estimates essential materials, utilities, wastes and effluents from system operation to be used for analyses of the site, local population, local area, material resources, costs and biosphere impacts. This assessment is of necessity restricted because the SC/ICM system will be part of a larger, undefined process and facility and because the facility is not site-specific. It would be expected that the site location and the related operations would have major environmental, social and economic impacts. Also, it is not possible to perform a cost/benefit analysis unless the full plant situation is addressed. Thus, this materials assessment is oriented toward providing information needed to perform an environmental report for an entire facility and site.

The information provided to determine the impact of the reference SC/ICM system on the environment is as follows:

Table 6.3.1, Essential Materials

Table 6.3.2, Utilities and Services

Table 6.3.3, Secondary Radioactives Wastes

Table 6.3.4, Facility Emissions.

The information above is for the normal operation of the facility using the acid waste flowsheet (Table 5.2.8). The facility is assumed to operate 300 d/yr. Refer to Section 6.1 for the effects of accidents. The acid flowsheet was used for these estimates, since it is generally the limiting case.

TABLE 6.3.1. Essential Materials

Material	Use	Annual Requirement(a)
Glass Frit	Waste Immobilization Media	4.9×10^5 kg
Canisters(b)	Containment of solidified waste during storage, shipping and disposal	562
Overpacks(c)	Containment of failed, filled packages	6
Caustic (19M)	In-cell decontamination	5 m^3
Nitric acid (12.2M)	In-cell decontamination	7 m^3
Helium	Leak check canister seal weld	570 sources
Argon (if used)	Inert blanket for canisters for In-Can Melter	$1 \times 10^5 \text{ m}^3$
Ammonia	Reactant in NO_x Destructor	1.5×10^5 kg
Silver Zeolite	Iodine adsorber	Negligible(d)
Complexants Oxalic Acid Na Tartrate	In-Cell Decontamination	(e)
Detergent	In-Cell Decontamination	(e)

(a) Based on flowsheet values for acid waste flowsheet for 300 days of operation at flowsheet capacity.

(b) Based on canister dimensions (Nominal): 10 ft x 18 in. ϕ , 3/8-in.-thick walls (internal height = 10 ft, internal area: 1.62 ft^2 , fill height = 80%, fill volume = 13.2 ft^3) plus 5% canisters for defective canisters and off-standard flowsheet conditions which add canisters.

(c) Assume 1% canisters need to be overpacked.

(d) Should be changed infrequently (about 1 to 2 years) and has small bed volume (about 8 ft^3).

(e) Optional.

TABLE 6.3.2. Utilities and Services

<u>Utility/Service</u>	<u>Source</u>	<u>Use Rate(a)</u>	<u>Annual Requirement</u>
Electricity	-Calciner, Melter Lights, Instruments, Equipment	500 kW	4×10^6 kW-h
Water	-Cooling Melter	600 L/min	3×10^8 L
	-Off-Gas (Including Condensate Recycle Tank)	260 L/min	1.5×10^8 L
	-Decontamination and Miscellaneous	Periodic	1×10^4 L
Steam	-Heating - Ventilation air, VOG and Process	6000 kg/d average	2×10^6 kg
Ventilation Air @ Ambient Temperature	-Cell Ventilation	1100 m ³ /min	6×10^8 m ³
Pressurized air (3 atm)	-Instruments and Feed Atomization	0.4 m ³ /min	2×10^5 m ³

(a) For full operation.

(b) Assume 10°F ΔT for cooling water.

(c) Ventilation air heated on the year-around average from 50°F to 75°F.

NOTE: Emergency Services: All services indicated above are required for emergencies.

TABLE 6.3.3. Secondary Radioactive Wastes

<u>Description</u>	<u>Volume, m³/yr</u>	<u>Radioactivity Ci/yr, MFP(a)</u>
Combustible and compactible waste	100	500
Failed equipment and noncompactible waste	100	5×10^4
Liquid Wastes Sumps	2000	1.5×10^6
Flush and Decontamination Cell and Equipment Exterior		
Process - Calcliner Condensate		

(a) MFP = Mixed Fission Products

TABLE 6.3.4. Facility Emissions

<u>Emission Description</u>	<u>Release Rate</u>	<u>Annual Quantity (a)</u>	<u>Annual Radioactivity to Atmosphere (a)</u>
Gaseous			
Ventilation Air Cell at 20°C ^(c)	1100 m ³ /min	6 x 10 ⁸ m ³	3.7 x 10 ⁻⁷ Ci MFP ^(b)
Vessel ^(d) Off Gas @30°C	30 L/min	1.6 x 10 ⁷ m ³	<1 x 10 ⁻¹¹ MFP
Calcliner ^{(e)(f)} Off Gas @20°C	2.4 m ³ /min	1.0 x 10 ⁶ m ³	1.8 x 10 ⁻¹¹ Ci MFP <4.4 x 10 ⁻³ Ci Ru Volatile <<2.7 x 10 ⁻⁴ Ci I (all passes through)
Chemical Emissions^{(e)(f)}			
Organics	0	0	--
NO _x	<0.5 kg/h	<3.6 x 10 ³ kg	
N ₂	96 kg/h	6.9 x 10 ⁵ kg	
NH ₃	<0.2 kg/h	<1.5 x 10 ³ kg	
O ₂	16.5 kg/h	1.2 x 10 ⁵ kg	
CO and CO ₂ ^(g)	Trace	Trace	
H ₂	Trace	Trace	
H ₂ O	36.8 kg/h	2.7 x 10 ⁵ kg	
Particulates in Gases ^(f)	2.8x10 ⁻¹⁴ kg/h	2.0 x 10 ⁻¹⁰ kg	
Cooling Water	0 ^(h)	0 ^(h)	0
Heat (from vitrification cell)	680 kW	6 x 10 ⁶ kW-h	0

(a) Assumes normal process operation for 300 d/yr at flowsheet rates (cell and vessel ventilation operates continuously). Quantities could be up to 30% greater due to startup, shutdown, non-normal operations, and deviation from assumptions.

(b) Assume average annual calcine release rate to cell which reaches cell filters: (2.1 kg to floor) (DF 10 to cell filters)(5 x 10⁴ DF cell filters)(5 x 10⁴ DF bldg. filters) = 8.5 x 10⁻⁸ gm (4.4 Ci/gm) = 3.7 x 10⁻⁷ Ci.

(c) Vitrification cell (Volume: 20,000 ft³) at 12 air changes/h.

(d) Calcliner.

(e) See flowsheet: Table 5.2.8 for high-level acid waste, maximum quantities (for neutralized flowsheet emissions can be calculated from Table 5.2.4).

(f) From calcliner off-gas system.

(g) From any organic solvent in HLLW. Emissions are zero for complete separation of solvent from liquid waste.

(h) Cooling systems assumed to be closed loop.

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7.0

PROCESS CONTROL REQUIREMENTS

7.0 PROCESS CONTROL REQUIREMENTS

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7.0 PROCESS CONTROL REQUIREMENTS

The process control requirements provide on-line process quality guidelines needed to generate a satisfactory product. The requirements indicated here are generic and may state guiding principles. This generic approach is necessary, since specific operating guidelines will depend on the particular feed composition and process design. Also, this section discusses tests that may be performed to assure product and canister conformance to potentially applicable criteria. Potential courses of action, should the canister and/or product not comply to the criteria, are also considered.

7.1 SPRAY CALCINER FEED SYSTEM PROCESS REQUIREMENTS

F. A. Miller

Processing parameters for the feed system are given in Table 7.1.1. A discussion of these parameters follows.

The feed system should provide a controlled flow of waste (at the proper pressure and of uniform composition) to the spray calciner. The waste feed flow rate should be maintained within 3% to 5% of the flow set point to provide the desired processing rate and frit-to-calcine ratio. The proper waste-feed pressure will depend on the size and type of nozzle. For the reference system with an internal-mix nozzle air-cap orifice of 0.312 in., 20 to 25 psig feed pressure is needed at the nozzle for the required flow rate and atomization.

To prevent solids accumulation in the bottom of the feed tanks and to provide a uniform glass composition, sufficient tank agitation should be

TABLE 7.1.1. Spray Calciner Feed System Process Parameters

<u>Variable</u>	<u>Requirement</u>	<u>Discussion</u>
Feed Flow Control	Maintain waste feed flow rate within 3% to 5% of set point.	Provides desired glass composition and processing rate.
Feed Pressure	Provide necessary feed pressure to atomizing nozzle to allow proper atomization: 20 to 25 psig for an internal mix nozzle with a 0.312-in. air-cap orifice.	Required feed pressure varies with type and size of nozzle. Refer to nozzle manufacturer's specifications for required feed pressure.
Feed Composition Uniformity	Less than 5% variation in any feed component from the top to the bottom of the tank.	Provides uniform glass composition. Prevents solids from settling and possible feed line pluggage.
Feed Temperature	Less than 50°C.	Required to prevent drying in calciner nozzle or feed line, which can result in a plug.

available to maintain less than a 5% variation in any feed component from the top to the bottom of a tank. The waste temperature should be maintained at less than 50°C to prevent excessive vaporization of the feed as it approaches the hot nozzle, which can result in a plug in the feed line or nozzle.

7.2 SPRAY CALCINER PROCESS REQUIREMENTS

F. A. Miller

Processing parameters for the spray calciner are given in Table 7.2.1. A discussion of these parameters follows.

TABLE 7.2.1. Spray Calcination Process Operating Parameters

<u>Variable</u>	<u>Requirement</u>	<u>Discussion</u>
<u>ATOMIZING NOZZLE</u>		
Atomizing air-to-waste feed mass flow ratio.	Greater than 0.2 air-to-feed flow ratio for an internal-mix nozzle air-cap orifice of 0.312 in.	Required flow ratio will vary with different types and sizes of nozzles. Droplets with mean volume diameters of 70 to 100 μm or less are desired.
Spray Pattern	Maximum diameter of the spray pattern must be less than the diameter of the spray chamber.	Required to prevent direct impingement of the spray onto the spray chamber wall that may result in caking.
<u>CALCINER</u>		
Wall Temperature	Greater than 25°C below calcine sintering temperature	Prevents calcine from adhering to the chamber wall.
Off-Gas Temperature	Feed rate and wall temperature selected must produce an off-gas temperature of greater than 200°C ^(a) for a reference-sized spray calciner (36-in.-dia x 10.5-ft-high spray chamber).	Temperature required to ensure calcine is sufficiently dry to produce free-flowing calcine. Required temperature may vary with size of chamber
<u>VIBRATOR</u>		
Frequency of Operation	Sufficient to prevent scale on the spray chamber wall that may reduce heat transfer. For low-sodium feeds, usually 1 to 3 two-s pulses/vibrator/h are used.	Frequency must be determined for different feed types.

TABLE 7.2.1. (contd)

Variable	Requirement	Discussion
<u>SINTERED-METAL FILTERS</u>		
Blowback Frequency	Sufficient to maintain filter pressure drop less than 15 to 20 in. H ₂ O for unequal-interval blowback pattern and 8 to 12 in. H ₂ O for equal-interval blowback pattern.	See text for discussion.
Blowback Pulse Duration	0.25-s pulse of ambient temperature air.	Experience has shown that 0.25-s pulses of compressed air appear to be as effective as longer pulses for cleaning filters.
Blowback Air Pressure	Greater than 40 psig.	Air pressures of 40 to 100 psig have been successfully used.

- (a) Other considerations, such as volatile species condensing on the filters may require higher off-gas temperatures. The effects of volatile species require further study.

7.2.1 ATOMIZING NOZZLE

The degree of waste feed atomization for a given nozzle depends on the air-to-feed mass-flow ratio. The required mass ratio has been determined, by operating experience, to be greater than 0.2 for an internal-mix nozzle with a 0.312-in. air-cap orifice. This required ratio will vary with type and size of the nozzle. A general rule is to refer to the nozzle manufacturer's specifications for the required flow conditions that will produce spray-droplet mean volume diameters of 70 to 100 μm when spraying water at room temperature.

The diameter of the nozzle spray pattern must not cause direct spray impingement onto the spray chamber wall. The direct impingement could cause buildup of wet calcine on the SC chamber walls. The spray chamber diameter

must be larger than the diameter of the turbulent region of the spray pattern specified by the nozzle manufacturer. At PNL, nozzles that produce a spray pattern of 13 to 15 in. in dia when spraying water at room temperature have been successfully used in a 36-in.-dia spray chamber. An optimum spray-pattern diameter, if one exists, has not been determined.

7.2.2 CALCINER FURNACE

Control of the spray chamber wall temperature by the furnace is needed to assure that the calcine feed slurry is converted to a powder that will freely flow into the melter. The powder must not build up on the calciner walls or cone section, which are sloped 90° and 60° , respectively, from the horizon. The extent of feed-component conversion to oxides (or calcination) is of secondary importance, since oxidation is completed in the melter.

To obtain a calcine that will readily flow into the melter, two conditions must be met: 1) the calcine must be maintained below its sintering temperature (the temperature at which the particles begin to stick or melt together), and 2) the calcine particles must be sufficiently dry. The processing guideline used at PNL is to maintain the spray chamber wall temperature at least 25°C below the experimentally determined calcine sintering temperature. This prevents the calcine from sticking to the hot wall and consolidating. Feed compositions with sintering temperatures from 450°C to over 900°C have been successfully processed by maintaining the wall temperature at least 25°C below the sintering temperature. Special techniques have been developed at PNL by which a frit component such as powdered silica is added to the feed to increase the effective sintering temperature of high-sodium feeds. This method has been used to increase the calciner operating temperature and processing rates for high-sodium feeds.

Experience has shown that the calcine moisture content should be below about 4% to assure that the calcine flows freely through the calciner cone section. Operating experience has demonstrated that an off-gas temperature (measured at the sintered-metal filters) of greater than 200°C will produce a dry calcine of less than 4% moisture for the PNL full-scale calciner. The

off-gas temperature is affected by both the spray chamber wall temperature and the feed rate of the waste. An increase in the wall temperature will increase the off-gas temperature, whereas an increase in feed rate will decrease the off-gas temperature. Wall temperatures ranging from 400⁰ to 800⁰C and feed rates of up to 400 L/h have been successfully demonstrated. The only processing requirement is that the feed rate and spray chamber wall temperature selected produce an off-gas temperature of greater than 200⁰C while still not causing the calcine to sinter.

7.2.3 VIBRATOR

The calciner is equipped with two vibrators (Model 1300AC, Cleveland Vibratory Company) or the equivalent mounted 180⁰ apart (140⁰ for conceptual design) at mid-height of the spray chamber. Wall vibration in the SC chamber prevents calcine buildup on the walls by shaking off loose calcine. If the spray calciner is operated within the control parameters discussed, extended operation can be achieved without vibration. While the longest period of operation without vibration has not been determined, up to 2-1/2 h of operation without vibration have been successfully completed. Normally, to maximize heat transfer by assuring minimal calcine buildup on the walls, each vibrator is operated 1 to 3 times/h with 2-s pulses at equally spaced intervals. The frequency of vibration required to maximize heat transfer must be determined for different waste compositions.

In the event that operating problems such as calcine sintering or poor atomization cause a scale that is not easily removed by vibration only, a thermal-shock technique can be used. This method requires that the chamber wall (and the scale) be heated up to the normal maximum operating temperature and then water-sprayed into the hot chamber through the atomizing nozzle for 2 to 5 min. Even the most stubborn scale has been removed using this method.

7.2.4 SINTERED-METAL FILTERS

Filter efficiency improves as a layer of calcine forms on the filters. This calcine layer acts as the filter media and prevents very small particles

from penetrating the sintered-metal pores, which can result in gradual plugging of the filters. Therefore, fewer filter blowbacks will increase the operating life of the filters by minimizing the time the filter surface is exposed to moving particles and calcine fines that may become lodged in the filter inner structure.

Two basic types of blowback patterns have been used--equal-interval and unequal-interval patterns. The filters are divided into several groups, with the filters in each group being blown back simultaneously from the same air supply line. For the unequal filter blowback patterns all filter groups are blown back within a few seconds, then a longer interval passes before the next set of blowbacks. The equal-interval blowback pattern sequentially blows back filter groups with equal time intervals (e.g., 1-min intervals) between blowbacks.

It is desirable to minimize the calciner pressure surges caused by pulses of blowback air. Variables that affect the magnitude of these surges are blowback pulse duration, blowback pressure, off-gas line flow resistance and the fraction of filters pulse, simultaneously. Experience has shown that short, 1/4-s pulses of ambient-temperature air are as effective as longer pulses for cleaning the filters. Static blowback pressures of 40 to 100 psig have been successfully used. One-fifth of the filters are blown back without pressurizing a small-scale calciner (to 70 L/h), while 1/11 of the filters in a large-scale calciner (300 to 400 L/h) are blown back simultaneously.

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7.3 IN-CAN MELTING PROCESS REQUIREMENTS

L. L. Petkus

In-can melter operating requirements are presented in Table 7.3.1. Further explanation of the requirements are provided below.

TABLE 7.3.1. In-Can Melting Process Parameters

<u>Variable</u>	<u>Requirement</u>	<u>Discussion</u>
Canister wall temperature	Maximum temperature must be below canister material-strength limits. Maximum operating temperature for 304L SS is 1075°C.	Safety factors for canister design (Simonen and Slate 1979)
	Minimum temperature must be high enough to solubilize all components and crystalline states. 1050-1075°C is normal operating range for most compositions.	Complete melting and mixing must take place for product quality.
Frit-to-calcine ratio	Ratio must be maintained within limits set by specific product-quality study. Normal frit-to-calcine weight ratio is about 3:1.	Product characteristics are sensitive to composition. A range of acceptable operation for most compositions is 20% to 80% by weight of calcine.
Feed rate	Feed rate should match the melting rate to minimize unmelted inventory in the canister and to maximize overall production. Glass has been successfully processed @ 75 kg/h.	Excess unmelted batch reduces melting rate.
Outgassing time	Normally, 2 h is used to allow sufficient outgassing	Empirical determination of product characteristics is necessary to allow sufficient time for product fining (i.e., clearing the glass of bubbles and unmelted solids).

TABLE 7.3.1. (contd)

Variable	Requirement	Discussion
Spray calciner to in-can melter differential pressure	Minimum differential must be maintained. 0-1 of H ₂ O normally maintained.	ICM must be at negative pressure to the cell.
Cooling rate	After glass formation in canister zone, the filled portion must be cooled at an adequate rate to maintain glass and canister quality. A filled canister cooling rate of 50-100°C is normally used.	Filled canister of glass must be cooled at a sufficient rate to avoid glass devitrification and stainless steel sensitization, and to minimize glass cracking and phase separation.

7.3.1 CANISTER WALL TEMPERATURE

The canister wall temperature is usually very close to the furnace temperature. The furnace set-point is therefore the control parameter. Because of the high temperatures in the ICM furnace and economic considerations, the canister is normally designed for use at maximum temperature of only 25° to 50°C above the furnace operating temperature. For example, a 304L SS canister is designed to withstand 1100°C and is operated at 1050° to 1075°C. The furnace is set at a maximum of 1075°C in all zones.

The minimum melting temperature must allow for incorporation of all feed components into the glass. It is usually best to have the operating temperature as high as possible to produce a homogeneous glass product. In a 304L SS canister, the range at 1050° to 1075°C is maintained to assure good melting. Low temperatures may cause non-homogenities and undissolved or unvitriified products. The minimum operating temperature for waste compositions must be experimentally determined.

7.3.2 FRIT-TO-CALCINE RATIO

Product development defines the proper frit-to-calcine ratio for a particular calcine. For most waste compositions a frit-to-calcine weight ratio of about 75:25 is used. The allowable variability in the ratio also needs to be established in product development studies. Local excesses of calcine can

result in an inferior glass product. If a layer of pure calcine greater than 2 cm deep forms in a canister, data indicates that unvittrified inclusions may result. The critical calcine depth for any particular frit may be different, depending on the solubility of the calcine and the viscosity of the melt. In tests, layers up to 4 cm thick were placed in a canister. After cooling, the canister was cut open and undissolved lumps of calcine about 2 cm in dia were found--mostly near the bottom of the canister.

7.3.3 FEED RATE

Addition of frit and calcine to the top at the melt should be controlled so that there is a minimum build-up of powder on top of the melt. This powder tends to insulate itself from the radiant heat from the canister walls. A minimum powder build-up helps maximize melting rate. In practice, a layer of 3 to 6 in. of powder usually covers the melt. To avoid continuous adjustment of the feed rate, an initial glass production rate is selected that will allow the canister to be filled to within one foot of the canister top without forming an excessive batch cover that would reduce heat transfer. A 24-in.-dia canister was filled at 75 kg/h using a defense glass composition with no large powder accumulation.

7.3.4 OUT-GASSING TIME

Once the canister is filled, usually to within one foot of the top, the feed is turned off or switched to the next canister. After filling, the batch must be allowed to finish melting and venting of all gases produced in the melt. Usually a period of 2 h is used to clear the glass of unmelted materials and bubbles. Adequate out-gassing will decrease the chances of having a sealed canister pressurize. However, out-gassing will also allow an increased amount of volatile species in the melt to volatilize from the glass and condense on cooler surfaces; thus, excess out-gassing time should be avoided.

7.3.5 SPRAY CALCINER/IN-CAN MELTER DIFFERENTIAL PRESSURE

A differential pressure of 0 to 1 in. H₂O between the ICM and the SC should be maintained to allow for control of melter off-gas pressure surges caused by sudden additions of calcine, such as during a filter blowback. Off gas on the two units is pulled from the melter into the spray calciner. The differential pressure is also used to detect plugging in the connecting section. The vacuum held on the melter is kept low to prevent significant air in-leakage.

7.3.6 COOLING RATE

Filled canisters must be cooled at a rate that minimizes phenomena that could compromise glass and canister integrity. Between the glass temperature of about 950°C and 500°C the glass should be cooled rapidly to avoid excessive devitrification (crystallization). However, the canister should not be cooled so quickly that significant glass-cracking results from created thermal stresses.

Cooling the glass as soon as possible after formation also inhibits any crystals, metals, or chemical nonhomogeneities in the glass from settling or accumulating. In the temperature range of 500°C to 750°C, 304L stainless steel tends to become sensitized and thus vulnerable to stress-corrosion cracking. Thus, the time the canister temperature is held in the 500°C to 750°C range should be kept to a minimum. The cooling of filled canisters through these sensitive temperature ranges at a rate of 50°C/h to 100°C/h has been found to be an appropriate compromise among all considerations (see "Cooldown," Section 4.5.3.2).

7.4 PRODUCT QUALITY VERIFICATION

H. T. Blair and S. C. Slate

Requirements have not been established by NRC or any other authoritative body on quality verification requirements. However, methods have been developed at PNL for product quality verification, and are discussed in Sections 4.3.15 and 4.5.3.5.

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7.16

7.5 REMEDIAL PRODUCT-QUALITY ACTIONS

D. E. Larson

In the course of plant SC/ICM operations, it is probable that some filled HLLW canisters will be produced that do not meet disposal repository, transportation, storage, and/or other requirements. Consideration must then be given as to the disposition of the unacceptable filled canisters. To date, this area has not been investigated in depth at PNL or by other concerned organizations. Actions required to handle filled canisters that do not meet specifications will eventually be determined by NRC regulations, potentially affecting facility handling requirements and disposal facility waste acceptance criteria. Since these regulations requirements, and criteria are not available, the subsequent discussion will only treat potential courses of action.

The waste product glass and/or the associated canister may not conform to applicable standards. The nonconformance could be caused by canister manufacturing defects, canister handling, and/or off-standard process conditions. Future criteria formulation must consider correction of off-standard conditions. If nonconformance conditions are detected, the following courses of action are available:

- no remedial action (follow normal life-cycle)
- overpack canister
- repair (correct canister defect, recycle glass).

For some filled-canister defects or for some major defects that occur rarely, the waste management system may be able to safely accommodate the nonconformity, and thus the associated canister can be disposed of in a normal manner.

Another alternative for handling out-of-specification filled canisters is to overpack them. The principle is that the additional container will compensate for or provide the barrier properties that were otherwise lost. The acceptability of this approach depends on the ability of the overpack to compensate for the properties lost by the defective canister. If the canister

itself is defective, the overpack approach is probably adequate, since the overpack technology is the same as or a reasonable extension of canister technology. But if the glass product is defective and the affected glass property is instrumental to acceptable package performance, such as glass durability, then the overpack approach may not be adequate. As indicated, the status of overpack technology is similar to and adapted from canister technology, and is discussed further by Simonen and Slate (1979). If this approach is deemed by regulations to be adequate, the waste management system must be designed both to overpack canisters and to handle the associated increase in package dimensions, the increase in weight, the reduction in package heat-transfer ability, and the overpacked packages.

If the canister itself does not meet specifications, it may be possible to repair the canister. For instance, if the lid-closure weld or the lid is defective it is within established technology to repair the weld by welding over the existing weld or by removing the defective weld (and removing and replacing the lid, if necessary) and making a new weld. Adapting this weld-repair technology to remote application should not be a significant problem. If the integrity of the balance of the canister does not meet required standards (either through physical damage or degradation of materials properties, such as by corrosion, loss of physical properties by overheating or overstressing, or allowing a nonconformance canister to be used) it may not be practical to repair the canister, given the level of capability envisioned for use in waste canister processing, handling, storage, transportation, and/or storage facilities.

If the canister needs to be replaced or if the glass needs to be reprocessed, it of course becomes necessary to remove the glass from the canister. A number of systems can conceivably be developed for glass removal from a canister. However, no systems have been studied in detail, nor has the technology been developed or demonstrated. After the glass has been removed from the canister, the canister will probably not be fit for re-use and will have to be discarded as failed hardware. The canister for disposal will be heavily contaminated with glass residue and may be in one piece, many pieces, or a molten mass. Depending on what conceptual scheme is used for glass removal,

the glass may be molten or in any size range of pieces. A system will have to be developed to handle the removal of glass for recycle or repackaging. It is expected that a significant development and demonstration effort will be needed to provide this option.

7.6 REFERENCES

Simonen, F. A., and S. C. Slate. 1979. Stress Analysis of High-Level Waste Canisters-Methods, Applications and Design Data. PNL-3036, Pacific Northwest Laboratory, Richland, Washington.

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