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Nuclear Waste Treatment Program Annual Report for FY 1985

H. C. Burkholder and J. H. Jarrett, Compilers

April 1986

**Prepared for the U.S. Department of Energy
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**Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
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NUCLEAR WASTE TREATMENT PROGRAM
ANNUAL REPORT FOR FY 1985

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EXECUTIVE SUMMARY

Two of the U.S. Department of Energy's (DOE) nuclear waste management-related goals are: 1) to ensure that waste management is not an obstacle to the further deployment of light-water reactors (LWR) and the closure of the nuclear fuel cycle and 2) to fulfill its institutional responsibility for providing safe storage and disposal of existing and future nuclear wastes. As part of its approach to achieving these goals, the Office of Terminal Waste Disposal and Remedial Action of DOE established what is now called the Nuclear Waste Treatment Program (NWTP) at the Pacific Northwest Laboratory (PNL) during the second half of FY 1982. To support DOE's attainment of its goals, the NWTP is to provide 1) documented technology necessary for the design and operation of nuclear waste treatment facilities by commercial enterprises as part of a licensed waste management system and 2) problem-specific treatment approaches, waste form and treatment process adaptations, equipment designs, and troubleshooting assistance, as required, to treat existing wastes. This annual report describes progress during FY 1985 toward meeting these two objectives. The detailed presentation is organized according to the task structure of the program, but this Executive Summary is organized by program element.

FIRST-GENERATION HIGH-LEVEL WASTE TREATMENT

The liquid-fed ceramic melter (LFCM) process is the leading candidate process for treating both current and future high-level liquid wastes in the United States. A revised draft of the LFCM vitrification technology testing and documentation plan was prepared. As indicated in the plan, the major output will be LFCM design and operations manuals, along with supporting data and reports. A draft outline of the LFCM design manual was prepared. Numerous papers and reports on various aspects of LFCM design, operation and product qualification were generated. Specific subjects covered include:

- technology of off-gas treatment for LFCMs
- physical and numerical modeling of joule-heated melters
- instrumentation for remote monitoring and control of LFCMs

- remote design features for a radioactive LFCM
- investigation of potential analytical methods for redox control in the vitrification process
- long-term testing of slurry metering pumps.

The first year of a 5-year nonradioactive and radioactive LFCM testing program was completed with the newly installed pilot-scale radioactive liquid-fed ceramic melter (RLFCM) system and various operational nonradioactive LFCM systems.

SECOND-GENERATION HIGH-LEVEL WASTE TREATMENT TECHNOLOGY

Second-generation waste forms and related process technology need to be developed for fresh LWR and LMFBR (liquid metal-cooled fast breeder reactor) reprocessing wastes generated after the year 2000. Effort was initiated this year, based on past work evaluating various high-level waste forms and processes. Specific activities included establishing an external technical review group, evaluating the performance of lead-iron-phosphate glass after manufacture under typical processing conditions, and initiating performance testing of Synroc C samples provided by the Australian Atomic Energy Commission. An evaluation was completed on the effects of high-temperature glass processing conditions on current-generation ceramic melters.

SPENT-FUEL TREATMENT

Work in this area was placed on hold pending a resolution of the need to develop treatment technology. The approach envisioned to develop treatment technology was documented, should it be needed.

TRANSURANIC WASTE TREATMENT

The objective of NWT program work on transuranic (TRU) wastes is to modify defense-developed contact-handled shredding, incineration, cementation and metal-melting technologies for remote-handled commercial wastes as part of defining and documenting optimum treatment strategies for commercial TRU wastes.

This will bring TRU waste treatment technology to the same level of development as LFCM vitrification technology. Specific accomplishments in 1985 are:

- Conceptual design completion for pilot-scale, remote vacuum coreless induction melting system. Applications include consolidation of remote-handled metallic TRU wastes and other remote-handled wastes (for example, spent-fuel consolidation wastes).
- Open literature reports on "Consolidation of Simulated Nuclear Metallic Waste by Vacuum Coreless Induction Melting," "Preliminary Analysis of Treatment Strategies for TRU Wastes from Reprocessing Plants," and "Shredder and Incinerator Technology for Treatment of TRU Wastes."
- Completion of draft requirements for TRU waste-form production, and draft plan for testing and documentation of TRU waste treatment technology development.

TECHNOLOGY SUPPORT

In addition to preparation of this series of annual reports, LFCM vitrification technology progress is reported quarterly (starting with the first quarter of fiscal year 1985). Also several draft reports, technical program plans, and program plans were prepared on nuclear byproducts technology.

Work on a mobile encapsulation and volume reduction system for wet low-level wastes was completed, was reviewed by industry, and was reported in the open literature.

WEST VALLEY SUPPORT

The final major vitrification system component, the canister turntable, was fabricated, tested, and sent to West Valley for installation and overall system testing. It is expected that the system will ultimately be used to vitrify high-level wastes (HLW) at West Valley.

A West Valley HLW glass composition was recommended that incorporates IE-96 inorganic ion exchanger in the melter feed. The composition was evaluated in engineering- and pilot-scale nonradioactive melter systems and as a

result has been selected as the reference West Valley HLW form composition. Work on glass composition development was published.

Removal of cesium from the West Valley HLW supernatant should allow disposal of the remaining solution as low-level waste. A reference cesium removal process was developed using an inorganic ion exchanger. Two ion exchangers were evaluated. In addition, an air displacement slurry (ADS) pump was developed to feed a mixture of glass-formers and HLW to the melter. The ADS pump has been selected by West Valley for their reference feed system. Twenty-three internal technical reports were submitted as part of the West Valley Support activity.

HANFORD WASTE VITRIFICATION PROJECT SUPPORT

The Hanford Waste Vittrification Project (HWVP) has contributed funds toward the shakedown and startup testing of the B-Cell RLFCM and repair of failed facility equipment. The information and capability resulting from these activities should be useful in future activities specific to HWVP.

FRG ASSE MINE TEST SUPPORT

In preparing for the 1986 and 1987 fabrication of 30 heat and radiation sources (canisters of radioactive borosilicate glass) for FRG nuclear waste repository experiments at Asse, several activities were completed. Included are:

- nonradioactive vitrification run with German feed composition and subsequent product evaluation
- clean-out and preparation of A-Cell and equipment design for canister decontamination and storage
- receipt of 5 MCi ^{90}Sr solution and 3 MCi ^{137}Cs solution and preparation of an additional 4 MCi of ^{137}Cs for shipment to PNL.

JAPAN TOKAI PLANT SUPPORT

General technology support has been provided by Japan-PNC as part of a technology exchange agreement. A PNC staff member has been in residence in

1985, working with PNL staff on the NWT program. A specific technology area of interest to PNC has been identified, and a preproposal for testing with simulated Tokai HLW has been prepared and discussed with PNC.

LOW-LEVEL WASTE COORDINATION

Starting in late 1985, PNL work on low-level and airborne radioactive wastes has been managed and reported as part of the NWT program. In 1985 four composite sorbent barriers for cesium, cobalt, and strontium in low-level waste (LLW) disposal sites were identified, and testing of engineered barrier effectiveness was started. A long-term field evaluation (using lysimeters) of different LLW forms is in progress. The test evaluates performance of waste forms in a shallow-land burial, arid climate environment. A guideline for selecting codes for ground-water transport modeling of LLW burial sites was published, and basic information needed to develop a performance assessment modeling program was prepared. Samples of copper-yttrium krypton waste forms were prepared and are being evaluated for krypton containment.

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1.0 TECHNOLOGY SUPPORT

1.1 OBJECTIVE

The objective of the Technology Support Task is to conduct special studies, usually short-term, that respond to specific commercial nuclear waste treatment needs.

1.2 SUMMARY - MOBILE ENCAPSULATION AND VOLUME REDUCTION SYSTEM -

J. L. Buelte and J. G. Carter

A study on a transportable vitrification process for low-level waste (LLW) was completed. Design criteria and the preconceptual design of the system were prepared, disposal costs were estimated, and utility interests in the transportable volume reduction service were assessed. In the preconceptual design, a joule-heated glass melter is used to convert the wet LLW into glass. The Mobile Encapsulation and Volume Reduction System (MEVS) can process 12,700 ft³/year of resins or 38,100 ft³/year of concentrated liquids from a minimum of three reactors. The capital cost for the MEVS is estimated to be \$4,700,000; the annual operating costs of the system based on servicing three reactors is \$1,500,000 for resins or \$2,300,000 for concentrated liquids. Total costs for transportation and burial are \$190 to \$220/ft³ of waste.

1.3 PRECONCEPTUAL DESIGN

The MEVS is a conceptual liquid-fed glass melting system with enough peripheral equipment to be self-sufficient in various environments (for example, during transportation, operation, or maintenance). It is based on an adaptation of previous high-level nuclear waste vitrification technology (Bjorklund and Brouns 1982).

The MEVS is specifically adapted for slurries of filter sludges, evaporator bottoms, and ion-exchange resins. Both noncombustible and combustible slurries can be handled without pre-evaporation or other pretreatment. The conceptual MEVS consists of a joule-heated glass melter, its associated feed system, an off-gas treatment system, and a product-handling and transfer station. The system is located in mobile trailers that can be transported to

nuclear reactor sites to process wet LLW generated and stored at the sites. The end product incorporates the noncombustible portions and the inherent radionuclides into glass, a stable, monolithic inert solid. The glass is poured into drums to minimize onsite storage requirements and reduce transportation and burial costs.

The joule-heated glass melter has been adapted to process both noncombustible and combustible slurries. Special feeding techniques help incorporate the radionuclides directly into the glass, minimizing particulate carryover and volatilization into the gaseous effluent stream. Radionuclides that are volatilized are scrubbed from the gaseous effluent via an off-gas treatment system. The scrub solution is decontaminated and recycled to the plant through an ion-exchange column in the MEVS. After being fully loaded, the ion-exchange resins in the column are recycled to the melter, thereby eliminating generation of a secondary waste stream.

The process can be categorized into six groups: the feed system, the melter system, the product-handling area, the off-gas treatment system, the control area, and the electrical and cooling support equipment. All components of the process are located in three transportable semitrailers (the process trailer, the support trailer, and the control trailer). The trailers have undercarriage assemblies so they can be transported by rail if desired. The MEVS is entirely self-contained and requires no facility-type services from the reactor for operation.

1.3.1 Process Trailer

Radioactive processing equipment is contained within the process trailer (Figure 1.1). This standard highway semitrailer measures 14.6 m long by 2.6 m wide by 4.1 m high (8 by 8.5 by 13.5 ft). Its maximum weight, including all process equipment, the trailer, and the towing vehicle, does not exceed 39,000 kg (86,000 lb).

All radioactive processing equipment is double-contained. The first level of containment is the radioactive processing equipment and piping; the second level is a module that completely envelops the radioactive processing equipment. The containment module and the trailer are designed with removable

FIGURE 1.1. Process Trailer for the Mobile Encapsulation and Volume Reduction System

panels at selected locations to allow contact maintenance of the radioactive processing equipment. The processing equipment includes:

- recirculating slurry pump that pumps wet waste from the plant to the melter feed tank
- 110-L (40 gal) feed tank with air sparger, in which glass-formers are added to the wet waste
- air displacement feed pump that meters slurry to the melter
- melter
- single-pass heat exchanger and pump for the melter cooling water
- turntable that provides a sealed drum filling and changeout station for glass-pouring operations
- receiving canister station that places filled drums into an overpack for storage and/or transport
- venturi scrubber to provide the first stage of cooling and cleanup of gaseous effluents

- two tandem nozzle scrubber units, one with a 12-in. inlet and the other with a 6-in. inlet
- two mist eliminators, one for each scrubber system, to remove water droplets from the gaseous effluents
- two single-pass heat exchangers to remove heat from the scrub solution
- scrub recirculation tank
- two scrub recirculation pumps
- resin column for discharge of the scrub solution back to the reactor plant
- condenser to remove additional heat from the gaseous effluents
- mist eliminator after the condenser to remove droplets generated in the condenser
- heater to heat the air before it enters the filtration system
- two redundant high-efficiency particulate air (HEPA) filter and iodine-absorber systems to provide primary and secondary filtration and iodine removal before gases are exhausted to the reactor.

The containment module is vented through a blower and HEPA filter system with the same capacity as that of the process effluent system. Therefore, the containment module ventilation system acts as a full-capacity backup to the main process effluent system.

A glass-former feed system, mounted atop the process trailer, is removed before transport. Although the process trailer does not include the induced draft blowers for the containment module and process effluent stream, the gases leaving the process trailer are fully decontaminated, thereby meeting the criteria of keeping all radioactive processing equipment in one trailer.

Lead shielding, 5 cm thick, is installed around the melter, product-handling areas, and feed tank prior to operation. It is removed before transport to maintain the weight limitations of 39,000 kg. At the reactor site, the shielding is mounted outside the process trailer around the melter and mounted

internally between the melter and effluent treatment system. The internal shielding can be dropped into place through a baffle in the roof of the containment module. The off-gas treatment system requires no shielding. The radioactive source in the melter and feed tank is conservatively assumed to be 100 R/hr using

maximum dose rate of 100 mR/hr at 1 m from the outside of the trailer. A operation, the melter is drained, the glass product removed, and the system is decontaminated to meet the 10 mR/hr transportation criterion at 2 m from the trailer with the shielding removed.

1.3.2 Control Trailer

The control trailer (Figure 1.2) measures 13.7 m long by 2.4 m wide by a maximum height of 4.1 m (45 by 8 by 13.5 ft); it is within the legal weight in most states of 36,000 kg (80,000 lb). A control room 5.5 x 2.4 m houses the distributed process control system that controls all critical operating functions and monitors and records all operating functions of the process. The distributed control system contains inherent redundancy features such as multiple operator interface units, dual plant communication loops, and backup multifunction controllers to ensure safe operation. The control trailer also contains the induced draft blowers for the containment module ventilation and

FIGURE 1.2. Control Trailer for the Mobile Encapsulation and Volume Reduction System

process effluent stream. The two blowers are interconnected such that the two ventilation streams can be directed through either blower should the other one fail. Therefore, the blowers for the process effluent system and the containment module ventilation system are completely redundant. A chemical makeup tank, used for storage and makeup for new scrub solutions, is located between the blower system and the control room. The plasma torch power supplies, used for restarting the melter, also are located in this area.

1.3.3 Support Trailer

The support trailer (Figure 1.3) is a standard flatbed trailer that measures 14.6 m long x 2.6 m wide (48 by 8.5 ft) with a total system capacity including tractor/trailer and load of 39,000 kg (86,000 lb). It houses all peripheral support equipment, including the electrical and off-gas cooling units. The heat exchangers in the process trailer use glycol as a cooling fluid, which is recirculated from the glycol cooler unit located on the support trailer. Blowers located in the glycol cooler unit discharge the heat from the glycol loop to the atmosphere. Three diesel generators provide primary and emergency electrical power. The first is a 400-kVA single-phase diesel generator for melter power. The other two are 230-kVA generators for primary and emergency backup power to the off-gas system. The support trailer also contains the 400-kVA transformer and silicon-controlled rectifier (SCR), which provide the varying voltage and current required for operation. The off-gas

FIGURE 1.3. Support Trailer for the Mobile Encapsulation and Volume Reduction System

system generators are connected directly to an automatic transfer switch and a motor control center that provides 480-V power to the blowers and motors of the off-gas treatment system. They also provide 480-V power to a step-down 50-kVA transformer that supplies lower voltage servicing through the distribution panel. The support trailer also contains a 10-hp air compressor to actuate the pneumatic valves located throughout the process.

1.3.4 Melter

The joule-heated glass melter (Figure 1.4) is designed to reduce the volume of both noncombustible and combustible slurries and incorporate their residual radionuclides into a stable glass matrix. The wet wastes are fed to a molten glass pool that is kept at 1000 to 1100°C by introducing an electrical current between Inconel 690® electrodes at opposite ends of the melting cavity.

FIGURE 1.4. Joule-Heated Glass Melter for the Mobile Encapsulation and Volume Reduction System

®Inconel alloys are products of the International Nickel Co., Huntington Alloy Products Division, Huntington, West Virginia.

The glass is contained within the melting cavity lined by a fused-cast refractory known as Monofrax K3®. As electrical potential is applied to the electrodes, an electrical current is established through the conductive molten glass, thereby acting as a resistive heating element and introducing power to the melt.

When combustible slurries are being fed, a drop tube in the lid of the melter is lowered 10 cm into the melt. As the slurry dries and combusts in the drop tube, combustion gases are forced into contact with the molten glass, thereby allowing mass transfer of radionuclides and particulates into the glass and attaining a high retention of radionuclides in the glass. This feeding technique has been tested in an experimental-scale glass melter with a drop-tube diameter of 3.8 cm at feed rates as high as 3 kg/hr. The 86-cm drop tube diameter in the MEVS conceptual design was scaled linearly with the diameter of the experimental melter drop tube to maintain identical residence times in the glass and achieve high retention values. The MEVS melter can process 70 kg/hr of resin slurries (which corresponds to the criteria given). Air cooling is provided at the bottom of the MEVS drop tube to maintain a viscous, relatively nonconductive layer between the drop tube and the molten glass and minimize the electrical shorting potential through the drop tube.

When noncombustible slurries are fed, the drop tube must be raised above the glass melt to allow formation of a cold cap. The drop tube is extracted 10 cm above the glass level via the air cylinder located on the lid of the melter. The overflow's air lift can reduce the glass level to attain additional separation between the bottom of the drop tube and the glass if necessary. The noncombustible slurry is mixed with glass frit in the mixing tank before being introduced to the surface of the glass melt. The heat from the glass pool evaporates the moisture and establishes a cold cap in which the glass formulation reactions take place. The nonvolatile waste constituents flux with the glass-formers, making a borosilicate glass composition.

The process is not amenable to waste solutions with significant concentrations of sulfates. Sulfate solubility in glass is limited to 0.5 to 1.0 wt%.

®Monofrax K3 is a registered trademark of the Carborundum Co.

Na_2SO_4 regeneration solutions could not be processed using the MEVS process. The resins could, however, be disposed of directly in the melter instead of being regenerated.

The melter cavity measures 1.37 by 1.67 by 0.41 m deep, resulting in an exposed surface area of 2.3 m^2 . The maximum concentrated liquid rate for a deep-bed condensate polishing system for a BWR results in a required rate of 210 L/hr. At maximum production rates, a minimum glass-production rate of 200 kg/hr would fill a canister of glass every 2 hr. These rates assume a 70% production factor with a 3-week shutdown period for transport and setup at each of three reactor sites. The melter was designed for a 90 L/hr-m^2 flux rate. The rates demonstrated for HLW vitrification range from 30 to 100 L/hr-m^2 ; however, HLW generally contains much more refractory components than does LLW. (LLW contains little if any iron, zeolite, and other refractory components.) Therefore, the 90 L/hr-m^2 rate will be easily achievable for LLW.

1.4 COST ESTIMATE AND SYSTEMS ANALYSIS

The preconceptual design of the MEVS provided the basis for capital and operating cost estimates of the process. The estimates were used to determine the total disposal costs, on the basis of waste volume, to allow comparison.

The estimate of capital cost was prepared by Kaiser Engineers Hanford Company (KEH). Capital costs include all labor and materials required to design, procure, fabricate, inspect, and license the MEVS process. All procurement and fabrication items are assumed to be fixed-price competitive procurements. A 26% contingency and an 8.6% escalation factor are included so that the costs represent a January 1987 completion date. Engineering and inspection services comprise 30% of the construction costs, based on past experience by PNL and KEH. These costs also include escalation and contingency factors. In comparing the estimated capital cost with those for other processes, one must carefully observe which factors are included. The combined procurement and fabrication costs for the MEVS were estimated to be \$2,700,000; accounting for escalation, contingency, engineering and inspection services, and licensing activities results in a total cost of \$4,700,000.

The annual operating cost for combustible slurries (resins and combustible filter sludges) is \$1,500,000. The annual operating cost for noncombustible slurries (concentrated liquids and noncombustible filter sludges) is \$2,300,000.

A conservative estimating approach was used for the operating cost estimate to ensure that all actual costs were considered. The process is assumed to be continuously monitored by two full-time operators in an "ABCD" shift schedule. A dedicated radiation protection technician is also assumed to be necessary 24 hr/day. The estimate allows for a day shift supervisory engineer, a transport crew, and staff for routine maintenance. A travel allowance is also assumed. In addition, a significant allowance is made for nonroutine maintenance (materials and labor) to replace processing equipment. The allowance is based on 33% of the capital investment of the melter, which requires replacement every 3 years, and 10% of the remaining capital items, which have a minimum 10-year operating life. The nonroutine maintenance factor should not be confused with capital recovery. The factor simply keeps the system in new condition. With the nonroutine maintenance factor, the entire system can be expected to be competitive with the longest term solidification systems (i.e., 30 years).

MEVS costs were compared with current practices by evaluating the entire span of waste management costs. The most common form of treatment presently used is to concentrate the wet wastes by evaporation and solidify the concentrated liquids, resins, and sludges by cementation. The cemented wastes are deposited in 55-gal drums or metal liners capable of holding 5.4 m^3 (190 ft^3). The cementation process actually increases the evaporated waste volume by a factor of 1.3, which also increases transportation and disposal costs. Total waste management costs from the evaporator through burial have been quoted by plant operators at \$155 to \$350/ ft^3 for concentrated liquids and from \$300 to \$350/ ft^3 for resin slurries. These costs are for contracted services.

Disposal costs for cementation and MEVS are compared with Table 1.1 in dollars per cubic foot of wet wastes before solidification. The MEVS operational cost is the annual operating cost divided by the annual waste processing volume. The MEVS processing cost includes also an allowance for full capital

TABLE 1.1. Comparison of Disposal Costs for Cementation and the Mobile Encapsulation and Volume Reduction System (MEVS)

	Disposal Costs, \$/ft ³ (a)		
	<u>Cementation(b)</u>	<u>MEVS</u>	
		<u>Resins</u>	<u>Concentrated Liquids</u>
<u>Processing</u>			
Operations	121	111	60
Capital Recovery and Return on Investment	(c)	68	25
<u>Transportation</u>			
Transport, Truck Rental, and Loading	20	3	14
Cask Rental	86	15	60
<u>Disposal</u>			
Burial	24	2	8
Radiation Surcharge	9	4	4
Curie Surcharge	13	13	13
Weight Surcharge	9	1	3
Perpetuity Escrow Fund	4	<1	1
Disposal and Business License Tax	9	1	3
Approximate Totals	<u>\$300/ft³</u>	<u>\$220/ft³</u>	<u>\$190/ft³</u>

(a) January 1985 dollars.

(b) Resins or concentrated liquids.

(c) Included in operations costs.

recovery and a 20% rate of return on investment. Transportation and burial costs are based on a cost breakdown given by Jacobs et al. (1984).

MEVS costs/ft³ for transportation and burial are lower than with cementation because of the high volume reduction factor. Fewer casks are needed and less volume at the burial site is required. The analysis assumes one cask per shipment and 190 ft³ of cement in each cask. Only 14 drums of glass can be transported in one cask, each containing 5.7 ft³ of glass (75% full) for a

total of 80 ft³. Nevertheless, because of the greater volume reduction factor, cost savings are realized for cask rental. Cost savings are more pronounced for the remaining disposal costs.

1.5 UTILITY ASSESSMENT

One objective of this program was to assess the interests of nuclear electrical utilities in the volume reduction service that MEVS would provide. This assessment showed that the utilities basically view the MEVS as adaptable to their present and near-term plans for disposal of radioactive waste. There appears to be much uncertainty as to the status of national disposal sites after January 1, 1986. According to the Low-Level Radioactive Waste Policy Act of 1980, each state will assume responsibility for wastes generated within its borders (Moore 1985). States currently operating national waste disposal sites may close them or put severe restrictions on acceptance of wastes as of January 1986 unless regional agreements for LLW are in place. Present indications are that the current national sites may remain open for another 4 years. Nevertheless, increasing burial costs are resulting in increased emphasis on volume reduction for onsite storage and/or disposal at national or regional burial sites.

Although response to the transportable self-contained process approach was positive, the utilities do not appear to be willing to commit capital or to hire more operating staff for radwaste treatment at this time. Contracted services for radwaste treatment appear to appeal to the utility managers. It allows the flexibility essential for adapting radwaste volume reduction processes to the utilities at this time.

Another desirable feature of the process is that the self-containment approach requires minimal interfaces and services from the nuclear power plant. The diesel generators, which provide operating and backup power for the melter and off-gas system, met with good response. Most utilities do not have spare 1200-A, 480-V buses to operate the system.

Off-gas cleanup prior to release was also essential for utility acceptance. The off-gas system allows the utilities to exhaust directly from the process trailer or to tie in with the plant stack to maintain a single exhaust point on the plant site.

During the utility assessment, it became apparent that the assumption that ion-exchange resins can be fed to the melter as a pumped slurry needs to be re-evaluated. Most resins are currently dewatered. It is more sensible to feed the resins to the melter as wet dewatered solids than to reslurry the resins, which would create additional condensate. The glass-former feeder located on the top of the process trailer could be adapted to feed wet solids.

The disposal of the condensate produced from the vitrification of wet wastes also needs to be reconsidered. The preconceptual design calls for a resin column decontamination of the condensate prior to discharge. The resins can then be recycled to the melter for full incorporation of radionuclides. However, the presence of sulfonate groups in ion-exchange resins will produce a dilute sulfate/sulfite scrub solution. It is not yet known what the sulfur concentration will be in the scrubber solution or whether the sulfur will impact the removal efficiency of the resin column. The uncertainty lies in the degree of solubility of sulfates in the glass, which is normally limited to 0.5 to 1.0 wt%. Verification tests are thus necessary to answer technical questions such as these and to provide information for definitive design. Also the acceptable release concentrations of sulfates for chemical waste disposal at a reactor facility need to be investigated.

Overall, the utility representatives' response was positive. They are not satisfied with the present state of commercially available technology for radwaste volume reduction and stabilization. Costs presented for the MEVS service in most cases provided an economic incentive for the MEVS. The overall response of the utilities was that if the reported costs are true, then indeed the MEVS will fill LLW treatment needs and should be supported for commercial development.

1.6 CONCLUSIONS

The MEVS has been preconceptually designed to fill a basic need for treatment of slurries, sludges, and ion-exchange resins in preparation for disposal. Provided the economics presented in this paper are representative of actual costs, it appears that electrical utility companies with nuclear power plants would be interested in a transportable volume reduction and stabilization service of this type. Utility representatives have indicated that presently available processes do not adequately fulfill their waste management needs. The economics presented in this report have been estimated on a conservative basis. When considering the total costs of disposal, which include processing, transportation, and burial, the costs of MEVS are about two-thirds the costs of commonly used techniques.

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2.0 TECHNOLOGY DEVELOPMENT

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2.1 OBJECTIVES

The objectives of the Technology Development Task for FY 1985 were:

1) define the documentation necessary for potential users of nuclear waste treatment technology to design and operate full-scale facilities with both efficiency and confidence, 2) establish specifications and requirements for high-level waste (HLW) and transuranic waste (TRUW) forms, 3) develop technology for treatment of commercial TRUW, 4) monitor the needs for the treatment of spent fuel, and 5) develop and monitor alternative technology for the treatment of HLW. To accomplish these objectives the task was divided into five major subtasks. These included Strategy, Performance, and Product Requirements; Byproducts and Spent Fuel; TRU Waste Treatment; Second-Generation HLW Technology; and Technology Documentation.

2.2 SUMMARY

In the Strategy, Performance, and Product Requirements subtask, a draft of potential requirements for TRU waste form production was prepared, an evaluation of treatment options for reprocessing wastes was published, comments were prepared for the Waste Acceptance Committee on proposed HLW and canister requirements, and work was started on an evaluation of treatment options for waste from consolidation of spent fuel. This information is summarized in Sections 2.3 to 2.5.

Two major activities within the Byproducts and Spent Fuel subtask were to complete an assessment of the availability and use of byproducts from spent fuel and a preliminary analysis of spent fuel treatment options. These activities are reported in Sections 2.6 and 2.7, respectively. The analyses indicate that there is a significant potential for the separation and use of byproduct materials.

Significant progress was made in selecting and developing waste processing technology for treatment of the various types of TRU wastes. This is outlined in the treatment strategy (Section 2.3). Development of a method to melt

metallic wastes is discussed in Section 2.8. Section 2.9 provides some early chemical durability results on a typical melted product. Mixed metals, organics, and oxide wastes can be treated by shredding and incineration. Testing of alternative equipment is reported in Section 2.10. HEPA^(a) filters are among the more difficult wastes to treat. A report on their characterization is contained in Section 2.11.

Second-generation waste forms are of increased interest, and our progress on the evaluation of several options is discussed in Sections 2.12 through 2.15. The potential of the low melting temperature of lead-iron phosphate glasses has been evaluated and is reported in Section 2.12. High-temperature glasses that offer some improvement in chemical durability are being developed. Progress in the development is reported in Section 2.13. The potential for production of these high-temperature glasses in current design melters was assessed and is reported in Section 2.14. A third major alternative form is SYNROC, which has been developed in Australia. Typical materials were received from Australia and are being tested. Early results are reported in Section 2.15.

The documentation of liquid-fed ceramic melter (LFCM) technology is of major importance and is supported in the fourth subtask. A plan for documentation of LFCM technology was prepared and is reported in Section 2.16. A similar plan for TRU waste treatment technology was also completed and is reported in Section 2.17. The design of the liquid-fed-ceramic melter for West Valley is being documented, and the documentation activity is discussed in Section 2.18. All the documentation is expected to be included in the final design manual for the LFCM. The early preparation of that manual is discussed in Section 2.19.

2.3 STRATEGY FOR TREATMENT OF TRU REPROCESSING WASTE - K. J. Schneider, W. A. Ross, J. L. Swanson, K. M. Yasutake, and R. P. Allen

A study was initiated and documented in a PNL report, "Preliminary Analysis of Treatment Strategies for Transuranic Wastes from Reprocessing Plants,"

(a) High-efficiency particulate air.

in collaboration with related work for DOE's Office of Civilian Radioactive Waste Management (OCRWM). The objective of the study was to analyze various treatment options for TRU waste at a fuel reprocessing plant and the cost impacts of these options on the total waste management system (i.e., treatment, storage, transportation, and disposal).

Projected transuranic waste streams from the Barnwell Nuclear Fuel Plant (Darr 1983), taken to be the reference fuel reprocessing plant, were grouped into the five categories of 1) hulls and hardware, 2) failed equipment, 3) filters, 4) fluorinator solids, and 5) general process trash and sample and analytical cell solid wastes. These wastes are composed of a wide variety of materials, including metal, cellulose, plastics, and rubber.

Six potential treatment options were selected for the five categories of waste. These options were selected to represent different overall objectives and varying methods for achieving them. The six basic treatment options are summarized in Table 2.1.

Schemes for treating each waste type were selected and developed for each treatment option. From these schemes, transuranic waste volumes were found to vary from $1 \text{ m}^3/\text{MTU}$ for no treatment to as low as $0.02 \text{ m}^3/\text{MTU}$, as shown in Table 2.2.

Based on conceptual design requirements, life-cycle costs were estimated for treatment plus onsite storage, transportation, and disposal of both high-level and transuranic wastes (and incremental low-level wastes) from 70,000 MTU (Table 2.2). For all treatment cases (Options 2 through 6), the additional costs for treatment were more than compensated for by the reduced cost of transportation and disposal, with net cost reductions in amounts ranging from \$0.1 billion to \$1.7 billion (in 1983 undiscounted dollars).

The strategy analysis in this study also took into consideration the potential requirements for waste forms and canisters (assuming geologic disposal) and waste processing characteristics. The waste-form considerations included recognition that the requirements being developed include those for defense TRUW, Class C LLW, and civilian HLW. Since the disposal method for TRUW has not yet been established and detailed characterization data for the

TABLE 2.1. Summary of the Six Reprocessing TRUW Treatment Options^(a)

Option	Title	Objective	Primary Treatments
1	No treatment	No treatment of wastes	Assay to certify TRU content
2	Minimum treatment	Reduce volume with simple technology	All wastes are mechanically compacted to reduce volume
3	Minimum number of processes and products	Treat wastes in similar manner to produce one type of simple waste form	All wastes are mixed with cement or grouted
4	Maximum volume reduction without decontamination	Treat wastes to produce minimum final waste volumes	Metals are melted, cellulose combustibles are incinerated, rubber and plastics are hot-pressed, and residues are melted
5	Maximum volume reduction with decontamination	Decontaminate TRUW to produce LLW	Wastes are decontaminated; residue is combined with HLW or treated separately ^(b)
6	Noncombustible waste forms	Reduce volume and eliminate combustibles	Metals are melted, combustibles are incinerated, and residues are cemented

(a) HLW is treated by vitrification in all options.

(b) Suboption 5A vitrifies decontamination solutions with HLW glass. Suboption 5B dries the decontamination solutions and hot-presses the decontamination solids from hull treatment.

TABLE 2.2. Reprocessing TRUW Volumes and Costs for Treatment Options

Option	TRUW Volume, m ³ /MTU	Life-Cycle Costs, Undiscounted 1983 B\$(a)			
		Treatment	Transportation	Disposal	Total
1. No Treatment	1.0	3.7	1.7	4.9	10.3
2. Minimum Treatment	0.24	4.0	0.6	4.2	8.8
3. Minimum Number of Processes and Products	0.63	4.0	1.5	4.6	10.2
4. Maximum Volume Reduction without Decontamination	0.078	4.7	0.4	3.6	8.7
5. Maximum Volume Reduction with Decontamination	0.021 ^(b)	5.5	0.4-0.6 ^(c)	3.9	9.8-10.0 ^(c)
6. Noncombustible Waste Forms	0.092	4.7	0.4	3.6	8.6

(a) Life-cycle costs for all TRUW + incremental LLW and HLW from 70,000 MTU.

(b) Includes increase in HLW volume, but excludes the increase in LLW volume.

(c) First number is for Option 5A; second is for Option 5B (see Table 2.1).

respective waste forms have not been obtained, the acceptability of waste forms cannot be fully judged. However, it seems likely that waste forms will be required to provide some degree of immobilization. Processing characteristics such as operational safety, process complexity, technology, status, and process flexibility of each treatment step within each option were also evaluated qualitatively.

The overall characteristics of the options studied were ranked in relation to system economics, waste-form characteristics, and processing characteristics (Table 2.3). Based on these evaluations, Option 6 appears to have the most favorable characteristics of the more extensive treatment options and ranks less favorably only in processing characteristics.

Major conclusions from the study are as follows: 1) all the treatment options appear to offer economic and waste-form incentives compared to no treatment; 2) volume reduction of the wastes generally (but not always) reduces overall system costs; 3) significant incentives exist for applying treatment options to TRU wastes that are more extensive than minimum or simple treatments; 4) fuel cladding hulls and hardware are the most important TRU waste

TABLE 2.3. Summary Ranking^(a) of the Reprocessing TRUW Treatment Options

<u>Option</u>	<u>Systems Economics</u>	<u>Waste-Form Characteristics</u>	<u>Processing Characteristics</u>	<u>Approximate Overall Ranking^(b)</u>
1	6	6	1	13
2	3	5	2	10
3	5	4	3	12
4	2	2	5	9
5	4	3	6	13
6	1	1	4	6

(a) Ranking of from 1 (most favorable) to 6 (least favorable of the group).

(b) Overall ranking was done by adding the prior three values for each option; the lower numbers are the most favorable.

stream from reprocessing because of their large volume, their high radioactivity, and the costs for their treatment, handling, transportation, and disposal; and 5) HEPA filters are a major waste stream that can be significantly reduced in volume, but their composition and construction complicates their treatment.

This study demonstrated that there are significant opportunities for combining wastes for treatment. Therefore, future R&D should consider all the waste streams, as was done in this study. Melting of metals, incinerating of combustibles, and cementing of residues are candidates for further development, based on the six basic options studied. These processes could reduce waste volume and waste management system costs, handle a large variety of wastes, and produce good-quality waste forms.

2.4 TREATMENT STRATEGY FOR NON-FUEL-RECYCLE TRU WASTES - K. J. Schneider, W. A. Ross, K. H. Oma, R. I. Smith, and L. R. Bunnell

A study has been initiated to evaluate the potential treatment strategies for transuranic wastes generated in the civilian sector without any fuel reprocessing. The study assumes that a central waste treatment capability is to be included in the proposed Monitored Retrievable Storage (MRS) facility. The proposed MRS facility, if implemented, will generate the largest amount of TRUW from civilian nuclear activities from its spent fuel handling, consolidating, and canisterizing, and it must have the capability to treat these internally-generated wastes. It seems reasonable to consider the proposed MRS facility as a potential central facility for handling and treating the smaller amounts of TRUW generated in the numerous commercial facilities prior to disposal of the wastes.

Projected transuranic waste streams from the proposed MRS facility and the other civilian sources were reviewed, and the original waste forms were placed in the following nine categories, based on their characteristics and amenability to potential treatment processes: failed equipment, spent fuel hardware, HEPA filters, combustibles, process filters and mixed combustibles and noncombustibles, resins, cemented wastes, concrete rubble, and solutions and sludges (from MRS operation only). These wastes are composed of a wide variety

of materials, which leads to numerous considerations relative to processes and schemes for converting them into other waste forms for transportation and disposal.

Eight potential treatment options were selected for the eight categories of TRUW. The options were selected to carry out different overall objectives and allow for use of different methods for treatment. The eight basic treatment objectives are: 1) no treatment (containerization only); 2) MRS reference (compaction, cementation, and size reduction); 3) intermediate volume reduction (supercompaction); 4) maximum volume reduction with decontamination (decontamination, incineration, and melting); 5) cementation; 6) treatment by one process (arc pyrolysis); 7) intermediate-quality waste form (incineration, melting, cementation, and sulphur-graphite matrix); and 8) highest-quality waste form (incineration, calcination, melting, and hot-pressing).

Numerous schemes for treating each waste type were evaluated, and specific schemes were selected for each treatment option. From these schemes, packaged transuranic waste volumes were found to vary from 2900 m³/yr for no treatment to as low as 180 m³/yr.

At year end, evaluations and ranking of the eight strategy options were initiated relative to process treatment, product quality, and costs.

2.5 TRU WASTE PRODUCTION REQUIREMENTS - G. B. Mellinger

A set of proposed production requirements for commercial TRU wastes was developed. These requirements were reported in a letter report entitled "Potential Production Requirements for Commercial Transuranic Waste Forms and Containers." The requirements are intended to be used as guidelines for those who are developing waste forms, processing technology, and containers for commercial TRU wastes. The requirements were developed from existing and proposed regulations that deal with the transportation and ultimate disposal of TRU waste in geologic repositories, as well as from draft acceptance requirements that were developed by the three geologic repository projects for HLW glass. The proposed production requirements in this document apply only to waste forms containing transuranic wastes from commercial sources.

The requirements deal with TRU waste-form characteristics and performance in storage, transportation, and disposal. A total of 22 requirements are proposed and are grouped into six categories: radionuclide-related requirements, accident performance, containment/transportation safety, thermal properties, restricted substances, and nonperformance items such as handling features and quality assurance. Within the categories, each item contains a statement of the proposed requirement, followed by a brief description of the need for the requirement and the basis for its development. Requirements have been made quantitative whenever possible.

Based on the proposed requirements, certain potential waste forms will be acceptable for production, and others will not. Those acceptable waste forms will, however, be able to accommodate all presently anticipated commercial TRU wastes. The acceptable waste forms will include consolidated (e.g., melted and cast) metals, unconsolidated metals, cast/hot-pressed glass/ceramics, and cement containing various wastes. The use of cement will allow the disposal of "problem wastes," such as pyrophoric materials and organic solids, without requiring high-temperature operations or equipment more sophisticated than that required for shredding and blending.

Some potential waste forms will not meet one or more of the proposed requirements. Fluorinator solids, primarily aluminum oxide and calcium fluoride, would result from the fluorination of uranium at a reprocessing plant. This material contains an unacceptably high content of unconsolidated fine particulate. Hot-pressed rubber/plastic waste forms would not meet the requirement for combustibility. Fluorinator solids, rubber, and plastic could, however, be incorporated in cement to produce a waste form that is acceptable based on the proposed requirements.

2.6 ASSESSMENT OF THE RECOVERY AND USE OF BYPRODUCTS FROM SPENT FUEL -

W. A. Ross, G. A. Jensen, G. L. Tingey, A. W. Prichard, S. M. Nealey,
and J. H. Jarrett

A preliminary assessment was made of the technology, public acceptance, and economic factors in the separation and use of byproducts from spent fuel. A letter report concludes that there is a growing use and need for byproduct

materials. It is projected that current sources of gamma radiation will be inadequate by 1988 and that new sources should be developed. Alternative gamma sources include: cesium from defense wastes and commercial spent fuel and ^{60}Co from Canadian and U.S. reactors, direct use of spent fuel, and machine-generated radiation. Of these alternatives, it is recommended that separation of cesium from spent fuel and the direct use of spent fuel be further evaluated. The current major gamma source is ^{60}Co , and it has most recently been almost totally supplied by Atomic Energy of Canada, Limited. Current requirements for gamma sources have resulted in the commitment of all cesium capsules previously produced at Hanford.

The current major use of gamma radiation is for sterilizing disposable medical supplies, a use expected to nearly triple in the next 5 years. Food irradiation is useful for destruction of pathogens or parasites, insect disinfection, and extension of the allowable storage periods for selected foods. Use of irradiation for treatment of food will result in less food loss and improvement in food quality. It may also help open new markets for selected products, such as shipment of apples and cherries to Japan.

Public acceptance of irradiation technology is uncertain; however, it seems likely since it meets some basic criteria for acceptance. These criteria include the following: 1) it provides real benefits, 2) careful testing of its use has occurred, 3) the technology can be controlled (no major disasters have occurred or are likely), and 4) those who would benefit from the technology are those who would take the risk.

Current regulatory actions are also encouraging since labeling requirements are being reduced, allowable doses are being increased, and approvals are easier to obtain.

The economics of byproduct utilization are tied to waste management costs. A preliminary cost comparison of waste management system costs indicates that byproduct recovery may be economically preferable to spent fuel disposal, particularly if other byproducts could be separated at the same time as the cesium. The results are preliminary and identify areas for additional work.

2.7 ANALYSIS OF SPENT FUEL TREATMENT OPTIONS - W. A. Ross, L. R. Bunnell, L. L. Clark, R. J. Guenther, and K. H. Oma

Four generic treatment options were evaluated for potential treatment methods should spent fuel treatment be needed. These generic options are as follows: 1) incorporate whole spent fuel rods in a durable matrix, 2) incorporate chopped spent fuel rods into a durable matrix, 3) convert the fuel into a powder or solution and then incorporate it into a durable waste form, and 4) separate the problem isotopes and useful byproducts from the spent fuel and incorporate the remaining wastes into a durable waste form. A method using comparison of pairs was employed with the following major criteria: cost, safety, public acceptance, and other considerations. Each major criterion was subdivided, and a weighting analysis method was used. Costs were broken down into treatment, development, transportation, storage, disposal, and byproduct resale value. Safety was subdivided into processing, transportation and handling, and repository performance. Public acceptance was considered to be based on perceived hazards and safeguards of plutonium. Other considerations were the availability of plutonium and uranium in the future and the state of technology.

Two major options were selected for further, more detailed, evaluation should spent fuel treatment be further considered. The two methods are to first treat whole, unvented rods by incorporating them into a durable matrix, and second to chemically separate the useful byproducts and problem isotopes from the spent fuel before processing the residuals into a waste form.

2.8 METAL MELTING DEVELOPMENT - D. R. Montgomery

PNL has completed the second year of a melting study using a vacuum coreless induction furnace to consolidate simulated nuclear metallic waste.

Vacuum coreless induction melting employs a graphite crucible that is bottom-poured by using a water-cooled copper freeze plug. The metal is poured into the canister or mold located directly under the crucible. The metal melted for this study included the eutectic alloy of nonoxidized zirconium and iron except for three heats, one of which consisted of a mixture of carbon steel, stainless steel, glass, and electric motor parts. The other two heats

were done to investigate the melting parameters of simulated pressurized water reactor (PWR) fuel-bundle skeletons. The last of these two heats was done with funding from the Monitored Retrievable Storage (MRS) program.

This year's study emphasized the redesign of the pouring nozzle to prevent a drop of metal from forming and solidifying at the nozzle exit. This drop had prevented a proper seal when the water-cooled copper freeze plug was replaced. Greater emphasis was also placed on the encapsulation of metallic general process trash by preplacing it in the canister and pouring the eutectic alloy of zirconium and iron over it. A conceptual design of a prototype furnace, along with a brief study report and cost estimate for fabrication, was completed by Kaiser Engineers Hanford Company. Thirteen heats plus three corrosion heats were done during this investigation, and produced the following results and conclusions:

- No failures of the water-cooled freeze plug were observed. The melting of the simulated PWR fuel-bundle skeletons was successful, except that not enough heat was conducted to the pouring nozzle to melt out the higher-melting-point metal and empty the crucible.
- A frequency of 3 kHz is better for melting in this application than a higher frequency such as 6 kHz, because of increased stirring of the melt, which prevents bridging.
- If the molten iron-zirconium eutectic metal cannot be poured and is allowed to solidify in the crucible, differential thermal contraction will break the graphite crucible.
- A second induction coil around the pouring nozzle, which is planned for the prototype furnace, will facilitate pouring of the metal from the crucible and at lower melt temperatures.
- The combination of a redesigned pouring nozzle and a modified technique of operation has solved the problem of the solidified drop at the nozzle outlet.
- The best melting rate was 53 kg/hr at 40 kW, with a power consumption of 0.75 kWh/kg.

- All encapsulation experiments were successful; the least dense ingot was 93.5% of theoretical, and the most dense was 98%.
- Stainless steel canisters with walls 1/4 in. thick were used exclusively without any problems.
- The one heat of carbon steel, stainless steel, glass, and electric motor parts reacted with the graphite crucible and eroded a hole through the bottom.

2.9 CHARACTERIZATION OF METAL MELTING PRODUCT - J. H. Westsik, Jr.

As part of the initial characterization of the metal melting product, specimens cut from an ingot of the Zircaloy®/stainless steel eutectic were exposed to deionized water, silicate water, and brine at 90°C in accordance with the MCC-1P leach test procedure. The test was run for 27 days rather than the standard 28 days. The specimens showed only small weight changes and very little release of material to the leachates. The ingot was prepared by melting a mixture of 18 wt% 316 stainless steel and 82 wt% Zircaloy 4 at a maximum temperature of 1371°C for 22 min. Nonradioactive tracers including 1.8 g $\text{Sr}(\text{NO}_3)_2$, 1.1 g CsNO_3 , and 5.7 g $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were added to 1001 g of metal mixture prior to melting. Table 2.4 shows the results of the test. None of the tracers were detected in the leachates at the conclusion of the test. Longer test intervals of 6 and 12 months are planned for FY 1986 to determine the long-term behavior of this waste form.

2.10 SHREDDING AND INCINERATION OF TRU WASTES - K. H. Oma

Treatment strategies for TRU wastes from commercial reprocessing have been identified and evaluated by Ross et al. (1985). Ross concluded that extensive treatment of the TRU wastes is warranted because of both lower system cost and improved waste-form characteristics. The evaluation recommended that wastes containing combustible materials be processed by shredding and incineration and that the resulting residue be incorporated in a cement waste form.

®Zircaloy is a registered trademark of Westinghouse Electric Corporation, Speciality Metals Division, Blairsville, Pennsylvania.

TABLE 2.4. Results of MCC-1P Leach Test on Zircaloy/Stainless Steel Waste Form

	<u>Deionized Water</u>	<u>Silicate Water</u>	<u>Brine</u>
Percent Weight Change	-4E-4	+4E-3	+8E-3
pH Change	+0.3	+1.9	+1.7
Normalized Elemental Mass Loss, g/m ²			
Fe	0.02	ND	0.18
Mn	ND(a)	0.33	ND
Ni	ND	ND	0.23
Zr	ND	ND	0.03

ND - Not detected.

A review of current shredder and incinerator technologies was performed. The review concluded that 1) the electrically-driven, low-speed shredder process was preferred over other shredder technologies for TRU waste pretreatment, and 2) the electrically-heated controlled-air, gas-heated controlled-air, and rotary kiln incinerators were preferred over other incineration processes for converting commercial TRU wastes to a noncombustible form. Based on the review, an experimental program was undertaken to demonstrate the preferred technology on simulated commercial TRU wastes. The objectives of the tests were to: 1) confirm that shredders and incinerators can be used effectively to process commercially generated TRU wastes and 2) select a reference shredding and incineration system for further testing and development.

Simulated wastes representing general process trash, sample and analytical cell waste, wood-framed HEPA filters, and metal-framed HEPA filters were used for the test program. Seven low-speed shredders and shredder configurations were tested and compared in terms of waste throughput, cutter force, cutter configuration, and fragment size. The three incineration processes were tested at commercial vendor sites using the shredded waste as feed material. Following the tests, the technical merit of each process was judged by a five-member panel using the Figure-of-Merit (FOM) evaluation method. The ratios of cost to

FOM were then used to select the most cost-effective reference shredder and incinerator process for further development.

The primary conclusions from this study are as follows:

- Shredding and incineration technology appears effective for converting simulated commercial TRU wastes to a noncombustible form.
- The gas-heated controlled-air incinerator received the highest technical ranking. On a scale of 1 to 10, the incinerator had an FOM number of 7.0. This compares to an FOM of 6.1 for the electrically-heated controlled-air incinerator and an FOM of 5.8 for the rotary kiln incinerator. The major advantages and disadvantages identified during the testing and evaluation of each incinerator are summarized in Table 2.5.
- The present-worth costs of the incineration processes for a postulated commercial reprocessing plant were lowest for the electrically-heated and gas-heated controlled-air incinerators, with costs of \$16.3 M and \$16.9 M respectively (1985 dollars). Due to higher capital and operating costs, the rotary kiln process had a present worth cost of \$20.8 M. These cost numbers are for comparative purposes only and are not adjusted for future inflation.
- The recommended process from the three evaluated for the commercial TRU waste application is the gas-heated controlled-air incinerator with a single stage of shredding for feed pretreatment. This process had the best cost-effectiveness ratio of 1.0 (normalized). The electrically-heated controlled-air incinerator had a rating of 1.2, and the rotary kiln rated a 1.5.
- Most of the simulated wastes were easily processed by the low-speed shredders; however, HEPA filters proved difficult to process. Wood-framed HEPA filters tended to ride on the cutter wheels and spacers without being gripped and shredded. Methods for feeding wood-framed HEPA filters and other wood-boxed items to the shredder need to be developed. Metal-framed HEPA filters and other difficult-to-shred items caused the shredders to periodically reach the torque limit and

TABLE 2.5. Major Advantages and Disadvantages of Incinerators

<u>Incinerator</u>	<u>Major Advantages</u>	<u>Major Disadvantages</u>
Electrically-Heated Controlled-Air	<ul style="list-style-type: none"> • Minimum off-gas treatment required due to low flow and low ash entrainment • Low ash/residue retainment in the primary chamber • Long equipment life • Able to process wide range of feed materials 	<ul style="list-style-type: none"> • Residue contains high fraction of fixed carbon • Process requires high level of feed pretreatment • Residue contains clinkers of carbon-rich wood • Remote maintenance is judged difficult
Gas-Heated Controlled-Air	<ul style="list-style-type: none"> • High burnout of fixed carbon is achieved • Process has been well developed for TRU and LL waste applications 	<ul style="list-style-type: none"> • (No major disadvantages identified)
Rotary Kiln	<ul style="list-style-type: none"> • Can process wide range of feed materials • Minimal feed pretreatment is required 	<ul style="list-style-type: none"> • Low retention of trace elements in residue • High off-gas treatment requirements due to high flow rate and high ash entrainment • Remote maintenance is judged difficult • Shorter refractory life contributes to increased maintenance and personnel exposure

go into an automatic reversal cycle; however, the filters were eventually processed by the units. Metal-framed filters will require a shredder designed for high cutter tooth force and/or larger shredded fragment size. Some of the dust on loaded HEPA filters was released during the shredding operation. Methods for fixing it on the filters should be evaluated and tested.

- All three incinerators were ineffective for oxidizing the aluminum metal used as spacers in HEPA filters. Aluminum metal will cause an undesirable hydrolysis reaction in a cemented waste form.

2.11 HEPA FILTER EVALUATION - Y. B. Katayama

The technical data from this evaluation are intended to aid in evaluating strategies for volume reduction of HEPA filters, a major waste stream of nuclear facilities. Two previously used metal-framed HEPA filters were disassembled and examined. Metal-framed filters are important because of uncertainties regarding their combustible content. The filters chosen were typical 24 x 24 x 11-1/2 in. units with glass filter media and solid polyurethane sealant between the filter media and metal frame. These filters had been used in the alkaline off-gas streams of a nonradioactive field experiment demonstrating in situ vitrification at PNL.

The results of incinerating the polyurethane sealant are listed in Table 2.6. Filter No. 1 had an additional 1 lb of burnable silicone-based grease in the filter-seal channel. The burnable portions of the metal-framed

TABLE 2.6. Ash Content of Polyurethane After Incineration at 900°C

	<u>Weight of Polyurethane, lb</u>	<u>Wt% ash</u>	<u>Remarks</u>
Filter No. 1	8-1/2	31	Soft, pliable, uniform color and texture
Filter No. 2	6	22	Outer layer of sealant darker colored and tougher than above

HEPA filters examined were about 15 wt%. Differences in the appearance, quantity, and physical property of the sealant are believed to be due to different service histories. During disassembly of the filters, greater buildup of caustic was observed in media of the second filter.

2.12 EVALUATION OF LOW-TEMPERATURE GLASSES AS SECOND-GENERATION WASTE FORMS - L. R. Bunnell and L. A. Chick

A recent publication (Sales and Boatner 1984) of Oak Ridge National Laboratory reported on work with low-temperature lead phosphate glass that performed impressively in leach tests and might offer substantial processing economies because of the lower temperatures.

We examined this glass, preparing it according to the reference. Leaching performance was evaluated according to standardized (MCC-1 and MCC-3) tests, and the glass does perform better than reference borosilicate glass (Table 2.6). The glass, however, is very subject to devitrification, as have the several phosphate glasses examined previously (Mendel and McElroy 1972). When devitrified by a schedule simulating the cooling of an average-sized canister used to receive molten glass (0.6 m in diameter), the glass behaves much worse in leaching tests, especially in regard to cesium (Table 2.7). The devitrification phases are complex and consist of at least six separate compositions, but no phase contains noticeable amounts of cesium, which is rejected and concentrated as soluble cesium silicate at the center of the crystalline mass, as shown in Figure 2.1.

More recently Sales and Boatner (1985) addressed the devitrification problem by decreasing the iron in the glass, and claim that cooling rates as low as 1°C/min will not degrade the leaching performance. PNL data generally indicate that cooling rates for reasonable-sized canisters will be lower than 1°C/min, especially with high-heat-producing glasses of major interest as second-generation nuclear waste forms. Such forms will receive relatively fresh reprocessing wastes, which produce substantial heat. The lower cooling rates will make devitrification more likely. Nevertheless, glass was prepared according to the new recipe and cooled at 1°C/min, then leach-tested. Although

TABLE 2.7. Comparison of Approved Reference Material-1 Standard Borosilicate Glass with Two Lead-Iron-Phosphate Glasses in Vitreous Form or After Stated Heat Treatments^(a,b)

Element	ARM-1 Borosilicate Glass, 30-Day MCC-3 Test	Pb-Fe-P Glass, Vitreous (as per Sales and Boatner 1984)	Cooled Simulating 0.6 m Canister	Pb-Fe-P Glass, Cooled at 1°C/min (as per Sales and Boatner 1985)
Si	0.39	NP ^(c)	NP	NP
B	0.79	NP	NP	NP
Pb	NP	0.004	0.003	0.17
P	0.52	0.06	0.43	11.83
Na	0.82	0.12	1.3	NP
Li	1.2	NP	NP	NP
Ca	0.01	0.11	0.28	NP
Sr	0.01	0.07	0.07	4.31
Al	0.18	NP	NP	NP
Fe	NP	0.01	0.01	0.21
Cs	0.10	0.14	61	50.13
Final pH	11	4.0	3.8	2.2

(a) All values are in units of normalized mass release, g/m².

(b) Test conditions: MCC-3; 90°C; 28 days unless otherwise stated, 45-100 + 200 mesh powder in 40 mL deionized water;

$$\frac{\text{Surface Area}}{\text{Volume}} = 1120 \text{ m}^{-1}$$

(c) NP = Not present in glass.

the crystals resulting from devitrification were small, they resulted in a substantial increase in cesium release, as shown in Table 2.7.

Our assessment of this waste glass type concludes that this good leaching performance can be realized only by keeping it vitreous, which means cooling it quickly from processing temperature. The Germans, faced with similar problems, originated the PAMELA process (Heimerl 1979), wherein the glass is made as marbles and encased in a matrix of lead. These steps add to process complexity and

FIGURE 2.1. Large Crystals in Lead-Iron-Phosphate Glass Subjected to Cooling Cycle Simulating 0.6-m Canister. Crystallization-induced volume changes produced large voids at the center, where most of the cesium is concentrated.

decrease waste loading per unit volume by about 40%, but may be worthwhile considering the glass' good durability.

2.13 HIGH-TEMPERATURE GLASSES AS SECOND-GENERATION WASTE FORMS - L. R. Bunnell and G. D. Maupin

In general terms, the chemical durability of a particular type of glass, i.e., borosilicate, should rise in proportion to its processing temperature. This is because "processing temperature" is really a function of viscosity, which is itself sensitive to the density of Si-O bonds in the glass. The fluxes added to decrease processing temperature do so by breaking Si-O bonds, thus decreasing the tightness with which cations are held in the glass structure. Statistically designed studies of glass formulations, such as Chick et al. (1984), indicate clearly that an increase in processing temperature is associated with better chemical durability. It is reasonable to expect that, for glasses of the general borosilicate type, increasing processing temperature to 1400°C should result in an order-of-magnitude performance increase.

During FY 1985, considerable experimentation was done on glass compositions having a viscosity of 100 poise^(a) at 1400°C and containing 25 wt% PW-4b calcine (Mendel 1977) to simulate the output of a relatively "clean" gadolinium-free reprocessing facility. Three approaches--an analog study, an empirical mixture study, and a substitution study--were all used so as to accomplish the most in the least time.

In the analog study, the SRL-165 and PNL 72-68 glasses were modified to high-temperature versions by decreasing fluxes, and leaching performance was measured by the MCC-3 leach test. SRL-165 is a high-durability borosilicate waste glass representative of current technology, and 72-68 is a very well-studied borosilicate waste glass. With boron used as an indicator of glass dissolution that would be free from precipitation effects, the high-temperature analog to SRL-165 outperformed the original by a factor of about 3.5 in a 28-day MCC-3 test. On the other hand, a high-temperature analog to 72-68 was better than 72-68 but worse than SRL-165 by a factor of 1.5. These fairly modest gains appear to indicate that the analog approach has little future as a means to achieve higher performance.

For the empirical mixture study, a statistically designed composition space was investigated using the computer model developed by Chick et al. (1984), which uses silicon release as an index to long-term glass performance. From this work, several candidates and an optimum composition were predicted. These compositions have been tested using MCC-3, and the optimum performed best, showing boron release rate six times lower than SRL-165 in a 7-day test.

The substitution study involved trading alkaline-earth oxides for boron and some alkali oxides in SRL-165. In one such glass where calcium and magnesium oxides were used, the molybdenum release rate (used because not all glasses contained boron) was a factor of 8 lower than SRL-165 in a 7-day MCC-3 test.

This work continues, aimed at attaining the stated order-of-magnitude decrease in release rate and still retaining the values of critical properties,

(a) Generally considered best for processing.

such as electrical conductivity, that enable use of LFCM technology. Such a glass would require minimal changes of established technology.

2.14 EVALUATION OF HIGH-TEMPERATURE MELTERS - K. H. Oma

It appears that with some modifications, current-generation LFCM technology can be used to produce a more durable higher-temperature glass. According to current correlation models (Chick et al. 1984), increasing the temperature at which the glass has a viscosity of 100 poise from 1150°C to 1450°C should improve leach resistance of the resulting glass by at least one order of magnitude. A melter to process this improved glass should be designed to operate at 1500°C or higher. No insurmountable obstacles related to melter design or construction materials have been identified for temperatures at or below about 1500°C. Tradeoffs must be made, however, as the melter will probably be larger, require higher maintenance, contain more expensive construction materials, and have a shorter design life. The more significant findings summarized from this evaluation follow:

- Current high-alumina lid refractories and K-3 glass contact refractories with a maximum temperature rating of well over 1500°C are routinely used in the commercial glass industry at 1400 to 1500°C. Thus no change to the primary refractory lining is foreseen.
- The cooled Inconel® electrodes are limited to ~1200°C and have typically been run below 1100°C. With air-cooling, the bulk-glass temperature can be run up to about 1300°C. Above this temperature, other electrode materials such as molybdenum, tin oxide, or Union Carbide LT-1 metal-ceramic should be considered. Molybdenum is the industry standard for melters at these temperatures.
- Inconel is used for several parts other than the electrodes in current LFCM designs. A substitute of platinum-rhodium or molybdenum can be made for service to above 1500°C. Platinum-rhodium should not be used in a reducing environment, and molybdenum is not suited for service in an oxidizing environment. The parts in question include

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the airlift tube, pour trough, pour tip, drain valve, suction tube, thermowells, pressure ports, and other miscellaneous parts. The K-3 refractory is a suitable substitute for the pour trough and pour tip.

- Silicon carbide heating elements used in the overflow section of the melter are good to 1500 to 1650°C for continuous service in air. More frequent replacement of the heating elements will be required when operated at these higher temperatures, but acceptable service life is anticipated.
- The standard stainless-steel canisters should be able to receive a high-temperature glass at present fill rates without any adverse effects.
- Cooling systems required for the melter will need to be scaled up to accommodate the increased heat load. Included would be cooling systems for the feed nozzle, electrodes, melter shell, canister turntable, off-gas line film cooler, etc. No technical difficulties or limitations are expected.
- Additional fission-product sorbers and particulate scrubbers may be required because the feed-to-off-gas decontamination factors are expected to be slightly lower at the higher melting temperatures.

2.15 SYNROC C EVALUATION - J. W. Shade

Comparative testing of Synroc C and uranium-doped 76-68 glass was done to gain general information on Synroc's potential durability compared to that of a well-known glass. The 76-68 glass contained 33% PW-8a calcine (Mendel 1977) and 4.16% depleted UO_2 while Synroc C contained 10 wt% PW-4b calcine and 0.50% UO_2 . The tests conducted were modified MCC-1 and -2 using monolithic test specimens and MCC-3 using specimens crushed to -40+80 mesh to obtain an undisturbed high specific surface area. Tests were conducted at 90°C and 150°C in MCC silicate water with a pH of 8.67 and MCC brine with a pH of 4.43. The MCC-1 and -2 tests were terminated at 28 days, but the MCC-3 tests will continue to 90 days.

Uranium concentrations in MCC-1 and -2 silicate water leachates filtered through 0.45- μm filters are shown in Figure 2.2. These results, reported in normalized milligrams per square meter, show that 76-68 yields uranium levels of about 1.0 to 1.5 ppm, typical for this glass. Only a small temperature dependence is observed, but this could be partly the result of minor quench effects for a low-solubility component. In comparison, uranium concentrations for Synroc approach detection limits, generally a few parts per billion. In normalized terms these are about 1.5 orders of magnitude lower than for 76-68. The two Synroc data points at 28 days that approach the glass concentrations may be questionable because a replicate yielded negligible values. Also preliminary MCC-3 data indicate uranium release values lower than for glass.

FIGURE 2.2. Uranium Concentrations in MCC-1 and -2 Silicate Water Filtrates from Tests with Synroc C and 76-68 Glass

Other elements released from these materials include barium, cesium, and molybdenum. Barium is present only in Synroc, but barium concentrations of about 0.4 ppm indicate that possibly some hollandite may be dissolving at 28 days. Normalized cesium release from Synroc is about 0.1 g/m^2 and is about 5 times higher for glass, while normalized molybdenum release at 90°C is about the same for both Synroc and glass, about 0.2 g/m^2 .

2.16 DRAFT PLAN FOR LIQUID-FED CERAMIC MELTER TESTING AND DOCUMENTATION -

J. H. Jarrett

The LFCM process is the reference U.S. process for treating both defense and civilian high-level liquid waste (HLLW). Several demonstrations of this technology are planned in the late 1980s and early 1990s. Development of the current technology has been under way for about 12 years and consequently is nearly complete. The design and operating parameters for safe, efficient operation have been defined and successful design concepts identified. The key areas where work remains are documentation of past development and design work, resolution of a few remaining technical issues, and demonstration of remote process and product quality control/verification models. Sufficient documentation to transfer the technology effectively and support licensing procedures is needed. Efforts in the next 5 years must concentrate on addressing these remaining issues if the work is to provide timely support of planned demonstrations as well as achieve technology testing and closeout of documentation in FY 1992.

This draft plan provides the Nuclear Waste Treatment Program (NWTP) approach to finalize and document the LFCM technology base for future applications. That documentation will allow future groups to utilize the technology efficiently to design, license, and operate an LFCM system, subject to confirmation during well-defined pilot-scale testing.

The overall objective of the activities outlined in this plan is to provide the information needed to: 1) complete development and testing of LFCM vitrification equipment by the end of FY 1989, 2) establish nonradioactive-to-radioactive LFCM equipment performance correlations by the end of FY 1990 so that a user of the technology can predict full-scale radioactive equipment

performance from nonradioactive test data alone, 3) establish a correlation between process control and quality of the glass product by the end of FY 1991 so that a user of the technology can deliver canisters of vitrified high-level waste to a licensed federal repository without destructive examination, and 4) provide documentation of vitrification technology design and operation by the end of FY 1992.

This draft plan provided input to the efforts on the outline of the LFCM design manual discussed later in this section.

2.17 PLAN FOR DOCUMENTATION OF TRU WASTE TREATMENT - J. H. Westsik, Jr.

A plan has been prepared that outlines the development of technologies for treating transuranic wastes from the reprocessing of spent fuel. The selection of processes for treating TRU wastes was described in the TRU treatment strategy report (Ross et al. 1985). The documentation plan then identifies the needed technology testing and development, defines the relationships needed for use in designing and operating future treatment facilities, and establishes an approach for documenting the technology in an efficient format for future use. An 11-year program is defined that concludes in FY 1996 with complete documentation of development and testing of first-generation TRU waste treatment technology.

Typical TRU wastes that would be generated at fuel reprocessing and fabrication plants would include fuel hulls and assembly hardware, HEPA filters, general process trash, sampling and analytical wastes, failed equipment, and fluorinator solids. In the recommended treatment, all metals would be reduced in volume by melting, all combustibles would be incinerated, and all the residual noncombustible wastes would be cemented with the incinerator ash and off-gas scrubber solutions.

The documentation plan emphasizes the treatment processes of shredding, metal melting, incineration, and cementation. Associated with each treatment process are design elements which must be completed and documented. These include waste-form composition, feed systems to the process, the process

itself, off-gas treatment systems, and product handling and quality verification. The plan recognizes that the collection, inspection, transportation, and disposal of TRU wastes must also be considered.

2.18 WEST VALLEY DESIGN REPORT - W. L. Partain

PNL, through the Nuclear Waste Treatment Program, has designed and built two vitrification systems in the past 3 years. One is the pilot-scale radioactive melter installed in the B-cell of the 324 Building at Hanford. The second system is for the West Valley Demonstration Program being conducted by the West Valley Nuclear Services Company, a subsidiary of Westinghouse Electric Co. at West Valley, New York.

The overall design description for the B-cell Melter is contained in PNL-5393, Design Features of the Radioactive Liquid-Fed Ceramic Melter System. The similar design description of the West Valley Development Program vitrification system is being prepared for publication in March 1986. The report PNL-5780 is titled Design and Operating Features of the High-Level Waste Vitrification System for the West Valley Demonstration Project (Siemens 1986). PNL, working closely with representatives from WVNS, designed the principal components of the vitrification system:

- concentrator/feed make-up tank
- de-entrainer/demister unit for the concentrator tank
- air displacement slurry pump for slurry transfer to melter
- submerged bed scrubber for the melter off gas
- liquid-fed ceramic melter
- closed turntable for canister positioning.

These two design reports provide a valuable overview of the current status of melter technology. The melter design employed in the B-cell is based on the well-proven nonradioactive series of development melters built and operated at PNL. The WVDP melter extrapolates the technology of the development melters and incorporates a new cavity configuration and electrode arrangement.

2.19 LFCM DESIGN MANUAL - W. L. Partain

A principal product of the Nuclear Waste Treatment Program is the documentation of the technology for the vitrification of high-level nuclear waste. The NWTP is organized through the LFCM Vitrification Technology Testing and Documentation Plan, which is also described in this report. This plan identifies R&D activities and provides a timetable for the documentation tasks. An outline of the LFCM Design and Operations Manual was developed to provide a framework for the documentation activities. An annotated outline was developed for the chapter dealing with melter design since this is a key aspect of the total documentation effort.

The outline is to be updated continuously, with the objective of slowly developing a very detailed, annotated plan for the final manual. The chapter describing the melter design is now being drafted, ahead of the timetable in the Plan, as a test to see how well the R&D activities described in the Plan support the documentation activities.

Applicable technical reports are being identified and collected into a dedicated resource file to be used in the writing of the Manual.

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3.0 TECHNOLOGY TESTING

R. A. Brouns - Manager

3.1 OBJECTIVES

The final step in LFCM development is to establish a predictive capability for the process performance that allows users of the technology to design and operate efficiently and with a high degree of confidence in the product quality. This is achieved through numerical and empirical modeling using large-scale nonradioactive and radioactive testing to help guide and validate the modeling effort. Concentrated testing over the next 3 to 5 years is required to support this effort effectively.

The overall objective of this task is to provide the information needed from nonradioactive testing to 1) complete LFCM vitrification equipment development, 2) establish correlations of nonradioactive to radioactive LFCM equipment performance so that users of the technology that can predict full-scale radioactive equipment performance from nonradioactive test data alone, 3) establish a correlation of process control to glass product quality so that canisters of vitrified high-level waste can be delivered without destructive examination to a licensed federal repository, and 4) document design and operation vitrification technology to bring the technology to a well-documented close.

Specific FY 1985 objectives included the following:

1. Develop the capability to predict how two factors--feed tank designs and feed formulations--individually and synergistically affect the homogeneity of melter feed.
2. Complete verification and documentation of the model for melter electrode/tank geometry design.
3. Collect data on pilot-scale equipment and flowsheet performance for comparison with radioactive performance data.
4. To ensure that an appropriate off-gas treatment system can be specified, develop the capability to predict radionuclide concentrations

in the off gas as a function of feed composition, equipment design, and operating parameters and compare the predictions with off-gas radiological release limits.

5. Develop remote instrumentation for melter monitoring and control to allow safe, efficient melter operation.
6. Begin development of models that predict the relationship between equipment design and operation and the overall product quality so that product verification can be achieved without product sampling or destructive examination.
7. Begin the development of a canister fill/cool model that predicts the relationship between canister fill rate, geometry and glass properties, and the quality of the glass fill.
8. To maintain acceptable melting behavior, establish control methods and analytical procedures for melter feed chemistry.

3.2 INTRODUCTION

To ensure that waste management is not an obstacle in the further development of commercial reactors and nuclear fuel cycle closure, the Nuclear Waste Treatment Program is developing a base technology for treating high-level waste. The reference technology selected by DOE is the liquid-fed ceramic melter (LFCM) process, producing a borosilicate glass waste form. Development of the LFCM technology has been under way since the mid-1970s. Consequently, design and operation parameters for safe, efficient operations have been defined and successful design concepts identified.

The purpose of this task is to bring the technology to a well-documented conclusion by completing development of the process and product models. These models will allow potential users of nuclear waste treatment technology to efficiently design and operate a vitrification plant, confident in the quality of the waste form produced. Development activities consist largely of non-radioactive testing and of numerical modeling to establish correlations between nonradioactive and radioactive equipment performance, process control and glass

product quality, and laboratory-scale and production-scale performance. Coordinated pilot-scale nonradioactive and radioactive tests are used to establish these correlations and models at the confidence level needed to attain acceptance of the technology. Nonradioactive tests using a pilot-scale vitrification system have been completed with a variety of waste compositions and under various operating conditions to fully characterize the system's performance. The radioactive validation of these correlations is planned as part of the radioactive LFCM demonstration task.

3.3 SUMMARY

Major progress was made in FY 1985 towards meeting the task objectives. Summarized below are the highlights of this work. Sections that follow give details of specific activities.

- Technologies for treating LFCM off-gas were reviewed and a status report was prepared. The report helped to identify remaining technical issues and data needs in this area.
- Two major tests of the pilot-scale vitrification system were completed in FY 1985. One test used a high-cesium and high-strontium glass that will provide heat and radiation sources for the Federal Republic of Germany (FRG) repository test program. Nonradioactive isotopes of cesium and strontium were used for this test. Data from the nonradioactive experiment will be compared with the radioactive (RLFCM) test data when the actual source canisters are produced in FY 1986. The second test was performed with a simulated WV glass, and its data will also be correlated with future radioactive liquid-fed ceramic melter (RLFCM) data.
- Additional testing of analytical techniques was conducted for controlling the redox state of the melter feed. The Mossbauer spectrometer was selected as the preferred analytical technique, and both nonradioactive and radioactive glasses were used in the tests.

- Data on canister thermal history collected during production of non-radioactive pilot-scale ceramic melter (PSCM) canisters were analyzed and compared to computer-predicted cooling rates to validate the cooling model.
- Initial studies were conducted of melter residence time effects. Melter glasses of various residence times were compared to their measured durabilities.
- Physical modeling data from studies of melter convection and temperature were compared to predicted behavior using the TEMPEST computer code simulation.
- Several remote control instruments for the melter process were tested. A reference control scheme was adopted based on these studies.
- Bench-scale mixing tests were completed using conventional slurry preparation systems, and the design for a large-scale prototype was prepared.

3.4 FEED MAKEUP AND TRANSFER - Activity Leaders: M. E. Peterson, H. T. Blair
Major contributors: D. H. Mitchell, W. O. Heath, L. A. Bray, D. McCarthy

Feed preparation and transfer systems consist of the equipment used to contain and process the high-level liquid waste (HLLW) between the point of entry into a vitrification facility and the melter chamber. The equipment includes tanks, concentrators, agitators, pumps, process monitors, transfer lines, and the cooled melter feed nozzle. These systems also include the equipment used to batch the glass-forming additives and to convey them into the feed makeup tank for blending with the HLLW.

During FY 1985, specific activities concerning feed preparation and transfer systems included:

- Completion of a mixing study that developed mathematical models, analytical techniques, and scale-up methods that can be used to estimate

the significance of compositional, geometric, and kinematic changes on the degree of mixing in full-scale tanks for processing melter feed.

- Development of a large-scale melter feed tank design including the agitator.
- Demonstration of a slurry level and specific-gravity measuring system that will work in concentrated slurries.
- Evaluation of simulated waste to determine the effects of simulation variables on the rheological and melting properties of melter feeds made with the simulants.
- Investigation to determine what causes foaming, which leads to feed processing difficulties.

3.4.1 Evaluation of the Mixing of Melter Feed

The feed preparation system's ability to produce and maintain a homogeneous melter feed within compositional tolerances strongly affects process control and quality control of the LFCM process. The purposes of this mixing evaluation were 1) to provide a quantitative description of a feed-mixing system's performance in terms of measurable process variables and 2) to prepare a set of fabrication drawings for the construction of a large-scale mixing tank during FY 1986.

Six independent variables were selected for testing after an extensive literature review: 1) type of upper impeller, 2) impeller diameter, 3) impeller rotational speed, 4) use/absence of wall baffles, 5) use/absence of internal heat transfer coils, and 6) the type of melter feed slurry evaluated.

Two upper impeller designs were evaluated: a 45° pitch four-blade turbine impeller and a three-blade, high-efficiency turbine impeller. The lower impeller was a four-blade flat turbine that can act as a sweeper to keep solids from depositing on the tank bottom. The impellers are shown in Figure 3.1.

Because the impeller diameter has a large effect on the mixing in the tank, three impeller diameters were selected for testing: 9.53, 11.43, and

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FIGURE 3.1. Bench-Scale Impeller Arrangements

19.05 cm. These diameters yield ratios of impeller diameter to tank diameter (0.25, 0.33, 0.5, respectively) that are commonly used in slurry applications.

The impeller's rotational speed is the most critical parameter in the scale-up of bench-scale data. Therefore, four equally spaced rotational speeds were selected to bracket the well-mixed and the unmixed conditions. The 9.53- and 11.43-cm-dia impellers were tested at speeds of 50, 140, 230, and 320 rpm. The 19.05-cm-dia impeller was tested at speeds of 10, 23, 36, and 50 rpm.

Wall baffles are commonly used in mixing to eliminate vortexing and to direct the flow. Tests were conducted with and without wall baffles to determine their effect on the solids distribution in the tank.

The use/absence of heating/cooling coils may affect the distribution of solids in the mixing tank. The coil design evaluated was the bayonet assembly used in the Defense Waste Processing Facility (DWPF) slurry-mix evaporator tank. The coils were evaluated only with the 9.53- and 11.43-cm-dia impellers. Coils designed for the 19.05-cm-dia impeller would not fit into the bench-scale tank. The bench-scale mixing system used to perform this study is shown in Figure 3.2.

An important step in the testing was to evaluate the physical and rheological properties of the simulated melter feed slurries. The final independent variable was the type of melter feed slurry used. Two slurries, a commercial waste slurry and a defense waste slurry, were selected. The slurries were tailored to simulate the physical and chemical properties of the melter feeds expected at the Hanford Waste Vittrification Plant (HWVP) and West Valley (WV) facilities. The rheological properties displayed by the two simulated slurries allowed them to be classified as yield-pseudoplastic non-newtonian fluids. Mathematical models have been developed to characterize this behavior. These models were applied to actual laboratory and bench-scale data and used to predict the level of turbulence present in the bench-scale mixing tank during each test. The level of turbulence was correlated with the degree of mixing achieved.

The dependent variable was the distribution of solids in the mixing tank. Samples were withdrawn from six locations in the mixing tank during each run. The total solids content in these samples was evaluated; it was compared with that of a homogeneously mixed batch of slurry.

Mixing-tank studies showed the following: 1) the solids distribution in an agitated tank becomes more uniform as the rotational speed of the agitator increases, 2) HWVP melter feed is easier to keep homogeneous than WV melter feed, 3) the high-efficiency turbine impeller design and a standard 45° turbine produce similar mixing results, 4) impeller diameter is significant only at low rotational speeds, 5) baffles improve mixing only at low rotational speeds, and 6) heating/cooling coils reduce the degree of mixing at low rotational speeds. Predictive equations were developed to quantify the magnitude of these trends.

FIGURE 3.2. Bench-Scale Mixing System

The bench-scale predictive equations were scaled up to predict the performance that is likely to occur in a large-scale mixing system. Scale-up of the bench-scale data included an assessment of the level of power needed to maintain solids in a uniform suspension and an estimate of the power required to resuspend solids once they had settled. Detailed evaluations of large-scale mixing system designs for the full-scale vitrification plants at the DWPF located at the Savannah River (SR) Plant and the component test stand (CTS) located at the WV Plant were conducted using the HW and WV slurries. The mixing system for the DWPF was designed for a Bingham Plastic slurry with a yield stress of 15 N/m^2 and an insoluble solids content of 48 wt%. The mixing system for CTS was designed for a slurry very similar to the slurry used in these bench-scale tests. Mixing-system designs used in mining and metallurgical industrial applications were also evaluated.

To scale up the bench-scale data, the diameter of the large-scale must be selected. Once the diameter is selected, the large-scale system is designed to be geometrically similar to the bench-scale system. The large-scale tank, a vertical cylinder with a flat bottom, had a diameter of 2.8 m and a design slurry depth of 2.8 cm. A power level of less than 1 hp (which induces a bulk fluid velocity of 1.5 to 4.8 m/min) will be sufficient to maintain the solids in the HW and WV melter feeds in a uniform suspension ($\pm 1\%$ of the mean value of total solids). This unusually low power requirement (and bulk velocity) is due to the very slow settling rates exhibited by the simulated HW and WV slurries (0.45 and 0.60 cm/hr, respectively). The yield-stress exhibited by each slurry is primarily responsible for the slow settling velocity of the solids in the slurry.

In addition to maintaining solids in a uniform suspension, the large-scale mixer must be able to resuspend solids if they settle because of a power outage or other disturbance. The scale of agitation necessary to resuspend solids is higher than the value needed to maintain solids in suspension. Historically, bulk fluid velocities of about 15 m/min are specified for mixing applications where a uniform suspension of solids is required. Power levels ranging from 5.0 to 9.5 hp, depending on the mixing-system configuration, must be applied to HW and WV slurries to achieve a bulk velocity of 15 m/min.

One goal of this evaluation was to select a reference prototype mixing system for full-scale verification tests. After selection of the reference, fabrication drawings were prepared for a large-scale mixing-tank shell that incorporates the geometric features necessary to properly mix simulated HW and WV melter feed slurries. The selection criteria used to specify the large-scale tank shell design are described.

The large-scale mixing tank will be used to prepare simulated HW and WV melter feed slurries. The tank must be located in the vicinity of existing vitrification process equipment. A decision was made to locate the large-scale tank in the space now occupied by an existing tank in the research facility. The largest tank diameter that can fit in this location is 2.8 m. This dimension was chosen for the large-scale mixing tank shell and used in the scale-up.

The mixing tank must have sufficient height to contain the fluid being processed and provide the freeboard necessary to prevent inadvertent spills of the contents. Industrial practice is to use an L/T ratio of about 1 for solids suspension applications. The L/T for the DWPF mixing tank is 1.08, whereas the L/T ratio of the WV tank is 0.80. An L/T of 1 for this large-scale tank provides for a fluid level of 2.8 m. The total height of the mixing tank shell was set at 3.4 m to allow for 0.6 m of freeboard.

The large-scale mixing tank shell was designed to have a flat bottom profile to conform to industrial practice and to the design installed at WV. The DWPF mixing tank has a slightly sloping bottom to facilitate the removal of mercury that may settle out in the tank. Since HW and WV slurries contain very little mercury, a sloping bottom was considered unnecessary for the large-scale tank shell.

The large-scale tank shell was designed to contain four, equally spaced wall baffles. The baffles were sized according to industrial practice, with a B_w/T ratio of 0.083 and a B_g/T ratio of 0.014, and are removable.

The tank shell and its support structure were designed to withstand a total load of 25,300 kg. This load includes the fluid's weight in the tank, as

well as the weight of the tank cover, agitator, slurry pump, and other auxiliary equipment that the tank shell must support. The tank wall thickness needed to support this load was calculated to be 0.6 cm.

The material of construction specified for all tank components was 300 series stainless steel.

3.4.2 Evaluation of a System for Measuring Tank Level and Specific Gravity

A system for tank-level and specific-gravity measurement was evaluated for application in concentrated HLLW processing tanks. The system operates on the same principle as a pneumatic bubbler tube level-measuring system does. The unique components of the system are the Holledge® metallic diaphragm sensors across which the pressure differential is measured. The diaphragm sensors prevent the air in the system from contacting the slurry, a problem that leads to drying of the slurry and plugging in conventional bubbler-type systems. The sensors integrated with the signal converters are shown in Figure 3.3.

The metal diaphragm sensors were exposed to agitated simulated melter feed slurry for 5 months with no visible damage to the diaphragm. Precisions of greater than 99% with a 95% confidence level were observed. Bias of both specific-gravity and level measurements existed. Use of sensors with factory calibrations and a microprocessor to account for nonlinearity can reduce the bias. The statistical evaluation of the system was affected by leakage of simulated waste into one sensor and contamination of the same sensor with metal filings. For the hot-cell application, all-welded sensor construction is recommended to prevent leakage, and special care in assembly is necessary to keep foreign materials out of the sensors.

3.4.3 Evaluation of Simulated Waste

Studies to develop the technology for vitrifying high-level nuclear waste must be performed with nonradioactive simulations of the wastes. A study was performed to evaluate the effects that the preparation of a simulated waste has on the physical properties of the simulation. Also of interest was how the nature of the simulation affects processing equipment tests and melting behavior.

®Holledge Ltd., Crawley, England.

FIGURE 3.3. Holledge Sensors Integrated with Differential Pressure Cells and Air Supply

A simulated high-fission-product waste was formulated based on a literature review of the projected wastes and their insoluble dissolver residues. Simulated nitrated and formated feeds for the WV vitrification system were also prepared by acidifying simulated plutonium and uranium extraction (PUREX)

sludge (Tank 8D-2) and Thorex acid (Tank 8D-4) wastes with nitric and formic acids. Glass-forming materials and ground zeolite were added to these simulated wastes to complete the melter feeds, which were then tested for viscosity and solids content. Preliminary melt rate studies were also done using several of these feeds. A comparison was made between the nitrated feeds made by acidifying simulations made from hydroxides and those made directly from metal nitrates that are used for current melter trials.

The significant results of this study are as follows:

- The rheology of WV feeds prepared by acidifying simulated hydroxide sludge was considerably different than that of the simulated feeds prepared from metal nitrate chemicals for current melter trials. The feeds prepared from hydroxides had higher viscosities (two to ten times) and smaller volumes of settled solids.
- Crucible melt rate tests showed that the fully nitrated WV feed simulations prepared for this study melted at the same rate as those prepared from metal nitrates for current melter trials despite the rheological differences of the feeds. Partially nitrated feeds melted at reduced but still acceptable rates. The formatted feeds melted with about the same behavior as the fully nitrated feeds; however, no attempts were made to optimize melting behavior.
- The rheology of WV formatted simulated feeds was very similar to that of feeds prepared from hydroxide sludge with no addition of nitric acid. This feed had relatively high viscosity and a small volume of settled solids that were easily resuspended.
- The settled solids content of simulated WV nitrated sludge made from hydroxide sludge was a function of nitric acid addition. The total settled solids were at a minimum when the acid was added at the stoichiometric requirement for complete nitration of the simulated waste. Further nitric acid addition increased the solids content of the simulation.
- The high nitrate (3.7 M NO_3^-) feed showed poor melting behavior as compared with the WV feed made from nitrate chemicals.

- The simulated high-fission-product melter feed produced an acceptable viscosity of ~6 cP with easily resuspended solids.

3.4.4 Investigation of Foaming in Simulated HLLW Melter Feeds

Experiments were performed to increase understanding of foaming behavior in melter feeds. Foaming occurs whenever air or other gases are entrained in melter feeds during air-lifting operations, vigorous agitation, etc. In most melter feeds, entrained air is spontaneously disengaged once mixing or air-lifting ceases, but certain feeds form stable foams. Uncontrolled foaming in melter feeds must be avoided because it seriously impedes waste processing.

A simulated high-fission-product melter feed, which consistently foams, was selected as a basis for study. The two parameters known to most strongly influence the formation of foam are surface tension and bulk viscosity. The approach to determine the causes of foaming in melter feeds was:

- Determine what species or impurities in high-fission-product feed are surface-active and to what extent they lower surface tension.
- Determine what species in high-fission-product feeds raise or lower feed viscosity.
- Determine how the parameters of surface tension and viscosity relate to foaming of feed and how these factors can be controlled to prevent it.

In the experiment, surface tension was measured for five different organic and inorganic high-fission-product feed constituents. The results are given in Table 3.1. Measurements were also made on six West Valley Support Task (WVST) feeds that do not form stable foams (Table 3.2).

The data in Tables 3.1 and 3.2 strongly suggest two things: 1) that foaming of feed can be correlated with surface tension and 2) that tributyl phosphate (TBP) is the most strongly surface-active constituent in high-fission-product feed and therefore is the primary cause of surface tension reduction. Further, the non-foaming WV feeds (and waste concentrate) had surface tensions varying from 65.9 to 77.1 dyne/cm as compared with 38.3 dyne/cm for the waste concentrate used to prepare high-fission-product feeds.

TABLE 3.1. Surface Tension of Miscellaneous Aqueous Solutions

<u>Samples</u>	<u>Surface Tension, dyne/cm</u>
Pure Water	72.14 ^(a)
BRET Waste Concentrate	38.3
TBP (0.13 g/L)	37.3
Na ₂ B ₄ O ₇ • 10H ₂ O (65.75 g/L)	70.3
Al (NO ₃) ₃ • 9H ₂ O (167.86 g/L)	75.7
NaNO ₃ (54.73 g/L)	73.4
NaDBP (1.55 g/L)	60.2

(a) Typical literature value.

TABLE 3.2. Surface Tension of Non-Foaming Melter Feeds

<u>Samples</u>	<u>Surface Tension, dyne/cm</u>
WVSP ECM 85-10	73.5
WVSP ECM 85-11	72.8
WVSP ECM 85-12	72.8
WVSP ECM 85-13	77.1
WVSP ECM 85-14	66.1
WVSP ECM 85-15	65.9
WVSP Waste Concentrate	76.3

To evaluate viscosity, various compounds were added to the high-fission-product waste concentrate to form various concentrations of feeds. Their viscosities were measured; results appear in Table 3.3.

To determine how the measured viscosity values correlate with foaming and stability of the foam, a method and apparatus (Figure 3.4) were developed for quantifying foam behavior. The approach is to continuously measure the electrical conductivity of a freshly prepared foam as it decays. This method allows foam behavior to be quantified in terms of two parameters: foaminess

TABLE 3.3. Viscosity of BRET-Based Feeds

Feeds	Bulk Viscosity, cP ^(a)	Temp, °C	Yield Viscosity, cP ^(b)
1F	3.2	21.4	6,240
2F	37.3	21.5	655,200
3F	6.7	21.6	22,776
4F	21.1	21.8	102,960
5F	20.0	21.8	257,400
6F	19.6	21.8	154,752
7F	13.3	25.6	79,872
			217,776

- (a) All measurements with capped-off Brookfield UL adapter, adapter, UL Spindle, 100 rpm, Brookfield RVDT Viscometer.
- (b) Measurements made with T-Bar spindle T-F on helipath stand at 25.2°C. All feeds were measured at 1.5 rpm except 2F and 7F, which were measured at 0.6 rpm.

and foam stability. Foaminess, expressed as the volumetric ratio of gas-to-liquid in a foam, $V_{G/L}$, is a measure of how much foam a liquid initially produces during sparging. Foam stability can be related to the initial rate of increase in $V_{G/L}$. With time, film drainage occurs in which liquid drains from the foam, causing the foam to decay and break. The rate of this decay was characterized from the plotted conductivity data by estimating the slope of the conductivity plot, dv , at the point where foam production by air sparging stopped and decay began. The data were fitted to literature-derived decay expressions, resulting in foam decay coefficients that were all in the same range as decay coefficients presented in the literature for various surfactant foams. Table 3.4 summarizes values of $V_{G/L}$ and dv/dt measured for the high-fission-product feed matrix. Based on this initial study, it was found that both feed surface tension and viscosity are the parameters that determine whether a feed foams.

FIGURE 3.4. Apparatus for Quantifying Foam Behavior in Melter Feeds

Specific conclusions of this investigation are:

1. Feeds must have a low surface tension (40 to 50 dyne/cm or less) to foam much. Feeds with higher surface tensions do not form stable foams.
2. Of the constituents in BRET feed, tributyl phosphate shows the greatest surface activity and is the primary cause of BRET waste's low surface tension.

TABLE 3.4. Foaminess and Foam Stability Data

Sample	a/b (a)	V _{G/L}	$\frac{dn}{dt}$ (mmho/sec)
REF	36.40	0.845	-10.53
1F	--(b)	0.780	-12.35
2F	37.29	0.855	-1.89
3F	36.63	0.851	-2.77
4F	37.59	0.854	-9.89
5F	36.96	0.777	-1.55
6F	36.27	0.835	-6.52
7F	36.86	0.855	-10.31

(a) Feed 1F produced a foam too unstable to estimate a/b.

(b) Coefficients for foam decay expression:
 $V_0 + \Delta V_L = (2a/b)(1-(bt+1)^{-1/2})$.

3.5 NONRADIOACTIVE CERAMIC MELTER TESTING - Activity Leader: J. M. Perez, Jr.

Major Contributors: L. A. Chick, M. E. Peterson, B. M. Wise

Current vitrification experiments are under way using laboratory-, engineering- and pilot-scale ceramic melters to: 1) complete development of vitrification hardware; 2) provide the information necessary to establish correlations between nonradioactive and radioactive equipment performance, process control and glass product quality, and laboratory-scale and production-scale performance; and 3) establish an extensive data base covering design and operations in order to support future licensing activities, and thus encourage private commercialization of this technology.

Two major nonradioactive PSCM experiments, designed as precursors to operations in the RLFCM, were conducted in FY 1985. The goal was to verify processability of the flowsheets and to allow direct comparison of test data. In this manner, operational differences between radioactive and simulated melter feed compositions can be determined. Each experiment used prototypic equipment such as the air-displacement slurry feed pump, the submerged bed and venturi primary off-gas scrubbers, and the high-efficiency mist eliminator and

hydrosonic scrubbers. As much as possible, experiments were designed to meet the data requirements of other NWTP research subtasks as well as the technical needs of the WVST and the HWVP. Many of the specific test results are reported in other sections of this report. The results of the FRG glass development, the melter performance, and the specific feed processing characteristics are reported in this section.

The first pilot-scale experiment, performed during March and April 1985, was conducted under the NWT Program for the FRG. Its purpose was to provide support for the RLFCM production of canisters containing high heat and radioactive dose loadings. For this experiment, a feed composition containing high amounts of cesium and strontium was developed and demonstrated. To support this experiment, two ECM experiments were conducted initially to test engineering procedures and candidate flowsheets.

The second experiment, during May and June 1985, was conducted to characterize the processing behavior of the simulated WV waste glass formulation to confirm its acceptability for use in the RLFCM. The test was performed also to meet numerous other objectives, which included defining the performance of the melter, off-gas, feed, and instrumentation equipment and establishing relationships between process controls and product quality.

3.5.1 FRG Glass Development

The development of glass for the FRG was challenging because it had to incorporate much higher concentrations of cesium and strontium than earlier glasses. To take advantage of previous work, the basic glass composition was modeled after the then-current WV glass composition. Obvious changes were made to account for the high cesium and strontium contents in the waste fraction of the glass. To conserve the use of radioactive cesium and strontium in the RLFCM operations, the following procedure was developed to quickly convert the RLFCM glass tank contents to the target cesium and strontium levels: First flush the melter with a glass composition that had acceptable physical properties (i.e., suitably low melting temperature and acceptable viscosity and electrical conductivity) but did not contain cesium and strontium. Then reduce the glass tank glass inventory by one-third. To the residual glass add a composition containing three times the target cesium and strontium concentrations.

Once the feed was added, the resulting glass composition would possess the proper cesium and strontium concentrations, but also have acceptable physical properties. As a result of these special processing procedures, three compositions needed to be developed. Table 3.5 gives the compositions of the anticipated waste streams and the final glass composition (FRG-8), the flush glass, and the high cesium and strontium feed compositions (spike feed), respectively.

TABLE 3.5. Oxide Formulations, wt%, of Cesium and Strontium Waste Compositions, FRG-8, Flush Glass and Spike Feed. Chick 1/30/85.

Oxide	Cs Waste Stream	Sr Waste Stream	FRG-8	Flush Glass	Spike Feed
SiO ₂	1.05	0.00	45.00	53.20	24.45
P ₂ O ₃	0.00	0.00	15.00	22.00	1.88
Na ₂ O	25.08	60.52	12.00	10.80	21.16
CaO	4.41	1.29	0.81	0.00	2.02
Al ₂ O ₃	0.47	0.15	2.40	0.00	6.86
Fe ₂ O ₃	2.17	0.30	10.08	14.00	2.16
PaO	7.12	3.03	1.20	0.00	3.44
MsO	2.98	0.12	0.53	0.00	1.23
Cs ₂ O	40.67	0.00	5.78	0.00	16.51
SrO	0.00	30.25	1.92	0.00	5.49
MnO ₂	4.75	1.51	0.77	0.00	2.20
ZrO ₂	0.47	0.00	0.07	0.00	0.19
PbO	4.75	0.30	0.69	0.00	1.98
Nd ₂ O ₃	1.76	0.61	1.10	0.00	3.14
La ₂ O ₃	2.27	1.21	1.20	0.00	3.43
CeO ₂	1.80	0.61	0.29	0.00	0.84
Cr ₂ O ₃	0.00	0.03	0.70	0.00	2.00
NiO	0.00	0.00	0.30	0.00	0.86
CdO	0.17	0.06	0.03	0.00	0.08
ZnO	0.17	0.00	0.02	0.00	0.07
P ₂ O ₅	0.00	0.00	0.00	0.00	0.00
Total	100.09	99.99	100.00	100.00	99.99

3.5.2 Experimental Ceramic Melter Testing

The experimental ceramic melter (ECM) is a small test melter used to perform preliminary scoping studies to evaluate slurry processing characteristics; it is shown as a diagram in Figure 3.5 and as a photograph in Figure 6.2. The melt cavity has an exposed melt surface of 0.054 m^2 and an operating depth of 15.2 cm. The resulting glass inventory is about 8.2 L. Under normal operating

FIGURE 3.5. Experimental-Scale Ceramic Melter

conditions, the glass melt is maintained at a bulk glass temperature of 1150°C. Slurry processing rates of up to 4 L/hr can be achieved with some slurries. During operation, glass is periodically transferred from the melt tank to a receiving canister via a glass riser and overflow trough. Glass enters the riser through a port in the side wall of the melt tank floor level. Glass discharge is assisted by an air-lift lance in the riser that bubbles air into the riser glass. The difference in apparent density of the glass/air mixture to the glass in the melt tank causes the glass in the riser to move up the riser and into the pour trough. The glass flows down the pour trough and into the receiving canister.

ECM testing consisted of evaluating a melter tank flush procedure and evaluating two slurry compositions. An objective of the nonradioactive testing was to demonstrate a procedure to conserve the amount of cesium and strontium required to bring the melt tank contents to the target concentrations. The melter was initially flushed with a chemical batch composition designed to have acceptable glass physical properties both while in the melter alone and when mixed with a composition containing a high concentration of the cesium and strontium waste streams. Physical properties include viscosity, electrical conductivity, and meltability. With this procedure, the RLFCM melt-tank glass inventory could be brought up to the target cesium and strontium concentrations without consuming cesium and strontium during repetitive flushings.

Following the flushing of the ECM melt tank, the tank volume was lowered to 67% capacity. A slurry of the composition shown in Table 3.5 was then metered to the melter. The concentrated slurry, containing about three times the normal cesium and strontium waste fractions, was fed to the melter over a 6.5-hr period.

Two slurry compositions were then fed to the ECM in two separate experiments (Tables 3.6 and 3.7). The compositions differed only in that zeolite ion-exchange material was present in one slurry to study the effect of zeolite on processability. The nonzeolite slurry contained additional unreacted chemicals so that the overall compositions remained identical. Sugar was added to all three feed slurries as a reductant to maintain the glass melt redox within a prescribed range as determined by the ferrous/ferric ion ratio. A ferrous/

TABLE 3.6. Nonzeolite Slurry Composition

Compound	g/L	Assumed Oxide	
		Compound	g/L
$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	61.81	Al_2O_3	8.40
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	178.51	Fe_2O_3	35.28
NaNO_3	71.13	Na_2O	42.00
$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	90.54	B_2O_3	52.50
H_3BO_3	36.26		
$\text{Ba}(\text{NO}_3)_2$	7.75	BaO	4.55
$\text{Ca}(\text{NO}_3)_2$	11.94	CaO	2.84
$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	11.80	MgO	1.86
CsNO_3	29.38	Cs_2O	20.23
$\text{Sr}(\text{NO}_3)_2$	13.72	SrO	6.72
$\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	7.52	MnO_2	2.70
$\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	0.53	ZrO_2	0.24
$\text{Pb}(\text{NO}_3)_2$	3.58	PbO	2.42
$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	12.90	Cr_2O_3	2.45
$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	4.09	NiO	1.05
$\text{Re}(\text{NO}_3)_3$	6.62	CeO_2	1.02
$\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	9.75	Nd_2O_3	3.74
$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	9.91	La_2O_3	4.20
		Pr_6O_{11}	0.11
SiO_2	157.50	SiO_2	157.50
Na_2SO_4	3.10	SO_3	1.75
Sugar	85.00		
		Total	351.56

ferric ratio of 0.1 to 0.3 was attempted. Off-gas sampling was conducted during the experiments to measure particulate and volatility losses.

These experiments are summarized in Table 3.8. All three slurry compositions melted well. No differences were noted in processing the nonzeolite versus the zeolite slurries. The cold cap was rigid but thin and melted readily. In all cases, the cold cap disappeared in less than 5 min, and within 1 hr the glass surface was clean of any residue.

TABLE 3.7. Zeolite Slurry Composition

Compound	g/L	Assumed Oxide	
		Compound	g/L
$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	15.45	Al_2O_3	2.10
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	189.49	Fe_2O_3	33.88
NaNO_3	57.60	Na_2O	39.20
$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	90.75	B_2O_3	52.50
H_3BO_3	32.55		
$\text{Ba}(\text{NO}_3)_2$	8.35	BaO	4.20
$\text{Ca}(\text{NO}_3)_2$	11.79	CaO	2.49
$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	13.36	MgO	1.51
CsNO_3	29.38	Cs_2O	20.23
$\text{Sr}(\text{NO}_3)_2$	13.72	SrO	6.72
$\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	7.52	MnO_2	2.70
$\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	0.53	ZrO_2	0.24
$\text{Pb}(\text{NO}_3)_2$	3.58	PbO	2.42
$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	12.90	Cr_2O_3	2.45
$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	4.09	NiO	1.05
$\text{Re}(\text{NO}_3)_3$	6.62	CeO_2	1.02
$\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	9.75	Nd_2O_3	3.74
$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	9.91	La_2O_3	4.20
		Pr_6O_{11}	0.11
SiO	129.85	SiO_2	133.35
Zeolite IE-96	35.70	Na_2O	2.80
		SiO_2	24.15
		CaO	0.35
		Al_2O_3	6.30
		Fe_2O_3	1.40
		BaO	0.35
		MgO	0.35
Na_2SO_4	3.10	SO_3	<u>1.75</u>
Sugar	70.00		
		Total	351.56

TABLE 3.8. Operating Summary of ECM-85-4 and ECM-85-5

	ECM-85-4		ECM-85-5
	Cs, Sr Spike	Nonzeolite	Zeolite
Total liters	25	140	94
Time, hr	6.5	40.3	27.8
Percent of time	100	100	100
Average feed rate, L/L	3.9	3.4	3.5
Average cold-cap coverage, %	70	60	70
Glass production calculation, kg	--	49	32.9
Glass temperature, °C	1115 to 1133	1113 to 1195	1126 to 1190
Power, kW	5.8 to 7.2	5.8 to 7.1	5.8 to 7.2
Resistance, ohms	0.61 to 0.73	0.49 to 0.75	0.61 to 0.91
Off-gas temperature, °C	210 to 290	185 to 330	195 to 295

Table 3.9 shows the off-gas DFs for boron and cesium; DFs are the ratio of the amount of a material entering a system to that evolved from it as an off-gas constituent. The boron DFs were similar to previous test data on boron volatility. The cesium DFs were higher than expected, indicating lower losses from the glass melt. As a result of these findings, boron and cesium concentrations were increased above the glass target levels during the upcoming PSCM experiment to account for losses via volatility.

A sample from the first glass poured after the cesium spike addition indicated that the melt tank had not mixed completely although 2 hr had been allowed for mixing before feeding the nonzeolite slurry. As a result, a longer mixing period was recommended for the PSCM experiment. Analysis of glass samples after the ECM experiment showed that none of the samples had a ferrous/ferric ratio greater than 0.001. Despite the under-reduced conditions of the melt, no foaming occurred, indicating a stable glass melt. No crystals were present in polished sections of the glass that were examined.

3.5.3 Pilot-Scale Ceramic Melter Testing

FRG PSCM-20 Experiment

A 10-day PSCM experiment (PSCM-20) was completed in April 1985 for the FRG under the NWTP. The PSCM is PNL's largest operating nonradioactive melter

TABLE 3.9. Boron and Cesium Decontamination Factors

<u>Feed Type</u>	<u>Boron DF</u>	<u>Cesium DF</u>
Cs, Sr spike	8	32
Cs, Sr spike	12	66
Average	10	49
Nonzeolite	56	160
Nonzeolite	47	100
Nonzeolite	22	170
Nonzeolite	21	150
Average	37	145
Zeolite	39	260
Zeolite	38	330
Zeolite	38	190
Average	38	260

system, with an exposed melt surface of 0.73 m^2 , an operating depth of 42 cm, and a resulting glass inventory of 280 L. Figure 3.6 is a side view of the melter. Temperatures in the PSCM are monitored with a thermocouple bundle placed inside a 2.5-cm Inconel® thermowell that is placed directly in the molten glass. A Hewlett Packard (HP) 9800 series computer (Figure 3.7) is used to control the melter power and thus keep the glass bulk temperature at 1150°C . The HP computer is used also as the melter data acquisition system. Temperatures, power, glass resistance, and other melter operating data are recorded every 2 min throughout each test allowing on-line data analysis. The primary objectives of the experiment were to do the following:

- Verify acceptable melting behavior of a waste glass composition containing high levels of cesium and strontium.
- Define the melter operating parameters and procedures.
- Determine pilot-scale cesium volatility and off-gas system equipment performance.

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8505760-2cn

FIGURE 3.6. Side View of Pilot-Scale Ceramic Melter

8505760-3cn

FIGURE 3.7. PSCM Computer System for I/O Control and Data Acquisition

- Determine a filling and cooling scheme that will produce a glass product with acceptable voids and glass fracture.

Results from off-gas studies and analysis of the eight test canisters filled during the experiment are discussed elsewhere in this report. Where appropriate, the test results are compared with results obtained from the two small-scale ECM tests that were conducted earlier to confirm the glass selection. Numerous operating parameters and objectives were defined by the information required for RLFCM operation.

In an attempt to avoid melting problems, the FRG canister glass was modeled after typical U.S. waste glasses with known processing behavior. The reference glass selected was an interim WV waste glass composition that included 10 wt% zeolite ion-exchange resin. The major difference between the designed glass composition (FRG-8) and the interim WV composition was the high levels of cesium and strontium and the lack of phosphate in the FRG-8 composition. Phosphate was eliminated to ensure that insoluble alkaline earth phosphate phases would not separate from the melt. Sugar was added to the slurries to reduce the glass melt and minimize the potential for melt foaming problems.

For efficient use of the radioactive cesium and strontium during production of the actual radioactive canisters, the experiment was also designed to demonstrate a means to achieve target levels of cesium and strontium in the first canister filled. To accomplish this, a procedure was developed that reduced the melter glass inventory to the extent that was easily achievable (about two-thirds full); and a slurry containing about three times the nominal cesium and strontium waste concentrations was fed to the melter until the normal operating level was reached. This slurry is designated the spike feed. Glass sampling to define the mixing time and off-gas sampling to determine the losses of cesium and strontium were conducted during this phase of the experiment.

During the FRG canister filling, the average feed rate was 21 L/hr. This rate was selected to duplicate the expected RLFCM processing rate. At other periods, the feed rate was increased to determine the maximum stable feed rate (per unit area) and further characterize off-gas emissions. The off-gas flow

was treated with an ejector venturi scrubber and a high-efficiency mist eliminator to duplicate the system that will be used during the radioactive production run.

Spiked Feed Processing Results. With one-third of the glass removed from the melter, the spiked feed was added until the normal melter operating level (at a melter vacuum of 10-15 cm water) was achieved and the tank inventory contained cesium and strontium levels representative of steady-state feeding. About 830 L of slurry was fed to the melter over a 22-hr period at an average rate of 34 L/hr (45 L/hr-m^2). Processing was stable with 70 to 80% cold-cap coverage. Based on these results, the average stable feed rate expected in the RLFCM is 23 L/hr--25% lower than predicted from ECM results, but still considered acceptable. The glass melt was stable with no foaming. A thin cold cap over the glass surface prevailed throughout the experiment. Little or no active venting was observed. The cold cap melted completely in about 50 min after feeding was stopped.

Analytical results of glass core samples taken of the melt tank after the addition of spiked feed showed that the glass tank was mixed and homogeneous after only 8 hr of idling. Therefore, convection bubblers to enhance mixing are not considered necessary.

FRG-8 Feed Processing Results. About 4750 L of slurry was fed to the melter, producing 1700 kg of glass over a 218-hr period. The maximum stable feed rate achieved during the first 24 hr was 32 L/hr (43 L/hr-m^2). Cold-cap coverage was maintained at 70 to 80%. Therefore, the RLFCM can expect to achieve a stable feed rate of 21 L/hr. Although this feed rate is 25% lower than predicted based on ECM results, it is still considered acceptable. Higher feed rates are considered possible, however, because of the thin cold-cap coverage.

No significant crystallization was seen in the glass samples. The eight FRG canisters were filled at an average slurry feed rate of 21 L/hr with a cold-cap coverage of about 50%. At both the 50% cold-cap coverage and 70 to 80% coverage, the glass melt was stable and little venting was observed through the 0.6- to 1.25-cm-thick cold cap.

Two sugar levels (90 g/L and 70 g/L) were used in the experiment to obtain reducing melt conditions as indicated by product glass ferrous/ferric ratios greater than zero. At 70 g/L, the ferrous/ferric ratio was 0.01; the ferrous/ferric ratio of 0.25 achieved at the 90 g/L sugar loading is within the range recommended in previous laboratory work to ensure a stable glass melt (0.1 to 0.3). Recent melter tests have shown that higher processing rates and stable glass melts can be achieved under less reducing conditions. Because no glass foaming occurred in either case, it is recommended that RLFCM operations use the lower sugar level. The variation in sugar level did not alter the processing rates or observed cold cap behavior, however. The maximum average feed rate during the low sugar period was 31 L/hr (41 L/hr-m²) with 70 to 80% coverage.

Determination of Cesium Volatility. A major objective of PSCM-20 was to determine the extent of cesium volatility from the glass to the off gas. Steady-state mass balance calculations were performed based on the results of analyses of feed, glass, and off gas. Samples taken from the melter tank after the addition of spiked feed, indicated that the canister-filling segment of the experiment was started with the concentration of cesium oxide in the melt tank 0.88 wt% below the target of 5.98 wt%.

The cesium oxide concentration in the first glass poured from the melter and in core samples taken from the second test canister had significantly decreased to a concentration of 4.7 wt%. This indicates that 21% of the total cesium oxide put into the melter was lost before the first glass was poured. The melter was in an idling mode for 5 days prior to feeding the FRG-8 composition. Losses of cesium oxide during idling account for the lower concentration of cesium oxide in the melt tank after the addition of spike feed and prior to feeding the FRG-8. During steady-state operation, the cesium concentration was 0.8 wt% less than target. This is a loss of 13% of the total cesium oxide put into the melter. Based on the mass-balance data, a conservative recommendation would be to add 15% more cesium oxide to the melter to account for volatility during steady-state conditions.

NWTP PSCM-21 Experiment. A pilot-scale melter test for the NWTP was conducted in May and June 1985. A simulated, WV feed was used for the test. The

simulated feed represented the WV alkaline PUREX sludge (Tank 8D-2) combined with the acidic Thorex waste (Tank 8D-4) and the IONSIV® IE-96 zeolite used to decontaminate the PUREX supernatant. The resulting glass formulation, designated WV205, consisted of ~10 wt% zeolite and ~23 wt% waste oxides with the remainder coming from raw chemical glass-formers. Sodium formate was used as a glass-former for redox control. Sugar was added at 19 g/L during part of the run to further reduce the melt.

An important objective of the run, to demonstrate acceptable processing behavior of the WV205 glass formulation, was met. The formulation used sodium formate as a glass-former to aid in attaining a reduced redox condition. Testing was conducted with and without an additional 19 g/L sugar reductant. Table 3.10 summarizes the PSCM-21 operating data. A simplified mass balance and feed makeup for WV205-type feed are shown in Table 3.11.

TABLE 3.10. PSCM Operating Data

Duration:	295 hr
Unplanned Downtime:	13.6 hr
Planned Downtime:	10.4 hr
Efficiency: ^(a)	95.2%
Maximum Stable Feed Rate:	
With Sugar:	~37 L/hr
Without Sugar:	~52 L/hr
Average Feed Rates Over Entire Test Periods:	
First 5 days with sugar:	30.0 L/hr
Second 5 days without sugar:	35.7 L/hr
Last 3 days with sugar:	37.5 L/hr ^(b)
Bulk Glass Temperature:	1150-1190°C ^(c)
Total Feed Processed:	9050 L
Total Glass Produced: ^(d)	3170 kg

$$(a) \text{ Efficiency} = 100 \left[1 - \left(\frac{\text{Unplanned Downtime}}{\text{Duration} - \text{Planned Downtime}} \right) \right]$$

(b) This period aimed largely at obtaining overfeeding.

(c) Temperatures were within range greater than 90% of the run.

(d) Calculated, assuming 350 g oxide/L feed.

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TABLE 3.11. WV205 Glass/Feed Composition

Compound	g/L	Assumed Oxide	
Compound		Compound	g/L
<u>Waste Chemicals</u>		<u>Waste + Formers</u>	
Fe (NO ₃) ₃ • 9H ₂ O	11.80	Fe ₂ O ₃	40.7
Fe (OH) ₃	36.75	P ₂ O ₅	8.83
Fe PO ₄ • 2H ₂ O	22.98	Na ₂ O	35.87
Na NO ₃	6.22	Cr ₂ O ₃	0.76
NaOH	0.16	Cs ₂ O	0.34
Cr(NO ₃) ₃ • 9H ₂ O	0.90	Ru ₂ O	0.27
Cr(OH) ₃	0.79	ZrO ₂	10.93
Cs NO ₃	0.46	MnO ₂	6.04
RuO ₂	0.27	NiO	2.43
ZrO(NO ₃) ₂ • 2H ₂ O	23.42	RE ₂ O ₃	0.41
Mn(NO ₃) ₂ • 4H ₂ O	17.23	Y ₂ O ₃	0.06
Ni(NO ₃) ₂ • 6H ₂ O	3.11	Al ₂ O ₃	5.55
Ni(OH) ₂	1.99	K ₂ O	12.28
Rare Earth (OH) ₃	0.23	BaO	0.19
Y(OH) ₃	0.04	B ₂ O ₃	34.86
Al(NO ₃) ₃ • 9H ₂ O	15.65	SO ₃	0.46
Al(OH) ₃	5.14	SrO	0.10
KNO ₃	0.54	CeO ₂	0.58
Ba(OH) ₂	0.21	CaO	1.70
Na ₂ SO ₄	2.49	MgO	4.04
Sr(OH) ₂	0.11	Li ₂ O	10.68
Ce(OH) ₃	0.63	TiO ₂	3.38
Ca(OH) ₂	2.23	SiO ₂	134.76
<u>Glass-Former Chemicals</u>		<u>Zeolite</u>	
Mg(NO ₃) ₂ • 6H ₂ O	25.69	Fe ₂ O ₃	1.36
Na ₂ C ₂ O ₄	36.44	Na ₂ O	2.73
Na ₂ B ₄ O ₇ • 10H ₂ O	100.13	Al ₂ O ₃	6.05
Li ₂ CO ₃	26.39	BaO	0.03
TiO ₂	3.38	SrO	0.01
SiO ₂	134.76	CaO	0.43
KNO ₃	25.85	SiO ₂	23.45
<u>Others</u>		MgO	0.27
Zeolite IE-96	39.18	TiO ₂	0.01
HNO ₃	8.82	Total	350
NaCl	0.11		
Sugar	19.0		

The experiment was divided into three parts. The initial 5-day period was conducted with sugar added at 19 g/L to achieve reduced glass melt conditions. The second 5-day period processed feed without the sugar additive to evaluate process stability under oxidized glass melt conditions. The final 3-day period was carried out with the sugar level restored. Maximum achievable feed rate was shown to depend upon the addition of sugar. Feed containing sugar had a maximum processing rate 30 to 40% lower than feed without sugar. Cold-cap behavior was similar with both feeds. The cap was thin (2.5 to 5 cm) and flexible; however, the percent coverage was much greater with sugar than without. The sugar-containing feed did process at higher rates during the last 3 days of the experiment than during the first 5; however, this last 3-day period aimed largely at analyzing overfeeding conditions.

The accumulation of secondary phases such as Na_2SO_4 or Ca-RE-PO_4 crystals was minimal during the run. Insoluble secondary phase formation, occurring during the processing of WV compositions, has been the focus of much work within the WVST this fiscal year. The phase formation is related to the presence of phosphate, calcium, and rare earths at concentrations above solubility limits for the glass under reducing conditions. During PSCM-21, the glass surface tended to have a mottled appearance typical of reduced WV glass melt. This mottled surface was less apparent when the no-sugar feed was used. Scanning electron microscope (SEM) analysis of melt surface samples taken after periods of sugar and no-sugar feeding showed that the main difference between samples appears to be the size of the crystals present. Crystals found in the sugar feed were as much as 10 to 15 times larger than with no-sugar feed. The accumulation of these crystals in the cold cap region appears to be the cause of the lower processing rate achievable with feed containing sugar.

Four foaming incidents occurred during the no-sugar portion of the run at ~1500 on 6/6/85, ~0600 on 6/7/85 and at ~1100 and ~1730 on 6/8/85. These episodes were caused by feed stoppages that led to rapid increases in the glass melt temperature when electrode power to the melter was not lowered sufficiently. When the electrode power was reduced to zero during feed stoppages, foaming was not observed. With the no-sugar feed, foaming incidents could probably be eliminated entirely if the proper glass-temperature control logic

was used. In general, the melting behavior of the WV205-type feed was excellent, much improved over the WV182 feed formulation tested in FY 1984 (Burkholder et al. 1985). Maximum feed rates more than doubled, and the cold-cap behavior was much improved, with no tendency to cone and pool. The processing is improved probably by several things, especially: minimization of calcium by switching from IE-95 to IE-96; minimization of rare earth by changing the formulation for thorium substitution; addition of potassium as a glass former; and the addition of titanium, magnesium, and lithium to the glass.

3.5.4 Summary

During FY 1985 over 600 hours of melter testing was conducted under the Technology Testing Task of the Nuclear Waste Treatment Program in support of task objectives. Testing was designed as a precursor to operations in the radioactive liquid-fed ceramic melter. The goal was to verify the processability of the flowsheets and to allow for direct comparison of test data.

Two ECM and two PSCM experiments were conducted. The ECM experiments demonstrated feed and glass compositions and engineering procedures required to process a composition containing high concentrations of cesium and strontium. Based on the positive ECM results, a 10-day PSCM test was conducted. On a pilot-scale, testing demonstrated a processable feed composition and suitable glass product. A method of quickly bringing the melt tank contents to correct specifications was demonstrated: the tank inventory was first reduced, and then a slurry concentrated in waste components was fed to the tank. Glass-product data indicate that a maximum cesium-oxide loss from the melter due to volatility is 13 wt% under processing conditions.

The second PSCM experiment was performed to evaluate the processability of a candidate WV melter feed composition as well as to generate operational data for melter, off-gas, feed system, and instrumentation equipment. The test processed 9050 L of feed during the 300-hr experiment. Processing rates of up to 71 L/hr·m² were achieved. Cold-cap behavior was very stable with minimal process upsets. There was very little indication of a stable secondary glassy phase forming, which has occurred with past WV melter feeds that used carbon-reducing agents.

3.6 EFFLUENT TREATMENT SYSTEM DEVELOPMENT - P. A. Scott and R. W. Goles

A comprehensive review of technology for treating melter-generated off gas was completed this year. The report surveys both domestic and foreign work and evaluates the performance characteristics of several treatment technologies. The characteristics of melter off gas are addressed in terms of the melter feed composition and melter operating conditions. Control of the melter and the feed system directly affects the off-gas composition and rates, and these relationships are delineated. Unresolved technical issues are addressed.

Pilot-scale and engineering-scale studies were conducted to characterize the gaseous effluents from melter operations and to evaluate the performance of equipment designed to treat the off gas. Two major tests were conducted using the off-gas system of the pilot-scale ceramic melter, and a series of parametric tests was conducted using the engineering-scale melter, known as the experimental ceramic melter (ECM).

A schematic of the off-gas equipment arrangement is shown in Figure 3.8. This arrangement provides several possible paths through the equipment so that various sequences can be implemented easily. Two different paths were used during the two PSCM experiments.

The first experiment, PSCM-20, was characterized by exceptionally high cesium loading in the melter feed. This provided opportunity to study this important radionuclide under unusual conditions. Cesium has been shown in past experiments (Goles and Sevigny 1983) to evolve from the melter by volatilization and then to condense in the off gas, forming aerosol particles. In this experiment, the cesium concentration in the melter feed was 5.75%, or about 40 times higher than previous experiments. During normal melter feeding conditions, the cesium DF was 140, which is higher than values obtained from experiments with lower cesium levels. Previous tests have yielded melter DF values from 14 to 73 (Goles and Sevigny 1983) for various feed compositions.

After the normal melter feeding period, the cesium in the melter off gas remained at about the same concentration for 12 days. Earlier tests with lower cesium levels have had off-gas concentrations of cesium that dropped abruptly soon after the cold cap had burned off and after the idling temperatures were

FIGURE 3.8. Arrangement of Air-Cleaning Equipment in PSCM Off-Gas System

established in the melter. This difference results from the increased contribution of cesium in the glass pool to off-gas emissions. At low melter feed concentrations, the brief high cesium concentration in the off gas results from rising temperatures in the melter plenum, which volatilize any cesium deposited there. While this also occurs for high glass loadings of cesium, the glass pool continues to emit cesium at a slowly declining rate.

During operation, the melter DFs for cesium correlated directly to size of the cold cap. This indicates that the cold cap suppresses or holds in cesium being volatilized from the glass pool. The cesium DF was found to be best during steady feeding rates; abrupt increases and decreases were both accompanied by higher emissions of cesium.

There is need for a reliable indicator of the glass redox condition to aid in melter process control. The ratio of NO_2 to NO in the off gas was found to be related to the redox state in one of the PSCM experiments. Following a reduction of reductant in the melter feed stream, the NO_2/NO ratio adjusted slowly to a new level. Had this adjustment occurred quite rapidly, the phenomenon would have been attributed to changes in the cold-cap chemistry. However, because the change was slow, the more slowly changing chemistry of the glass pool offered a more logical explanation. This relationship needs further definition to be useful for process control.

A film cooler was used again on one of the PSCM experiments. This device cools and protects the off-gas pipe at the entrance of the melter off gas to the off-gas line by injecting a boundary layer of air or steam. Following 10 days of melter operation, the inside wall of the film cooler was significantly cleaner than in previous tests. A revision in the instrumentation that controls the air-injection rate had stabilized these rates so that they did not enter the turbulent regime. The coating on the interior wall was soft and easy to remove.

Tests on the submerged bed scrubber showed that the scrubbing effectiveness was not severely affected by changes in gas flow rates. With the film cooler operating, the total noncondensable gas-flow rate was increased nominally from 80 to 120 cfm (using air injection at the film cooler). DFs for the

lower and higher rates were about 20 and 30, respectively. The lower collection efficiency for a higher gas flow is due primarily to reentrainment of particles collected in the scrubbing liquid (water).

Tests on the high-efficiency mist eliminator were conducted to determine the relative efficiency of aerosol collection for changes in direction of gas flow and for the use of a water spray to irrigate the fiber packing. All previous tests had been conducted with the gas flow entering the outside of the cylindrical cartridge and exiting on the inside. No difference in collection efficiency could be attributed to the direction of flow. The use of a water spray to irrigate the packing had very negative results. Apparently the water promotes migration of the collected particulate material through the fibers, which is reentrained on the discharge side. The gas-flow rates for the tests conducted were at the upper limit of normal design, making reentrainment a more predominant factor.

A series of tests was conducted on scrubbing NO_x from the off gas using a water-irrigated structured packing. Scrubbing efficiencies were quite low, ranging from 2.0 to about 17.0% NO_x removal for a range of flow rates and NO_x concentration in the scrubbing water. Absorption was nominally 5.0%.

A series of four tests was conducted in the ECM to evaluate volatility of cesium and ruthenium as a function of the oxidation potential in the melter feed. There appeared to be a correlation between the oxidation state of the glass feed and the rates of off-gas emission during melter processing. As the oxidation state of the glass feed increased, the cesium and ruthenium loss rates to the off-gas system also increased. This result was more pronounced for ruthenium than for cesium. Other factors, such as cold-cap coverage, in-leakage of air to the melter, and temperature, are probably more important to the off-gas behavior of cesium than is oxidation potential of the glass feed.

Cesium and ruthenium DFs ranged from 119 to 739 and 26 to 601, respectively, while ferrous/ferric ratios in the feed varied from 0 to 1.1. The ferrous/ferric ratio is a measure of the reduced state of the melter feed.

Volatility of both cesium and ruthenium was suppressed by high sugar (reducing) loading in the feed. The major mechanism for loss of cesium from the feed was transport of particulate through the off-gas system.

3.7 PHYSICAL AND NUMERICAL MODELING OF JOULE-HEATED MELTERS -

Activity Leaders: L. L. Eyler and R. J. Skarda

PNL has conducted research in HLLW vitrification for DOE since the mid-1960s. Because of the expense and time required to test different prototype designs, physical and numerical modeling techniques are used to study various options to help optimize the melter configuration and estimated generalized design correlations. A computer model (TEMPEST) capable of accurately predicting performance of waste vitrification melters was developed. Qualification and validation of the computer model for joule-heated melters is important for providing designers of future vitrification plants the necessary melter analysis tools. For that reason, physical melter model experiments have been conducted to provide a data base for evaluating numerical-solution procedures and prediction results.

3.7.1 Physical Modeling Description

The physical modeling effort in FY 1985 continued the work performed in FY 1984 (Skarda, Hauser, and Fort 1985). Modeling work in FY 1984 was performed to support the HWVP (Gurley and Minor 1985). The two melter systems modeled were the B-Plant Immobilization Pilot Plant (BIPP) melter and the PSCM. The PSCM is a PNL operating, pilot-scale research melter having a melt surface area of 0.73 m^2 . The BIPP melter was part of a proposed conceptual design used for early design studies associated with the HWVP.

Various BIPP electrode operating configurations were investigated in FY 1985, with the emphasis on providing a data base for validating the numerical model of the BIPP melter. The code being validated uses finite-difference approximations of time-dependent equations governing conservation of mass, momentum, energy, and electric potentials in three-dimensional geometries. Code predictions were compared to experimental test data in several BIPP electrode configurations. Tests were performed in a model melter design in which a dual pair of electrodes is present. Each pair can be operated at a

controlled power level. Tests were made at two different electrode spacings and three upper-to-lower electrode power ratios (U/L EPRs). Results were obtained for several power splits between the electrode pairs. Two aspect ratios (melter fluid depth-to-width ratios of 0.38 and 0.47 were tested). Detailed results of this investigation are presented in Eyler et al. (1985).

The test plan for this work included performing experiments in the BIPP physical melter model to satisfy specific test objectives. These experiments included studying the effects of electrode spacing and electrode power skew using independently powered pairs. Modeling fluid and melter model parameters were determined by physical scaling laws to simulate proposed operation of the BIPP melter.

Six tests were originally planned using two electrode spacings and three power skews as listed in Table 3.12. Planned data acquisition included fluid temperatures, electric potential, flow velocity, and wall heat flux to provide a rather complete set of data for evaluating numerical predictions. Planned tests are identified in Table 3.12 as test runs BRUN-1 through BRUN-6. During these tests, only temperature and electric-potential data were acquired. Subsequently, test runs BRUN-7 through BRUN-9 were conducted to acquire flow-visualization data.

3.7.2 Numerical Modeling Description

The physical behavior of waste glass processing in a joule-heated melting furnace involves rather complex interaction between fluid flow, heat transfer, and electrical current. Generally the physical processes will exhibit a three-dimensional and transitory behavior, depending on the melter operating conditions and design parameters. Matters are further complicated because the transport properties associated with the flow of material, heat, and electricity are highly temperature-dependent and can vary over several orders of magnitude within the melter during operation.

As complex as these processes are, they can nevertheless be accurately described using well-known mathematical formulations based on fundamental physical laws and the principles of continuum mechanics. Obtaining solutions to

TABLE 3.12. Test Plan Summary

Run No.	Electrode Power Skew	Model Electrode ^(a) Spacing, cm	Modeling Fluid Level, cm	Electrode Potential Reference
BRUN-1	100% Top 0% Bottom	6.35	17.94	Floating ground
BRUN-2	0% Top 100% Bottom	6.35	17.94	Floating ground
BRUN-3	50% Top 50% Bottom	6.35	17.94	Floating ground
BRUN-4	100% Top 0% Bottom	2.54	14.61	Floating ground
BRUN-5	0% Top 100% Bottom	2.54	14.61	Floating ground
BRUN-6	50% Top 50% Bottom	2.54	14.61	Floating ground
BRUN-7 ^(b)	50% Top 50% Bottom	6.35	17.94	Absolute ground
BRUN-8 ^(b)	75% Top 25% Bottom	6.35	17.94	Absolute ground
BRUN-9 ^(b)	50% Top 50% Bottom	6.35	17.94	Floating ground

(a) BIPP spacing is 4x model spacing.

(b) Additional tests performed for flow visualization.

the resulting highly nonlinear partial differential equations is accomplished using numerical methods with the aid of a high-speed digital computer.

The TEMPEST computer code was developed by PNL to simulate a wide variety of multidimensional, transient fluid flow and heat transfer phenomena in reactor systems. The joule-heated melter version of the code solved the governing continuity, momentum, energy and electric-field equations in either two or three dimensions using a combination of implicit and explicit finite-difference procedures. The code uses finite-difference approximations of the governing time-dependent equations. Code prediction results were then compared to model test

data. For qualification, comparisons were made to data in several configurations. Included were: a model of a one-armed, electrically conducting body; physical melter model results using a single electrode pair; and data acquired in this present model work using a physical melter model with two individually controlled electrode pairs.

3.7.3 Conclusions and Recommendations

Physical melter modeling using a dual-electrode-pair configuration provides a means of testing electrode spacing and ratio of power to each pair. It also provides a data base for testing numerical models. Experimental results obtained in the present work led to the following observations and conclusions:

- The dual-electrode-pair system provides additional control of mixing in the molten glass not available in a single-electrode-pair system.
- An upper-to-lower electrode power ratio (U/L EPR) of 1.0:0.0 is a poor operating configuration because temperature stratification occurs between upper and lower fluid regions, which inhibits mixing.
- Results of using an U/L EPR of 0.0:1.0 indicated very high local temperatures directly in front of the powered electrode pair. This may indicate excessive cross-firing between pairs, which could shorten electrode life.
- Only moderate cross-firing and thermal stratification occurred for cases in which the U/L EPR was 0.5:0.5.
- The largest temperature variations with time occur in central regions of the fluid. This results because of the enhanced cooling of the modeled (top surface) cold cap.
- Flow-visualization results are inconclusive.

Conclusions drawn from results of numerical simulation presented are broken into categories. For theory and numerical basis, conclusions are:

- Operational modes and solution procedures used in the melter version of TEMPEST are working correctly for the test applications evaluated.

- In a test of the electric-field solution, the predicted current in a one-arm body model is 3.32 μA . Measured data was 3.33 ± 0.1 μA . Surface enhancement is predicted to be 2.56 compared to a measured value of 2.6 ± 0.1 .

From simulation of physical melter model experiments with a single electrode pair, conclusions include:

- Voltage drop agreements varying from 3 to 20% underprediction are found, with bulk temperatures agreeing within $\pm 1^\circ\text{C}$.
- Accurate results are obtainable when two-dimensional simulation of physical melter model experiments is used with sufficient noding resolution. Three-dimensional models of three-dimensional tests, however, are found to be generally more consistent.
- Flow-field predictions qualitatively follow observations, as indicated by viewing a computer-generated video movie.

From simulation of physical melter model (e.g., BIPP) experiments with a dual electrode pair, conclusions include:

- Predicted voltage drop results for tests with an U/L EPR of 0.0:1.0, 1.0:0.0, and 0.5:0.5 vary in agreement from an underprediction of 30% to "exact" agreement for two-dimensional models.
- Particular attention to thermal boundary condition is required because of strong dependence of electrical conductivity on temperature.
- Temperature field data in the modeling fluid are typically at $\pm 10^\circ\text{C}$ variance with data for two-dimensional models.
- Agreement of overall voltage drop and temperature field data is significantly improved in a three-dimensional model of a 0.5:0.5 power-split test. This results because of more correct accounting of heat transfer through front and back walls.

- Electric field data and predictions are in good qualitative agreement when normalized to corresponding overall voltage drops. Local deviations are directly attributable to differences in local temperature because of temperature-dependent electric conductivity.
- Comparison of local electric-field data in power-split ratios other than 0.0:1.0 or 1.0:0.0 cannot currently be made with TEMPEST.

From simulation of the idling and feeding operation modes of the pilot-scale ceramic melter, conclusions include:

- Attaining thermal equilibrium or quasi-steady conditions is a prerequisite for correct predictions. This requires that special attention be given to thermal boundary conditions.
- Accurate thermal properties of melter glass are required to improve confidence in predictions.
- Additional investigation of prescribed thermal boundary conditions, time-step dependence, and noding resolution are needed in order to improve confidence in prediction of melter operation.

Several recommendations can be made based on present experimental work, as follows:

- Flow visualization should be an integral part of the physical melter model experiments. Visual observations can be used not only for obtaining velocity data, but can also aid in interpretation of other data obtained during experiments. Additional work is required to determine the best tracer particles in modeling fluids.
- Accurate data on overall heat balance should be obtained. This could be done by sufficiently instrumenting cooling channels, and it would assist in the evaluation and specification of thermal boundary conditions for numerical models.
- Prolonged operation at an U/L EPR of 1.0:0.0 should be avoided because extensive stratification can result from this power configuration and inhibit mixing.

- Power controller configuration should be set up to eliminate the possibility of cross-firing between electrode pairs.

Concerning the melter version of TEMPEST, recommendations include the following:

- Operational modes and use of the melter version of the TEMPEST computer code should be documented in the form of a users' manual.
- Dual-electrode-pair (combined) electric-field output should be made available to the user. This requires that the code be modified.
- Difficulties are encountered in electric-field solution convergence at startup. An automated (numerically considered) methodology should be developed to adjust power levels, etc., in response to ill-defined initial conditions.
- Determination of bulk fluid temperature should be included as part of the computation.
- The electric-field solution procedure and operational modes should be upgraded to be compatible with the most current TEMPEST developments in other programs.
- A standard set of inputs for electric-field and melter test problems should be developed and a quality assurance program commenced for maintaining and qualifying future code evaluation and model development.

Concerning physical melter simulation, recommendations include:

- Further investigation and development of a methodology for qualifying the attainment of equilibrium or quasi-steady conditions should be addressed.
- Two-dimensional modeling advantages and limitations need to be better defined because this approach can significantly improve computational efficiency for parameter testing of melter design and analysis.
- Flow-visualization experimental data should be obtained in the dual-electrode-pair physical melter model. This would allow qualifi-

cation of predictions of basic fluid-flow characteristics (flow direction, magnitude, etc.).

For simulation of operating melters and melter designs, recommendations include:

- The PSCM model and simulation results need to be re-evaluated in more detail; in particular, specification of thermal boundary conditions and determination of fluid properties need to be better addressed.
- Thermal radiation modeling in TEMPEST needs to be improved to provide better physical definition of heat transfer within the glass melt and at the cold-cap surface.

3.8 PROCESS/PRODUCT MODELING AND CONTROL - Activity Leader: W. L. Kuhn
Major Contributors: D. W. Faletti, J. H. Westsik, L. J. Ethridge,
P. W. Reimus, and R. K. Farnsworth

3.8.1 Process Instrumentation and Control

Process instrumentation and control activities conducted during FY 1985 included:

- examination of instrumentation data from previous years' melter experiments to determine whether, and how well, the instrumentation indicated the operating condition of the melter
- testing and evaluation of new instrumentation concepts, including new thermocouple positions in the glass thermowell, an infrared camera, pneumatic level-detection system, acoustic monitor and a time domain reflectometer
- development of a temperature control algorithm that uses feedback on glass temperature to control electrical power to the melter.

Evaluation of Existing Melter Instrumentation

The objective of this work was to evaluate whether, and how, existing instrumentation could be used as indicators for critical phenomena within the melter such as cold-cap coverage and foaming. The evaluation was limited to

data already digitized and on magnetic tape, e.g., glass and plenum temperatures but not off-gas system variables.

As has been generally recognized, foaming is characterized by increased temperature in the glass melt. Still to be resolved is how to identify this temperature increase amid all the random temperature fluctuations associated with the convection current in the melter. Glass transfers from the melter cause temperature increases at the thermocouples located in the area of the discharge trough and face and at the glass thermocouple located 4 cm above the melter floor near the discharge entrance. Plenum temperatures indicate the cold-cap coverage. Typically, the higher the plenum temperature and the greater the temperature gradient in the plenum, the smaller the cold cap. It appears that during overfeeding, the temperature profile inverts, with cooler temperatures closer to the cold cap.

Evaluation of New Instrumentation Concepts

A melter viewing system, consisting of an infrared camera and associated electronics, has been demonstrated to provide clear pictures of the melter interior and cold-cap surface during melter operation. Additional design work is needed to provide adequate cooling to critical components within the melter cavity and to provide pictures of the entire glass surface so that cold-cap size can be quantitatively estimated. The pneumatic level-detection system functions well for measuring glass specific gravity and glass level in the melter. Further testing is needed to assess its capabilities for indicating overfeeding, bridging of the cold cap, and foaming. Clustering of thermocouples at the expected level of the cold cap may provide an early indication of foaming. Acoustic monitoring is being examined for detection of foaming and overfeeding, and time domain reflectometry is being considered for detection of glass level, foaming, and salt formation. The acoustic probe appears to respond to changes in the glass/cold-cap region, but no strong correlations have been established. The time domain reflectometer has been plagued by problems with the electronics of the system, and its evaluation is incomplete.

Temperature Control Algorithm

A temperature control algorithm is being developed to control electrical power to the melter using a glass-temperature feedback loop to the controller. Natural fluctuations in the temperature need to be accounted for through averaging, and the control system must check for failed thermocouples. A cascade control scheme is used with glass temperatures in the outer primary loop and melter power in the inner secondary loop. The primary control loop can provide proportional, proportional-integral, proportional-derivative, or proportional-integral-derivative (PID) control of the signal to the power controller.

The temperature control algorithm was used throughout PSCM-21 and during part of PSCM-22. Proportional control worked well during steady-state operation although the PID control appeared to provide better temperature control during transients associated with startup. The algorithm did not respond fast enough to foaming observed during PSCM-21, and operator intervention was required to make the necessary power reductions to reverse the foaming. The algorithm was modified for PSCM-22 to respond to foaming as indicated by the thermocouples clustered in the cold-cap region. The change, however, could not be tested because no foaming was observed.

3.8.2 Canister Modeling

Canister modeling activities conducted during FY 1985 included the following:

- designing an experiment (PSCM-20) for a nonradioactive pilot-scale melter to gain information about the expected extent of cracking in canisters produced in the RLFCM for the FRG
- designing the experiments for PSCM-20, PSCM-21 and PSCM-22 for a non-radioactive pilot-scale melter to gain data on transient temperature for use in validating the TEMPEST computer code
- examining canisters from the PSCM-20 experiment for the degree of cracking

- assessing our application of the TEMPEST code by comparing the predictions of the code to the experimental data obtained in PSCM-20 and PSCM-21, including identifying limitations of the code's accuracy and recommending further computer code development and experimental activities.

Design of Experiments to Predict Cracking

The purpose of the PSCM-20 experiment was to gain information needed to determine the process conditions (e.g., pour schedule, use of overpacks, etc.) that would produce canisters with an acceptably low amount of cracking. Though only limited changes could be made to RLFCM operations, except for the pour schedule and the use of overpacks, the objective was to keep cracking to the practical minimum and to obtain information on what this minimum would be.

A criterion was developed to permit (given the time-temperature history of a radioactive (heat-generating) canister) selection of an appropriate thermal history in a nonradioactive canister that would predict the cracking in a radioactive canister. A "quick freeze" stress model widely used in the glass industry was applied to the problem. Although the extent of its applicability to cracking in waste glass canisters has not been thoroughly investigated, the criterion provided a reasonable basis for the experimental design of the PSCM-20 cracking experiments.

Design of Experiments To Validate the TEMPEST Code

Transient temperature data were obtained to assess how the TEMPEST code could be used to predict the thermal history in a canister. Six canisters in PSCM-20, three canisters in PSCM-21, and one canister in PSCM-22 were instrumented to obtain the data. The studies of parameters included the canister diameter (12, 13, and 24 in.), the pour method (batch and continuous), and the thickness of internal and external insulation. During the PSCM-20 experiment, two canisters were filled within a simulated turntable assembly (a group of shells having heat transfer resistances similar to that of an LFCM turntable), which provided a physical model of the heat-transfer behavior expected in the RLFCM.

Another important experimental design activity was determining the acceptable range of pour schedules for the RLFCM. This included determining the effects of a 24-hr shutdown. The canisters were filled in three equal pours and in six equal pours. The cracking was not affected.

Comparing the experimental results from the pours using the simulated turntable with the TEMPEST code showed that TEMPEST, though exact only for symmetrical problems, gave acceptable results for the unsymmetrical simulated turntable. These comparisons showed also that the values of emissivities and contact coefficients used were acceptable.

Canister Examinations

The eight canisters filled during PSCM-20 were cut to permit inspection over the radial-axial cross-section of the canisters. The longitudinally cut surface of each canister was visually inspected, and a qualitative estimate of the cracking was made. The amount of cracking is considered to be slight, with much of the glass found in 5- to 10-kg pieces.

TEMPEST Validation

The predictions of the TEMPEST code were compared with data obtained from five selected canisters filled during PSCM-20 and PSCM-21. The variables studied included canister diameter (12, 13, and 24 in.), canister height (45, 56, and 85 in.), insulation thicknesses internally (0 to 1/2 in.) and externally (0 to 3 in.), and use of both continuous and batch filling. In addition, one canister was filled within the simulated turntable to determine the ability of the TEMPEST code to model heat transfer within a structure similar to a turntable.

The two adaptations of the TEMPEST code used in this study were called the batch-fill and the continuous-fill models. The batch-fill adaptation of TEMPEST was used to model the three 12-in. canisters, which were filled in three pours of roughly equal size. Then the continuous-fill adaptation of TEMPEST was used to model the continuously filled 13-in.-diam canister and the batch-filled 24-in. canister. The 33 batch pours used to fill the 24-in. canister were modeled using the continuous-fill adaptation of TEMPEST because of the labor savings with the reduced input.

The batch-pour adaptation of TEMPEST was sufficiently accurate to be useful for many LFCM applications. It gave temperatures near the centerline that were accurate to 50-125°C over most of the cooldown. However, during periods immediately following a pour, TEMPEST overpredicted temperatures by as much as 250°C. These deviations were caused by a large underprediction of the cooldown immediately following a pour and by another, less severe, underprediction of the cooldown rate at times greater than 10 hr after a pour.

The continuous-pour adaptation of TEMPEST predicted temperatures more accurately than the batch-pour adaptation did. Temperatures near the centerline were within 50°C or better over most of the cooldown. This was true also for temperatures further from the center and for periods far removed from the time the glass surface passed a given position.

3.8.3 Mass Balance Modeling

A transient mass balance over an LFCM melter was modeled in order to understand the effect of the melter residence time on damping fluctuations in the feed composition and to understand the sensitivity of the predicted outlet glass composition on the residence time.

If a melter is operating at steady state, the outlet glass and inlet feed compositions will be the same, based on the nonvolatile species intended to form the glass. During actual operation, however, various fluctuations in the process can be expected such that the glass composition in the melter will be fluctuating continuously about some mean value. If the melter is assumed to be a well-mixed tank, then the outlet composition for a given species is related to the inlet composition by a mass balance comprising a first-order ordinary differential equation. The equation can be solved to give a general relationship between the inlet feed and outlet glass compositions. The equation was used to check the importance of deviations from the assumed well-mixed tank model.

One likely source of fluctuation in the glass composition is fluctuation in the feed composition, e.g., due to variations in the waste stream or the addition of glass-forming materials. The solved differential equation can be used to explore the effect that the residence time has on damping fluctuations

in the composition as the glass mixes in the melter. Assume that the inlet composition is fluctuating sinusoidally about some mean value:

$$C' = C'' + A \sin (wt)$$

where A is a constant describing the magnitude of the fluctuation, and w is a constant describing its frequency, and where $w = 2\pi/P$, where P is the period of the assumed cyclic fluctuation. When the root mean square (RMS) average of the fluctuation in the outlet glass composition is divided by the RMS average of fluctuation in the inlet feed composition, the result is:

$$\frac{\text{RMS}[C - C'']}{\text{RMS}[C' - C'']} = (1 + 2\pi T/P^2)^{-3/2}$$

This is evaluated as follows:

<u>P/T</u>	<u>Ratio of Fluctuations</u>
1	0.004
2	0.03
3	0.08
5	0.24
10	0.61

We conclude that fluctuation must continue a long time (e.g., five times the residence time) for fluctuations in the inlet (feed) composition to propagate significantly to the outlet glass composition.

3.9 MELTING PROCESS CHEMISTRY - Activity Leader: D. S. Goldman

Major Contributors: S. C. Marschman, and M. A. Reimus

The objective of the Melting Process Chemistry Studies Subtask was to investigate methods to help optimize and control melter feed chemistry. This work was performed in an effort to simplify process control and improve productivity. Emphasis was placed on determining some of the causes of processing problems and on developing techniques to relate laboratory measurements

to actual glass-melting performance. An attempt was made also to establish methods for effectively addressing glass-melting problems.

One activity was investigation of cold-cap formation in glass melters. Often during melting of a feed slurry, a thick, impermeable cold cap may develop at low reductant concentrations, which impedes heat transfer to the feed, slowing the melting process. This may also trap gas between the bottom of the cold cap and the melt surface, which further impairs heat transfer. Reducing agents such as sugar have been shown to improve the cold-cap melting characteristics of many nuclear waste glass formulations, but little effort had been given to defining the mechanisms that impact melting. This study investigated methods to determine the melting rate of various glasses and the behavior of the cold cap formed by these glasses.

A laboratory test procedure was developed to evaluate the melting performance of simulated nuclear waste glass streams. The test procedure used bottom-heated refractory crucibles to melt nuclear waste feeds. Melting rates of the feeds are determined by holding the crucibles in a furnace at temperature and extracting them as a function of time. The crucibles are sectioned, and the amount of cold cap remaining is measured and converted to a melting rate. This method proved satisfactory for determining melting rates but cannot predict the long-term effects of melter operation such as the formation of layers of residue on the melter surface. Thus efforts were turned to developing a technique by which long-term melting problems could be predicted.

The effort to address actual time-dependent melter problems resulted in the design and construction of a laboratory mini-melter. The design and development required much of FY 1985, and the melter was brought on line near the close of the fiscal year. The mini-melter, however, has been shown to work well using liquid feed streams and should prove to be a useful tool in scale-up of laboratory results. It will be developed during FY 1986 as a tool for predicting long-term melting problems associated with various simulated nuclear waste glass feed streams.

The redox state of nuclear waste glass has been shown to affect the cold-cap formation and glass-melting rate. Glasses that are too reducing tend to favor formation of a secondary metallic phase, which may accumulate at the

bottom of the melter and possibly cause electrical shorts in the furnace. Glasses that are too oxidizing tend to foam, which may lead to melter shutdown. Wet chemistry methods are well established and may be used for determining the redox state of glass through the determination of the ferrous/ferric ion ratio of a glass. These techniques, however, would be cumbersome and difficult to use in a hot cell.

Thus another effort of this subtask was to determine the usefulness of Mossbauer spectroscopy for remote, easy-to-operate redox determinations. Development of the technique yielded several results. First, it was determined that ferrous/ferric ratios obtained from the Mossbauer spectroscopy technique were about 20% greater than those obtained by wet chemistry techniques. This deviation was found to be linear, and a correction factor was developed for use in correlating Mossbauer data to wet chemistry data. Second, it was discovered that the ferrous/ferric ratio of glasses could be determined from measuring intensity data from three velocity locations, one representing the background and two representing the ferric and ferrous resonant peaks. This decreased the time to produce a ferrous/ferric ratio from several hours to less than 1 hr. This potential has led to the development of a new generation of high-speed Mossbauer systems for determining specific redox couples, such as ferrous and ferric iron by Ranger Scientific, Inc.

While the Mossbauer technique performed well on nonradioactive glasses, problems were encountered with radioactive glasses. The technique was found useful in determining the ferrous/ferric ratio of waste glasses containing uranium and thorium. Fully radioactive glasses, however, could not be analyzed. Featureless spectrums were obtained from Mossbauer experiments performed for as long as 5 hr. The conclusions drawn from these radioactive experiments was that beta and gamma radiation emitted from the waste glasses caused enough interference to effectively mask any detection of the Mossbauer effect. Thus the use of Mossbauer spectroscopy for determining the redox state of nuclear waste glass was abandoned.

Ion chromatography was identified late in FY 1985 as a possible candidate for the determination of the redox state of nuclear waste glass. Preliminary experiments have shown that ferrous/ferric ratios may be accurately determined

using this technique, and they will be investigated further during FY 1986. Careful examination of this technique and others will be performed in FY 1986 to establish which method will most likely yield accurate redox-state determinations.

Another important consideration in developing nuclear waste glass compositions is durability of the glass. It has been shown that durability is related to the residence time of the glass in the melter. Optimization of this residence time leads to increased productivity and reduced operating costs. One objective of this task was to determine the residence time of glass in the PSCM. Another goal of this task was to perform short-term laboratory tests with simulated nuclear waste glass feeds and compare their glass durability to those obtained from glasses melted in the PSCM and ECM.

To determine the residence time in the PSCM, a barium tracer was added to the WV PSCM-19 test. The residence time was determined to be 3.06 days. This value agrees closely with the value of 2.98 days that was predicted based upon melter geometry and processing rate (24.5 L/hr). An attempt was made to model the residence time of the PSCM using a modification of the TEMPEST computer code. It was found, however, that excessive computer time was required to develop an accurate description of the entire melter volume. Few particles exited the melter at the completion of extended runs, although the development of convective cells with time was clearly evident. Funding restrictions prohibited further development of this computer code.

Experiments were performed to determine whether melter residence time and product properties could be correlated. PSCM and ECM melts were leach-tested using the MCC-1 28-day leach test. Induction-coupled plasma (ICP) analyses were performed on each of the PSCM and ECM glasses, and slurry feeds were prepared in the laboratory to match these compositions. These feeds were melted and held at temperature for 4 hr, 15.6 hr, and 2.5 days. These glasses were leach-tested using the MCC-1 leach test to determine their chemical durability. Generally, little difference was seen between the durability of glasses processed in the melters and those melted for 3 or 4 hr in the laboratory, and good correlations were obtained. Statistical analysis did indicate a variation

of chemical durability between glass produced in different melters; however, experimental errors not taken into account could have affected this result.

An important result of this work was the demonstration that the chemical durabilities were similar whether the glasses had been melted in the laboratory for several hours or had been collected from the PSCM with a mean residence time of several days. This similarity suggests that sufficient residence time exists in a larger melter, such as the PSCM, to produce a homogeneous product. Experimental results have also shown a dependence of durability on residence-time effects of glasses processed in laboratory crucibles from liquid feeds. The compositions of the glasses were found to change with residence time in the furnace due to volatility of certain oxides. These compositional changes may be the sole cause of the observed durability increase with time, as durability is extremely dependent on composition. Further experimentation is needed to determine the exclusive effect of residence time on the chemical durability of nuclear waste glass.

3.10 DEVITRIFICATION SCALE-UP - Activity Leader: L. A. Chick

The objective of this activity was to show that scale-up of devitrification behavior from the laboratory to a full-scale canister is valid. This was to be achieved by comparing the microstructures of glass samples taken from full-scale instrumented canisters with laboratory glass samples that duplicated the chemical composition, redox state, and thermal history of the canister glass samples.

A search of the available instrumented canisters found that only the FRG instrumented canisters from PSCM-20 were fully instrumented, sectioned, documented, and available for sampling. Samples of glass from four of the FRG canisters were obtained. When possible, the glass samples from the areas with the slowest cooling rate (mid-canister, centerline) and the fastest cooling rates (top of the glass, near the canister wall) were obtained. These samples were then sectioned, polished, and optically examined. ICP analyses were also performed on each glass sample.

No crystalline material was found in any glass samples obtained from the FRG canisters. This is in contrast with thin sections of heat-treated glass

samples of the FRG glass composition made during laboratory glass development. The glass-development samples were found to have significant amounts of both cubic and hexagonal crystals. ICP analysis indicated that the compositions of the laboratory and canister glass were essentially the same. Comparison of the thermal histories of the canister and the laboratory glasses showed that the laboratory glasses were heat-treated at much slower cooling rates than any of the canister glasses. These observations indicate that the laboratory tests allow time for crystal nucleation and growth, while canister glass heat treatments do not allow time for these processes. These observations also confirm previous observations that the amount of devitrification observed in laboratory-produced and heat-treated glasses is significantly higher, and thus could be used as a conservative estimate of the amount of devitrification that could be expected in canister glasses.

3.11 REFERENCES

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4.0 RADIOACTIVE LIQUID-FED CERAMIC MELTER OPERATIONS

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4.1 OBJECTIVE

Remote radioactive engineering-scale testing of the liquid-fed ceramic melter (LFCM) system is a necessary and logical step in the progression to full-scale production capabilities at designated U.S. sites to ensure that the process and equipment perform as intended. The objective of this test program is to demonstrate satisfactory radioactive waste immobilization operations that will provide an adequate data base for future full-scale production facilities. In addition, specific sponsor-related objectives such as producing isotopic heat and radiation sources using the radioactive liquid-fed ceramic melter (RLFCM) system will be completed.

4.2 SUMMARY

Seven experiments were performed during the radioactive shakedown testing of the RLFCM system which occurred in FY 1985. During this year all equipment underwent significant testing during more than 300 hours of feeding of over 3200 L of radioactive slurry. The control system for the reference feed pump (air displacement slurry pump) had to be changed due to inefficient operation. The melter glass sampling system was frequently modified to accommodate the extremely harsh working environment ($>1000^{\circ}\text{C}$).

The shakedown testing was completed using radioactive feed simulating that at West Valley, New York. A test lasting 175 hr and vitrifying 75,000 Ci of activity in ~ 300 kg of glass was completed. The canister glass level detection system was demonstrated to have a sensitivity to detect glass level to $\sim \pm 0.1$ in. The data acquisition and display system was also successfully working and continues to be developed into a useful data retrieval and diagnostic

resource. Effluent sampling systems were established and tested, and they demonstrated results showing much more sensitivity than possible during non-radioactive testing.

In addition to the RLFCM system testing, more than 3.0 MCi of ^{137}Cs and 5.0 MCi of ^{90}Sr solutions were successfully transferred to the 324 radiochemical facility. There they will be used in the production of isotopic heat and radiation-source canisters during FY 1986 for the Federal Republic of Germany (FRG). Also, negotiations were completed and the facility prepared to receive spent fuel elements in early FY 1986 to be used in preparing melter feed spikes after the campaigns to produce the FRG canisters are completed.

4.3 INTRODUCTION

Since 1973, the liquid-fed ceramic melter process for converting high-level liquid wastes (HLLW) to borosilicate glass has been under development and testing in the United States. Its early success, inherent simplicity, and ease of operation and maintenance led to its adoption as the reference HLLW vitrification process in the U.S., Japan, and the FRG. Currently the LFCM is the Department of Energy's (DOE) reference process for planned defense and commercial nuclear waste solidification facilities, including the West Valley Demonstration Project (WVDP), the Hanford Waste Vitrification Program (HWVP), and the Defense Waste Processing Facility (DWPF) at the Savannah River Plant. Because of the LFCM's wide acceptance as the reference waste vitrification process in the U.S., the DOE requested that PNL design, construct, and operate a prototypical radioactive pilot-scale waste solidification facility employing the LFCM process. Pilot-scale radioactive testing is necessary to provide design and operating data that can be applied to production-scale projects. The RLFCM equipment was installed in FY 1984 (Burkholder and Rusin 1985) and has undergone shakedown testing in FY 1985 using increased levels of activity in each test.

4.4 GENERAL SYSTEM DESCRIPTION

The pilot-scale RLFCM is a radioactive testing facility consisting of a vitrification system and supporting equipment systems for preparing liquid

waste and treating off-gas and condensate. The vitrification system, which consists of an RLFCM, a canister-positioning turntable, and a glass-level detection system, is depicted in Figure 4.1.

Radioactive waste slurries are prepared by blending radioactive waste and glass-forming chemicals in the waste preparation equipment. They are fed from a feed makeup tank to the RLFCM using a slurry feed system. In the RLFCM the liquid waste is dried and melted to form a borosilicate glass. The bulk glass temperature in the RLFCM is maintained at 1100 to 1200°C during operation and at ~1050°C during idling. Off-gas from the vitrification process, consisting of inleakage air, water vapor, chemical decomposition products, and some entrained particulate, is treated through successive stages of scrubbing, quenching, filtration, and absorption. The decontaminated off-gas is then discharged to the building stack.

The molten-glass product formed in the RLFCM overflows into stainless steel canisters positioned beneath the RLFCM by a turntable, which holds up to three canisters. The glass level in a canister being filled is monitored by a gamma-detection system. Once filled, a canister is rotated from the filling position while another is rotated into the filling position. The filled canister is allowed to cool and is then removed from the turntable.

4.5 TESTING RESULTS

4.5.1 Feed System

The high-level waste slurry feed pump tested in the Radioactive Liquid Fed Ceramic Melter (RLFCM) Program during FY 1985 was the air displacement slurry (ADS) pump (Figure 4.2). The feed rate of the pump, as demonstrated in previous nonradioactive testing, is capable of spanning a range of 10 to 185 L/hr. This range, coupled with its demonstrated high reliability, was determined to be adequate for use with the RLFCM which has a maximum processing capacity of 40 L/hr.

Two pump control systems were tested during FY 1985. The first of these was a constant air volume system using a master-slave air cylinder assembly

FIGURE 4.1. Schematic Flow Diagram of the Pilot-Scale RLFCM Vitrification System

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FIGURE 4.2. ADS Pump

sized at 1 L in a syringe-like principle to provide the motive air supply to the pump chamber which forces the slurry to the melter. This system was continually hampered with operating difficulties. The major problem was its intolerance to minor air leakages through the remote connectors. This problem could not be easily eliminated with systems in a radioactive cell. The melter was fed using this control system for 204 hr and pumped an estimated 1800 L of slurry. Flow rates ranged between 2 and 16 L/hr.

The second control system demonstrated was a constant pressure system (Figure 4.3). The change to this system in the fourth quarter was made to gain better control of the flow rate to the melter over a greater range of rates. This system uses an air supply from the operating gallery to provide the motive air supply to the pump chamber. A three-way solenoid valve located in the cell allows air to the pump chamber when in its normally closed position. The normally open position of this solenoid allows the pump chamber to vent back to the feed tank as it fills with slurry. This system, operated 125 hr, pumped an estimated 1991 L of slurry. Feed rates of 10 to 25 L/hr were typically maintained, and rates up to 34 L/hr were demonstrated. The two control systems are shown schematically in Figure 4.3.

During FY 1985, the ADS pump and control systems were used during nine experiments for a total of ~329 hr of operation, summarized in Table 4.1. Testing of the ADS pump using the constant volume control system occurred during RLFCM-1 (nonradioactive) through RLFCM-3C (radioactive). The constant air volume system was initially installed because 1) it allows no potential for blowback contamination to the operating galleries, and 2) cold development of the second system was not yet complete. Its major disadvantage was its intolerance to leaks in the system: once the one liter of air in the slave cylinder was dissipated during each cycle, there was no potential for make-up air.

Two sources for leaks are present in the constant volume system. One of these is the remote connectors themselves. Leakage through the block connectors was observed visually with the aid of a liquid soap solution applied to the block connectors. Although the leaks are not significant, enough air leakage occurred to limit the maximum possible air supply to the pump chamber. The

TABLE 4.1. ADS Pump FY 1985 Operating Experience

	RLFCM-1, Nonradio- active	RLFCM-2, Nonradio- active	RLFCM-1, Radioactive	RLFCM-2, Radioactive	RLFCM-3A, Radioactive	RLFCM-3B, Radioactive	RLFCM-3C, Radioactive	RLFCM-4, Radioactive	RLFCM-5, Radioactive	Totals
Run Duration, hr	56.2	5.9	2.5	25.7	1.6	9.2	89.4	0	174.7	368.3
ADS Pump on Time, hr	56.2	5.9	2.5	25.7	0	8.9	62.5	0	125.3	287.0
Efficiency, ^(a) %	100	100	100	100	0	96.6	77.9	0	78.8	64.4
Average Feed Rate, L/hr	9	2	12	16	0	17	11	0	16	13.2
Liters Processed	493	12	30	418	0	150	697	0	1991	3791
ADS Pump Control System	Constant Volume (mild steel)	Constant Volume (mild steel)	Constant Volume (mild steel)	Constant Volume (mild steel)	Constant Volume (stainless steel)	Constant Volume (stainless steel)	Constant Pressure	Constant Pressure		
Feed Line Size, in.	0.25 x 0.035	0.25 x 0.035	0.25 x 0.035	0.25 x 0.035	0.25 x 0.035	0.25 x 0.035	0.375 x 0.035	0.375 x 0.035	0.375 x 0.035	
Reason for Run Termination	Planned Shutdown	Planned Shutdown	Planned Shutdown	Seizing (due to rust) of cylinder assembly	Plug Devel- oped at Feed Line/ Flowmeter Interface	Slurry Leakage at ADS Pump/ Feed Line Flange	Planned Shutdown	NA	ADS Pump Solenoid Valve Failure	

(a) Efficiency = $100 \left[1 - \left(\frac{\text{Unplanned Downtime}}{\text{Duration} - \text{Planned Downtime}} \right) \right]$

other source of air leakage is through the check valve located at the base of the slave cylinder. In the constant air-volume system the purpose of the cylinder assembly is twofold: to provide the motive air supply during Step 4 and to provide the vacuum on the pump chamber during Step 2 to draw slurry into the chamber. The check valve is intended to prevent slurry being drawn back into the slave cylinder by not allowing too great a vacuum. In actuality, it prevents the pump chamber from completely filling with slurry. The opening of the check valve during each cycle for an uncontrollable duration permits varying quantities of air to enter the slave cylinder. The end result is that varying amounts of slurry enter the pump chamber, causing an unstable flow rate.

The ADS pump using the constant air pressure control system was tested during RLFCM-4 (radioactive) and RLFCM-5. This system proved more reliable than the constant air volume system. Minor air leakage, such as through block connectors, was not a problem. A disadvantage of this system is the potential for pressurizing the melter when the volume in the feed tank is allowed to drop below the minimum pumpable. When this occurs, air at the operating pressure is routed directly to the melter. Pressure swings are observed in the RLFCM melter corresponding to the cycling of the ADS pump.

4.5.2 Melter Operation

Figure 4.4 summarizes the operation of all RLFCM experiments as depicted by the melter tank temperature. This figure is an archive data triple plot of the indications recorded from three thermocouples in the glass tank since the melter was first started in August 1984. The three thermocouples are staggered in a common, vertically oriented thermowell positioned on the melter center line about 1 in. in front of the glass discharge throat. They are located 3, 6, and 9 in. above the melter floor, and the glass level is normally 14 in. deep.

Nine experiments have been conducted with the melter since its installation and are indicated by the vertical lines running through the temperature plots. Experiments 1-C and 2-C used a nonradioactive feed slurry to demonstrate the melter facility's operability before authority to initiate hot operation was granted. The remaining experiments RLFCM-1 through RLFCM-5 used

FIGURE 4.4. RLFCM Operation As Depicted by Melter Tank Temperature

radioactive slurry feeds and were used to shake down the melter system and identify improvements in the feed delivery and off-gas treatment systems.

RLFCM-5 was the final shakedown experiment in FY 1985. Its major objectives were to operate the melter for a minimum of 100 hr and to realize an on-line efficiency of at least 80%. The experiment lasted 175 hr and had an overall efficiency of 78.8%. A total of 1990 L of slurry feed were processed immobilizing 75,000 Ci of activity in 300 kg of glass. Some of the more significant melter operating parameters are shown in the composite plots of Figure 4.5.

Figure 4.5A is a record of the adjustments made to the power control system setpoint adjustments during the experiment in order to maintain the desired melter glass temperature range of $1150^{\circ}\text{C} \pm 25^{\circ}\text{C}$. The resistive feedback temperature control system was used throughout this experiment except for those periods identified as MANUAL control. Figure 4.5B shows the response of the control system to these changes. Figure 4.5D shows the average glass temperature during the experiment, with the target glass temperature and the temperature range indicated by horizontal solid and dashed lines.

Figure 4.5C shows the power delivered to the melter electrodes during the experiment. The two horizontal lines at 35 and 40 kW indicate the idling power requirements at ~ 1100 and 1130°C and are useful in identifying the periods of feed transfer into the melter, the approximate feed-transfer rates, and the cold-cap burn-off periods. Figure 4.5E is useful in identifying the onset of glass foaming conditions in the melter.

RLFCM Glass Sampler

Glass samples were successfully obtained from the glass stream falling from the melter discharge trough lip during transfers of glass into the receiving canister. The samples were caught in a graphite sample boat attached to the end of a piston rod and extended by means of a pneumatic cylinder piston into the falling glass stream (Figure 4.6). Development of this device is

FIGURE 4.5. Plots of Certain Melter Operating Parameters

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FIGURE 4.6. Glass Sampler

continuing in an effort to extend the life of the the precision-finished piston rod, which is destroyed by prolonged exposure to the 1000°C environment of the discharge section.

Air-Lift Glass Discharge System

The RLFCM glass air lift is a heavy-wall Inconel 690® tube, 3/4 in. in diameter, inserted deep into the glass in the vertical riser tube (through a nozzle in the melter lid). It becomes a very efficient air-lift pump when purged with a low air flow that can pump glass out of the melter tank at a rate high enough that the temperature of the glass falling into the canister is only 50 to 100°C lower than the average melter tank temperature and the glass remains very fluid.

The air-lift pump performed quite well during the initial shakedown experiments, pumping at about 0.5 L/min with an air-flow rate of 3 scfm at a pressure of 20 in. water content. No calibration of discharge rate versus air-flow rate has been established. Glass drainage from the Inconel-690 discharge trough lip was limited to a maximum of about 2 min after the air-lift air flow was terminated.

Data Acquisition and Display System

Figures 4.4 and 4.5 typify data capabilities being developed from the data acquisition and display system (DADS) for the RLFCM facility. A total of 208 analog sensors are sampled once every 5 sec for a period of 5 min (60 samples), once every 15 minutes. The average and the standard deviation values of each of these 60 sample groups are calculated, converted into engineering units, and stored on disk as soon as the sixtieth sample is taken. The 5-min sampling periods bracket the hour and quarter-hour periods, and the sampling times for the average and standard deviation values are recorded as the even hour and quarter-hour values. Immediately after the average and standard deviation values are transferred to disk and tape storage, the calculated values, based on one or more of the average analog values just recorded, are determined.

®Inconel alloys are products of the International Nickel Co., Huntington Alloy Products Division, Huntington, West Virginia.

These calculated values are termed "pseudo sensors," and they also are stored on disk and magnetic tape without standard deviation values. Space has been allotted for 42 pseudo sensor values.

Random access space has been allotted on the disk for 400 sets of average analog sensor values (208) and their standard deviation values, and for 42 pseudo sensor values. This is a wraparound space, with the last data values determined overlaying data values that were determined 400 scans previously. Thus the disk maintains the last 4 days of data for the 250 analog and pseudo sensor values.

A plotting routine, drawing on the data stored on disk, enables an operator to display either the averaged analog sensor values or the calculated pseudo sensor values plotted versus the sampling time. Currently the operator can specify the y-axis limiting values, and the tic mark intervals, but the x-axis remains fixed at 100 hr with minor tic marks every hour, major tic marks at 00:00 hr, and the date indicated at 12:00 hr. Plots can be made with one, two, or three plots per page, all with an identical x-axis.

The data stored on magnetic tape is intended primarily for archive use. However, since it has the same format as the data stored on disk, it can be used as a source of operational data for periods longer than the 4-day limit of the random access disk storage data. This feature is ideal for such long-range studies as the degradation of the melter tank liner, shifting temperature distributions within the melter refractories, or for recapping melter performance parameters over a long period.

4.5.3. RLFCM Effluent Emission and Off-Gas Characterization System

RLFCM sampling development efforts during FY 1985 were to set up equipment and capabilities during shakedown testing to characterize effluent emissions from the melter and the performance of the off-gas system at least as well as was done during previous, cold LFCM simulations. All analytical methodology employed in cold testing has now been transferred and applied to the RLFCM. The condensible and noncondensable sampling systems that have been designed to

accomplish this objective are described here. The limited sampling data collected by this equipment in FY 1985 is also discussed.

System Design for Sampling Condensible Effluent

The purpose of the RLFCM condensible off-gas sampling system is to characterize melter emission and off-gas system performance with regard to aerosols and condensible gas process effluent. The magnitudes and the loss mechanisms associated with essentially all radioactive feed component emissions are characterized using this system.

The number of independent sampling loops developed to support the RLFCM was chosen specifically to allow simultaneous decontamination factor (DF) measurements across the melter, quench scrubber and high-efficiency aerosol removal device. Each of these three parallel sampling loops is composed of in-cell effluent collection devices and out-cell flow control equipment. The in-cell components are designed to remove all radioactive process effluent by filtration and gas-scrubbing techniques before the gas is conveyed to the out-of-cell control equipment. Consequently all radioactivity will be contained within the hot cell, thus minimizing dose rates associated with sample collection and handling. The components making up the three sampling-flow control loops are illustrated in Figure 4.7.

Noncondensable Effluent Sampling System

The noncondensable gas composition of the RLFCM exhaust will be established using a gas mass spectrometer. The mass spectrometer and all its associated control instrumentation is rack-mountable and has been deployed on the second-floor B-Cell gallery. The melter exhaust gas sample presented to this instrument is in the form of a flowing, nonpressurized bypass stream that must be both clean and dry. A gas-processing system has been designed to achieve these conditions while minimizing undesirable effects upon gas composition. This system is composed of gross and polishing demisters, a filter, a permeation dryer, and two absolute filters in series. Of these components only the permeation dryer and the absolute filters will be located out of the hot cell. These out-of-cell components will be housed in the B-Cell sample room hood, although no significant contamination of the components is anticipated.

4.17

FIGURE 4.7. RLFCM Sampling System Schematic

The entire gas-processing system is completely passive and requires little more than compressed air service. These systems are schematically represented in Figures 4.7 and 4.8.

In-Cell Sampling

Off-gas samples were successfully taken from the melter plenum and downstream of the EVS during the final shakedown experiment (RLFCM-5) using the remote sampling equipment described above. The sampling data obtained were, overall, quite similar to typical results obtained in the strains characterizing the effluent from the nonradioactive melter. Table 4.2 summarizes these off-gas data in terms of DFs, that is, the ratios between the rates at which substances enter a device and the rates at which they are evolved. Due to unacceptable uncertainties associated with some of the measured sampling parameters, individual feed component DFs were expressed in terms of the overall gravimetric, or mass DF of the device being characterized. These resultant relative elemental DFs were then renormalized by a conservative estimate of this overall DF. The bases for assigning overall DFs to the melter and ejector venturi scrubber (EVS) were past nonradioactive tests, specifically PSCM-9 and PSCM-19. The performance values assumed for the melter and EVS were 250 and 10, respectively. In addition to the above assumptions, melter feed compositional data were not available; consequently, the RLFCM-5 feed make-up specifications defined in the melter run plan were used as a basis for calculating relative melter feed component DFs.

Despite the use of approximations, the performance data listed in Table 4.2 are in good agreement with results obtained during previous cold testing. However, unlike previous cold characterization work, semivolatile behavior can be established with orders of magnitude more sensitivity using nuclear analytical techniques. This is clearly illustrated in Table 4.3, which summarizes the radionuclide content of the condensate sample fraction of the melter off-gas effluent sampling system. Except for ^{154}Eu , all the radionuclides present in the condensate are considered semivolatile and, consequently, may have penetrated the upstream aerosol sample filter as a vapor.

FIGURE 4.8. RLFCM Noncondensable Gas Sampling and Analysis System

TABLE 4.2. RLFCM-5 Melter and EVS Normalized DFs

Element	DF	
	Melter	EVS
Al	700	22
B	630	6.7
Ba	320	11
Ca	300	3.4
Ce	560	--
Cr	18	7.2
Cs	62	4.2
Fe	<640	--
K	30	3.6
La	320	--
Li	56	13
Mg	160	4.4
Mn	920	4.5
Mo	67	12
Na	1600	6.2
Nd	460	--
Ni	230	5.0
Ru	53	27
Si	<3000	--
Sr	470	33
Te	71	4.4
Ti	990	17
Zr	200	6.7

TABLE 4.3. Radionuclide Content of Melter Condensate Sample

Isotope	dpm/mL	ppm	Cold Limit, ppm
^{106}Ru	1.8E5	2E-5	0.02
^{125}Sb	5.7E2	2E-7	0.05
^{137}Cs	8.8E3	4E-5	0.05
^{154}Eu	4.7E2	8E-7	0.002

Although these semivolatiles are easily detected and quantified radiochemically, their concentrations are orders of magnitude below conventional analytical detection limits, as is also shown in Table 4.3.

The data in Table 4.3 can be used in conjunction with aerosol sampling data to assess the percentage of ^{106}Ru melter off-gas emission that is evolved in the vapor state. This value, $10^{-4}\%$, is orders of magnitude lower than one could estimate on the basis of cold studies alone. Of greater significance is the degree to which gaseous ruthenium can penetrate the low-efficiency quench scrubber. No gaseous ^{106}Ru was detected downstream of the EVS during the present study; however, sampling volumes were low, and ruthenium volatility was effectively suppressed by the organic loading in the feed as discussed above. Nevertheless, the RLFCM will easily provide the necessary sensitivity for establishing melter exhaust processing needs for volatile effluents such as:

^3H , ^{79}Se , ^{99}Tc , ^{106}Ru , ^{125}Sb , ^{129}I and ^{137}Cs .

4.5.4 Remote Canister-Level Detection

The design of the RLFCM provides for a turntable for the glass canisters that consists of a three-position motor-driven carousel located within a containment vessel. This containment vessel is coupled directly to the overflow section of the RLFCM and, as such, provides a vacuum seal for the melter. Since the canisters are totally contained within the turntable enclosure, remote, contactless microprocessor-controlled methods were developed to establish the height and extent of glass fill in the canister as well as the turntable's positioning of the canister beneath the RLFCM. All in-and-out of cell equipment supporting this remote technology was installed by the end of FY 1984. All functional aspects of this system were tested and evaluated during the present reporting period.

The glass-level detection system is composed of a translatable in-cell gamma-ray source, out-of-cell gamma-ray detection/analysis equipment, and a microprocessor controller/interpreter (Figure 4.9). The microprocessor sequentially positions the gamma-ray transmission source adjacent to 11 fixed out-of-cell detectors with the melter canister interposed. At each detector

FIGURE 4.9. Glass-Level Detection System

elevation, a one-minute count begins automatically; the resulting counting rate is transferred to the microprocessor, where the value is compared with a previously established background rate. This comparison serves to establish both the presence of the glass level and the extent of cross-sectional fill in the canister. Since out-of-cell detector response will depend on source positioning as well as interposed glass, the system's diagnostic abilities will be limited by the reproducibility of source positioning. Operation of the system has been investigated, and the results are discussed below.

Operational characteristics of the canister-level detection system were tested during the RLFCM-2 test. The data generated by this system during 24 hr of uninterrupted service have been evaluated. During this 24-hr surveillance, two transfers of glass were made, both of which influenced the counting data associated with the first (lowest) canister level. The response of the system to the glass level is summarized in Figure 4.10. The effective cross-sectional fill at Level 1 after each transfer was calculated on the basis of a glass density of 2.5 g/cm^3 and a canister inside diameter of 12 in.

The reproducibility of counting rate associated with each of the 11 detectors was also evaluated over the 48-hr test period. These data are shown in Figures 4.11, 4.12, and 4.13 for the 11 levels or detector positions as percent deviation from the mean. Mean values and associated variations were determined only from comparable data. The data associated with Detector 1 (Level 1) were calculated using three separate mean values while all others were based on a single value derived from about 260 separate observations. The reproducibility was generally excellent, with most detectors exhibiting variations of count rate less than $\pm 2\%$. This variability is, however, much greater than the statistical variations inherent in counting data and, consequently, is a direct measure of positional reproducibility of the source stage.

Figures 4.14 and 4.15 characterize the functional relationship between counting rate and source-positional displacement from the level reference point for each of the 11 level detectors. Although the data are limited, it is clear that for most detectors positional displacements as small as 0.1 in. greatly affect counting rate. As a result, the positional reproducibility of the source translator must be, on the average, significantly better than ± 0.1 in.

FIGURE 4.10. Level 1 System Response to Two Consecutive Melter Glass Transfers

The larger-than-average variability associated with the data from Detector 2 can be accounted for totally on the basis of its corresponding response function in Figure 4.14. The reference position for this detector lies between two relative counting rate maxima. Consequently, the detector counting rate for this level would be expected to be much more sensitive to uncertainties in the source position than would other levels. However, the variability in the counting rate of Detector 11 cannot be similarly explained on the basis of its positional response function (Figures 4.13 and 4.15). Its behavior seems to be linked to glass transfers; that is, the discontinuities in data associated with Detector 11 are similar to those exhibited by Detector 1 and are coincidental to the glass transfers that occurred during RLFCM-2. Thermal dimensional changes of the canisters during glass transfers are probably responsible for the observed counting rate changes at position 11 in that the canister neck is not a uniform absorber. This effect will be investigated in future RLFCM tests.

FIGURE 4.11. Counting Rate Reproducibility for Levels 1 Through 4

FIGURE 4.12. Counting Rate Reproducibility for Levels 5 Through 8

FIGURE 4.13. Counting Rate Reproducibility for Levels 9 Through 11

FIGURE 4.14. Source Positional Counting Rate Data for Levels 1 Through 6

FIGURE 4.15. Source Positional Counting Rate Data for Levels 7 Through 11

In summary, operation of the RLFCM canister glass level detection system was fully evaluated during FY 1985. Reproducibility of source positioning was found to be excellent, usually better than ± 0.1 in. As a result, variations in counting rate for most levels were less than 2%. Since a 2% variation in counting rate is equivalent to the effect of a glass absorber 1/16 in. thick, the accuracy of the RLFCM level detection system is more than adequate to detect and diagnose small nonuniformities in the canister glass fill.

4.5.5 Preparation for Receipt of Cesium and Strontium

Isotopic heat and radiation sources in the form of ^{137}Cs and ^{90}Sr solutions were successfully obtained in FY 1985 for the FRG canister campaigns to be held in FY 1986. During this time over 3 million curies of ^{137}Cs and 5 million curies of ^{90}Sr were received at the 324 Building. These figures represent sufficient strontium activity to produce all the FRG canisters and enough cesium activity for the first ten canisters. Additional quantities of cesium (up to 4 million curies of ^{137}Cs) will be received during the first two quarters of FY 1986 to ensure that isotopic heat and dose specifications can be met.

The first quarter of FY 1985 was dedicated almost entirely to testing equipment and modifying the 324 Building's shielded receiving facility to ensure safety during handling of solution. Detailed studies of solution were performed to determine the rate of hydrogen evolution due to radiolysis. These results were used later to specify cask-fill levels, cask-vacuum requirements, and maximum load-to-unload time intervals. A backup emergency cooling-water system was implemented and demonstrated to be effective in ensuring that a continuous water supply was always available to the solution storage tanks. New facility-monitoring instrumentation was installed to provide redundant surveillance capabilities. Finally, all systems were tested as part of a mock transfer of solution. The first radioactive shipment, 400,000 Ci of ^{137}Cs , was successfully unloaded at the facility in January 1985. Figure 4.16 depicts the cask used to ship the cesium and strontium solutions.

FIGURE 4.16. Shipping Cask

Receipt of cesium solutions continued into March, when the final cask shipment was unloaded at its designated storage location. In June, strontium shipments began; they continued through July, when they were terminated due to lack of storage space. As material is consumed as part of the initial FRG canister production campaigns in FY 1986, additional cesium will be received to build up the isotopic inventory to its necessary level.

The chemical composition of each solution is given in Table 4.4. Before its use as RLFCM feedstock material, this waste will be preblended, concentrated, and denitrated. The solution will then be combined with nonradioactive cold chemicals to produce the desired feed composition for the isotopic heat and radiation sources for the Federal Republic of Germany.

TABLE 4.4. Reference Chemical Analysis of Cesium and Strontium Nitrate Solutions

<u>Element</u>	<u>CsNO₃</u>	<u>Sr(NO₃)₂</u>
Al	5.59 E-3	9.58 E-3
Ba	2.02 E-2	8.31 E-3
Ca	4.72 E-2	4.96 E-2
Cd	3.03 E-4	6.5 E-3
Ce	1.59 E-3	8.0 E-4
Cr	--	6.39 E-3
Fe	2.32 E-2	3.51 E-2
La	8.63 E-3	2.92 E-2
Mg	4.36 E-2	1.24 E-2
Mn	<1.13 E-2	9.53 E-3
Na	4.89 E-1	5.0 E-1
Nd	3.56 E-3	6.50 E-3
Pb	1.2 E-2	2.3 E-3
Si	3.5 E-3	--
Zn	1.14 E-3	--
Zr	<1.01 E-3	--
Cs	1.46 E-1	1.56 E-3
¹³⁷ Cs	600 Ci/L	Negligible
Sr	2.35 E-3	1.13 E-1
⁹⁰ Sr	Negligible	475 Ci/L
Oxide Loading	~52 g/L	~44 g/L

4.5.6 Spent Fuel Receipt Preparation

During FY 1985 a contract was signed with Wisconsin Electric Power Company, which operates the Point Beach Nuclear Power Plant, to supply three PWR spent fuel assemblies. These spent fuel assemblies will be dissolved and used as feed spikes in future waste vitrification activities following the campaign to produce the FRG canisters. Table 4.5 provides the characteristics of the fuel assemblies. The NLI-1/2 cask which is being supplied by Nuclear Assurance Corporation (NAC) was selected for use in shipment.

TABLE 4.5. Spent Fuel Characteristics

WE ID	ANSI Serial	Burnup	Enrichment		Criticality Date		Current Grams								Initial Grams	
			Initial	Current	Initial	Last	U	²³⁵ U	²³⁶ U	Total Pu (a)	²³⁹ Pu	²⁴⁰ Pu	²⁴¹ Pu	²⁴² Pu	U	²³⁵ U
H07	LM036A	32,889	3.1920	0.8883	11/22/76	10/9/81	383,891	3,410	1,665	3,589	2,073	837	486	193	401,182	12,806
H12	LM036F	32,979	3.1920	0.8828	11/22/76	10/9/81	383,426	3,385	1,667	3,593	2,073	839	487	194	400,742	12,792
H25	LM036U	32,945	3.1920	0.8851	11/22/76	10/9/81	384,933	3,399	1,668	3,595	2,075	839	487	194	401,359	12,811

(a) Plutonium data subject to change when ²⁴¹Pu decay is calculated as of 3/31/85. Also subject to further ²⁴¹Pu decay is calculation as of date of shipment. Data on ²³⁸Pu content is unavailable.

The 324 Building facility was ready to receive fuel at the end of FY 1985, and a successful dry run was completed. All required procedures were updated and all required storage and handling equipment were readied for use. Fuel shipments are expected to be completed in the first quarter of FY 1986.

5.0 A-CELL FACILITY PREPARATION

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and D. N. Berger

5.1 OBJECTIVE

The objective of the A-Cell Facility Preparation Task is to provide a facility for welding testing characterizing, decontaminating, storing, and shipping radioactive canisters of glass produced during operation of the pilot-scale RLFCM.

5.2 SUMMARY

A necessary component of the RLFCM Program is the capability to characterize, store and decontaminate canisters filled with glass and to prepare them for shipment. Preparation of the canisters of glass for shipment is requiring installation of several pieces of equipment: 1) leak-testing equipment to check for complete closure of the canister; 2) a gage for checking maximum diameter and straightness of canisters; 3) an electropolishing unit to remove contamination not removable by the high-pressure water/steam spray; 4) a gamma-scanning system for determining homogeneity; 5) an infrared scanning system to determine surface temperature; and 6) storage racks. Some of this equipment is being bought and modified for remote use while some is requiring design and fabrication.

5.3 INTRODUCTION

The liquid-fed ceramic melter (LFCM) is the reference vitrification process for the High-Level Waste (HLW) Immobilization Facility, and can be used to vitrify both liquid and solid wastes. The LFCM process has been under development at the Pacific Northwest Laboratory (PNL) since 1973 for defense and commercial applications. Its development and verification requires the testing of specific equipment and operating strategies in a remote vitrification facility using radioactive waste. The RLFCM will provide needed documentation of

design, data, and operating experience for use by architect-engineers involved with future commercial waste treatment facilities.

Characterization, decontamination and storage of the canisters of waste glass are necessary components of the RLFCM program and have been assigned to the A-Cell Facility Preparation Task within the Nuclear Waste Treatment Program. This activity will require the use of hot-cell space because the glass will contain large quantities of radioactivity. The 324 Building's A-Cell, adjacent to B-Cell where the RLFCM is located (see Figure 5.1), is a logical choice. Cleanout and renovation of A-Cell have been necessary to make space available as the cell contained obsolete equipment used in previous programs. Extensive radionuclide decontamination of the cell was necessary to ensure that canisters decontaminated for shipment are not recontaminated.

5.4 EQUIPMENT DEVELOPMENT, DESIGN AND FABRICATION

The design philosophy of the A-Cell Decontamination Testing and Storage Facility was to ensure that equipment fabricated would be as generic to the Nuclear Waste Treatment Program as possible, to meet the foreseen requirements of present and future waste programs. Thus A-Cell equipment design criteria have attempted to meet the characterization needs of waste canisters based both the U.S. acceptance criteria and the needs of the Federal Republic of Germany (FRG). Figure 5.2 depicts the steps necessary in the decontamination, testing and storage of glass canisters produced by the RLFCM.

5.4.1 Decontamination System

Electropolishing was chosen as the means to decontaminate the canisters of waste glass. This choice was made on the basis of available expertise within PNL, decontamination experience, and the disposal of electropolisher waste products.

The electropolishing system is the most complex piece of equipment required by this facility. Since an electropolishing system large enough to decontaminate an RLFCM canister of glass had not been designed or demonstrated, considerable effort was necessary to establish design criteria and verify the

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FIGURE 5.1. Radiochemical Engineering Cells in 324 Building

FIGURE 5.2. Necessary Steps To Decontaminate, Test, Store, and Ship Canisters

performance of engineered design features. The necessity to make it remotable has increased the difficulty of design and fabrication.

Many factors in this decontamination concept can affect the surface finish. Electropolishing is done in 150°C orthophosphoric acid followed by the use of 100-psig steam (about 170°C) to remove the residual phosphoric acid from the canister surface. The cathode/anode geometry and the electrolyte temperature are design parameters that remain essentially constant. The dissolved metal concentration gradually increases, and there is preliminary indication that a solubility limit exists. The concentration of water in the electrolyte gradually decreases due to evaporation and electrolysis (generation of hydrogen and oxygen). Significant cathode corrosion also occurs with prolonged exposure to high-temperature phosphoric acid. These changes in the phosphoric acid electrolyte affect electropolishing chemistry (i.e., salt formation on the anode surface and parasitic reactions) and conductivity through the electrolyte (affects power requirements).

Several technical issues had to be resolved before final design and fabrication of the electropolisher was possible. Most difficult was the requirement to electropolish at elevated temperatures (150°C) so as to avoid possible cracking of the glass within FRG canisters due to the high temperatures at surface and centerline. Electropolishing at 150°C required extensive development that included:

- electropolishing tests at elevated temperature
- tests to remove thermal oxide at elevated temperature
- studies of electrolyte boiling
- tests of surface degradation/corrosion.

Smooth surface finishes have been achieved in phosphoric acid baths up to about 215°C. At higher temperatures runaway corrosion can occur on clean stainless steel surfaces. At 150°C, smooth surface finishes have been obtained in phosphoric acid baths with nominal concentrations of up to 100% (115% is the practical upper limit due to partial dehydration of the phosphoric acid).

The electropolisher was designed to decontaminate canisters of glass produced in B-Cell, which may range from 8 to 16 in. in diameter and 4 to 9 ft in

height. The resultant tank is large and is constructed of Hastelloy® C-276 to permit electropolishing at 150°C. The bottom of the vessel is equipped with an agitation device and a liquid distributor with nozzles directed to agitate the solution-suspended solids off the bottom for transfer and removal by filtration. A spray ring for canister cleaning is positioned at the top of the vessel. An air sweep is provided near the canister-receiving port to prevent release of mist and gas to the hot cell. This will be treated by the A-Cell process off-gas system and released to the cell.

The heating system for the electropolisher is designed to heat 9300 lb of 85% phosphoric acid to 150°C. The vessel is insulated, and cooling coils are provided to maintain the temperature of the tank contents within the operating range during electropolishing. Penetrations into the vessel are of the same material as the vessel.

Incorporated in the same rack as the electropolisher tank is a rinse tank for removing the electrolyte film from the glass canister after electropolishing. The rinse tank's capacity is sufficient to hold a canister 16 in. OD x 9 ft long and the volume of electrolyte displaced by the canister. The top of the tank has an 18-in.-dia opening for the glass canister and ample remaining space for service connectors. Air will sweep the canister-receiving port, preventing moisture and contamination from being introduced in the cell air. Air sparging will agitate the rinse solution: one spray ring at the top and another at the bottom of the vessel will be used to spray down the electropolished canisters. The vessel will be similar in design to the electropolisher tank, but constructed of 304L stainless steel rather than Hastelloy C-276. The tank will contain coils for heating and cooling the tank. Figure 5.3 is a simplified drawing of the electropolisher and rinse tank.

Solution from the electropolishing vessel will be recirculated for tank agitation and passed through a filter to remove solid particles. Clarified filtrate will be routed back to the electropolishing vessel jet pumps located at the bottom of the vessel. The system for separating solids will consist of a feed pump, a cartridge filter, and two jet pumps. A filter backflush system

®Hastelloy is a registered trademark of Cabot Corporation, Kokomo, Indiana.

FIGURE 5.3. Electropolisher and Rinse Tank

will also be provided. The recirculation system requires the pump to recirculate 150°C, 85% phosphoric acid at a rate of 20 gpm. The filter medium is sintered Hastelloy C-276.

The pumped recirculation system is also an integral part of the system for agitating the tank contents. The pump and its associated piping provide the motive fluid to drive a jet-pumping system to agitate the tank contents and a spray nozzle to provide a fluid sweep over the canister bottom for displacing trapped air.

The off-gas system will include a condenser, an entrainment separator, an electric heater, a filter, and a blower to filter or condense the gases, vapors, or mists entrapped in the sweep air from the electropolishing and rinse tank. The blower is sized to maintain a velocity of 150 ft/min through the canister loading port of the electropolisher tank and rinse tank. The condenser can cool to approximately 90°F the wet air that is produced in operating the electropolisher and rinse tanks. A moisture separator is located downstream of the condenser to remove moisture entrained by gas flow through the

condenser. The electric heater reheats the gas to slightly above saturation temperature prior to filtration. A high-efficiency particulate air (HEPA) filter is located downstream of the heater.

Plans for the acquisition and control of data call for the use of micro-processors and digital technology to provide physically and functionally distributed control and display with a minimum of hardware and to be compatible with RLFCM and HWVP test systems. A cathode ray tube-based operator console is planned that will have process graphic and retrieval capability for processing data.

5.4.2 Canister Characterization Systems

The nondestructive characterization testing of waste canisters, based on U.S. site acceptance criteria and the needs of the FRG, requires that several pieces of equipment be designed for remote use in A-Cell and the air lock. The current requirements for characterizing canisters are:

- leakage after closure by welding
- surface temperature
- gamma profile
- dose rate
- ovalness and straightness
- weight
- surface contamination

5.4.2.1 Leak Detection

After filling and welding, the FRG canisters must be leak-tested to ensure freedom from weld defects that could release contamination during transport or repository storage. The FRG requested the leak-testing operation include the following:

- use of a mass spectrometer leak-detection system with helium as the tracer gas
- placement of the canister in a special vacuum chamber to provide maximum leak-detection sensitivity

- preparation of a leak-testing approach and procedures that provide the type of data and associated quality assurance validation required for repository licensing
- provision for independent third-party review of the approach, procedures, and leak-testing operations.

Possible approaches to leak-testing using helium for the FRG canisters were evaluated, including various methods to introduce helium before and after welding. Also, extensive calculations were performed to identify effects of process and canister variables on achievable test sensitivities and to define the optimum set of test parameters. The results of this work indicate that adequate detection sensitivity for both the preliminary B-Cell leak tests and the more stringent air lock measurements can be obtained by the pre-weld introduction of a helium source with an approximate leak rate of 5×10^{-4} atm cc/sec. Substantial variations in welding and subsequent handling/decontamination times, canister void volumes, and other process parameters will still permit detection of a 1×10^{-6} atm cc/sec leak.

A system designed to meet the above requirements of the helium leak-check system consists of a vacuum-tight helium leak-check vessel that will contain the canister, a vacuum pump, and a mass spectrometer. All equipment except the vessel containing the canister will be located in the cask-handling area of the 324 Building. The helium leak-check vessel (Figure 5.4) will be located in the air lock adjacent to the cask-handling area.

5.4.2.2 Measurement of Surface Temperature

An infrared thermometer that can measure skin temperature from emitted infrared radiation will be located in a sleeve in the wall of A-Cell. The infrared radiation emanating from a small-volume element of the canister will be measured and mapped along the central axis of the canister. This measurement will help in determining the strontium distribution within the canister and/or detecting voids or areas of low density in the glass. A guide will be provided to align the canister with the infrared monitor.

FIGURE 5.4. Helium Leak-Check Vessel

5.4.2.3 Gamma Profile

The distribution of cesium in the canisters will be established through measuring the γ -ray activity of ^{137}Cs emanating from a small-volume element of the canister. Mapping of this γ -ray activity along the central axis of the canister will establish the cesium distribution. A guide will be provided to align the canister with the gamma monitor.

The signal from the gamma detector will be supplied to a multichannel analyzer that will discriminate between ^{137}Cs and the gamma energy of other radioisotopes. The multichannel gamma analyzer will also be used to monitor other gamma energies produced by bremsstrahlung. Gamma radiation from sources to the sides of the detector will be absorbed by the shielding plug.

5.4.2.4 Measurement of Dose Rate

The dose rate from the canister will be measured in the air lock with a Keithley ionization chamber mounted on a stand. Readout of the dose rate will be outside the air lock in the cask-handling area. During measurement the canister will be suspended from the crane a predetermined distance from the ionization chamber.

5.4.2.5 Measurement of Ovalness and Straightness

The ovalness and straightness gage will be provided by the FRG. The gage and support will be modified somewhat to make it compatible with the operation of other A-Cell equipment and will position the canister for measurements of temperature and gamma activity.

5.4.2.6 Canister Weighing

A strain-gage load cell with a capacity of 4000 lb and an accuracy of $\pm 0.1\%$ of full scale will be hung from the crane hook for weighing glass canisters.

5.4.2.7 Measurement of Surface Contamination

A holder will be fabricated for swipes that can be handled by a manipulator for wiping canisters to detect loose contamination. To determine contamination levels, the swipes will be removed from A-Cell or the air lock through existing transfer passageways.

5.5 CANISTER STORAGE

Temporary canister storage in rack modules will be placed in cell space not occupied by decontamination and test equipment. Each storage position will accommodate canisters of 8 to 16 in. in diameter and 4 to 9 ft in length. The storage racks and rack components are designed for replacement with the overhead crane.

5.6 A-CELL LAYOUT

A-Cell is 21 ft wide, 9.25 ft deep, and 34 ft high, with the two shielding windows located one above the other. The second-floor window is provided with two master-slave manipulators for the operation of equipment within the cell, while the first-floor window has only one manipulator. The decontamination and characterization equipment will be located in front of the windows so it can be seen during operation and be accessible to the manipulators and crane. Most operations will take place in front of the second-floor window. The storage racks will be located on the floor of the cell and accessible only by use of the crane. A layout of the equipment within A-Cell is shown in Figure 5.5.

5.12

FIGURE 5.5. Layout of Equipment Within A-Cell

5.7 FACILITY PREPARATION

The cleanout of A-Cell (location shown in Figure 5.1) required all of FY 1985. Equipment removed from the cell included waste barrels; several Waste Solidification Engineering Prototype (WSEP) canisters; test pods; storage racks; a small water basin; a calorimeter; miscellaneous filters; work trays; and drill motors. As all equipment to be removed from the cell was radioactive; it was necessary to reduce its size sufficiently to fit into a shielded waste box for transporting to the Hanford 200 Area Burial Grounds for disposal.

Access to A-Cell is through two successive sets of hinged steel Dutch doors. One door connects the air lock to A-Cell, and the other connects the air lock to a cask-handling area, the central service area for transporting radioactive materials within the 324 Building. Equipment is handled by the use of two systems. A crane with a rating of 5 tons operates on a rail that permits it to serve A-Cell, D-Cell, and the air lock; and heavy duty master-slave manipulators are located at each viewing window.

5.7.1 Size Reduction

Remote size reduction of equipment in A-Cell was accomplished chiefly by use of a PNL-developed saw fabricated from a commercially available reciprocating pneumatic hacksaw. The saw was rather slow and required constant attention by the operator to ensure it did not bind. The use of a diamond blade installed in an electrically operated skillsaw did not prove particularly effective; held in place by a master-slave manipulator, it was very difficult to control. The use of abrasive blades on a plasma torch was not allowed as particulates produced would plug the cell's exhaust filters.

As size reduction by remote operations was extremely slow, the small water basin, pods and storage racks were decontaminated and "shadow"-shielded so that demolition activities could take place in the air lock and thus save time. Abrasive blades were used and demolition was done quickly and efficiently.

5.7.2 Waste Boxes

Shielded waste disposal boxes were used to transport the cut-up equipment to Hanford's 200 Area Burial Grounds. Two types of boxes were approved for shipment of waste classified as nontransuranic high-activity solid waste. A

lightly shielded waste box was fabricated to contain lightly-contaminated equipment. A heavily shielded waste box was fabricated for shipments of highly-contaminated equipment.

The lightly shielded waste box (see Figure 5.6), commonly referred to as the 6-1/2-ton box, was fabricated from steel plate with all welded joints with an overpack constructed from wood. The heavily shielded waste box (see Figure 5.7), commonly referred to as the 22-ton waste box, was fabricated from steel plate with lead plate attached to the outside walls. All joints are fully welded and the overpack is constructed from steel plate.

5.7.3 Waste Removal

The major items of equipment removed from A-Cell were:

- tank
- ten 55-gal drums
- 20 WSEP canisters
- one calorimetry pod
- one small water basin
- one work-station rack
- one pod storage rack
- two canister storage racks.

For waste hauls from A-Cell to the 200 Area Burial Grounds, twenty boxes (fifteen 6-1/2-ton and five 22-ton) were filled with a total of ~61 m³ of waste. All shipments were safely made with no overexposure to any operating staff.

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FIGURE 5.6. Lightly Shielded Waste Box (6-1/2 tons)

8303517-2cn

FIGURE 5.7. Heavily Shielded Waste Box (22 tons)

6.0 WEST VALLEY SUPPORT

J. R. Carrell - Manager

6.1 OBJECTIVES

The Western New York Nuclear Services Center (WNYNSC) is the only commercial nuclear fuel reprocessing plant to have operated in the United States. Underground tanks at the site contain high-level waste (HLW) produced, in part, by a commercial fuel reprocessing campaign. The State of New York has assumed responsibility for these wastes. The Department of Energy (DOE) is assisting, through the West Valley Demonstration Project (WVDP), in retrieving and solidifying these wastes. The site contractor for the WVDP is West Valley Nuclear Services, Inc. (WVNS).

The overall objective of the West Valley Support Task (WVST) is to provide the technical support required by the WVDP, including the transfer of DOE-developed HLW treatment technology. Specific objectives include 1) designing an acceptable glass-waste form for West Valley waste and providing characterization data that support its acceptability and 2) assisting WVNS with the technology and equipment required to successfully vitrify the West Valley waste.

The following sections summarize the FY 1985 activities of the WVST in support of the above objectives. These sections cover work done in vitrification process development, head-end process support, equipment design support, and glass characterization.

6.2 SUMMARY

The final major vitrification system component, the canister turntable, was fabricated, tested, and sent to West Valley for installation and overall system testing. It is expected that the system will ultimately be used to vitrify high-level wastes (HLW) at West Valley.

A West Valley HLW glass composition was recommended that incorporates IONSIV® IE-96 inorganic ion exchanger in the melter feed. The composition was evaluated in engineering- and pilot-scale nonradioactive melter systems and as a

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result has been selected as the reference West Valley HLW form composition. Work on glass composition development was published.

Removal of cesium from the West Valley HLW supernatant should allow disposal of the remaining solution as low-level waste. A reference cesium removal process was developed using an inorganic ion exchanger. Two ion exchangers were evaluated. In addition, an air displacement slurry (ADS) pump was developed to feed a mixture of glass-formers and HLW to the melter. The ADS pump has been selected by West Valley for their reference feed system. Twenty-three internal technical reports were submitted as part of the West Valley Support activity.

6.3 VITRIFICATION PROCESS DEVELOPMENT - Activity Leader: R. A. Brouns

Major Contributors: J. M. Perez, R. W. Goles, B. M. Wise,
and L. J. Ethridge

The vitrification process and equipment is being developed and tested to determine the optimum design and operating parameters for the glass melter, slurry feed system and primary effluent treatment equipment. The data obtained in this activity will support selection of the vitrification hardware and the approach to processing.

The reference approach to the vitrification process was initially defined in FY 1983. During FY 1984 the reference vitrification process and equipment were further refined and additional performance data were gathered. An emphasis was placed on identifying and solving glass-foaming and other waste-specific melting problems. A major effort was also aimed at developing a melter feed composition and equipment to handle direct incorporation of the zeolite ion-exchanger used for decontaminating the supernatant in one of the HLW tanks.

The major effort in FY 1985 was in making the final selection of the glass composition to be used for the West Valley process and in demonstrating this choice in a pilot-scale experiment. Detailed examinations of an instrumented canister filled with glass during one of the PSCM runs was also completed.

6.3.1 Ceramic Melter Testing

In FY 1982, Pacific Northwest Laboratory (PNL) began testing of the ceramic melter in support of the planned 1988 startup of the West Valley campaign to vitrify the PUREX and Thorex wastes. Since then, the assumed flowsheet and waste composition have evolved considerably. In the current flowsheet, radiocesium will be recovered from the alkaline PUREX supernatant with a zeolite (IONSIV IE-96) ion exchanger. The cesium-loaded zeolite will be added to the washed PUREX sludge and the Thorex waste for vitrification. Glass-formers will be added to this blended waste mixture, and the resultant feed will be vitrified in a ceramic-lined melter. The current reference flowsheet is shown in Figure 6.1.

Initial tests with the pilot-scale melter (PSCM), including PSCM-9 (August 1982) and PSCM-15 (May 1983), processed a simulated Tank 8D2 alkaline sludge

FIGURE 6.1. Simplified Schematic of West Valley Vitrification System

waste and glass frit mixture. At that time the flowsheet assumed that the Thorex waste would be processed separately later. It was later assumed that cesium would be recovered from the 8D2 supernatant using an inorganic resin that would be eluted, thus delivering the cesium back to the process as an acid solution. For the PSCM-16 melter trial (August 1983), a feed was used that simulated nitric acid and acidified PUREX sludge plus Thorex waste. Glass-former chemicals replaced the previously used frit for rheological considerations.

In the first quarter of FY 1984 it became apparent that, because of advances in supernatant processing, zeolite (initially IE-95) would be incorporated into the melter feed. At that time, laboratory testing was started to determine how zeolite could best be incorporated into the waste glass. Experimental Ceramic Melter (ECM) testing was begun in the third quarter of FY 1984. The first PSCM test of the zeolite feed was PSCM-19, performed in August 1984. Initial ECM and PSCM tests suggested that a calcium-phosphate phase on the surface of the glass melt was severely limiting maximum processing rates. For that reason, a change was made to IE-96 zeolite, essentially a calcium-free version of IE-95 with very similar exchange properties. It was from this point that FY 1985 melter testing began.

6.3.2 Experimental Ceramic Melter Testing

The ECM is a joule-heated, ceramic-lined melter (Figure 6.2 and the diagram in Figure 3.5) with an exposed glass surface area of 0.054 m^2 and a slurry-processing capacity of up to 4 L/hr. The simulated waste slurry is metered to the melter via a variable-speed peristaltic pump. Off-gases are initially scrubbed in a packed column before passing into the laboratory auxiliary off-gas system.

During FY 1985, 13 experiments were performed with the ECM using West Valley or related feeds. The objective was to identify a feed that would incorporate the West Valley PUREX sludge and Thorex waste and the zeolite ion exchanger used to decontaminate the PUREX supernatant. Variables investigated were: reductant level, incorporation of zeolite, acid type and level, alkali type and level, boron level and rare earth, calcium, chromium, and phosphorus

FIGURE 6.2. Experimental Ceramic Melter (ECM)

levels. Additionally, emphasis was placed on confirming the correlation between laboratory melt rate and redox control tests and actual ECM performance.

The FY 1985 ECM runs are summarized in Table 6.1. The glass compositions used in the tests are given in Table 6.2. The first three tests (ECM-85-1, 2 and 3) were performed to optimize the WV183 glass formulation. ECM-85-4 and ECM-85-5 tested a high-cesium glass developed for the FRG program that was designed to be as much like WV183 as possible. Zeolite was added to one of these glasses to determine its effect on melt performance. ECM-85-7 tested an SRL analog glass with formatted waste. The melter trials ECM-85-8 through ECM-85-13 tested a series of glass formulations with fully and partially nitrated feeds. The significant results of these experiments are as follows:

- Formation of calcium-rare earth- PO_4 phases on the glass surface is the major cause of poor melting performance.
- Chromium phases appear to have little or no impact on melting performance.
- PO_4 phases continue to exist during idling.

TABLE 6.1. Summary of FY 1985 West Valley-Related Experimental-Scale Ceramic Melter Tests

ECM Test	Glass Formulation	Feed Formulation	Test Duration, hr	Online, %	Average Feed Rate, L/hr	Average Glass Temperature, °C	Cold Cap Behavior	Comments
ECM-85-1	WV183	Nitrated plus sugar	23.8	57	2.3 ^(a) 1.5 ^(b)	1160	Rigid; tendency to bridge; average ~70%	Viscous surface layer
ECM-85-2	WV183	Nitrated plus sugar, sulfate	24.0	98	2.1 ^(a) 2.8 ^(b)	1160	Thin; less rigid; some venting; average ~80%	Viscous surface layer
ECM-85-3	WV183	Nitrated plus sugar, sulfate	76.8	88	1.7 ^(a) 1.8 ^(b)	1160	Similar to ECM-85-2 but with bridging; average ~55%	Viscous surface layer
ECM-85-4	FRG-8	Glass formers for zeolite	40.3	100	3.4	1150	Rigid but thin with many vents; average ~60%	Very good melt behavior
ECM-85-5	FRG-8	Zeolite	27.8	100	3.5	1160	Rigid but thin with many vents; average ~70%	Melt behavior identical to ECM-85-4
ECM-85-6	WV192 WV183 Update	Nitrated	46.3	92	3.0	1175	Rigid but thin with many vents; average ~50%	WV192 is WV183 with less rare-earth elements used for U and Th substitution
ECM-85-7	WV202 SRL TDS-165 analog	Formated	24	100	2.8	1180	Rigid but thin with many vents; average ~75%	Some scum and molten salts
ECM-85-8	WV199	Partially nitrated	34	94	2.1	1150	Rigid but thin with many vents; average ~70%	Formed glassy insoluble phase; rubbery
ECM-85-9	WV199	Fully nitrated	18.6	100	2.4	1160	Very rigid; little venting; average ~60%	Formed glassy insoluble phase; rubbery
ECM-85-10	WV203 PSCM-16 analog	Partially nitrated	41.4	100	3.0 ^(a) 3.4 ^(c)	1130	Very active; flexible; average ~40%	Small amount of scum
ECM-85-11	WV202 SRL TDS-165 analog	Partially nitrated	36.5	100	2.3	1170	Rigid; some venting; average ~70%	Surface scum very rigid
ECM-85-12	WV204	Partially nitrated	37.8	97	2.5	1160	Rigid; thick; moderate venting; average ~60%	Surface scum very rigid
ECM-85-13	WV205 SRL interim glass	Partially nitrated	42.5	98	2.8 ^(a) 3.2 ^(b)	1150	Thin; flexible; active venting; average ~60%	Small amount of scum

(a) Average for entire test.

(b) Stable feed rate for last 8 hr.

(c) Average for last 20 hr of test.

TABLE 6.2. Glass Compositions for FY 1985 Experimental-Scale Ceramic Melter Tests

Glass Oxides	FY 1985 Experimental-Scale Ceramic Melter Tests								
	1, 2, and 3 ^(a)	4 and 5 ^(b)	6 ^(c)	7 and 7E ^(d)	8 and 9 ^(e)	10 ^(f)	11 ^(g)	12 ^(h)	13 ⁽ⁱ⁾
Al ₂ O ₃	2.36	2.39	3.29	2.80	3.31	3.31	3.31	3.31	3.31
B ₂ O ₃	15.53	14.93	15.58	7.50	15.56	8.80	7.56	7.50	9.96
BaO	0.06	1.29	0.06	0.07	0.06	0.06	0.06	0.06	0.06
CaO	0.63	0.81	0.61	0.62	0.61	0.61	0.61	0.61	0.61
CeO ₂	0.17	0.29	0.16	0.07	0.16	0.16	0.16	0.16	0.16
Cr ₂ O ₃	0.68	0.70	0.22	0.71	0.22	0.22	0.22	0.22	0.22
Cs ₂ O	0.10	5.75	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Fe ₂ O ₃	12.23	10.04	11.75	11.90	11.84	11.84	11.84	11.84	11.84
K ₂ O	0.08	--	0.07	0.08	0.07	0.50	0.07	0.50	3.51
Li ₂ O	--	--	--	4.50	--	3.75	4.55	4.00	3.05
MgO	0.08	0.53	0.16	0.08	0.16	1.30	0.16	1.16	1.31
MnO ₂	0.48	0.77	1.71	0.91	1.73	1.73	1.73	1.73	1.73
Na ₂ O	14.74	11.95	14.76	10.50	14.23	14.65	10.22	12.50	11.03
NiO	0.45	0.30	0.69	0.85	0.70	0.70	0.70	0.70	0.70
P ₂ O ₅	2.60	--	2.50	2.72	2.52	2.52	2.52	2.52	2.52
RE ₂ O ₃	2.92	2.29	0.12	0.25	0.12	0.12	0.12	0.12	0.12
RuO ₂	--	--	0.08	0.10	0.08	0.08	0.08	0.08	0.08
SiO ₂	44.67	44.80	44.73	52.30	45.22	45.64	52.68	49.50	45.20
SO ₃	0.14	0.50	0.13	0.64	0.50	0.50	0.50	0.50	0.50
SrO	0.03	1.91	0.03	0.04	0.03	0.03	0.03	0.03	0.12
TiO ₂	--	--	--	--	--	0.60	--	--	0.97
Y ₂ O ₃	0.02	--	0.02	--	0.02	0.02	0.02	0.02	0.02
ZrO ₂	1.68	0.07	3.10	3.16	3.12	3.12	3.12	3.12	3.12
Other	0.35	0.68	0.13	--	--	--	--	--	--
Total	100.00	100.00	100.00	100.00	100.36	100.00	100.00	100.00	100.00

- (a) ECM-85-1, -2, and -3; WV183 glass; fully nitrated feed with no HNO₃ added; ~10 wt% IE-96 zeolite.
 (b) ECM-85-4 and -5; FRG-8 glass (WV192 with high Cs and no P); nitrated feed with no zeolite (ECM-85-4) or ~10 wt% IE-95 zeolite (ECM-85-5).
 (c) ECM-85-6; WV192 glass (updated WV183); nitrated feed.
 (d) ECM-85-7 and -7E; WV202 glass, SRL TDS-165 analog glass with old waste; formatted hydroxide feed.
 (e) ECM-85-8 and -9; WV199 glass; partially (ECM-85-8) and fully (ECM-85-9) nitrated hydroxide feed; 25 and 50 g/L sugar; ~10 wt% IE-96; Na oxalate glass former.
 (f) ECM-85-10; WV203 glass, PSCM-16 analog; partially nitrated hydroxides; 50 g/L sugar; ~10 wt% IE-96; Na oxalate glass former.
 (g) ECM-85-11; WV202, SRL TDS-165 analog; partially nitrated hydroxides; 22 g/L sugar; ~10 wt% IE-96; Na oxalate glass former.
 (h) ECM-85-12; WV204, PSCM-16, SRL TDS-165 hybrid; partially nitrated hydroxides; 22 g/L sugar; ~10 wt% IE-96; Na oxalate glass former.
 (i) ECM-85-13; WV205, SRL interim glass analog; partially nitrated hydroxides; 36 g/L sugar; ~10 wt% IE-96; Na oxalate glass former.

- Increased nitrate level enhances melting performance modestly (~10-20%) when proper redox is maintained.
- Zeolite does not degrade melting performance.
- Formate-based feeds melt comparably to nitrate-based feeds.
- Higher alkali, lower viscosity glasses improve melter performance by increasing flux and suppressing phase separations.

Based on the above and on results from other areas of the West Valley Support Task, PNL recommended that West Valley adopt the WV205 glass formulation for use in the FY 1985 pilot-scale ceramic melter test. The WV205 formulation works well because it has a high alkali content which improves fluxing and suppresses the formation of surface phases and yet is found to have excellent durability. PNL recommends that this feed be processed as a partially nitrated slurry using only nitric acid recovered from the melter off-gas scrubber. The scrubber should be operated in the condensing mode to capture HNO_3 most efficiently. The feed will be nitrated to the fullest extent possible without adding more acid to the system and increasing NO_x emissions.

6.3.3 Pilot-Scale Ceramic Melter PSCM Test

A pilot-scale melter test using the WV205 feed was conducted in May and June of 1985 under the Technology Testing Task. The WVST provided funding to extend the experiment an additional 60 hr. The formulation, designated WV205, consisted of ~10 wt% IE-96 zeolite and ~23 wt% waste oxides, with the remainder coming from raw chemical glass-formers. Sodium formate was used as a glass-former for redox control. Additionally, sugar was added at 19 g/L during part of the run to further reduce the melt.

The PSCM operating data was summarized in Table 3.10. A total of ~9050 L of simulated feed was processed during the ~300 hr test. The feed without sugar processed significantly faster than the feed with sugar (~71 L/hr·m² versus ~51 L/hr·m² maximum feed rate). In general, the melting behavior of the WV205 feed was excellent, much improved over the WV182 feed formulation used during PSCM-19. Maximum feed rates more than doubled and the cold cap behavior was much improved, with no tendency to cone and pool as in PSCM-19. The PSCM-21 experiment is described in detail in the Technology Testing Task section of this report.

6.3.4 Instrumented Canister Analysis

The objective of using instrumented canisters during the PSCM experiments is to develop and demonstrate means by which liquid-fed ceramic melter (LFCM) process instrumentation and a knowledge of process phenomena can be used to control and assess the quality of the glass product. The August 1984 run, designated PSCM-19, was conducted to achieve a number of objectives. Filling an instrumented full-scale canister, roughly representing a typical West Valley canister, was among these. The data collected from this canister was used to assess the glass product and to add to the data base, which includes canister data from PSCM-14 and PSCM-15 (McElroy and Burkholder 1984).

The results of composition and temperature measurements were used to assess our ability to predict compositions from simple mass balance calculations and our ability to predict canister temperatures. Based on these assessments, improved sampling matrices and test plans were developed for use in future runs. A qualitative comparison of devitrification with the temperature histories was made and compared with previous West Valley canister studies.

Data on glass composition, devitrification, and temperatures pertaining to the PSCM-19 instrumented canister were generated. The temperature data were obtained by placing thermocouples at several radii and several elevations in the canister. The data on the glass were obtained by coring samples of glass from the canister and analyzing them for composition [induction-coupled plasma (ICP) and x-ray fluorescence analyses] and crystallinity [scanning electron microscopy (SEM) and x-ray diffraction analysis].

The conclusions drawn from these data are:

1. The batch-pouring procedure was an effective technique for filling canisters at the low glass production rate of 7 kg/hr experienced during PSCM-19. Batch pouring did not cause melter upsets or other operational problems.
2. The full-scale product was generally superior to that of PSCM-14 or PSCM-15 with respect to voids, devitrification, and cracking. This is mainly attributable to the batch-pouring procedure.

3. Because of the higher pour rate during batch filling, the glass filled the canister more completely than for the lower, continuous-pour rates used in PSCM-15. The filling was equal to or better than the filling observed in the PSCM-14 canister.
 4. Batch-poured glass experienced cooling rates of about 100°C per hour, which is much greater than the average 20°C per hour rate seen in glass poured continuously. Less than half of the devitrification (spinel) seen in previous instrumented canisters was seen in the samples taken from the PSCM-19 canister.
 5. A significant fluctuation of several components, especially boron, was seen in the feed samples. This large fluctuation in the composition was not seen in the glass samples due to damping of rapid fluctuations by mixing in the melter. There was, however, some indication of a gradual increase in boron concentration in the grab samples taken toward the end of the run and in the corresponding core samples, which is consistent with the high average boron in the feed.
 6. More work on the statistical design of sampling schemes is recommended in order to gain greater certainty in the predictions of glass compositions based on the feed composition data. In conjunction with the sampling scheme, continued investigation of the mixing in feed tanks and the technique for sampling is also recommended.
- 6.4 COMPONENT TEST STAND (CTS) PROCESS SUPPORT - Activity Leader: L. K. Holton
Major Contributors: B. M. Wise, L. A. Bray, W. O. Heath, and T. R. Myers

A reference supernatant treatment process has been developed for West Valley Tank 8D2 high-level waste. The alkaline supernatant will be treated with IONSIV IE-96 ion exchanger to recover the cesium. A pilot-scale ion-exchange column was used to determine the hydraulic properties of IE-96. The sludge in Tank 8D2 was simulated, and investigations were completed to prepare formatted and nitrated feeds for vitrification. A small sample of Tank 8D2 supernatant has been analyzed; the sample compares favorably with synthetic feeds used to select the reference process.

PNL has the responsibility to aid West Valley Nuclear Services in selecting and designing the West Valley Demonstration Project supernatant treatment system. In FY 1983, several processes were evaluated by PNL (Bray et al. 1984). In FY 1984, a reference supernatant process (inorganic zeolite ion exchange) was chosen by West Valley. The process will treat the alkaline supernatant (pH 10) stored in the West Valley HLW Storage Tank 8D2. The process is designed to recover the cesium activity, thus converting the alkaline sodium waste liquid (6 to 7 M) to a radioactive low-level waste (LLW) for onsite disposal. The HLW solids remaining in Tank 8D2, along with the cesium-loaded zeolite and a small volume of Thorex acid waste, will then be mixed and used as melter feed for vitrification.

The selected pretreatment option for Tank 8D2 alkaline supernatant consists of an ion-exchange system using a series of columns that provides a cesium decontamination factor (DF) of 10^3 to 10^4 . If 100% of the zeolite is utilized, about 80,000 kg of zeolite will be required to treat 2×10^6 L of waste.

The sludge phase remaining in Tank 8D2 after removal of the alkaline supernatant will be blended with a small volume of Thorex acid waste from Tank 8D4 and the cesium-loaded zeolite for vitrification. Additional nitric acid or formic acid may be required before vitrification to aid in rheological and redox behavior.

Several investigations were made in support of the West Valley reference pretreatment system, including:

- constructing and testing a pilot-scale ion-exchange column
- evaluating an alternative ion exchanger for supernatant treatment processing
- evaluating the acid digestion of zeolite
- analysis of actual Tank 8D2 supernatant
- simulating nitrated and formated feeds for the West Valley vitrification system.

6.4.1 Engineering-Scale Ion-Exchange Column Tests

The current reference process for decontaminating Tank 8D2 supernatant involves ion-exchange columns that will be installed in process tanks at West Valley.

Installation, calibration, and column tests were completed. The column is designed like that proposed by West Valley, but is smaller (diameter of 2 ft versus 3 ft, cylindrical section height of 10 ft versus 10.5 ft). The cylindrical section of the column is fabricated from Plexiglas® so that the exchange bed can be directly observed. The column top and bottom are fabricated from ASME dished heads. The vessel distribution/collector system consists of a series of Johnson screens^(a) with internal piping for the backwash distributor/service collector and inlet distributor, and Johnson screens without internal piping for the backwash collector. The column installation, top fittings, and bottom fittings on the Plexiglas column are shown in Figures 6.3, 6.4, and 6.5.

The purpose of the engineering-scale ion-exchange column study was to obtain the data needed to complete the final design of the West Valley supernatant treatment system and to verify the proposed column design. This general objective was divided into the following components:

- Determine the bed utilization efficiency of the test column - This information was needed to complete material balances for the front-end system and to predict system performance. A resin that changed colors was used in a series of column loadings to determine the shape of the interface between loaded and unloaded exchanger, thus giving column efficiency and suggesting column design changes that would improve efficiency.
- Determine the hydraulic properties of the zeolite in the column - Data collected in these tests will be used to determine necessary flow rates and pressures and to size pumps for the actual system. Upflow bed expansion and downflow pressure drop versus flow rate were investigated.

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(a) Manufactured by Johnson Division-UPO, Inc., St. Paul, Minnesota.

8408342-7cn

FIGURE 6.3. Overall View of Pilot-Scale Zeolite Ion-Exchange Column

8408342-6cn

FIGURE 6.4. Head Fitting for Pilot-Scale Zeolite Ion-Exchange Column

8408342-4cn

FIGURE 6.5. Bottom of Pilot-Scale Zeolite Ion-Exchange Column

- Evaluate the zeolite changeout efficiency for the column - The proposed design for the columns at West Valley includes a sluice outlet on the bottom of the column. This configuration was tested to determine a workable sluicing procedure and to determine the actual changeout efficiency and potential operating difficulties.
- Determine the behavior of zeolite fines - Zeolite fines may be generated during transfer of zeolite to the ion-exchange columns at West Valley. A test was performed to determine whether fines would cause operating difficulties in the test system. A test of downflow pressure drop was included to simulate the column loading procedure.
- Identify potential operating difficulties with the test system - This objective was met by observing the tests and noting any difficulties.
- Recommend system design changes to improve system performance - These recommendations were based on the problems identified during the tests.

The significant findings of this work include:

- As tested, the column bed utilization is greater than 90% at 50% breakthrough. The volume not utilized included all the exchanger under the service collector and some of the exchanger above the distributor. That above the distributor could be attributed to column-wall effects and distributor inefficiencies.
- Tests of downflow pressure drop showed that at flow rates of interest the bed pressure drop was negligible. It was not possible to determine the pressure drop accurately with the test system due to the small pressure differences. Previous work has indicated that the pressure drop will be in the range of 2 to 10 in. H₂O/ft bed during column loading.
- When added at 6 wt%, zeolite fines increased the downflow bed pressure drop beyond the 5 psi allowable in the test system due to structural constraints. Backwashing the bed, however, lowered the pressure drop to allowable levels.

- It was possible to sluice all but a very small amount of zeolite (several grams) from the column. The following procedure worked quite well. The bed was backwashed to expand it and then the bottom alve was opened. The backwash water was left on during sluicing. After the bulk of the zeolite and water were removed from the column, water spray from the backwash distributor was used to rinse out the remaining zeolite.

6.4.2 Durasil Evaluation

At the request of WVNS, PNL investigated Durasil® ion exchangers as alternatives to zeolite for decontaminating the West Valley alkaline supernatant. Durasil 10A and 210 were suggested for study; cesium loading performance, water leaching, and acid elution were evaluated. The results indicate that Durasil 10A and 210 can be expected to achieve a cesium loading of 10 to 12 cv equivalents when used to treat West Valley Tank 8D2 supernatant. The West Valley reference ion exchanger (IE-96) is expected to achieve a cesium loading of 26 to 30 cv equivalents.

Samples of Durasil 10A were tested for retention of cesium using simulated West Valley alkaline supernatant. Batch relative distribution ratios (R_d) were determined for three small samples. The cesium R_d values were 11.7, 24.3, and 13.4 after a 16-hr batch contact with Durasil 10A and synthetic supernatant (pH 10.4).

A 20-cm³ column of Durasil 10A was tested using simulated West Valley alkaline supernatant (pH 10.4) (Figure 6.6). The feed flow rate was 0.2 cv/hr; a 50% cesium breakthrough occurred at 12.5 cv. Water washing (10 cv), sodium elution (0.1 M HNO₃), and cesium elution (3 M HNO₃) were tested based on Duratek advice. The first 2 cv of H₂O were composited (pH 10.35), and 0.5 mL (centrifuged volume) of postprecipitated silica gel was observed in the sample. Approximately 2.6% of the loaded cesium was eluted with the water wash cycle. The sodium wash removed about 71% of the loaded cesium. The 3 M HNO₃ strip solution removed the remaining 26% of the cesium. Results for Durasil 10A and

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FIGURE 6.6. Cesium Breakthrough Profile for Alkaline Supernatant and Durasil 10A

IE-96 are compared in Figure 6.7. IE-96 has a 50% cesium breakthrough at 27.5 cv as compared with 12.5 cv for Durasil 10A.

Three loading/elution cycles were completed using the same column of Durasil 10A. West Valley alkaline supernatant feed was loaded to 50% cesium breakthrough, followed by a water wash, 3 M HNO_3 elution, and the exchanger was then reconditioned using 0.15 M sodium tetraborate. The Durasil 10A cesium capacity was reduced after each cycle as shown in Figure 6.8. The 50% cesium breakthrough was reduced from the initial 12.5 cv to 5 cv and 3.8 cv for the

FIGURE 6.7. Comparison of Cesium Loading and H_2O Profiles for IE-96 and Durasil 10A

FIGURE 6.8. Cesium Loading Profile for Durasil 10A as a Function of Loading Cycle

next two loading cycles. A postprecipitate was observed in the first fraction of water wash for each cycle. The 17-cm-tall ion-exchange column lost 0.5 cm of bed height after three cycles. This loss and the observation of postprecipitated material indicate that Durasil 10A is soluble in West Valley alkaline supernatant. A 3 M HNO₃ elution profile is shown in Figure 6.9. The majority of the cesium was released in the first 3 cv, but the remaining cesium "tails" during the next 15 to 20 cv.

FIGURE 6.9. Elution of Durasil 10A Using 3 M HNO₃

A sample of Durasil 210 was also tested for cesium retention using the West Valley alkaline supernatant. The 45 to 80 mesh exchanger was prepared by Duratek in the NH_4^+ -form. Duratek suggested that the cesium loading would increase if the West Valley supernatant was adjusted to pH 8 using HNO_3 and that the stability of the exchanger to OH^- attack would improve. No improved cesium loading was found (about 10 to 12 cv at 50% breakthrough at both pH 8.3 and pH 10.4). Postprecipitation of silica, however, was not observed at pH 8.3 during water washing, and exchange stability was improved. Postprecipitation of the Durasil 210 was observed at pH 10.4. Severe gassing of the exchanger was observed during initial alkaline supernatant (pH 8.3) loading of the Durasil 210. The gassing was eliminated by partially converting the Durasil 210 (NH_4^+ -form) to the Na^+ -form using 10 cv of 5 M NaNO_3 .

The results for a loading, water wash, and 3 M HNO_3 elution cycle with Durasil 210 are shown in Figure 6.10. The cesium-loading profile shows an earlier initial breakthrough than for Durasil 10A (Figure 6.8, first cycle) but a similar 50% cesium loading breakthrough of 10.5 cv. A second test column with NaNO_3 -washed Durasil 210 and pH 8.3 feed (eliminating gas formation) resulted in essentially the same loading profile at 12 cv (Figure 6.11).

Batch relative distribution ratios were obtained for Durasil 210 at 6°C and 25°C for synthetic West Valley alkaline supernatant and for pH 10.4 and pH 8.3 feeds diluted 1:3 and 1:10. The R_d results were about 20 for pH 10.4 feed and about 10 for pH 8.3 feed (Table 6.3). This difference, however, was not observed in the above column tests. No enhanced column loading for Durasil 210 would be expected for feeds diluted 1:3 or 1:10 based on the results shown. IE-96 results also are shown in Table 6.4 for comparison, indicating that unlike the Durasil 210 exchanger, dilution and lower temperatures enhance the zeolite loadings.

Batch distribution tests were completed to determine the R_d of cesium-loaded Durasil 210 in contact with demineralized water at 6°C, 25°C, and 70°C. The average R_d for Durasil 210 was about 10^4 ; the average IE-96 R_d was $>10^6$ (Table 6.4).

FIGURE 6.10. Cesium Breakthrough Profile for Alkaline Supernatant and Durasil 210

FIGURE 6.11. Cesium Breakthrough Profile for Alkaline Supernatant at pH 8.3 and pH 10.4

The evaluation of other ion exchangers, Durasil 210 and 10A, indicated no advantages for recovering cesium from West Valley alkaline supernatant as compared with the reference, IE-96.

6.4.3 Acid Digestion of Zeolite

Process requirements for preparing a melter feed for vitrification are being evaluated. As now conceived, Tank 8D2 sludge will first be washed with water to remove excess sodium and sulfate. The washed sludge will then be

TABLE 6.3. Cesium Batch Distribution Values for Durasil 210 and IE-96^(a)

Dilution	Durasil 210				IE-96			
	6°C		25°C		6°C		25°C	
	pH 8.3	pH 10.4	pH 8.3	pH 10.4	pH 8.3	pH 10.4	pH 8.3	pH 10.4
1:1	18.9	19.9	6.6	21.4	50.7	62.5	39.5	43.8
1:3	59.6	94.5	26.4	87.2	231	232	123	151
1:10	147.3	290.0	109.8	249.7	980	986	455	362

(a) Conditions: 45 to 80 mesh, NH_4^+ -form, H_2O -washed Durasil 210.

TABLE 6.4. Cesium Distribution Between Loaded Exchangers and H_2O as a Function of Temperature^(a)

Temperature, °C	Distribution Coefficient, R_d	
	IE-96	Durasil 210
6	--	7.4×10^4
25	3×10^6	1.7×10^4
40	1×10^6	--
70	4×10^6	4.6×10^3
120	7×10^6	--

(a) Condition: 16-hr contact.

transferred from Tank 8D2 to a concentrator and blended with Thorex acid waste and water-slurried cesium-loaded zeolite. Nitric acid may also be blended with this mixture if feed rheology or melter performance benefits would result.

As part of this study, IE-96 zeolite was digested with HNO_3 acid to determine acid requirements and melter performance. To determine the acid-leaching requirements, three tests were conducted using 10 M HNO_3 at 25°C or 70°C and 5 M HNO_3 at 25°C; 10 cv of acid were used to leach the IE-96 zeolite. The acid was passed through the column of zeolite at 0.5 cv/hr. The initial zeolite weight was determined to be 740 g/L of exchanger. The final weight ranged from 488 to 529 g/L (29 to 34 wt% lost) after acid digestion.

The undigested and final quantities of digested zeolite were analyzed for oxide content (Table 6.5). The results show that 10 M acid is more efficient at elevated temperatures in removing iron from the zeolite structure. About 0.2 wt% and 2 wt% Fe₂O₃ remained in the silica structure after elution with 10 M HNO₃ at 70°C and 25°C, as compared with 3.3 wt% Fe₂O₃ in the undigested exchanger. The analyses of eluate showed that 15 to 20 moles of HNO₃ are required per liter of IE-96 for maximum removal of iron, calcium, aluminum, and sodium.

Zeolite resulting from the 10 M HNO₃-70°C column acid digestion test was blended into a melter feed and tested in a laboratory-scale crucible to determine melting performance. When compared with undigested zeolite feeds, the melting performance was poor.

TABLE 6.5. Analysis of IE-96 Exchanger with HNO₃ Digestion^(a)

Oxide, wt% ^(b)	Standard	5 <u>M</u> HNO ₃ , 25°C	10 <u>M</u> HNO ₃ , 25°C	10 <u>M</u> HNO ₃ , 70°C
Al ₂ O ₃	15.4	2.4	2.35	1.4
B ₂ O ₃	0.1	0.6	--	--
BaO	0.1	0.02	0.02	0.01
CaO	1.3	0.39	0.40	0.39
Fe ₂ O ₃	3.3	2.0	1.8	0.23
MgO	0.6	0.24	0.19	--
Na ₂ O	6.8	0.48	0.29	0.27
SiO ₂	60.1	82.2	82.6	85.4
SrO	0.04	0.02	0.02	0.02
TiO ₂	0.26	0.26	0.31	0.23
Other	1	1	1	1
H ₂ O	11	11	11	11
Final Weight, g/L	740	514	529	488

(a) Conditions: 10 cv HNO₃ at 0.5 cv/hr; initial IE-96 = 740 g/L.

(b) Adjusted results to 11 wt% H₂O.

Zeolite IE-96 was digested with nitric acid to determine acid requirements and resulting melter performance when the zeolite was blended with West Valley sludge. About 15 to 20 moles of HNO_3 were required per liter of IE-96 for maximum cation removal. When compared with undigested zeolite added to the melter feeds, the melting performance for digested zeolite was poor.

6.4.4 Analysis of West Valley Tank 8D2 Supernatant

About 25 mL of Tank 8D2 alkaline supernatant was sent to PNL after cesium decontamination in the West Valley hot cells using a PNL-fabricated ion-exchange column containing 30 mL IE-95. The decontaminated sample (cesium DF of about 10^6) is being used to obtain a variety of analytical data. A cation analysis using inductively coupled argon plasma spectroscopy (ICP) is shown in Table 6.6. Density and viscosity values for synthetic and actual alkaline supernatant are compared in Table 6.7 for four temperatures. The sodium and specific-gravity values indicate, based on previous sampling results, that the West Valley supernatant had concentrated in the tank by evaporation. The viscosity data for actual and synthetic supernatant agree well (Figure 6.12).

TABLE 6.6. Analysis of West Valley Alkaline Supernatant by ICP

<u>Element</u>	<u>Concentration, mg/L</u>	<u>M/L</u>
Al	(5) ^(a)	--
B	65	0.006
Ca	(2)	--
Ce	(8)	--
Cr	680	0.013
Fe	(2)	--
K	5100	0.13
Mg	(1)	--
Mo	210	0.002
Na	196,640	8.55
Nd	(5)	--
P	240	0.008
Rh	(7)	--
Si	80	0.003
Te	(5)	--
Zn	(1)	--

(a) Parentheses indicate approaching detection limits.

TABLE 6.7. Measurements of Physical Properties for Synthetic and Actual West Valley Alkaline Supernatant

Temperature, °C		Viscosity, cP		Density, g/mL	
Synthetic	Actual	Synthetic	Actual	Synthetic	Actual
6.5	6.5	6.58	7.15	1.33	1.40
25	25	4.32	3.38	1.32	1.39
40	40	2.70	2.34	1.31	1.38
85	65	1.27	1.29	1.275	1.36

Viscosity and Density of NaNO_3 at 25°C

NaNO_3 , M	Viscosity, cP	Density, g/mL
3	1.129	1.159
5	1.539	1.255
7	2.159	1.366

6.4.5 Review of Nitrated and Formated Feeds

During the vitrification stage of the WVDP, WVNS will remove the PUREX sludge from Tank 8D2, blend it with Thorex waste from Tank 8D4 and the zeolite generated by decontaminating the Tank 8D2 supernatant, add glass-forming chemicals and acid, and then vitrify the resulting feed in a ceramic melter. In the current reference process, the melter feed is a nitrated slurry, obtained by blending the hydroxide Purex sludge, acidic Thorex waste, and other melter feed components with excess nitric acid. This process is not the only option, however; and several alternatives were the subject of the work described below:

- Determine the optimum process conditions for making nitrated melter feeds - This work involved preparing simulated PUREX (Tank 8D2) sludge and simulated Thorex (Tank 8D4) acid wastes, digesting them in acid, and preparing melter feeds from them. The optimum addition of nitric acid was determined by comparing the rheological properties of the digested wastes and the resultant melter feed. The properties investigated included viscosity and percent settled solids. Observations were made of the feed-making process, including the concentration step.

FIGURE 6.12. Viscosity of Synthetic and Actual West Valley Supernatant with Temperature

- Determine the optimum process conditions for making formed melter feeds - This work was performed in the same manner as the nitric work. Formic acid was chosen because of the extensive experience at Savannah River Laboratory (SRL) and PNL with the formic acid flowsheet.
- Verify the rheology of melter feeds made directly - Nitrated feeds for PNL melter runs are made with nitrate chemicals instead of nitrating the metal hydroxides found in the West Valley wastes. Comparisons were made between the rheology of the feeds prepared for this study and feeds prepared for current PNL melter experiments to determine whether the simulated melter feeds are representative. Laboratory crucible melt tests also were performed to compare the melting behavior of the feeds.
- Determine the flowsheet impacts of formed versus nitrated melter feeds - Mass balances for nitrated and formed flowsheets were completed. Expected quantities of nitrates, carbon, and water were compared in the balances. Results of the laboratory melting studies on formed and nitrated feeds were used to determine possible impacts on melter performance.

6.4.5.1 Nitrated Feeds

Simulated wastes are currently prepared for vitrification studies at PNL by combining metal nitrates, phosphates, and oxides. In the case of West Valley, ground zeolite, glass-forming chemicals, and sucrose are then blended into the waste mixture to form the vitrification feed. Laboratory rheology, pumping, and redox control studies have each relied on this form of preparation.

To verify this feed approach, simulated West Valley PUREX acid waste was prepared based on analysis of the West Valley Tank 8D2 contents (Table 6.8). To prepare Tank 8D2 sludge, the acid waste was adjusted with NaOH, Na_2CO_3 , and NaNO_2 and digested for 100 hr at 95°C (to simulate years of in-tank heating and digestion). The resulting solids were separated by centrifuge and then washed with water. The sludge was washed four times (24 hr each time) using 180 mL of

TABLE 6.8. Final West Valley Alkaline Sludge
and Supernatant Composition

<u>Component</u>	<u>M/L</u>
Cl ⁻	0.04
NO ₃ ⁻	3.45
Al	0.017
Ni	0.011
Cr	0.027
K	0.19
Fe	0.306
Cs	0.00138
Sr	0.00056
Rb	0.00037
Ba	0.0006
Zr	0.0023
Sm	0.008
Mn	0.012
F ⁻	0.0013
P	0.1
Na	6.6
SO ₄ ⁼	0.25
Mo	0.0015
NO ₂ ⁻	2.09
CO ₃ ⁼	0.345

H₂O/cycle/initial liter of sludge plus supernatant. The water wash step may be used at West Valley to lower the Na₂SO₄ and NaNO₃ content of the West Valley sludge before vitrification.

To determine the effect of nitric acid's acidification of sludge, four sludge samples were prepared using the above procedure. To prepare 1 L of West Valley feed for vitrification, washed sludge (resulting from 3.3 L of sludge and supernatant) and synthetic Thorex acid waste were combined with varying volumes of nitric acid. These mixtures were then digested at 95°C and analyzed for free acid and total nitrate (Table 6.9). No acid was added to Sample 1;

TABLE 6.9. Acidification of West Valley Sludge Used To Prepare 1 Liter of West Valley Melter Feed

	Sample 1	Sample 2	Sample 3	Sample 4
Centrifuged Sludge Weight, g	274	304	280	286
Sludge Volume, mL	227	227	227	227
Thorex Addition, mL	56	56	56	56
HNO ₃ Addition, moles	0	0.56	1.14	2
Solids Volume After HNO ₃ Digestion, mL	227	33.3	4.25	18.3
Solids Weight After Digestion, g	274	39	4.3	20.7
H ⁺ Analysis, moles	Basic	Basic	Neutral	0.14
NO ₃ ⁻ Analysis, moles	0.41	1.17	1.76	2.16

0.56, 1.14, and 2 moles of HNO₃ were added to Samples 2, 3, and 4, respectively. The values of 0.56 and 1.14 moles of HNO₃/L were chosen because they represent about 50% and 100% of the theoretical amount of nitric acid required to nitrate the basic sludge. The volume of centrifuged solids after digestion varied with final OH⁻ or H⁺ ion concentration. The initial sludge volume was reduced from 227 mL if no acid was added to 4.25 mL when the sludge had been neutralized with 1.14 moles of HNO₃ (Sample 3). As the sludge became acidic, a new precipitate formed (Sample 4) composed of iron and rare-earth phosphates.

To prepare 1 L of West Valley vitrification feed, the washed and nitrated sludges were combined with ground zeolite (IE-96) and glass-forming chemicals to an equivalent of about 300 g of oxide/L (Table 6.10). The resulting nitrated feeds were used to determine melting properties and feed rheology.

Samples of nitrated sludge prepared for vitrification (Table 6.10) were tested to determine viscosity (centipoise) and yield stress point (Pascal) as a function of nitration. The four nitrated feed samples (Table 6.9) were also compared with current vitrification feed (WV183) prepared by combining metal nitrates, phosphates, and oxides.

Rheological results (Table 6.11) show that all feeds prepared by simulating actual West Valley sludge have higher viscosity and yield stress point

TABLE 6.10. Addition of Glass-Forming Chemicals to West Valley Sludge or HNO_3 -Treated Sludge to Prepare 1 L of WV183 Melter Feed

Chemicals Added to Table 6.10 Solution	Amount, g
SiO_2 (-325 mesh)	130
$\text{Na}_2\text{B}_4\text{O}_7$	146
Na_2SO_4	6
Zeolite (a)	39.7
$\text{Ca}(\text{NO}_3)_2$	5.8
$\text{Na}_2\text{C}_2\text{O}_4$	44.3
Sucrose	25

(a) Ground zeolite: 16.8 wt%, -200 +325 mesh; 22.5 wt%, -325 mesh; balance >200 mesh.

TABLE 6.11. Rheological Data for Melter Feeds Prepared Using Nitrated Sludge Versus WV183

	Sample Numbers				
	1	2	3	4	WV183
Shear Rate, sec^{-1}	Viscosity as a Function of Shear Rate, cP				
120	17	39	65	107	9
200	13	29	45	71	7
400	9	21	28	40	(6)
Yield Stress, Initial	1.2	2.0	5.3	11.0	0.6
Pa, Final	0.4	1.4	3.2	7.4	0.3
Moles HNO_3 , Added/L of Melter Feed	0	0.56	1.14	2	--
H^+ Analysis, moles	Basic	Basic	Neutral	0.14 H^+	--
NO_3^- Analyses, moles	0.41	1.17	1.76	2.16	2.2

values than WV183 melter feed. Sludge-prepared feed that was not nitrated compared more closely with WV183 feed. As nitric acid was added to the sludge, the viscosity at 120 sec^{-1} shear rate and the initial yield stress point increased more than tenfold as the vitrification feed became acidic (see Sample 4 in Table 6.11). In all cases, the sludge-prepared feeds suspended the ground zeolite for more than 24 hr. The WV183 feed quickly dropped the zeolite/silica out of solution.

Melting rate tests were performed with Samples 2 and 4 and with the current WV183 melter feed to determine the effect of acid content on melting rate and to verify the validity of the current method for making feed for melter trials. A clay crucible with 40 g of a standard glass composition (PSCM-16) was placed in the top of a vertical tube furnace. After temperature stabilized, the melt temperature at the surface was $1030^{\circ}\text{C} \pm 10^{\circ}\text{C}$. Next, 15 mL of feed was poured into the crucible; after 2 min, an additional 15 mL of feed was poured into the crucible. The crucible was removed from the furnace about 2 to 7 min after the last addition of feed. The cooled crucible was sectioned vertically along a diameter. A photographic enlargement was then made, an acetate sheet was placed over the photograph, and the cold cap was traced and cut from the acetate sheet. This cutout was then weighed. This process was repeated, and the results were plotted as a function of time to obtain a melting rate trend for that particular feed.

The redox potential of the feed was adjusted using sugar prior to the melting rate test to produce a ferrous/ferric ratio in the resulting glass of between 0.1 and 0.4. Ratios in this range minimize the potential for melt foaming and metal formation. The procedure used to determine the redox information was similar to that used to determine the melting rate, except that the feed was sequentially added to an empty crucible in the furnace at 10-min intervals until about 18 g of glass was produced. The melt was left in the furnace for 30 min after the last addition of feed. The resulting glass was ground into powder; and, in some cases, it was analyzed to determine the ferrous/ferric ratio using a colorimetric wet-chemical procedure. Otherwise, the color of the glass powder was used to indicate the ratio. West Valley glass powder with a ferrous/ferric ratio of 0 is light brown. Its color

changes to charcoal as the ferrous/ferric ratio becomes positive, although the size of the ratio is not readily discernible. Thus, this charcoal-colored sample was chemically analyzed to determine the ferrous/ferric ratio, and existing correlations were used to optimize the sugar concentration for the subsequent melting-rate test.

Nitrate anion-ion chromatograph analyses of Samples 2 and 4 indicate 1.17 M and 2.16 M of NO_3^- , respectively. Consistent with these values, it was determined that these feeds required 25 g/L (0.88 M C) and 60 g/L (2.10 M C) of sugar, respectively, to produce acceptable ferrous/ferric ratios. Inductively coupled plasma (ICP) analyses indicate that these feeds were formulated close to the target WV183 composition (generally within 1 wt%). The amount of feed available for evaluation of melting rate precluded duplicate testing. Sample 4, the fully nitrated feed, exhibited excellent melting behavior with slopes near -40 and cold-cap burnoff times between 4 and 5 min (Figure 6.13).

FIGURE 6.13. Cold-Cap Burnoff Times for Formated and Nitrated Feeds

That slope is similar to the standard WV183 formulation made from commercial nitrate chemicals. Sample 2, the partially nitrated feed, exhibited slower melting. However, since the carbon-to-nitrate ratio was low (0.88/1.17 mol ratio), this work should be repeated. For comparison, PSCM-16 feed (a standard glass feed) had a slope near -20, a cold-cap burnoff time near 7 min, and a processing rate of about 44 L/hr in the PSCM.

6.4.5.2 Formated Feeds

The study of formated feeds discussed here covers experimental procedures, rheology of the samples, melting rates, and behavior of the prepared feeds. Three West Valley sludges were prepared that were similar to those prepared for the nitrated studies. The washed sludges were used to prepare formated West Valley vitrification waste (Table 6.12). The formic acid was added to a water solution of sludge, glass-formers, Thorex waste, and zeolite at 80 to 90°C. The initial test was based on forming all mono- and divalent ions in the feed. About 50 to 80 mL of formic acid (HCOOH) was added to the waste mixture and digested. The resulting waste was evaporated to a volume of 1 L.

TABLE 6.12. West Valley Sludge Used To Prepare 1 L of Formated Melter Feed

	<u>Amount</u>
Centrifuged Sludge Weight	~300 g
Centrifuged Sludge Volume	~220 mL
Thorex Waste Volume	112 or 56 mL
SiO ₂ (-325 mesh)	130 g
Na ₂ B ₄ O ₇	146 g
Na ₂ SO ₄	6 g
Na ₂ CO ₃	35 g
Zeolite ^(a)	39.7 g
Ca(NO ₃) ₂	5.84 g
Approximate Amount of H ₂ O	500 mL

(a) Ground zeolite: 16.8 wt%, -200 +325 mesh;
22.5 wt%, -325 mesh; balance >200 mesh.

A sample of formatted feed prepared for vitrification using sludge was tested to determine viscosity and yield stress point values as compared with current vitrification feed prepared by combining metal nitrates, phosphates, and oxides (WV183). Melting-rate tests were performed with Sample 6 as described in the previous section.

The rheological results (Table 6.13) show that the formatted feed has higher viscosity and yield stress point values than WV183 but that it is similar to the Sample 1 feed with no HNO_3 added to the sludge (Table 6.11). The rheological data for the formatted feed show the same shear stress with increasing or decreasing shear rate and is the only feed tested that shows a Bingham flow.

The rheology of formatted feeds is very similar to that of feeds prepared from hydroxide sludges with no addition of nitric acid. These feeds have relatively high viscosities, have a small volume of settled solids, and are easily resuspended.

Melting studies with the formatted feed show that 10 g/L of sugar was required to bring the redox level to the desired range, which is consistent with the much smaller amount of nitrate in the feed and the increased carbon due to the formate. Melting tests indicated that the formatted feed melted at the same rate and had characteristics similar to those of fully nitrated feed made from sludge or from metal nitrate (see Figure 6.13).

TABLE 6.13. Rheological Data for Melter Feeds Prepared Using Formatted Sludge Versus WV183

	Sample Number	
	6	WV183
Shear Rate, sec^{-1}	Viscosity as a Function of Shear Rate, cP	
120	16	9
200	12	7
400	8	6
Initial Yield Stress Point, Pa	1.0	0.6
Final Yield Stress Point, Pa	1.0	0.3
NO_3^- Analysis, <u>M</u>	0.52	2.2

6.4.5.3 Computer Mass Balances for Nitrated and Formated Flowsheets

The mass balances for nitrated and formated flowsheets revealed several significant differences. The formated flowsheet balance indicated less NO_x (about 31%) leaving the process due to a smaller input of nitrate. The formated balance also showed small quantities of combustibles (CO and H_2) exiting the melter. These quantities would increase significantly in the balance if more feed were formated instead of nitrated. These combustibles may not exist in actual melter operation due to the increased nitrate levels, and thus oxidizing potential, of the West Valley feed. No data are currently available to support this speculation, however. It should be noted that the formated feed is inherently more complex because it contains hydroxides, formates, nitrates, sugar, and oxalate. Redox control of this feed is potentially more difficult because of its complexity.

In the formated flowsheet, the assumptions concerning the operation of the submerged bed scrubber (SBS) are quite important because they determine the total quantity of formate and nitrate in the feed. The more effectively the SBS operates, the more HNO_3 is recycled until there are no mono- and divalent hydroxides left to react with the formic acid addition. In the formated flowsheet, there is some incentive to operate the SBS in a way that does not capture HNO_3 effectively. In the nitrate flowsheet, however, operating the SBS to recover HNO_3 as effectively as possible is desired because less makeup HNO_3 is required and less total NO_x must exit the vitrification process.

Comparison of the preliminary mass balances for the fully nitrated and formated vitrification feed processes indicated that the formated feed significantly reduces (about 69%) NO_x levels exiting the vitrification process. Total carbon levels were also reduced with the formated flowsheet. The water balance is very close to that of the nitrated feed, however. The mass balance shows also that production of combustibles (CO , H_2) in the melter may pose a safety hazard in the formated flowsheet. Further study may show, however, that these combustibles do not form due to the increased nitrate level in the West Valley feed as compared with SRL feeds.

6.4.6 Rheology Studies for West Valley Project

Two separate investigations were conducted in FY 1985 in support of the West Valley Front-End Process: 1) a method to simulate the rheology of the Tank 8D2 sludge and 2) a method to improve the rheology of the Tank 8D1 sediment. Both activities are described below.

6.4.6.1 Development of Simulated Tank 8D2 Sludge

The objective of this work was to provide a method for preparing a non-radioactive simulant of the radioactive sludge at the bottom of West Valley Tank 8D2. The simulant is to be used in nonradioactive scale-model tank testing. Two different types of sludge simulant were developed.

The first type of simulated sludge is a gel that tends to redisperse into clumps that require high shear and/or acidification for reslurrying. This sludge may represent worst-case behavior and may be useful in testing schemes for tank acidification. The second type of simulated sludge also forms a gel but redisperses into separate particles and is thus much easier to reslurry. As such it is like the clay simulants already in use by WVNS and may represent best-case behavior.

Both simulants were developed to be very simple to prepare, the first consisting of three basic ingredients, the second only two. When added in different proportions, the ingredients can be used to prepare a wide range of sludge flow behavior from stiff and unyielding to soupy.

The first simulation consisted of Ludox TM®, a 50 wt% suspension of colloidal (22 nm) SiO₂, a flocculating salt solution, and an algae-derived xanthan gum thickener called Kelzan®. To prepare a sludge simulant, the salt solution is mixed with a stock solution of Kelzan and ultrasonically agitated to fully disperse the Kelzan molecules. Deionized water was used to prepare all solutions. Two different salt solutions were used to prepare simulant sludges. The first was a solution of 125 g/L NaOH in deionized water. The second salt

®Ludox TM is a registered trademark of the E. I. du Pont de Nemours Company, Wilmington, Delaware.

®Kelzan is a registered trademark of Kelco, a division of Merck and Company, Inc., Chicago, Illinois.

solution, used exclusively later in the development of the simulated sludge, was an undiluted (full strength) 8D2 supernatant simulant prepared by PNL for a separate WVST study.

A sludge simulant is then prepared by pouring Ludox TM into the solution of salt and thickener, whereupon the salt causes the 22-nm SiO_2 particles to coagulate spontaneously, forming a gel. The rheology of the Ludox/Kelzan/salt solution gel depends entirely on the proportions of the three constituents. In fact, the utility of this type of simulant is that only three constituents are required to achieve a wide range of gel stiffnesses. In short, this method is simple and versatile.

A potentially valuable property of the Ludox/Kelzan/salt sludges is that they tend to break up in relatively irreducible clumps. The other type of sludge simulant (discussed below) tends to resuspend back into the individual particles from which it was derived. The two simulants, even when prepared so that each exhibits the same yield viscosity,^(a) simulate the above-mentioned two possible resuspension modes. Since solids that have sat for years may tend to be bridged and cemented together, and therefore break into relatively irreducible clumps requiring acidification and/or grinding before processing, our clump-forming sludge simulant may well represent a worst-case scenario. Also, since acidification coupled with agitation will tend to break the clumps into smaller agglomerates/primary particles, this type of simulant sludge would be useful for evaluating 8D2 acidification schemes.

Since actual 8D2 sludge contains more $\text{Fe}(\text{OH})_3$ than any other single insoluble constituent (48 wt%), our second type of sludge simulant was based around $\text{Fe}(\text{OH})_3$. Because the 9.6 wt% $\text{Fe}(\text{OH})_3$ suspensions we worked with had relatively low viscosities (about 4,000 cP), some type of thickening was required. At first Ludox TM was added in the hope of forming a thick gel. This mixture, however, usually exhibited a lower viscosity than either constituent alone. Further, only a very small amount of $\text{Fe}(\text{OH})_3$ slurry was required to liquefy relatively thick Ludox/salt gels. In one test, 1 mL of $\text{Fe}(\text{OH})_3$ liquefied a 25-mL gel sample. One explanation is that a phenomenon

(a) Maximum plastic viscosity of "startup" viscosity as shear rate approaches zero.

of particle-particle attraction occurs in mixtures of $\text{Fe}(\text{OH})_3$ and SiO_2 . This is possible because in solutions of basic pH, $\text{Fe}(\text{OH})_3$ and SiO_2 particles carry opposite surface charges, causing the two types of particle to be attracted to one another. The $\text{Fe}(\text{OH})_3$ would tend to "scavenge" the much smaller SiO_2 particles, reducing the total number of primary particles, disrupting the SiO_2 gel network, and thus liquefying the gel. If this were the case, it may even be possible to scavenge and thus "remove" SiO_2 with $\text{Fe}(\text{OH})_3$ or vice versa. Some experimentation, however, would be required to substantiate this.

Based on the hypothesis that oppositely charged particles can scavenge one another, we switched from trying Ludox as a rheological additive to trying another insoluble species, one that would have the same (positive) surface charge as $\text{Fe}(\text{OH})_3$. The likely choice was FePO_4 since it has a positive surface charge and is the second major constituent of the 8D2 sludge, comprising 24% of the insolubles.

The combination of $\text{Fe}(\text{OH})_3$ and FePO_4 was found to lead to a wide variety of sludge rheologies. Unlike the Ludox/salt/Kelzan simulants, this sludge redisperses into individual particles like the clay simulations already in use by WVNS.

The final simulant sludges were prepared to exhibit yield viscosities matching those measured for a sample of actual hot 8D2 sludge using an identical test method (Brookfield viscometer with WVNS R&D spindle). The yield viscosity of the actual hot sludge was calculated as 1,086,000 cP, while the two types of simulants measured 1,084,000 cP for the clump-forming simulant and 1,119,000 cP for the redispersible simulant. Since the target yield viscosity of 1,086,000 cP for the actual hot sludge was arrived at by only a single set of data, a matrix of simulants was prepared along with a method for preparing them such that, as more information regarding actual sludge rheology becomes available, either a simulant from our matrix or an extrapolation from it can be used to simulate actual Tank 8D2 sludge.

Figure 6.14 is a plot comparing the viscosity-versus-time behavior of the hot sludge sample measured by WVNS with those values measured for two sludge

FIGURE 6.14. Comparison of Hot Sludge Versus Simulant Sludges

simulants prepared by PNL. As can be seen, the peak viscosities of both simulants closely match that of the hot sludge. Tables 6.14 and 6.15 summarize the composition and peak, or yield, viscosity behavior of the final matrices of the two types of sludge simulants.

6.4.6.2 Improvement of Resuspension Properties of Tank 8D1 Spent Zeolite

The objective of this work was to evaluate rheological additives for the purpose of improving the resuspension behavior of the Tank 8D1 spent zeolite sediment. Six additives were tested, and of these, two polymers with high molecular weight were found effective in improving sediment resuspension. One particular polymer was found to be the most effective in aggregating fines and thus preventing the formation of a compact, nonresuspendible sediment at a

TABLE 6.14. Final Matrix of Clump-Forming Simulated Sludge

Compound	25	26	27	28	29	30	31	32	33	34
Ludox, mL	25	25	25	25	25	15	16.5	18	15	15
SiO ₂ , g	0	0	0	0	0	7.0	6.0	5.0	7.0	7.0
8D2 Supernatant, mL	7	8	9	10	11	5	5	5	4	6
Kelzan, (a) mL	10	10	10	10	10	10	10	10	10	10
Deionized H ₂ O, mL	8	7	6	5	4	17.2	15.5	14.0	18	16
Yield Viscosity, cP x 10 ⁶	>1.88	>1.88	1.08	>1.88	0.84	0.62	0.47	>1.88	~1.88	1.47

(a) 10 g/L stock solution.

TABLE 6.15. Final Matrix of Redispersible Simulated Sludge

Compound	50	51	52	53	54
FeOH ₃ , (a) mL	50	50	50	50	50
FePO ₄ , g	3.62	4.52	5.42	7.23	9.04
Weight Ratio (b)	1.5	1.2	1.0	0.75	0.50
Yield Viscosity, cP x 10 ⁶	0.82	1.12	0.68	1.57	1.88

(a) 9.6 wt% dispersion.

(b) Ratio of FeOH₃ to FePO₄.

polymer loading of 0.1 g/L. The rheological properties associated with the final polymer-treated tank contents are:

- sediment yield viscosity of 188,000 cP
- overall slurry viscosity of 1.04 cP
- tank supernatant viscosity of 1.3 cP.

In addition to rheological analyses, an analysis of the sediment's compactability was also performed using a centrifuge. It showed the polymer-treated zeolite sediments to be 1.78 times more compactable and only 77% as

dense as sediments not treated. High compactability and low sediment density are both desirable and indicate the ease of sediment resuspendability. Additionally, a potentially novel method was developed for measuring in-tank resuspension behavior of sediments using a scale-model tank (Figure 6.15) equipped with an agitator. In this method, conductivity electrodes sense the presence of suspended particles, allowing the rate and extent of particle resuspension to be measured. The polymer-treated sediment was found to reslurry faster and with more particles in suspension than the untreated sediment.

Figure 6.16 is a simplified process flow chart of the part of the vitrification front-end process that will be used to remove cesium from Tank 8D2 supernatant. In this part of the process, the supernatant waste fraction will be pumped out of Tank 8D2 into supernatant feed Tank D-001, cooled in Tank E-001 and then introduced into the top of one of four ion-exchange columns. In our simplified flow diagram, only column A (C-001) is shown. The supernatant is pumped into a distributor located at the top of the column, which evenly distributes the 8D2 supernatant over a bed of unloaded IE-96 resin. As the supernatant passes through the bed, Na^+ ions in the IE-96 exchange with Cs^+ ions in the supernatant, thereby removing the cesium. The supernatant exiting the bottom of column A is then pumped into a distributor at the top of column B for further removal of cesium. When the IE-96 bed becomes loaded with Cs^+ ions, the bed is flushed with water to remove any 8D2 supernatant held up in interstices. This flush water, along with the interstitial supernatant, is pumped back to Tank 8D2. The bed is then blown down with utility air to remove all remaining interstitial water.

To remove the spent IE-96 bed, the bed is first expanded by injecting sluice water from Tank 8D1. A valve at the bottom of the ion-exchange column is then opened, and the contents of the column are gravity-sluiced directly into Tank 8D1. To avoid excess water in Tanks 8D1, the sluice water is recycled by means of pumps G-004 and G-003. After the spent IE-96 resin is removed from the column, new resin is slurried into the column by a delivery system not shown in Figure 6.16.

FIGURE 6.15. Tank-Mixing Test Apparatus

FIGURE 6.16. Supernatant Treatment System, Ion-Exchange Section

It is expected that about 44 column volumes, or 48,440 kg, of zeolite will be required to remove the cesium from 8D2 supernatant. The spent zeolite sluiced out of the columns and into Tank 8D1 will remain at the bottom of 8D1 until the cesium has been completely removed from the 8D2 supernatant. On completion of 8D2 supernatant treatment, it is expected that Tank 8D1 will contain about 48,440 kg of spent IE-96 solids in a dilute aqueous solution having a total combined volume of about 380,000 L. The zeolite loading in Tank 8D1 will be about 127.9 g IE-96/L of 8D1 supernatant. The 8D1 supernatant fraction will consist primarily of water with trace amounts (~100:1 dilution) of 8D2 supernatant.

Tank 8D1 is an existing underground tank having a diameter of 70 ft and a height of 27 ft. Assuming that on completion of 8D2 supernatant treatment the tank will contain 380,000 L of zeolite in water, the liquid height in 8D1 will be about 3.5 ft. There are five centrifugal pump-type mixers in Tank 8D1. Each mixer has two output nozzles, 180° apart, each with a pumping capacity of 600 gpm at 1750 rpm. The sediment in 8D1 must be resuspended using these mixers.

Polymers can help resuspend a sediment if they are present during its original formation. Very long polymers, with molecular weights in the millions, act as strings that tie fines together into much larger, irregularly shaped clumps. These clumps do not pack well, resulting in expanded, more voluminous sediment. How much the sediment expands depends on the quantity of fines present in the original particulate material. Expanding the sediment bed will prevent the presence of extremely small ($<2\text{ }\mu\text{m}$) interstices. These interstices can greatly impede resuspension of sediment because their small cross-sectional area results in very high pressure drops as water is forced through them. Since resuspension amounts to forcing water into the sediment bed, thereby separating individual particles, small interstices can cause beds to be nonresuspendable if the interstitial pressure drop is greater than the pressure drop available through the shear field produced by the mixing equipment. Small interstices therefore hold sediments together by imposing large, shear-resistive pressure drops. Such behavior is known as capillary resistance since the interstitial diameters are analogous to capillary tube diameters. Anyone who has attempted to blow water out of a small capillary tube, 0.2 mm or less in diameter, can appreciate the concept of capillary resistance. The dilatancy of certain sediments is attributable entirely to capillary resistance.

Let's assume that there will be enough fines present in IE-96 leaving the ion-exchange columns to produce some capillary resistance and further assume that the existing 8D1 mixing equipment may be unable to produce enough shear to overcome such capillary resistance. How much polymer will it take to prevent such a nonresuspendable sediment from forming? By the results as presented earlier, it takes about 0.1 g/L polymer to prevent formation of a

shear-resistive sediment. Assuming a 127.9 g/L final zeolite loading in Tank 8D1 and that 48,442 kg zeolite will be present, the total amount of polymer required will be:

$$\frac{1 \text{ L}}{0.1279 \text{ kg}} \times 48,442 \text{ kg} \times \frac{0.1 \text{ g}}{\text{L}} = 37,900 \text{ g}$$

or about 40 kg of polymer required for the duration of 8D2 supernatant treatment process.

In determining how best to add polymers to Tank 8D1, a few things must be considered. In the simplest terms, the polymers we are interested in consist of long strings of carbon atoms interspersed with ionic attachment groups. In addition to attaching to zeolite particles, these polymers can attach to other surfaces such as the tank walls, pumps, etc. If all the polymer were added in one initial charge to Tank 8D1, for instance, before adding any spent zeolite, it is likely that much of it would no longer be in solution. As each successive column of spent zeolite is dumped into 8D1, more and more polymer would be adsorbed out of solution. Early in processing, the liquid in 8D1 would be depleted of polymer. Also, due to the high cesium levels in 8D1, it is likely that polymers in solution would undergo some type of radiolysis, resulting in chain fragmentation, fragment recombination, etc. Furthermore, polymers left in solution more than one month tend to degrade unless refrigerated. Therefore, there is no advantage in trying to maintain a concentration of polymers in solution, awaiting the next batch of zeolite on which to adsorb.

Thus it appears best to add the polymers incrementally as needed, specifically along with each new batch of spent IE-96. There are a few choices as to where to add the polymers, directly into Tank 8D1 before each batch of spent IE-96, or directly into each column so they enter 8D1 along with the spent resin. Either way might be acceptable. Before discussing this further, however, it is helpful to consider the form in which polymers should be added.

The best way to add polymers to any process is to first mix them with a minimal amount of water, producing a heavy polymer syrup. The thickest practical syrup usually contains about 10 g/L polymer (see Table 6.16). The

TABLE 6.16. Viscosity of Polymer Stock Solutions

<u>Sample</u>	<u>Concentration, g/L</u>	<u>Viscosity, cP</u>	<u>Temperature, °C</u>
NX-130	10	71.8	8.3
NP10	10	6.2	8.2
N120P	10	34.3	8.1
Kelzan	10	2115.4	6.8

thicker the polymer syrup, the more difficult it is to pump, and more importantly, the more vigorously it has to be agitated to mix it uniformly with the bulk liquid in which it is diluted. On the other hand, the more dilute the polymer syrup, the more extra water must be added to the process. Since about 40 kg polymer would be needed for treating the expected 48,440 kg zeolite and about 44 batches of spent zeolite will probably need to be polymer-treated, each zeolite batch will require roughly 1 kg of polymer. This means about 100 L of 10 g/L polymer syrup or 1000 L of 1 g/L polymer syrup would need to be added along with each column of spent zeolite. Thus, between about 4,400 and 44,000 additional liters would have to be added to Tank 8D1, raising the liquid level an additional 1/2 in. to 5 in. An intermediate polymer syrup of 4 g/L polymer could be added in 400-L quantities per batch of zeolite for a total excess liquid addition of 17,600 L, raising the 8D1 liquid level ~2 in., or from about 3.5 ft to 3.7 ft. Such a syrup would have a fairly low pumping viscosity and probably not require excessively vigorous mixing with the bulk fluid.

The polymer syrup would be mixed outside the cell by adding the polymer in either flake or solution form to water in a small agitated vessel. Laboratory experience indicates that ultrasonic agitation is the most effective type, although any relatively low-shear agitator may be acceptable. High-shear fluid-impaction agitators should not be used since the high shear will fragment the polymer chains, rendering them ineffective. Instead, a standard impeller/propeller-type mixer should be used. Ultrasonic agitators impose virtually no shear and result in much more rapid and thorough mixing, but are generally more expensive. For the same reasons, a low-shear pump should be used to transport

the polymer syrup into the cell. A positive displacement pump like a diaphragm or peristaltic pump should be used rather than centrifugal pumps.

The two most likely places to introduce the polymer syrup would be via direct injection into Tank 8D1, with the 8D1 mixer/pumps operating, or via direct injection into the sluice/water lift Tank D-004. One advantage to adding the polymers to the sluice/lift tank would be that they would contact more closely the spent zeolite within the column during the zeolite sluicing/removal operation. The polymers may even assist the sluicing operation. If they are added to Tank D-004, it would be best to install a submerged, baffled inlet in the tank to help disperse and mix the polymers in with the sluicing water in the column. The advantage of adding the polymers directly to Tank 8D1 is that mixers are already available and a separate chemical add line may not be required as there is probably already an existing 8D1 chemical add line. Moreover, adding the polymers to Tank 8D1 before the new batch of spent zeolite is dumped in approximates the method used in lab testing.

6.5 COMPONENT TEST STAND (CTS) DESIGN SUPPORT - Activity Leader: D. H. Siemens Major Contributors: D. N. Berger, M. E. Peterson, and M. R. Elmore

6.5.1 Air Displacement Slurry Pump

In the past 2 years, PNL has designed and developed an air displacement slurry (ADS) pump to meter a mixture of HLLW and glass-formers to the glass melter as part of the vitrification process. The pump was designed to deliver slurry at rates of 10 to 200 L/hr. The slurry contains up to 50 vol% solids, including the abrasive glass formers. Gamma radiation dose rates of 10^6 rad/hr from the slurry rule out the use of elastomers, which are commonly part of the internal construction of metering pumps designed for use with abrasive slurries. The ADS pump operated successfully for 4000 hr at flow rates of 15 to 180 L/hr. The all-metal pump components are estimated to have lifetimes of at least 6 months as determined by evaluating the effects of abrasion during this 4000-hr period.

The design of a remotely operated ADS pump evolved from the West Valley Demonstration Project. During the past year, West Valley selected the ADS pump as their primary feed system. The pump was to be installed in the feed makeup/

concentrator tank and used to deliver a mixture of HLLW and glass-forming chemicals to the melter. Their selection of the ADS pump was based on the success of previous testing with the nonremote pump and the potential for significant cost savings for equipment as compared to other types of metering pumps. Therefore, PNL designed the ADS pump to operate remotely for this application.

The following discussion of the remote ADS pump is in three sections: 1) principles of operation, 2) design requirements, and 3) design features.

6.5.1.1 Principles of Operation

Figure 6.17 shows how the ADS pump operates. The displacement chamber is submerged in the concentrator tank with the chamber assembly located 0.5 in. from the tank bottom. Slurry flow through the chamber is regulated by a two-way pneumatically activated valve; flow is motivated by a three-way electric solenoid valve that alternately vents and valves compressed air into the chamber. A complete pump cycle can be simplified into four steps. During the first step of the cycle, the two-way valve is driven upward, opening the entrance from the tank and closing the feed line to the melter. The second

86A180-4

FIGURE 6.17. ADS Pump Operation

step is the fill step. Slurry enters the chamber as a function of the tank head. Air in the chamber is vented back to the tank through the three-way solenoid valve. The two-way valve is driven downward during Step 3. This closes the entrance from the tank and opens the line to the melter. Step 4 is the discharge step of the cycle. Compressed air is valved into the chamber, forcing the slurry from the chamber through the feed line to the melter. The flow rate is controlled by varying the air pressure and cycle time.

6.5.1.2 Design Requirements

The PNL ADS pump was easily handled using conventional methods. Operation in a remote environment required design modifications. Basic design requirements were established as follows: 1) the pump must be completely replaceable and maintainable using only a remotely operated overhead crane and impact wrench, 2) only proven remote flanging technology could be used, and 3) components that are anticipated to have a shorter useful life than the main body of the pump must be separately replaceable. No major changes in the design of the pump chamber were needed for remote operation. The length of the chamber was made larger to obtain higher flow rates of 200 L/hr. Abrasion tests, conducted after ~4000 hr of operation, indicated the pump chamber's service life to be in excess of 6 months.

To meet the above requirements, three major design changes were made to the nonremote pump: 1) the entire pump was designed and mounted on a remote flange, 2) the electric solenoid valves were installed in a replaceable jumper, and 3) a replaceable activating assembly for the two-way valve was designed. The electric solenoid valves and pneumatic activators are anticipated to have a shorter life than the main pump body and, therefore, were made separately replaceable. The nonremote ADS pump used a single, double-acting pneumatic cylinder that was connected to the drive rod and two-way valve using standard couplings. The solenoid valves were installed using standard pipe fittings.

6.5.1.3 Design Features

The remote ADS pump consists of three components: 1) the main pump body, 2) the service jumper, and 3) the activator jumper. These components are

discussed below in the order in which they are installed in the concentrator/feed makeup tank.

The main pump body consists of the pump chamber (Figure 6.18), which is supported on a remote tank flange. This chamber is constructed entirely of metal, using age-hardened stainless steel to lengthen the service life in the abrasive slurry. Guide bushings ensure the alignment of the valve and seats. A drive rod and rocker arm assembly are used to activate the two-way valve.

A 6-in. remote tank flange (Figure 6.19) was used to support the pump chamber. This flange design has been successfully used in remote application at the Hanford Site and elsewhere since the early 1940s. In addition to supporting the pump, the flange is used also to effect a seal to the tank nozzle in which the pump is installed. A graphite-impregnated asbestos gasket is used. With this flange, retainers are provided to prevent the closure nuts from being lost during handling, and for keeping the nuts in the correct attitude for thread engagement at assembly. The nuts are put into the retainers

86A180-5

FIGURE 6.18. ADS Pump Chamber

86A180-3

FIGURE 6.19. Remote Flange of ADS Pump

before installation. Design is such that the nuts remain on top of the flange bolts until tightened down using the impact wrench during installation of the pump. Alignment dowels and flange bolts are provided on the tank nozzle portion of the flange assembly. Damage to the flange bolts during installation is prevented by appropriately sized alignment holes in the pump-mounting flange. An electric-powered impact wrench, nominally 450 ft-lb, is used to tighten the closure nuts on the flange bolts. Also mounted on the remote tank flange is a PUREX connector for the feed line to the melter, a PUREX connector for the air and vent lines for the pump chamber, and the rocker arm actuator for the two-way valve.

The second component of the remote ADS pump is the service jumper (Figure 6.20). The service jumper brings the air, water, and electrical services for the operation of the pump into the cell. Mounted in the service jumper are the two electric solenoid valves for operating the pump. The three-way electric solenoid valve valves and vents compressed air to and from the pump chamber. The four-way solenoid valve supplies the air to the pneumatic activators for operating the two-way valve. PUREX connectors are used to connect this jumper to the main pump body and to the activator jumper. The service jumper, installed on the main pump body, is shown in Figure 6.21.

86A180-2

FIGURE 6.20. Service Jumper

86A180-7

FIGURE 6.21. Service Jumper Installed on Remote Flange

A vertical push-pull motion is required to operate the two-way valve, which is located on the inlet of the pump slurry chamber. To provide this motion in a replaceable jumper, two double-acting pneumatic cylinders and an activating assembly were used. The two double-acting cylinders are mounted on a support structure, and the air service is provided from the service jumper by the PUREX connector. The PUREX connector also provides support for the cylinders. An actuator rod extends from the two-way valve up through the pump-mounting flange. The upper end of the rod is connected to a rocker arm that has a fulcrum at the approximate center of the arm. The cylinder assembly is secured in place by using the impact wrench to make up the PUREX connector. The cylinder actuator rods rest on the rocker arm. Air is connected only to the downstroke of each cylinder. With this arrangement, the cylinder actuator rods are in constant contact with the rocker arm, thus providing smooth push-pull operation for the two-way valve without a direct connection between the two-way valve actuator rod and the pneumatic cylinders. Figure 6.22 shows the actuator jumper. The remote ADS pump, complete with all the jumpers, is shown in Figure 6.23.

In summary, the design features of the remote ADS pump are: 1) the pump was designed and mounted on a remote flange, 2) the electric solenoid valves were installed in a replaceable jumper, and 3) the activating assembly for the two-way valve was designed and installed in a replaceable jumper. The remote ADS pump, fabricated and installed in the West Valley Demonstration Project, is currently being tested. Tests to date have been successful.

6.5.1.4 ADS Pump Controller

During the past year, West Valley requested that PNL design and fabricate a microprocessor controller for the ADS pump. Originally the pump was to be controlled using the MICON. Details in the delivery of the MICON system required a temporary controller for the remote ADS pump. PNL has already designed and fabricated a controller and modified it for the West Valley application.

86A180-1

FIGURE 6.22. Actuator Jumper

86A180-6

FIGURE 6.23. Remote ADS Pump with Jumper

The criteria for the design and operation of the controller were as follows:

- Vary the flow rate between 50 and 200 L/hr.
- Sequence the four steps of the pump cycle in proper order and allow for the duration of each step (in seconds) to be varied. Steps 1 and 3 need to be as short as 0.5 sec, Step 2 needs to vary between 1 and 40 sec, and Step 4 needs to vary between 5 and 180 sec.
- Automatically water-flush the pump chamber after the pump has been stopped.
- Manually water-flush the pump chamber.
- Manually control the two-way valve such that it can be opened or closed, when desired, after the pump has been stopped.
- Manually water-flush the pump with the two-way valve in the open position such that the screen is back-flushed.
- Emergency-stop the pump with no water-flush occurring.
- Vary the air pressure that goes into the pump chamber between 0 and 20 psi. This variation should be in the form of a third-order polynomial, $Y = p + k_1x + k_2x^2 + k_3x^3$, where p is an initial pressure setting that can be varied, k_1 , k_2 , and k_3 are constants that are set by the operator depending on the desired flow rate, and x is an instantaneous time in Step 4 of the cycle.
- Vary the fill time (Step 2) as a function of the tank level. A minimum tank level where the pump output is independent of the tank level must be determined and put into the program. An input from a level measuring device is required. When the minimum level is reached, the fill time should be varied according to a third-order polynomial of the form $y = I + k_1x + k_2x^2 + k_3x^3$. I is the minimum fill level, k_1 , k_2 , and k_3 are constants that are set by the operator, and x is an instantaneous time in Step 2 of the cycle.

The software for the controller was developed and the controller was fabricated by PNL. After fabrication was complete, the functional test of the

controller was conducted using the nonremote ADS pump. The controller satisfied all the design criteria listed above. It was shipped to West Valley, where it is being used on the remote ADS pump.

6.5.2 PUREX C-Sampler

A C-Sampler was designed by PNL for canyon remote operation. It consists of a basic C-Sampler design adapted to a standard PUREX three-way connector. Its remote design permits sampling of process tanks inaccessible to manipulators without running lines from the tank to a distant sampling point. The 3-way PUREX connector provides lines for 1) steam or air for the jet, 2) a suction line from the process tank, and 3) a return line to the tank. The design allows a sample bottle to be positioned on the sampler at a window via manipulators and then the sampler to be installed on a tank by means of a crane and impact wrench.

The PUREX C-Sampler was fabricated by J. A. Jones, and preliminary functional testing was conducted by PNL. Testing consisted of repeatedly installing and removing the sampler from a test stand using a crane and ~500 ft-lb electric impact wrench. This was done to evaluate the ability of the sample bottle-holder mechanism to function as intended, that is, to hold the sample bottle in proper position for sampling, during full impact installation and removal.

A mounting adapter was fabricated to provide a test stand for the sampler during testing. Figure 6.24 shows the sampler on the test stand in the 324 Building where the preliminary testing was conducted. The adapter, a pipe with the male portion of the PUREX connector attached, was installed on a flange of the melter mock-up in the 324 high bay to simulate a process tank lid. The sampler was then repeatedly mounted on the test stand, tightened with the impact wrench, loosened, and removed by crane. During each cycle the position of the sample bottle and condition of the bottle holder was examined for problems caused by impact with the wrench.

In general, the bottle holder mechanism performed properly. A minor problem did occur during initial testing: the sample bottle holder was not held in the proper position by the toggle clamp. Figure 6.25 shows the proper location

FIGURE 6.24. PUREX C-Sampler in Place on the Test Stand for Functional Testing of the Bottle Holder Mechanism

FIGURE 6.25. Detail of the C-Sampler Showing the Sample Bottle Location and Bottle Holder/Clamping Mechanism

of the toggle clamp and the sample bottle on the C-Sampler. The problem was corrected by a minor adjustment to the toggle clamp, and the sampler was subsequently retested and found to perform properly. Upon conclusion of preliminary testing at PNL, the sampler was shipped to WVNS for additional testing on a process tank.

6.6 COMPONENT TEST STAND (CTS) GLASS TECHNOLOGY SUPPORT -

Activity Leader: L. A. Chick

Major Contributors: D. S. Goldman and L. R. Bunnell

The objective of this task is to design glass compositions that can be most easily processed in a liquid-fed ceramic melter to produce nuclear waste glasses of high chemical durability. This role included identifying and working to solve several problems such as glass foaming, surface-layer formation, and settling of dense crystals. Solutions to these problems were often interactive, with solutions to one problem producing undesirable effects in some other area.

Meeting the above objective required that CTS Glass Technology Support implement numerous changes during FY 1985. Figure 6.26 shows the chronology of these changes. At the beginning of the year, the WV182 glass composition had been tentatively selected on the basis of a statistically designed mixture study (Chick et al. 1984). Normally, a few small iterations in raw materials or processing parameters would precede production of the chosen composition. Actually, however, far more experimentation was necessary to perfect the West Valley glass.

The first problem, encountered in the PSCM-19 test, was formation of a calcium-phosphate surface scum that impeded melting. This scum was essentially eliminated by choosing a zeolite, IE-96, with lower calcium content. Minor compositional changes continued and resulted in WV192, which contained chromium-iron oxide crystallites (hematite and spinel), but no detectable phosphate. These phases can settle and could cause electrical shunting of the electrodes if they accumulated until continuous.

FIGURE 6.26. Diagram Showing Chronology of Events in FY 1985 Leading to Design and Final Selection of the WV205 Composition

An updated waste stream composition containing less chromium prompted a five-glass study in which boron and lithium were varied. WV202 was chemically the most durable of these five, but tended to form a phosphate-based scum with rare earths during melter idling. About this time, the need to reduce NO_x emissions prompted a switch from feed made with nitric acid to one made with formic acid. The need for yet higher melting rates led to more testing and further compositional changes, as embodied in WV203 and WV204. Slightly increased alkali contents for lower viscosity, to gain higher melting rates, resulted in composition WV205. Laboratory testing of this composition showed acceptable melting rates and minimal formation of scum. These qualities were verified in an ECM run, and WV205 was chosen for the feed used in the PSCM-21 run in June 1985; WV205 is now the West Valley reference composition.

The substantial number (23) of composition changes would have been impossible to make on a rational basis without the data base acquired during the mixture study of Reference 1. Using this data base, the computer program could predict the effect of any change in composition. Using a plot like the one of Figure 6.27, for instance, one can predict the effect of many different compositional changes upon electrical conductivity. Although 23 compositional changes were made in FY 1985, many more than that were "tested" without ever mixing any chemicals or melting any glass.

The original feed for PSCM-21 contained 35 g/L of sugar, added for redox control. This amount was determined by using a previously measured correlation between ferrous/ferric iron ratio and foaming tendency. During the PSCM-21 test, a stable melting rate of about 45 L/hr was achieved with this sugared feed. For a time during PSCM-21, the melter was fed with nonsugared feed. Surprisingly, the melting rate increased to about 60 L/hr. Subsequently, laboratory crucible testing demonstrated that sugar did slow the melting rate, for reasons yet unknown. Eliminating the sugar, however, produced a more oxidizing environment, with ferrous/ferric ratios changing from about 0.2 to near zero. This change carries a risk of foaming incidents; two of these, in fact, occurred during the feeding of nonsugared feed in PSCM-21. The incidents were minor and easily controlled, but they point up the fact that the West

FIGURE 6.27. "Effects Plot" Resulting from the Statistically Designed Mixture Study. This permitted prediction of the effects that changing the given elemental composition would have, in this case, on electrical conductivity.

Valley melter will operate closer to foaming conditions than would be the case with sugared feeds. If foaming should later become a problem, several reductants have already proved effective in eliminating the problem. Sugar might even be added in lesser amounts as additional insurance against foaming, with little effect on melting rate.

During this work, all milestones in the FY 1985 Technology Program Plan were met. These were as follows:

- Recommend glass composition for PSCM run
- Issue letter report on potential analytical techniques for redox control
- Issue letter report summarizing FY 1985 melting behavior studies
- Issue letter report on waste variability studies plan
- Issue summary report on waste variability studies

- Provide initial glass property prediction model as program to West Valley
- Provide initial batching calculation computer program.

6.7 REFERENCES

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7.0 LOW-LEVEL WASTE COORDINATION

L. T. Lakey - Manager

The objectives of the Low-Level Waste Coordination Task are to identify and conduct appropriate long-term research and development programs for DOE on low-level and airborne radioactive wastes. These programs/subtasks include both theoretical and experimental studies on all facets of low-level waste management, with emphasis on volume reduction, waste forms, packaging, hydrologic transport, and dose assessment.

7.1 ENGINEERED SORBENT BARRIERS - J. L. Buelte and H. D. Freeman

7.1.1 Objective

The objective of this study is to provide and evaluate new and cost-effective technology for restricting the migration of radionuclides from low-level wastes using sorbent and ion-exchange materials as engineered barriers.

7.1.2 Summary

Sorbent materials are being studied for DOE's Low-Level Waste Management Program as engineered barriers for low-level waste disposal sites. The study comprises experimental evaluations in the following two stages:

- Screening studies that evaluate the performance of a wide variety of sorbent materials
- Effectiveness evaluations that verify the effectiveness of sorbent barrier materials as a system under simulated field conditions.

Screening studies have identified sorbent materials for cesium, cobalt, and strontium. The sorbent materials were selected based on criteria developed for this program and the empirical results of screening studies. The results of the study made it apparent that no single sorbent material is effective for all radionuclides considered. Therefore, four composite sorbent barriers were identified for effectiveness evaluations in columns 0.6 m in diameter (Milestone 1B in Life of Task Schedule). The large columns represent field conditions more accurately, generate permeability data, and enhance detectability of radionuclides in the leachate passing through the sorbent barriers.

The four sorbent barriers include composites of activated charcoal, greensand, A-51 zeolite, and red pottery clay. Exposure of the first two barriers and one control material in the effectiveness evaluation columns was completed in FY 1985.

7.1.3 Screening Studies of Potential Sorbent Materials

The objectives of the screening studies were to: 1) identify potential sorbent materials; 2) develop criteria for selecting materials to be tested; 3) obtain distribution coefficients (K_d s) from batch contact studies; and 4) test the effectiveness of barrier formulations in matrix interaction studies.

Selection Criteria

Before the results of the screening tests could be analyzed, selection criteria were developed to rank the relative performance of the sorbent barrier formulations developed during the study. These criteria will be used also to rank the performance of the sorbent barriers in the larger scale effectiveness evaluations. The four selection criteria are discussed below:

- relative cost effectiveness
- long-term stability
- selectivity for radionuclides over more prevalent cations
- availability.

The relative cost effectiveness criterion was based on the cost of the sorbent material required to increase the effective K_d to a value sufficient to meet 10 CFR Part 20, Appendix B, Table II water concentrations for soluble contaminants. Based on a leachate composed of 1 $\mu\text{Ci/L}$ each of ^{137}Cs , ^{60}Co , and ^{90}Sr , required reduction factors are 20 for ^{60}Co , 50 for ^{137}Cs , and 3300 for ^{90}Sr . The long-term stability criterion is 300 yr, based on the half-lives of ^{90}Sr and ^{137}Cs , allowing them to decay to safe levels. The selectivity criterion will be applied where the effects of competing ions interfere with the 300-yr lifetime of the sorbent barrier. Lastly, the candidate sorbent materials must be available in large enough quantities for use at low-level waste disposal sites.

Batch Contact Studies

The batch interaction tests used simulated LLW leachate spiked with 1 $\mu\text{Ci/L}$ each of ^{60}Co , ^{85}Sr , and ^{137}Cs , with and without 1 ppm EDTA. The minimum critical reduction factors necessary for a barrier of a given thickness to meet discharge limits within established drinking water standards for strontium, cesium, and cobalt have been calculated from a model. The batch tests established minimum equilibrium distribution coefficients, K_d s of the sorbents and soils; these were then used to calculate the mass fractions of soil and sorbents for particular barrier formulations. The resulting costs of the sorbent barrier formulations determined by the mathematical model and measured K_d s ranged from $<\$0.01/\text{kg}$ to $\$5.10/\text{kg}$. The most promising materials were the synthetic zeolite A-51® for strontium ($\$0.40/\text{kg}$), greensand and red pottery clay for cesium ($<\$0.01/\text{kg}$), and activated charcoal and Dowex 21K® ion-exchange resin for cobalt ($\$0.11/\text{kg}$).

Matrix Interaction Studies

Four different simulated leachates were used for the matrix interaction tests in small columns to determine the effects of competing ions and radionuclide concentrations. A 2 x 2 matrix of competing ions such as calcium, sodium, and magnesium at 10 and 1000 ppm and radionuclides at 1 and 100 $\mu\text{Ci/L}$ formed the four leachates used in the column tests. The leachates all contained 1 ppm EDTA and were adjusted to pH 5. The major observed effect in these studies was that the leachates with the high concentrations of competing ions effectively reduce the sorption of strontium for all sorbent barrier formulations. Cesium breakthrough was not seen at 60 pore volumes, and cobalt was evident in only two of the 24 column tests. The results indicate that additional screening studies are required to identify a cost-effective sorbent for strontium.

®The synthetic zeolite A-51 is manufactured by Union Carbide, Morristown, New Jersey.

®Dowex 21K is a registered trademark of Dow Chemical Co., Midland, Michigan.

Nevertheless, four of the most promising sorbent barriers could be selected for further study. Based on the selection results of the batch tests and the matrix interaction tests, the following four barriers were selected for evaluations of their effectiveness:

- 88 wt% soil, 6 wt% activated charcoal, 1 wt% greensand, and 5 wt% A-51 zeolite
- 85 wt% soil, 6 wt% activated charcoal, 5 wt% red pottery clay, and 4 wt% A-51 zeolite
- 72 wt% soil, 26 wt% activated charcoal, and 3 wt% greensand
- 68 wt% soil, 26 wt% activated charcoal, and 6 wt% red pottery clay.

The first two barriers were tested in the 0.6-m-dia columns in FY 1985, and the other two will be modified in FY 1986 to increase their effectiveness for sorbing strontium before continuing the effectiveness evaluations.

7.1.4 Effectiveness Evaluations of Selected Sorbent Materials

The purpose of the effectiveness evaluations is to verify the performance of the four sorbent barriers identified in the screening studies. Since the selection of these barriers was based on experimental results from batch contact interactions and laboratory-scale column studies, field conditions were not adequately represented. In addition, because of the high detection limit in small sample volumes, the laboratory-scale screening studies do not identify sorption trends under conditions of low breakthrough of radionuclides. The effectiveness evaluations are designed to depict many field conditions more accurately by using large-diameter (0.6 m) columns. The columns will duplicate water infiltration, physical pressure from the weight of the solid wastes above the sorbent barrier, and hydrostatic head of the leachate expected in the field. They will also produce larger sample volumes of leachate passing through the sorbent barrier to significantly improve analytical detectability of radionuclides. In some cases, the laboratory-scale column studies have not generated enough leachate through the sorbent materials to be detectable in low radionuclide concentrations.

The four sorbent materials are being tested in two phases in three 0.6-m-dia exposure columns. The first phase was completed in FY 1985. Two sorbent barriers and one control material (Hanford soil) were exposed to radioactive leachates for 5 months. The breakthrough of radioactive contaminants from the sorbent barriers was compared with the breakthrough from the control material with no sorbent material amendments. This approach will verify the effectiveness of the amendments of sorbent material.

Although the first phase of the effectiveness evaluations is complete, not all data had been analyzed or reduced at the end of FY 1985. Preliminary gamma-counting results of the leachate breakthrough samples, however, provide sorbent barrier reduction factors for each radionuclide. One sorbent barrier, the mixture of zeolite, activated charcoal, and greensand, exceeded the required reduction factors of 3300 and 50 for both strontium and cobalt respectively, whereas the control material of Hanford soil did not. The other sorbent barrier, composed of different ratios of zeolite, activated charcoal and red pottery clay, achieved reduction factors of 110 and 750 respectively for strontium and cobalt. Cesium, on the other hand, achieved a reduction factor in Hanford soil and both sorbent barriers of greater than 1500. The established criterion for cesium is a factor of 50, so it appears that greensand and red pottery clay are not necessary to retard cesium migration under these conditions.

Except for the fact that strontium breakthrough was not as severe as expected, the effectiveness evaluations support the findings of the screening tests. In addition, the effectiveness evaluations provide much more sensitive data to detect breakthrough trends with high reduction factors. The leachates are currently being analyzed for competing ions to determine the selectivity of the sorbent barriers.

7.2 SPECIAL WASTE FORM LYSIMETERS - ARID - R. L. Skaggs

7.2.1 Objectives

The primary objective of this program is to conduct waste-form leaching tests in a field facility in order to determine typical source terms generated

by commercial solidified low-level waste. The solidification agents being tested include cement, vinyl-ester styrene, and bitumen. Through field and laboratory research, the chemical and physical processes that control the concentrations of radionuclides in the soil solution surrounding the waste in an arid climate will be identified. Methods for representing source-term boundary conditions in radionuclide transport models will be determined.

7.2.2 Summary

The Special Waste-Form Lysimeters - Arid Task was begun in FY 1983 for the long-term field evaluation of solidified low-level waste forms intended for shallow-land burial. A similar task is ongoing at the Savannah River Laboratory (SRL) for a humid climate. A field lysimeter facility, consisting of ten lysimeters around a central instrument caisson, has been constructed in which to perform the field testing. Waste samples have been emplaced in the facility, which became operational at the end of the second quarter of FY 1984. Two bitumen waste forms were added to the facility in September 1984.

All laboratory-scale solidified samples for the leach tests have been prepared by Brookhaven National Laboratory (BNL) and the leach tests have been completed. A letter report to be prepared by BNL will describe procedures, data and analysis of the BNL leach tests.

PNL completed organic analysis of three of the four liquid-waste samples in March 1985. The hydrophobic and hydrophilic organic fractions of the wastes were analyzed by gas chromatography and combined GC/mass spectrometry. As reported by Walter and Graham (1985), a variety of both hydrophobic and hydrophilic organics were found in the samples. The two most abundant classes of hydrophobic compounds were alkylphenols and alkylphenyl phosphate esters. The hydrophilic compounds consisted mainly of organic acids.

Baseline data on the lysimeter soils have been collected and are reported in a topical report (Walter, Graham and Gee 1984). These data include water-retention characteristics, hydraulic conductivities, and the particle-size distributions for soils collected from the lysimeters during the backfill operation. Chemical and radiological analyses are conducted quarterly on leachate collected and measured from the drains in the bottom of the lysimeters. A

sudden snow melt in the second quarter of this fiscal year flooded three of the ten lysimeters. A total of over 700 L of leachate was drained from the flooded lysimeters while the remaining seven lysimeters, having escaped the overland flow of ponded water, produced less than 100 L of leachate over an 18-month period. In October 1985, based on preliminary counts using a NaI counter, detectable levels of ^{54}Mn and ^{60}Co were found in leachate collected from the bottom drains of seven of the ten lysimeters.

The geochemical code MINTEQ, developed at PNL, was selected to model the interaction of ground water with commercial solidified low-level wastes (Graham and Peterson 1985). This code can calculate ion speciation/solubility, adsorption, oxidation-reduction, gas phase equilibria, and precipitation/dissolution of solid phases. Based on characterization of the waste streams, it was determined necessary that thermodynamic data for cobalt, antimony and cesium solid phases and aqueous species be added to the MINTEQ data base. The geochemical model developed from the laboratory data will then be applied to predict the release from a field-lysimeter facility that contains full-scale waste samples. The contaminant concentrations migrating from the wastes predicted using MINTEQ will be compared to the long-term lysimeter data. This comparison will constitute a partial field validation of the geochemical model.

7.2.3 Lysimeter Study

The Special Waste-Form Lysimeter Study is designed to quantify the release and migration of radionuclides from solidified commercial low-level waste. A field-test facility has been built to contain selected waste forms in specially constructed lysimeters. Solidified low-level waste samples from commercial power reactors have been emplaced in the facility (Table 7.1). The waste forms are being characterized by laboratory leach tests, including MCC-3S, MCC-4S, and ANS-16.1, to obtain estimates of radionuclide release. Also solubility studies are being conducted to determine the amount of contaminant available for transport after release. Data collected from this research will be used to relate laboratory measurements of waste-form characteristics to the release and migration rates observed in the field. Comparisons can be made between results obtained from this arid site facility and those of the humid site at Savannah River Laboratory.

TABLE 7.1. Waste Forms Obtained for the Special Waste-Form
Lysimeters - Arid Program

<u>Waste Stream</u>	<u>Reactor</u>	<u>Solidifying Agent</u>
Boric acid concentrate waste	PWR(a)	Masonry cement
Boric acid concentrate waste	PWR	Bitumen
Evaporator-concentrate (regenerative) waste and ion-exchange-resin waste	BWR(b)	Portland Type III cement
Evaporator-concentrate (regenerative) waste and ion-exchange-resin waste	BWR	Vinyl ester-styrene

(a) Pressurized water reactor.

(b) Boiling water reactor.

The field lysimeter facility is designed to accommodate ten waste forms. Ten closed-bottom lysimeters, 3 m deep by 1.8 m dia, are arranged around a central instrument caisson, 4 m deep by 4 m dia (Figure 7.1). The central caisson houses all equipment for collecting data and samples and provides access to sampling ports in each lysimeter for selective sampling of the soil and waste forms. Leachate from each closed-bottom lysimeter drains to the central caisson, where it can be collected, measured, and sampled.

Suction candles (ceramic cups) placed in the bottom and around the waste will be used to collect soil water samples periodically for chemical analysis. Moisture content and soil temperature are being monitored at 12-hr intervals. The data are sent over a phone line to a computer; a backup cassette tape data-storage system is also in place. Radiological analyses will be performed in situ and through selective sampling. These will provide the Low-Level Waste Management Program with direct field results regarding leach and migration rates from actual commercial solidified waste.

PNL has completed the organic analyses of the liquid fraction of the boric acid concentrate waste (from a PWR) that was solidified with masonry cement.

FIGURE 7.1. Conceptual Drawing of the Field Lysimeter Facility
for the Special Waste-Form Lysimeters - Arid Program

Various organic chelating agents were identified in the hydrophilic organic fraction of the sample. Two of them, ethylene-diaminetetraacetic acid (EDTA) and citric acid, are typically used in the decontamination operations at nuclear facilities. Also completed are the organic analyses (liquid and solid fractions) of the BWR waste streams (evaporator-concentrate waste and evaporator-concentrate waste with ion-exchange-resin waste) and the solid residue from the PWR waste stream (boric-acid concentrate waste). The PWR solid residue contains chelating agents similar to those found in the liquid fraction of the sample. The organic contents of the BWR waste stream are qualitatively different. The major components are phenols and phosphate esters. Such compounds are used as plasticizers and hydraulic fluids. The solid portion of the BWR evaporator-concentrate waste also contained a significant concentration of EDTA.

In addition to field monitoring, which is the task's central purpose, a series of laboratory testing and geochemical modeling exercises is under way. These tests will help to predict expected leach rates and help to interpret the field data. The ion speciation/solubility and mass transfer geochemical code MINTEQ will be used to model the waste stream, the waste form, and any column effluent and batch solutions. The geochemical modeling efforts are being focused on the effects of organics radionuclide behavior in the environment. Specifically, the goals of the laboratory and modeling work will be to identify the mechanisms controlling the rate of release of radionuclides from the waste form.

7.2.4 References

Graham, M. J., and S. R. Peterson. 1985. "An Overview of the Geochemical Code MINTEQ: applications to Performance Assessment for Low-Level Wastes." Presented at the Seventh Annual Department of Energy Low-Level Waste Management Program Participant Information Meeting, September 9-13, 1985, Las Vegas, Nevada.

Walter, M. B., and M. J. Graham. 1985. "Special Waste Form Lysimeters-Arid Annual Report 1985." Presented at the Seventh Annual Department of Energy Low-Level Waste Management Program Participant Information Meeting, September 9-13, 1985, Las Vegas, Nevada.

Walter, M. B., M. J. Graham and G. W. Gee. 1984. A Field Lysimeter Facility for Evaluating the Performance of Commercial Solidified Low-Level Waste. PNL-5253, Pacific Northwest Laboratory, Richland, Washington.

7.3 PATHWAY AND DOSE-TO-MAN ASSESSMENT PRACTICES - D. A. Myers

7.3.1 Objective

Provide the National Low-Level Waste Management Program (NLLWMP) with a means to compare radiological dose pathways models used at DOE low-level waste sites.

7.3.2 Progress During FY 1985

Progress on the Pathway and Dose-to-Man Assessment Practices Task during FY 1985 was in two directions. First, a milestone was met in the completion of PNL-4980, Guidelines for Selecting Codes for Ground-Water Transport Modeling of Low-Level Waste Burial Sites by C. S. Simmons and C. R. Cole in May 1985. This document provides a step-by-step procedure and guidance in selecting numerical codes to simulate groundwater transport at low-level waste (LLW) sites. Foremost in the development of this document is the recognition that the ground-water pathway is the predominant means by which radionuclides can move to the accessible environment.

Second, concurrent with preparation of PNL-4980, an outline of basic information needed to develop a performance assessment modeling program was prepared. This outline was developed into a request for information and was sent to DOE LLW sites with a request that the information be developed in essay form and forwarded to PNL. Sample essays were developed and included in the materials sent to the sites.

To minimize the potential for bias in reviewing and evaluating the information supplied by the sites, a Technical Review Committee (TRC) was formed to address the materials to be supplied by the sites. This committee is composed of seven members with technical expertise in fields ranging from partially saturated flow dynamics to health physics. Its membership was limited to persons with no direct connection with DOE LLW programs, but with experience in

related work. The TRC was used to comment on a system of review or evaluation criteria to be used in providing a consistent basis for evaluating the several independent LLW programs.

7.4 KRYPTON ION IMPLANTATION - E. D. McClanahan, R. W. Moss, E. R. Bradley, E. N. Greenwell, and E. L. McDonald

7.4.1 Objectives

The objectives of this program for FY 1985 were to: 1) carry out radioactive laboratory-scale implantation experiments with ^{85}Kr ; 2) complete target power supply evaluation; 3) demonstrate simultaneous operation of multiple ion implantation modules; 4) make provisions for the periodic monitoring of krypton-loaded storage specimens over an extended period ~5 to 10 years; and 5) terminate and document the development effort.

7.4.2 Summary

Pacific Northwest Laboratory (PNL) has implanted 380 curies of krypton-85 in a series of three experiments to provide three capsules containing the copper-yttrium-krypton waste form for long-term elevated-temperature krypton release tests. These capsules were placed in shielded casks equipped with heating elements and thermocouples for maintaining and monitoring the capsule storage temperatures. A sampling procedure was developed for periodically measuring the krypton-85 release rate. Tests at elevated temperatures are in progress.

To verify the feasibility of operating pilot-scale equipment developed for the BRET^(a)-scale krypton trapping units, a target power supply/current interrupter evaluation task and a simultaneous operation of multiple krypton trapping/storage devices (KTSDs) task were completed. Three alternative design approaches for the target power supply/current interrupter were tested and evaluated for their suitability in providing the dc power to BRET-scale krypton ion implantation/sputtering units. Two of the three power supply/current

(a) The Breeder Reprocessing Engineering Test-scale unit developed at PNL can process the krypton from ~0.1 MTHM/day from Fast Flux Test Facility fuel cooled 180 days. That amounts to about 1 L Kr/hr at STP, although the unit can pump as much as 1.5 L Kr/hr at STP.

interrupters were found acceptable and their relative merits noted. A manifold with a capacity to operate three BRET-scale gas trapping units was completed. PNL demonstrated that these trapping units can operate simultaneously without the need for a separate vacuum pump to maintain stable trapping operation. During the multicurie-scale experiment, a stable mode of operation was discovered whereby a single KTSD could operate without an additional pump. This method was tested successfully on the BRET-scale equipment, thus providing a second option for scale-up.

Four reports considered necessary to close out the Krypton Ion Implantation Program are in various stages of preparation. Completion of the last report is scheduled for April 1986.

7.4.3 Introduction

Ion implantation of krypton in sputter-deposited metals is a promising method of storage of ^{85}Kr . The major advantages of this technique include: 1) very high krypton loading [$\sim 30 \text{ cm}^3$ of Kr (STP)/g or over 200 cm^3 of Kr (STP)/ cm^3 of deposit], 2) low-pressure ($\sim 1 \text{ Pa}$) and low-temperature ($< 20^\circ\text{C}$) operation, 3) very stable waste form, and 4) a waste form with relatively high thermal conductivity. The design for a disposable krypton-trapping unit for BRET-scale application was completed in FY 1984. This unit was designed to be capable of being connected remotely to a station providing the necessary utilities for its operation. The same station also would accept a larger module suitable for commercial-scale operation ($\sim 5 \text{ MT/day}$ reprocessing plant). The BRET-scale trapping unit equipped with a composite target, whose copper/yttrium surface area ratio is 4.1, is capable of trapping 1.1 L (STP) of Kr per hour with a trapping efficiency of $6.0 \times 10^{-2} \text{ L (STP) per kWh}$.

To complete the data base on the ion-implantation sputtering process, the work accomplished this fiscal year included: 1) testing the effects of radiation on both the implantation process and preparing specimens for long-term krypton release characteristics of the sputtered copper-yttrium-krypton product, 2) verifying the availability of reliable and easily maintainable target power supply/current interrupters, and 3) establishing that the process can be scaled up without the necessity for auxiliary vacuum pumps and the corresponding need to recycle exhausted krypton.

7.4.4 Radioactive Laboratory-Scale Implantation Experiments

Six hundred curies of ^{85}Kr were allocated for preparing three ^{85}Kr -loaded copper-yttrium samples; however, radioactive decay and losses in product purification reduced the total amount to 450 curies. This amount was divided equally for preparing three ^{85}Kr -loaded copper-yttrium samples for long-term thermal release measurements at 150°, 250°, and 350°C. Since the specific activity of the ^{85}Kr feed (4.2%) was representative of a commercial reprocessing plant stream, the experiments themselves were expected to reveal operational problems attributable to the high beta activity. Prior to the three hot runs, a nonradioactive krypton implantation run was carried out to simulate the exact run conditions and identify procedural problems and the need for additional radiation shielding. The nonradioactive krypton-loaded storage device is undergoing accelerated thermal release tests to identify when significant krypton release might be expected irrespective of radiation damage or rubidium growth into the waste form.

Figure 7.2 shows a simplified schematic piping diagram for the equipments used for the nonradioactive and the 150-curie-scale experiments. The KTSD module and shielding arrangement is shown in Figure 7.3. The details of the procedure used for carrying out these experiments may be found in PNL-SA-13239. Prior to commencing the radioactive phase of this work, a Safety Evaluation Document was prepared and reviewed which concluded that additional safety analysis was unnecessary. An informal presentation was held for DOE-RL (Program and Safety) to describe the procedures and related safety aspects of the work.

The nonradioactive and the three radioactive krypton implantation runs were completed on schedule. The operation of the radioactive runs was improved with each successive run by adjusting the sequencing of the power supplies and the pressure controller to the point that manual override of these controls was unnecessary on the third run. An inadvertent target-to-anode short in the third run prevented trapping more than 82 curies in the deposit but did not interfere with the safety in the disassembly step. The balance of the 150 curies in that shipment was returned to Oak Ridge National Laboratory.

FIGURE 7.2. Schematic Piping Diagram for 150-Ci ^{85}Kr Experiment

FIGURE 7.3. Krypton Trapping Storage Device (260 cm^2 substrate area)

The completion of these tests demonstrated the following: 1) the high beta radiation field does not adversely affect the ion implantation/sputtering process; 2) radioactive particulate material was not detected during disassembly of the KTSD; 3) the KTSD operated the entire portion of the radioactive portion of the run with the aid of an auxiliary pumping system and hence a 100% recovery factor; 4) the KTSD could be stopped and restarted if necessary;

5) the pumping speed of the KTSD could be varied continuously from zero to greater than 8 std cm³/min; and 6) the whole-body exposure received by the operator was low--~25 mr/run.

7.4.5 Target Power Supply/Current Interrupter Evaluation

The target power supply/current interrupter furnishes the energy to sputter-deposit the metal matrix in which the krypton gas is implanted. The output of the target supply/current interrupter should be 2500 V. The current capacity required is determined by the positive ion-current density of the discharge (typically 100 A/m²) and the target area. Hence the BRET-scale KTSD would require a capacity of ~10 A. Due to the nature of the gas discharge used in this process, plasma arcs, resembling short circuits, have to be dealt with to prevent damage to the power supply/current interrupter and the trapping unit so as to minimize the disruption and maintain the stability of the trapping process. Since the target is the largest of five power supplies required to operate a KTSD, its efficiency and reliability/maintainability are critical to the operation.

Three types of 2500-V - 25-A dc power supply/current limiters were selected for evaluation and are shown schematically in Figure 7.4a-c. The first, a commercially built unit described as an integral power supply-shunt-type limiter, is shown in Figure 7.4a. The second unit, a commercially manufactured integral power supply-series-type limiter, is shown in 7.4b. The third unit, shown in Figure 7.4c, was a standard commercial supply with an external PNL-designed current limiter.

The details of this work are included in a PNL report in a draft form. The final report is to be completed in April 1986. All three power supply/current interrupter units performed satisfactorily from the standpoint of power delivery and arc suppression. It was observed, however, that the recovery time for return to the normal krypton-trapping rate following severe arcing conditions was dependent on the method used for arc suppression. The relatively long time to recover output voltage with the shunt-type unit resulted in intolerable pressure fluctuations in the system. Since this unit has the

FIGURE 7.4. Power Supply/Current Interrupter Concepts

lowest capital cost (about a factor of three lower than the second unit) and highest electrical efficiency (95%), a target power supply/current interrupter for production use may warrant further development to correct this deficiency. Other approaches to circumventing this deficiency include modifying the target design to minimize the enhanced emission effect and/or the use of a more sophisticated means of controlling the krypton pressure. The integral power supply-series-type interrupter provides the ultimate in flexibility to meet any process demand because of its direct control over the output voltage and current. The PNL unit can provide most of this flexibility with greater electrical efficiency at about half the capital cost of the commercially built integral power supply-series-type interrupter.

7.4.6 Simultaneous Operation of BRET-Scale Krypton Trapping Modules

To eliminate the need of an independent pump to maintain the critical pressure range for stable operation of a KTSD, it was desirable to demonstrate the simultaneous operation of two or more (depending on the arcing frequency) KTSDs on a common manifold. This would be achieved if one KTSD would be operating at full capacity at any given time. The use of a vacuum pump to stabilize pressure control in the KTSD would require recycling up to 10% of the krypton process stream and contending with maintenance of ^{85}Kr -contaminated pumps. Radiolytic decomposition of pump fluids could cause other problems.

During the nonradioactive mockup phase for the multicurie "hot" runs, a means was developed for controlling the 260-cm² substrate area KTSD without the need of auxiliary pumping. Stable operation of the KTSD is complicated by the unique interdependence of the pressure-regulating controls and those for the power supplies regulating the discharge density, the target voltage, and the substrate-bias or ion-implantation voltage. It was decided to adapt the control means described in PNL-SA-13239 to the BRET-scale KTSD (See Figure 7.5). Two 1000-cm² and one 1500-cm² substrate area KTSDs with copper-yttrium targets (shown in Figure 7.6) were individually tested and found to function satisfactorily at their rated power when isolated from the pumping station. Two of the KTSDs were then restarted in sequence and run concurrently 3.5 hr with no external pumping. While the KTSDs worked independently of one another, it was

FIGURE 7.5. BRET-Scale Krypton Trapping Storage Device (1000 cm² substrate area)

85F757-2cnB

FIGURE 7.6. Multiple KTSDs, Power Supplies, and Control Equipment

noted that the pressure fluctuations during arcing were reduced. The successful operation of both single and multiple trapping modules without auxiliary pumping removes a serious potential obstacle to scale-up of the ion-implantation sputtering process. Three conditions were found necessary to promote stable operation when arcs were occurring: 1) both the target and substrate current limiters must have "off" periods of less than about 10 msec; 2) following an arc, the substrate limiter must signal the krypton feed-control valve to close completely as rapidly as possible and the krypton control valve must return to its original opening (just prior to the arc) when the arc clears; and 3) in the case of an arc resulting in a loss of pressure control, normal operation is regained more quickly if the substrate supply voltage is lowered to about 200 V, then raised slowly to the setpoint until the excess gas has been trapped and the pressure is under control again. The first condition was met by making a one-time adjustment in the timing circuits of the power-supply current limiters for two of the KTSDs.^(a) The second condition was satisfied by circuit modifications to the commercial pressure control unit but could be improved with the use of a more sophisticated unit. The third condition was met for this test by a simple manual adjustment. This could and should be controlled automatically.

7.4.7 Monitoring of KTSDs

Long-term stability of the sputter-deposited krypton-metal matrix is important in evaluating the sputter-deposition process for immobilizing radioactive ^{85}Kr gas. Laboratory experiments using nonradioactive krypton trapped in a nickel-lanthanum sputter-deposited matrix have shown that krypton gas is released from the metal matrix at low rates by a diffusion process (McClanahan et al. 1984). Gas release rates and the stability of the metal matrix may, however, be affected by the radiation field and transmutation products in an actual storage container of ^{85}Kr . Consequently, experiments have been started to measure the release of ^{85}Kr gas from multicurie krypton-copper-yttrium deposits and assure the stability of the alloy at elevated temperatures that bracket the anticipated long-term storage conditions.

(a) It was not possible to meet this requirement on the power supply-shunt-type limiter, used for the substrate supply on the third KTSD, and therefore no attempt was made to operate this unit.

Elevated-Temperature Storage

Three multicurie krypton-copper-yttrium deposits that are contained in the KTSDs will be used to determine the stability of the metal matrix during storage at elevated temperatures over a period of 5 to 10 years. Temperatures of 150, 250, and 350°C were selected to bracket anticipated storage conditions. The three units are currently being stored at 150°C in lead-shielded casks, and the amount of krypton released from each unit will be measured after 3 months' storage. One unit will be returned to 150°C while the temperature of the others will be increased in 100°C increments to reach their final storage temperatures, 250 and 350°C, respectively. Gas release will be measured at 3-month intervals during the initial heat-up periods and at 6-month intervals thereafter.

A diagram of the storage cask configuration is shown in Figure 7.7. The cylindrical cask was fabricated from stainless steel sheet in a double-walled configuration. Lead shot was used to fill the 1.50-in.-thick wall cavity and combined with a solid lead lid (1.5 in. thick) provides the necessary radiation shielding. Radiation levels were reduced from about 50 R/hr at contact with the KTSD to less than 25 mR/hr at the cask surface.

The KTSD is positioned within a clam-shell heating element which is centered near the bottom of the cylindrical cask. Inlet and exhaust lines with valves outside the cask are provided for measuring release of krypton gas. The internal pressure of the unit is measured with a pressure gauge attached to the exhaust line. This gauge is monitored weekly and provides an early warning of unexpectedly large krypton release from the metal matrix or of a leak in the containment. Thus, a significant increase or decrease in pressure would indicate a problem with the unit and the experiment would be terminated.

Temperature of the units is measured with chromel-alumel thermocouples and controlled with variable transformers. The temperature-power characteristics of each storage cask was experimentally determined by spot-welding thermocouples directly to the side of a nonradioactive KTSD and measuring the wall and furnace temperatures as a function of power level. The data from these experiments were used to establish the proper furnace temperature and power level to obtain the desired KTSD wall temperature for long-term storage.

FIGURE 7.7. KTS D Cask and Heater

^{85}Kr Release Measurements

Procedures have been developed and used to measure the amount of ^{85}Kr released from a 10-Ci ^{85}Kr -Ni-La deposit that was stored at ambient temperature. The same procedures will be used to measure ^{85}Kr release from the 150-Ci ^{85}Kr -Cu-Y deposits stored at elevated temperatures.

A schematic diagram of the gas-measuring system is shown in Figure 7.8. The radioactive deposit is contained within the KTSD, which has inlet and exhaust lines with valves for connecting to the gas-measuring system. The system consists of an expansion chamber of known volume, a manometer to measure the system pressure, two small ($\sim 20\text{ cm}^3$) sample-containers for gas analysis, a dry nitrogen or argon gas source for purging the system, and a Triton® gas monitor calibrated for ^{85}Kr . A mercury manometer and a glass expansion chamber were used for the initial experiments. These components, however, have been replaced by a capacitance manometer and stainless steel chamber to simplify the procedures and reduce operating personnel's exposure to radiation.

Two methods for measuring ^{85}Kr release were evaluated. The first method was based on the technique commonly used to measure the release of fission gas from the oxide fuels in nuclear fuel rods. Gas from the KTSD was expanded into the evacuated system and the resulting pressure was measured with the manometer. Volume of the expansion system was designed to provide subatmospheric pressure in the system even for the unlikely release of large quantities of krypton during storage (up to 20% for the 150-Ci deposits). The KTSDs are typically stored under 1 atm nitrogen or argon gas, and for the expected low release of krypton gas the system pressure after expansion would be less than 0.5 atm. This negative pressure minimizes the potential for accidental release of ^{85}Kr from the sample containers during transport and analysis.

The ^{85}Kr concentration of the gas was measured by multidimensional gamma-ray spectrometry of two gas samples. Sample containers were fabricated from 16-mm-dia Pyrex® tubing, $\sim 10\text{ cm}$ long, sealed at one end and fitted with a vacuum stopcock and a ground glass joint at the other end. The volume of each

®Triton is a registered tradename of Johnston Laboratories, Inc., Cockeysville, Maryland.

®Pyrex is a registered tradename of Corning Glass, Corning, New York.

FIGURE 7.8. Schematic Piping Diagram for Measurements of ^{85}Kr Release

sample container was determined by the difference in weight between the container when it was evacuated and when it was filled with water. The measured volumes of five containers ranged from 18.8 to 19.5 cm³.

Gas samples were removed from the system after expansion and were counted on two gamma-ray spectrometer systems. A ⁸⁵Kr standard was prepared in one of the extra sample containers and used to calibrate the spectrometer systems. Identical sample and standard geometries were used to minimize the effects of geometry on counting efficiency. Counting times ranged from 30 to 40 min, and similar results were obtained for both samples on each of the two systems. The measured ⁸⁵Kr concentration was 0.0234 ± 0.0004 $\mu\text{Ci}/\text{cm}^3$ for both samples.

The total ⁸⁵Kr gas released from the metal matrix was calculated from the sample gas analysis and the combined volumes of the gas expansion system and KTSD by the relation

$$\text{Total } ^{85}\text{Kr Release} = C(V_1 + V_2)$$

where $C = ^{85}\text{Kr}$ concentration, $\mu\text{Ci}/\text{cm}^3$

$V_1 =$ Expansion system volume, cm³

$V_2 =$ KTSD volume, cm³.

Volumes of the expansion system and KTSD were determined from the well-established pressure/volume relationships of ideal gases. Gas from a calibrated volume at atmospheric pressure was expanded into the evacuated expansion system, and the resulting pressure was measured with the manometer to determine the volume of the expansion system. This expansion was made after the system had been connected to the KTSD and includes the volume of the piping up to the KTSD valve. Internal volume of the KTSD was determined, after the gas-release measurements were completed, by expanding nitrogen gas at atmospheric pressure from the KTSD into the evacuated system. A barometer was used to measure atmospheric pressure when the measurements were conducted.

A Triton gas monitor, calibrated for ⁸⁵Kr, was used to measure gas release by the second method employed. The gas contained in the expansion system and KTSD was exhausted through the monitor by purging the system with nitrogen. A

flow of pure nitrogen gas at 50 std cm³/min was established before the krypton-containing gas was introduced to the monitor. Gas from the expansion system and KTSD was then vented through the monitor. A parallel flow of pure nitrogen was maintained during the initial purging to ensure that the ⁸⁵Kr concentration in the gas did not exceed the measuring capacity of the monitor, 0.0125 μCi/cm³. The ⁸⁵Kr activity was recorded on a strip chart and the peak area integrated to obtain the total ⁸⁵Kr content.

The results from the gas-release measurements show minimal krypton release from the sputtered krypton-nickel-lanthanum deposit after storage at ambient temperature for 1.6 years, Table 7.2. The total release of ⁸⁵Kr measured by gamma-ray spectrometry was 33.9 μCi, which corresponds to a release fraction of only 2.1×10^{-5} after 10 years of storage. This is a factor of ten lower than previously estimated from elevated-temperature release data of nonradioactive krypton-nickel-lanthanum deposits (McClanahan et al. 1984) and indicates that the deposit's stability was not affected by the radiation field or decay products. Release data for ⁸⁵Kr are needed to assure the stability of the copper-yttrium alloy at elevated temperatures bracketing the anticipated long-term storage conditions. These data will be obtained from the 150-Ci ⁸⁵Kr-Cu-Y deposits currently being stored at elevated temperature.

The low value for the ⁸⁵Kr release measured by the Triton gas monitor is thought to relate to a higher pressure in the ionization chamber of the monitor during calibration. The Triton is equipped with an internal pump to provide a continuous flow of gas through the monitor. During calibration, a ⁸⁵Kr standard was pumped through the monitor at atmospheric pressure via a closed-loop system. However, when connected to the gas-measuring system, the flow restriction provided by the needle valve reduced the pressure in the monitor and

TABLE 7.2. Krypton Release from a Sputtered Krypton-Nickel-Lanthanum Deposit After 1.5 Years' Storage at Ambient Temperature

<u>Measurement Method</u>	<u>Total ⁸⁵Kr Release, μCi</u>	<u>Extrapolated Release Fraction After 10 yr Storage</u>
Gamma-Ray Spectrometry	33.9	2.1×10^{-5}
Triton Gas Monitor	1.6	1.0×10^{-6}

thereby invalidated the calibration. The internal pump will be deactivated during future experiments. Better agreement between the two methods of measuring ^{85}Kr release is expected.

7.4.8 References

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8.0 ACRONYMS AND ABBREVIATIONS

ADS	Air-displacement slurry
ALARA	As Low As Reasonably Achievable
BRET	Breeder Reprocessing Engineering Test
BWR	Boiling-Water Reactor
CFR	Code of Federal Regulations
CTS	Component Test Stand
cv	column volume(s)
D&D	Decontamination and Decommissioning
DADS	Data Acquisition and Display System
DF	Decontamination Factor
DOE	Department of Energy
DWPF	Defense Waste Processing Facility
ECM	Experimental Ceramic Melter
EDTA	ethylene-diaminetetraacetic acid
EPA	Environmental Protection Agency
EVS	Ejector Venturi Scrubber
FRG	Federal Republic of Germany
HEME	High-Efficiency Mist Eliminator
HEPA	High-Efficiency Particulate Air
HLLW	High-Level Liquid Waste
HLW	High-Level Waste
HWVP	Hanford Waste Vitrification Program
LFCM	Liquid-Fed Ceramic Melter
LLW	Low-Level Waste
LLWTF	Low-Level Waste Treatment Facility
LMFBR	Liquid Metal-Cooled Fast Breeder Reactor
LWR	Light-Water Reactor
MCC	Materials Characterization Center
MEVS	Mobile Encapsulation and Volume Reduction System
NAC	Nuclear Assurance Corporation
NLLWMP	National Low-Level Waste Management Program
NRC	Nuclear Regulatory Commission

NWTP	NWTP Waste Treatment Program
OCRWM	Office of Civilian Radioactive Waste Management
PNL	Pacific Northwest Laboratory
PSCM	Pilot-Scale Ceramic Melter
PWR	Pressurized-Water Reactor
RLFCM	Radioactive Liquid-Fed Ceramic Melter
TC	Thermocouple
TRC	Technical Review Committee
TRU	Transuranic
WV	West Valley
WVDP	West Valley Demonstration Project
WVNS	West Valley Nuclear Services
WVST	West Valley Support Task

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