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Commercial Waste Treatment Program Annual Report for FY 1983

J. L. McElroy and H. C. Burkholder, Compilers

February 1984

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**Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830**

**Pacific Northwest Laboratory
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COMMERCIAL WASTE TREATMENT PROGRAM ANNUAL PROGRESS REPORT FOR FY 1983

Compiled by
J. L. McElroy and H. C. Burkholder

February 1984

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Pacific Northwest Laboratory
Richland, Washington 99352

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EXECUTIVE SUMMARY

The Department of Energy (DOE), in the last half of FY 1982, established the Commercial Waste Treatment Program (CWTP)^(a) at the Pacific Northwest Laboratory (PNL). The mission of the program is to establish the technology for treating and immobilizing spent fuel and high-level, transuranic and related special wastes from the civilian nuclear energy program. The CWTP develops waste treatment system technology and components, tests treatment systems, assists in deploying the technologies, produces waste packages for testing in storage and disposal, and maintains a resource of capabilities and facilities for waste treatment-related activities.

This annual report describes progress during FY 1983 relating to technologies under development by the CWTP, including:

- development of glass waste form and vitrification equipment for high-level wastes (HLW)
- waste form development and process selection for transuranic (TRU) wastes
- pilot-scale operation of a radioactive liquid-fed ceramic melter (LFCM) system for verifying the reliability of the reference HLW treatment process technology
- evaluation of treatment requirements for spent fuel as a waste form
- second-generation waste form development for HLW
- vitrification process control and product quality assurance technologies.

An assessment was prepared on international commercial waste treatment technologies. Borosilicate glass has been evaluated as a commercial HLW form, and waste-form specifications have been drafted for the production of HLW glass. The glass evaluation is being reviewed by National Waste Terminal Storage (NWTS) sites. Improved glass compositions have been developed for both West Valley

(a) In January 1984 the program was renamed the Civilian Nuclear Waste Treatment Program (CNWTP).

sites. Improved glass compositions have been developed for both West Valley Nuclear Services (WVNS) and light water reactor (LWR) reprocessing facilities, using the Barnwell Nuclear Fuel Plant (BNFP) as the reference. The characteristics of the liquid feed to the LFCM were studied, and the feed system behavior was improved. The safety of liquid feeding was further studied by assessing the potential for, and consequences of, a molten-salt water reaction. The development of a decontamination technique for cladding hulls was begun, and an assessment of alternative TRU metal melting methods was completed with selection of the vacuum-induction method. A draft strategy document for development of second-generation HLW treatment technology was prepared. An evaluation of spent fuel as a commercial high-level waste form has been initiated.

Technology testing activities have focused on the preparations for a radioactive liquid-fed ceramic melter pilot plant. This work has included equipment design and fabrication, cell cleanout and documentation. Design of the ceramic melter, canister turntable, feed rack, and scrub rack was completed and fabrication initiated. Cell cleanout and preparation of radioactive pilot-plant equipment was 40% complete at year end. Many waste hauls were made, which included spent fuel hardware, Three Mile Island (TMI) equipment, spray calciner equipment, and large quantities of miscellaneous obsolete cell hardware. A design description document and an Environmental Evaluation were completed as well as a Safety Analysis Report (SAR) Supplement. An Operational Readiness Plan (ORP) was completed and approved. Criticality safety specifications and an internal review of natural hazards (i.e., earthquake and tornado) were also completed.

In the deployment assistance area, support for TMI reactor cleanup operations was provided through zeolite vitrification, mobile direct counting and radiochemical laboratories, and multi-element beta dosimeters. Four canisters of glass were produced from vitrification of TMI submerged demineralized system (SDS) zeolite liners. Samples were taken from the vitrified zeolite and were characterized. Durability was determined using Materials Characterization Center (MCC) leach tests. The leaching behavior of all components appears to be similar to that shown by the nonradioactive demonstration glass and is

comparable to that of PNL-76-68 glass. Four reports have been issued describing the nonradioactive and radioactive demonstration and product characterization. PNL has supplied a mobile direct-counting laboratory and a mobile radiochemical laboratory to provide rapid onsite analyses of material during the TMI cleanup operations. Multi-element beta dosimeters were provided for four different experiments in the TMI-2 Containment Building, and the results were analyzed.

Three pilot-scale ceramic melter (PSCM) runs were completed using a simulated West Valley waste. A submerged bed scrubber (SBS) was designed, fabricated and tested. The conceptual design of the vitrification off-gas treatment system was completed and documented. The results of alkoxide characterization and melter testing were documented. Process chemistry data were developed to evaluate a front-end process to be utilized for sodium removal from the neutralized HLW at West Valley. An engineering examination of four supernatant treatment processes was completed, including the generation of preliminary engineering flow diagrams and material flows. The four supernatant treatment processes were compared based on their ability to provide minimum decontamination performance for four key elements, and documentation was completed. The methods developed for supernatant decontamination included inorganic ion exchange, organic ion exchange and precipitation.

An engineering-scale sludge washing demonstration was conducted with simulated sludge and simulated sludge containing precipitant chemicals to verify laboratory-scale sludge washing results, and the results were reported. Conceptual drawings were completed of the remotely operable melter components and integral systems. A waste canister turntable was fabricated and modifications to it were made as a result of initial testing.

Assistance to the Breeder Reprocessing Engineering Test (BRET) Program was provided by completing the selection and preconceptual design of the BRET HLW vitrification system. A working formulation for the waste glass was developed. Input to the BRET safety and environmental assessment was completed.

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1.0 TECHNOLOGY DEVELOPMENT

W. A. Ross - Manager

1.1 OBJECTIVES AND OVERVIEW

The objectives of Technology Development for FY 1983 were to: 1) provide key requirements, specifications, and bases for the development, selection, and application of waste treatment systems; 2) develop glass formulations for West Valley Nuclear Services and Barnwell Nuclear Fuel Plant and obtain necessary product characterization data; 3) develop technical information to support design and operation of waste vitrification systems; and 4) select and develop transuranic waste treatment systems. To accomplish these objectives, Technology Development was divided into four corresponding activities.

The system analysis activity completed four reports during the year; three of them are at the comment draft stage and are discussed in Sections 1.2, 1.5 and 1.7. An economic assessment of glass and ceramic waste-form systems was published and is summarized in 1.6. Sections 1.3 and 1.4 summarize the initial results of experimental studies that were started to support the performance document.

In the glass development and characterization activity, two reference glasses were developed during the year. A major development activity resulted in selection of a glass for West Valley, as reported in 1.8. A smaller glass development activity for the Barnwell Nuclear Fuel Plant was also completed (Section 1.9). The importance of a glass gel surface layer in providing a diffusion barrier was evaluated in Section 1.10. This task also performed the work reported in Section 1.3 noted above.

The vitrification systems development activity has focused on safety and operational control methods and requirements for a liquid-fed ceramic melter (LFCM). The results of a hazard assessment from a potential liquid feed-molten salt reaction are reported in 1.11. The development of improved liquid feeds and pumps and their performance in a pilot-scale run are reported in 1.12. Our approach to product and process quality control is reviewed in 1.13. Section 1.14 summarizes the results from melter control and instrumentation developments and assessments.

The TRU product and process development activity focused on treatment of metallic wastes, which are expected to be the most expensive reprocessing wastes to be handled. Two approaches to cost reduction are being developed. For the first, metallic melting, 23 potential methods were reviewed and a vacuum induction melting technique was selected for further development (Section 1.15). The second concept is the decontamination and disposal of fuel hulls as LLW; its development is reported in 1.16. The potential radionuclide release from fuel hulls in both their as-generated and in a melted condition is being measured (Section 1.17).

As can be noted above, a wide spectrum of activities is being conducted in Technology Development, and significant progress was made during its first year.

1.2 GLASS PERFORMANCE DOCUMENT - R. D. Peters and K. J. Schneider

A draft document, PNL-4570, has been prepared to evaluate the radiation protection performance of the vitrification process and the resulting borosilicate glass waste forms in the context of current waste management system designs and regulations.

The evaluation was conducted by first defining reference vitrification, transportation, storage and disposal systems using the current literature. The performance of these systems in protecting present and future humans and their environments was next analyzed using established modeling techniques and data from the current literature. Where applicable and documented, the modeling results of other investigators were used directly. Finally, the results of these analyses were compared with the provisions of existing and proposed Environmental Protection Agency (EPA) and Nuclear Regulatory Commission (NRC) rules.

Waste management systems producing and using borosilicate glass are predicted to meet existing dose-based radiation protection standards (10 CFR 20, -50, and -72, and 40 CFR 190) even when conservative values are used for system performance parameters. These results, summarized in Table 1.1, show doses to maximum individuals from normal vitrification, transportation and storage operations not to exceed 0.1 mrem per year. Doses to maximum individuals from

TABLE 1.1. Calculated Annual Radiation Exposures to the Public from High-Level Waste Management with a Borosilicate Glass Waste Form, mrem/yr

<u>Part of Waste Management System</u>	<u>Anticipated Dose</u>		<u>Calculated Abnormal or Accident Dose</u>
	<u>Criterion</u>	<u>Maximum Calculated</u>	
Disposal in			
Basalt	<25	2.0	--
Granite	<25	0.9	--
Salt	<25	--	2.0
Tuff	<25	2.0	--
Vitrification	<25	0.1 ^(b)	12.0 ^(c)
Storage in			
Water	<25	0.0001 ^(b)	0.0003 ^(c)
Air	<25	<0.0001 ^(b)	<0.0001 ^(b)
Transportation by			
Truck	<500 ^(e)	0.03 ^(b,d)	300.0 ^(b)
Rail	<500	0.02 ^(b,d)	1300.0 ^(b)

- (a) Dose to the maximum-exposed individual based on existing regulations for nondisposal fuel cycle facilities.
 (b) Average dose/yr of 70-yr whole-body dose to the maximum-exposed individual.
 (c) Average dose/yr of 50-yr whole-body dose to the maximum-exposed individual.
 (d) Assumes the activities are one-half by each method.
 (e) Application of ALARA will probably reduce the value.

vittrification or storage accidents could be as high as 12 mrem per year, and an extremely severe, but very unlikely, transportation accident could cause doses as high as 1,300 mrem per year. Using repository host rock parameters indicated by the available literature, calculations indicate that maximum doses to maximum individuals from disposal in salt, basalt, tuff, and granite host rocks do not exceed 2 mrem per year and occur more than 500,000 years after repository closure.

Disposal systems using borosilicate glass are predicted to satisfy the provisions of the Federal Register draft of EPA disposal rule, 40 CFR 191, for

all four host rocks when best-estimate values are used for site-performance parameters. The key site parameters are the ground-water travel time from the repository to the accessible environment and the nuclide sorption coefficients. The existing information suggests that the ground-water travel times are greater than 10,000 years for all disposal sites currently under investigation on a best-estimate basis, and this consideration alone ensures compliance with 40 CFR 191.

The fractional release rates from waste package systems using borosilicate glass are predicted to be smaller than the 10^{-5} per year value in the NRC disposal rule, 10 CFR 60, for all four host rocks when favorable performance parameter values are used, the compliance boundary is located in the host rock 100 meters from the repository cavity, and the analysis is cut off at 10,000 years. When one or more of these three qualifications is not applicable for water-saturated host rocks, the fractional release rates are predicted to be larger than the 10^{-5} per year standard for up to three nuclides (^{99}Tc , ^{135}Cs , and ^{226}Ra) in some years. In fact, for nuclides, like ^{226}Ra , that grow into the waste by radioactive decay after 1,000 years, an "actual" 10^{-8} per year fractional release rate is sometimes required to meet the "nominal" 10^{-5} per year standard. Salt disposal systems meet the 10^{-5} per year standard without qualification because water is not flowing past the emplaced waste packages under normal conditions. It may be possible to find sites in the other host rocks that approximate this "no flow" condition, but the literature supports the use of "flow" conditions for non-salt disposal media. Because the largest predicted doses from disposal are smaller than even a conservative application of existing dose-based radiation protection standards, because several authors (National Academy of Sciences 1983; Burkholder 1983) have provided technical bases for fractional release rates that are larger than the NRC's 10^{-5} per year limit, and because the NRC can approve larger fractional release rates at its option, it seems likely that borosilicate glass will be in compliance with 10 CFR 60 as ultimately implemented.

Therefore, borosilicate glass waste forms in simple canisters are likely to have adequate performance when used in waste management systems of current

design and should be designated "acceptable" for application as required to solve nuclear waste management problems.

As a result of this document two experimental studies were conducted (see Sections 1.3 and 1.4) that have supported the models and data used in the disposal analysis.

1.3 EXPERIMENTAL MODELING OF NEAR-FIELD DISCHARGE - L. A. Chick

To address recently proposed NRC criteria (US NRC 1981) limiting the allowable release from a nuclear waste form, long-term predictive models must be developed. Defensible models must be based upon experimental data taken under repository-relevant conditions. To date, such a model does not exist. As an initial approach, we have developed an experimental system to validate the basic physical principles of solubility-limited, liquid-diffusion-controlled transport (Chambre et al. 1982). A simplified, near-field "repository environment" was constructed using a cylinder of Li_3PO_4 as the waste form surrounded by nonsorbing teflon beads as the rocky backfill. The test chamber was ~1 ft in diameter and ~4 ft long, weighing over 170 lb when assembled. The pore velocity was held constant at 16.6 m/yr. Steady-state discharge appears to be reached after ~2 days, giving an expected outlet concentration of 1 ppm. The measured discharge concentration stabilized after 44 hr to ~1.2 ppm Li, in excellent agreement with the calculated value. More experimental data, though, are needed to draw conclusions about the model's validity. Our experimental approach, however, does show promise for synthesizing readily available leaching, geochemical sorption and solubility data into a defensible mathematical-experimental model for repository licensing.

1.4 SOLUBILITY OF TETRAVALENT ACTINIDE HYDROUS OXIDES UNDER REDUCING AND HIGH-TEMPERATURE CONDITIONS - D. Rai and J. L. Ryan

Under reducing conditions, the solubility of tetravalent actinide compounds can be used to set limits on maximum aqueous concentrations in equilibrium with waste forms such as waste glasses. However, accurate values are not available for 1) solubility product of the tetravalent actinide hydroxides, 2) tetravalent hydrolysis constants, and 3) tetravalent carbonate complexes

needed for solubility calculations. Most values reported in the literature are either estimated or based on very questionable old data. The presence of $M(OH)_5^-$ species is predicted under alkaline conditions, making the solubility of actinides under alkaline conditions appear unrealistically high. However, Ryan and Rai (1983) studying U(IV) hydrous oxide found no evidence for such species $[U(OH)_5^-]$ and observed solubilities to be very low. Therefore studies with Np(IV) hydrous oxide were initiated to determine the solubility and the influence of hydroxo and carbonate complexes.

The general method used in this study is discussed in detail by Ryan and Rai (1983). Briefly, the study involved adding approximately 0.025 ml of Np(IV) solution (~11 mg) in HCl to a basic solution of 0.05M $Na_2S_2O_4$. The $Na_2S_2O_4$ was used to maintain neptunium in the Np(IV) state. The pH values of the suspensions were adjusted to range from ~7 to 14.5, and all experiments were conducted in a N_2 atmosphere.

The results (Figure 1.1) showed that neptunium concentrations in equilibrium with Np(IV) hydrous oxide at pH values >8 were essentially all below detection limits ($10^{-8.3}M$). Similar to U(IV) (Ryan and Rai 1983), no evidence

FIGURE 1.1. Solubility of Np(IV) Hydrous Oxide in the Presence of $Na_2S_2O_4$ (The pH values >13 are only approximate, calculated from total NaOH concentration added to the samples.)

was found for the amphoteric behavior of Np(IV). A few samples at pH values around 7 (Figure 1.1) had neptunium concentrations of about $10^{-6.7M}$. Np(IV) hydrous oxide is not expected to be this soluble at near-neutral pH values, and the observed high concentrations may be due to the ineffectiveness of the $Na_2S_2O_4$ to maintain neptunium in Np(IV) state at this pH. Other redox agents will be tried in the future to answer this question. The results nevertheless show that solubility-limited maximum concentrations of neptunium under reducing-alkaline conditions will be very low and similar to the value used in the document on glass performance.

1.5 WASTE-FORM PRODUCTION SPECIFICATIONS - W. A. Ross

A set of 17 specifications for waste-form production requirements was drafted. The specifications are intended to provide a base for discussion among producers of solidified high-level waste, transporters, and repository site developers and operators. They address the basic areas of production requirements: behavior during transportation, handling, and temporary storage, and long-term repository performance. The specifications will allow development of testing methods, and generation of data needed to ensure that requirements of each group can be met at minimum cost. Agreement upon specifications will simplify design and allow a base of experience to be developed during the R&D phases of the waste management programs.

Additional supporting information is being developed for the specifications before they are distributed for comment and review.

1.6 ECONOMIC COMPARISON OF CRYSTALLINE CERAMIC AND BOROSILICATE GLASS FOR HLW DISPOSAL - R. W. McKee, P. M. Daling and L. E. Wiles

A study was conducted to evaluate the relative economics of utilizing a crystalline ceramic for disposal of commercial HLW as compared to a borosilicate glass. The two waste forms were compared on the basis of relative costs for disposal of HLW from a 70,000-metric ton equivalent (MTE) system. The entire waste management system, including waste processing and encapsulation, transport, and final repository disposal, was included in this analysis. The repository concept is based on the current basalt waste isolation project

(BWIP) reference design, which employs a concept of waste emplacement in horizontal boreholes. The boreholes are ~200 ft long and each holds up to 17 HLW canisters. A bentonite-basalt mixture is utilized for backfill around the canisters. The bentonite sorbs and swells when contacted by water, helping to prevent ground water from reaching the HLW canisters.

To determine whether the design assumptions would affect the relative economics for the two waste forms, several design basis alternatives were evaluated including:

1. immediate versus delayed addition of the bentonite/basalt backfill, which impacts allowable canister loading,
2. a range of basalt thermal conductivities, which affects the allowable canister thermal loading, and
3. a range of waste compositions which, in turn, affects the volume of solidified waste.

The optimum canister size and waste load for both waste forms were determined for all of the above conditions using a thermal analysis procedure. The cases with the largest canister and highest waste loading and those with the smallest canister and lowest waste loading were selected for total system cost analysis. Any significant cost advantage for one waste form over the other should show up at one or the other of these extremes.

The cases selected for complete system cost analysis are summarized in Table 1.2 and the results are presented in Table 1.3. The two C cases represent the conditions allowing the largest canisters to be used, and the two F cases represent the conditions requiring the smallest canisters. Repository costs favor the borosilicate glass waste form while transportation costs favor the crystalline ceramic waste form. The determining component is the waste processing cost, which favors the borosilicate glass process because of its relative simplicity. A net cost advantage of ~10% to 15% is indicated for the glass waste form.

TABLE 1.2. Emplacement Conditions and Canister Characteristics Selected for Complete 70,000 MTE System Cost Analysis

<u>Case</u>	<u>Immediate Backfill</u>	<u>Basalt Conductivity</u>	<u>Waste Concentration</u>	<u>Waste Form</u>	<u>Canister Heat, kW/Can</u>	<u>Canister Dia, Ft</u>	<u>Number of Canisters</u>
C-1	No	High	Low	Glass	4.68	1.36	16,800
C-2				Ceramic	4.16	0.84	17,700
F-1	Yes	Low	High	Glass	1.16	0.48	64,500
F-2				Ceramic	1.08	0.29	69,600

TABLE 1.3. Life-Cycle Waste Management System Cost Comparisons for Glass and Ceramic Waste Forms (Constant January 1983 \$1M Dollars)

<u>Case</u>	<u>Waste Form</u>	<u>Processing Costs</u>	<u>Transportation Costs</u>	<u>Disposal Costs</u>	<u>Total System Costs</u>
C-1	Glass	790	360	3110	4260
C-2	Ceramic	1700	200	3100	5000
F-1	Glass	780	310	4750	5840
F-2	Ceramic	1540	200	4870	6610

1.7 SECOND-GENERATION WASTE FORMS - L. R. Bunnell

A strategy has been written for a program to develop second-generation waste forms, and this strategy has been submitted to DOE. The approach is very flexible, and includes a total of six options, listed below:

1. LWR fast-track - 1990 design and construction readiness
2. LWR moderate - 1995 design and construction readiness
3. LMFBR fast-track - 1990 design and construction readiness
4. LMFBR moderate - 1995 design and construction readiness
5. Monitoring and innovation
6. No action.

The strategy contains points for and against each option, basic activities that would be pursued to meet the objectives, and preliminary budgets. Planning is under way for a 1984 program of modest size. Adoption of any of the options (except #6) will result in the availability of much more information on which

to decide whether any second-generation waste form is enough superior to glass, in both processing and performance, to warrant its use.

1.8 WEST VALLEY GLASS DEVELOPMENT - L. A. Chick

A statistically designed study was performed to develop a glass for vitrification of the combined HLW stream at the West Valley, New York, facility. The simulated waste composition and the seven component composition region studied is shown in Table 1.4. The actual West Valley waste stream is broken into four parts in the experimental design. Thus the effects of iron, aluminum, and sodium oxides can be studied separately from those of thorium, plutonium, uranium, and others which were included as fixed fractions of the variable component referred to as "waste mix." Chosen from this composition region were 103 glasses to be melted and tested. Test results were used to calculate empirical models that predict glass properties as a function of composition. The models were then employed to find the optimum composition for the West Valley application.

Properties tested and modeled include melt viscosity and electrical conductivity, crystallinity after three different heat-treatments, and leaching behavior in seven different tests. Stepwise least-squares regression was used to fit partial third-order polynomial glass compositions. Modeling was statistically successful (adjusted R-squared values from 0.87 to 0.95) for viscosity, electrical conductivity, slow-cooled, and isothermal-annealed crystallinity, and five of the seven leach tests.

The optimization utilization models express the following properties:

- T100p - temperature at 100 poise melt viscosity. LFCM operation requires T100p near 1150°C.
- EC100p - electrical conductivity at the 100-poise temperature. LFCM operation requires EC100p between 0.15 and 0.5 inverse ohm-cm.
- SCC - relative crystallinity produced during a slow-cooling schedule designed to mimic the canister centerline history. SCC was found to be an indicator of crystallinity occurring between 900 and 1150°C, that is, in the melter pouring section or during melter idling. It

TABLE 1.4. West Valley Study Waste and Recommended Glass and Glass Formers Compositions, wt%

<u>Oxide</u>	<u>Simulated Study Waste</u>	<u>Range for Study</u>	<u>Recommended Glass</u>	<u>Recommended Glass Formers</u>
SiO ₂		35-60	45.40	63.10
B ₂ O ₃		0-20	2.40	3.30
Na ₂ O	7.70	7-30	15.50	18.60
CaO		0-15	10.20	14.20
Al ₂ O ₃	1.23	0-12	0.90	0.80
Fe ₂ O ₃	48.02	0-24	13.50	
ThO ₂	15.33		4.31	
P ₂ O ₅	11.72		3.29	
UO ₂	4.96		1.39	
Cr ₂ O ₃	3.20		0.90	
SrO	0.63		0.18	
ZrO ₂	0.84		0.24	
Cs ₂ O	0.63		0.18	
MnO ₂	1.98		0.55	
NiO	1.49		0.42	
CeO ₂	0.52		0.15	
Nd ₂ O ₃	0.78		9.22	
MoO ₃	0.81		0.23	
K ₂ O	0.16		0.04	
Waste mix		0-22		
Total	100.00		100.00	100.00

was found that predicted SCC should be kept below 0.1 to avoid the possibiity of crystallinity occurring in the melter.

- Si4pH - a combined leaching measure composed of silicon release in the Soxhlet, pH3 buffered static, 150°C static, and 28-day static tests and the final leachate pH in the MCC-3 agitated powder test. These data were standardized to give equal weight to each test and

linearly combined into the $Si4pH$ parameter, which ranged from less than 2 for the very best high-temperature glasses up to 9 for the very worst glasses treated.

The recommended optimum glass composition is shown in Table 1.4 in terms of individual oxides and study components, respectively. Also listed is the glass former or "frit" composition that would be added to the waste stream to make the optimum glass. It should be noted that further testing will be performed in FY 1984 to determine whether it would be beneficial to substitute Li_2O for part of the Na_2O . A detailed report of the glass development effort and observed correlations will be prepared and published during FY 1984.

1.9 BARNWELL GLASS DEVELOPMENT - L. A. Chick

In 1977, glass 77-260 was developed for vitrification of the Barnwell Nuclear Fuel Plant high-level waste in the in-can melter at $1050^{\circ}C$. This year, a new glass was developed for an updated Barnwell waste composition to be vitrified in the liquid-fed ceramic melter at $1150^{\circ}C$. For this comparison to the new glass, 77-260 was remade with the new waste composition. Table 1.5 shows the updated waste composition used for glass development and the compositions of the new glass, 83-B-15, and the new version of 77-260, 77-260C. The viscosity of 83-B-15 is about 100 poise at $1150^{\circ}C$, and the electrical conductivity is about $0.25 (Ohm-cm)^{-1}$, both properties appropriate for LFCM processing. Representative leaching data obtained by the static MCC-1 tests at $90^{\circ}C$ show that the new Barnwell glass releases are between five and eight times less than for the 77-260C glass. The exception to this is for strontium in deionized water.

1.10 PROTECTIVE LEACHING-LAYER STUDIES - L. A. Chick

A series of experiments was performed to learn whether the reaction or "gel" layer which forms on glasses provides protection from further leaching. Many investigators have assumed this is the case since the rate of elemental release in static tests decreases with time as the reaction layer thickens. It has been proposed that leaching under these conditions is, therefore, controlled by diffusion through the reaction layer. Six glasses were tested to investigate the role of the reaction layer. First, each glass was leached in

TABLE 1.5. Composition of Barnwell Glasses

<u>Oxide</u>	<u>Current Simulated Barnwell Waste</u>	<u>Glass 77-260C</u>	<u>Glass 83-B-15</u>
<u>Glass Formers</u>			
SiO ₂		36.00	48.00
B ₂ O ₃		9.00	9.00
Al ₂ O ₃		2.00	5.00
Li ₂ O		0.00	4.50
Na ₂ O	20.30	14.70	9.59
TiO ₂		6.00	0.00
CaO		3.00	0.00
<u>Waste Components</u>			
Gd ₂ O ₃	30.22	9.98	9.06
Nd ₂ O ₃	8.66	2.86	2.60
P ₂ O ₅	7.04	2.32	2.11
ZrO ₂	6.16	2.03	1.85
MoO ₃	5.59	1.84	1.68
CeO ₂	3.72	1.23	1.12
RnO ₂	3.22	1.06	0.97
Cs ₂ O	3.01	0.99	0.90
BaO	2.17	0.72	0.65
La ₂ O ₃	1.62	0.53	0.49
Fe ₂ O ₃	1.61	0.53	0.48
Pr ₆ O ₁₁	1.58	0.52	0.47
Sm ₂ O ₃	1.21	0.40	0.36
1ViO	1.10	0.36	0.33
SrO	0.99	0.33	0.30
MnO ₂	0.72	0.24	0.22
Y ₂ O ₃	0.67	0.22	0.20
Cr ₂ O ₃	0.41	0.14	0.12
100.00	100.00	100.00	100.00

the normal manner for MCC-1, producing a curve for cumulative release versus time. The slope of these cumulative release curves decreases with time, as expected. To test whether the slope decrease was due to reaction layer growth, a sample of each glass was leached for 42 days, with the water being replaced each 7 days. In this test, since the reaction layer thickness is allowed to increase, the release would be expected to diminish with each successive 7-day leaching if the reaction layer has a protective effect. Figure 1.2 shows the boron release for glass 79-417, which was typical of the five glasses. The middle curve is the normal cumulative release showing decreasing slope. The bottom curve is the successive releases for the 7-day leaches of the same sample. Indeed, these releases do decrease slightly with each successive leaching. However, the top curve, which is the cumulative sum of the 7-day releases, illustrates that the apparent protective effect seen in the bottom curve accounts for only a small part of the slope decrease of the middle curve. The protective layers from these samples are being observed on screening electron microscope, and other related tests are still being analyzed. Based, however, on these preliminary results, it can be said that the primary cause for the normal leach rate decrease is not a protective effect of the reaction layer.

1.11 POTENTIAL FOR HAZARD DUE TO MOLTEN SALT LAYERS - W. L. Kuhn

When two liquids, one much hotter than the boiling point of the other, contact, there is the potential for a vapor explosion. This is the rapid vaporization of the more volatile liquid after the two fluids become intimately mixed by a disturbance. In an LFCM process there is the potential that excessive pressurization in the melter cavity would result from such a vapor explosion involving an aqueous layer lying on a layer of molten salt floating on the glass.

A very conservative analysis, in which all the available aqueous layer is vaporized, showed that the resulting pressurization would be proportional to the influent rate of the aqueous liquid (e.g., feed, water). Assuming the dimensions of the currently proposed West Valley LFCM, the maximum pressurization resulting from a 1-gpm influent rate would be about 50 to 70 psi.

FIGURE 1.2. Boron Release Rate for Glass 79-417, Typical of the Five Glasses

However, we view this result as unduly conservative since we believe that a relatively thin layer of water cannot all simultaneously enter into a single vapor explosion.

Since we believe the pressure estimates are unduly conservative, during FY 1984 we will attempt to show through combined experiments and theory that the entirety of a thin aqueous layer will not enter into a single vapor explosion. We expect this will decrease pressurization estimates by a factor of 10 to 100.

1.12 FEED AND PUMP DEVELOPMENT - H. T. Blair

This task is to develop and demonstrate equipment and procedures for containing, mixing, transporting, and controlling the rate of delivery to the melter of the blend of acid waste and glass formers. Acid wastes are

relatively easy to process, but complications arise when glass formers are added. Experience has shown that when glass formers were added as frit to simulated commercial wastes which were 2 to 4 molar nitric acid, the mixture would gel or the frit formed a sediment difficult to suspend. These gels and sediments plugged feed transfer lines and hampered operation of pumps or air-lifts used to convey the feed.

Two approaches were taken to developing a successful acid feed system. First an extensive review of the various pumping concepts was conducted that included literature searches, contacting pump manufacturers and the users of pumps in slurry applications, surveying what was being done in other nuclear waste development programs in the U.S. and technology exchanges with foreign R&D facilities. Various pumps were purchased or fabricated and tested with simulated feeds in a test station and in conjunction with the operation of the liquid-fed ceramic melter at PNL. The second approach was to evaluate ways of adding the glass formers and of treating the waste and glass former mixture to produce a pumpage easier to process.

A milestone was set to test an acid feed system for the slurry-fed melter by September 1983. The waste stored at West Valley, New York, was chosen as the reference waste for this test, and a glass composition was developed for this waste. It was determined that the glass formers could be added to the simulated reference waste, which was acidified to 2 M nitric acid, in the forms shown in Table 1.6 to produce a slurry resistant to both excessive gelling and settling.

A 10-day run was made in the pilot-scale ceramic melter using this feed composition in August 1983. Because of the improved rheology of the feed, a two-stage airlift rather than a pump was successfully used to convey and control the liquid feed to the melter at an average rate of 46 L/hr.

Since completion of the run in August, further studies have been conducted with the addition of the silica in the form of stabilized colloidal suspensions. These have completely eliminated settling problems and should greatly reduce abrasive wear in the feed system.

TABLE 1.6. Glass-Former Composition for Slurried Melter Feed
for Vitrifying West Valley Acidified Waste

<u>Melter Feed</u>	<u>g/L</u>	<u>Glass Composition Assumed Oxide</u>	<u>wt%</u>
Glass Formers			
SiO ₂ (-325 mesh)	147.65	SiO ₂	44.93
Na ₂ SiO ₃ • 5H ₂ O	2.29	Na ₂ O	4.30
Na ₂ B ₄ O ₇	43.93	B ₂ O ₃	9.21
LiNO ₃	54.91	Li ₂ O	3.61
Mg(NO ₃) ₂ • 6H ₂ O	27.35	MgO	1.30
ZrO(NO ₃) ₂ • 6H ₂ O	2.17	ZrO ₂	0.30
La(NO ₃) ₂ • 6H ₂ O	2.66	La ₂ O ₃	0.30
TiO ₂	<u>2.00</u>	TiO ₂	<u>0.60</u>
Subtotals	282.96		64.55
Waste components	<u>543.61</u>	Waste oxides	<u>35.47</u>
Total	826.67		100.02

1.13 PRODUCT QUALITY CONTROL - W. L. Kuhn, S. C. Slate, L. J. Ethridge

The relationship between process control, product quality control, and product quality assurance has been described in a paper, "Using Process Instrumentation to Obviate Destructive Examination of Canisters of HLW Glass" by W. L. Kuhn and S. C. Slate, which was presented at Waste Management '83, Tucson, February 27 - March 3.

The position is taken that the quality of the product can be assured for storage, transport, and disposal without destructive sampling. Instead we recognize that the product's performance correlates closely with the composition of the glass and its cooling history in a canister, and that in fact these two factors only can be controlled by operators of a vitrification process. Adequate design and control of the process enables control of the composition and the thermally defined structure (i.e., devitrification, cracking, etc.) of the glass. Experimentally determining the correlations between product quality characteristics (which determine performance) and composition and structure links quality control to process control. Documenting these correlations and

recording the process variables during vitrification reveals the level of statistical confidence for the quality characteristics; at an adequate level of confidence quality assurance is attained.

Work to date has verified that the LFCM process produces a very uniform product when a large batch of premixed melter feed is used. Demonstration of adequate HLW and feed sampling methodology and of favorable dispersive properties of the feed is planned, and will be important to ensuring product composition by using mass balances. A detailed thermal code is being developed to predict the cooling history of canisters. Simple analytical expressions have already been used to explain the long-term cooling rate seen in pilot-scale testing.

1.14 MELTER CONTROL AND INSTRUMENTATION - R. L. Treat

Methods were considered for ensuring the complete and uniform filling of canisters with HLW glass. Effective methods include the application of proven design features and the use of special instrumentation suited to HLW processing. Instrumentation was identified for 1) proportioning wastes and glass formers, 2) detecting glass level, and 3) monitoring glass pouring rate, viscosity, and process conditions before beginning to pour the glass. It was concluded that a variety of effective methods exist for ensuring the complete and uniform filling of canisters. The selection of methods must, however, be tailored to the specific set of conditions and requirements for each HLW glass-melting application.

A novel instrument for indicating glass viscosity was tested and showed promising results. It injects gas into molten glass at very low rates, and viscosity is inferred by the rate at which bubbles are released into the glass. Release of a bubble is indicated by a pulse on a gas-pressure recorder.

The effects of chemical variability on melting process operability and glass product performance were also assessed. This assessment required a definition of melting process equipment and criteria for acceptable equipment operability and product performance. It was generally concluded that chemical variability will have little effect on melter operability and product quality. However, the effects of chemical variability on four areas of concern

could not be adequately evaluated due to lack of supporting data. Those areas of concern are 1) potential for melter short-circuiting, 2) potential for molten salt formation, 3) potential for melter foaming, and 4) potential for irregular rates of steam release. It was recommended that work be conducted to improve our knowledge of chemical variability in the melting process, particularly where separation of settled and floating phases may occur. It was also recommended that the composition of organic chemicals in the waste be better defined. Tests based on improved knowledge of chemical variability were recommended to assess the effects on the four areas of concern that could not be evaluated.

1.15 SELECTION OF METAL MELTING METHOD - D. R. Montgomery

A document entitled Review and Evaluation of Metallic TRU Nuclear Waste Consolidation Methods was written by D. R. Montgomery and J. F. Nesbitt. Its purpose was to identify, evaluate, and rate consolidation methods that could reduce the volume of metallic TRU nuclear waste generated in a fuel reprocessing facility. Both compaction and melting techniques were rated. Each consolidation process was evaluated based on its feasibility for handling and processing the metallic wastes produced if the Barnwell Nuclear Fuel Plant were operated. From the wide variety of melting concepts and consolidation systems that might be applicable for consolidating metallic nuclear wastes, the following processes were selected for evaluation:

- inductoslag melting
- rotating nonconsumable electrode melting
- plasma arc melting
- electroslog melting with two nonconsumable electrodes
- vacuum coreless induction melting
- cold compaction.

Each process was evaluated and rated on the criteria of process, state and type of development required, safety, process requirements, and facility requirements. It was concluded that the vacuum coreless induction melting process is the most viable process to consolidate nuclear metallic wastes. The

numerical ratings for each process by principal criteria, a total rating for each, and its ranking based on its total numerical rating when compared to other processes are presented in Table 1.7.

The ratings and numerical values shown for each criterion are the results of independent evaluations made by individuals with broad experience in radioactive waste processes, remote handling, remote process facility operation, and/or metal melting and casting.

Based on the information gained from the document, it is recommended that a large-scale cold mockup facility be established to refine and test the melting system selected prior to production operation. The mockup facility could also be used to test other similar equipment, and it would be a valuable tool for troubleshooting subsequent production problems. As a second option to the mockup facility, scaled-down tests have been identified that could be done by retrofitting PNL's present Inductoslag ingot furnace.

1.16 FUEL HULLS DECONTAMINATION - R. P. Allen and M. W. McCoy

This activity is to develop and demonstrate a decontamination technique capable of decontaminating large volumes of spent fuel hulls to levels that will allow their disposal as low-level waste.

A process that mechanically removes the oxide layer from autoclaved Zircaloy® tubes was developed. The first step of this two-step process is to split open the Zircaloy tubes using a cryogenic fracturing technique. This permits free access to the oxide layer on the interior surfaces of the tube sections. The autoclaved Zircaloy tubes will fracture into four sections, shown in Figure 1.3, when struck while cooled to the temperature of liquid nitrogen. The oxide layer is then removed from the Zircaloy tube sections in the second step using the centrifugal barrel finishing technique. Centrifugal barrel finishing is a standard technique used in the metal finishing industry for cleaning small, intricate items. In this technique the tube sections, along with silicon carbide abrasive and a little water, are placed in barrels that are mounted in pairs on a turret. During operation, the turret is revolved in one

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TABLE 1.7. Composite Rating Matrix for Consolidation Processes

	<u>Inductoslag Melting Ingot</u>	<u>Inductoslag Melting (casting)</u>	<u>Nonconsumable Electrode Melting</u>	<u>Plasma Arc Melting</u>	<u>Electroslag Melting</u>	<u>Vacuum Coreless Induction Melting</u>	<u>Cold Compaction</u>
Appendix	A	A	B	C	D	E	F
Complexity of process	302	362	359	320	254	435	320
State and type of development	240	254	264	244	210	284	229
Safety	227	228	212	222	210	262	282
Process requirements	157	156	217	189	140	226	242
Facility requirements	210	190	195	192	202	240	168
Total rating	1136	1190	1247	1167	1016	1447	1241
Ranking	6	4	2	5	7	1	3

FIGURE 1.3. Typical Section from Cryogenic Fracturing of Autoclaved Zircaloy Tube Section (photo ~1/2 scale)

direction, the barrels in the opposite direction. This motion causes the Zircaloy tube sections to slide one on the other in the abrasive slurry, effectively removing the oxide film.

Studies were completed that indicate disposal of the fuel hulls as low-level waste is possible if the surface contamination is removed, and that this decontamination process for fuel hulls is economically feasible.

1.17 LEACHING OF FUEL HULLS - Y. B. Katayama

Spent fuel hulls are being leach-tested in 90°C deionized water by an MCC-1 procedure. Comparison of as-processed hulls to consolidated, melt-compacted hulls is being made.

The hull material was taken from hull storage barrels filled during the Nuclear Waste Vittrification Project (NWVP) at PNL. Six PWR fuel bundles discharged from the Point Beach Reactor, with burnups of 20,000 to 30,000 MWD/MTU were used for waste preparation during the NWVP. Batches of fuel rods, representing about 86 kg of uranium, were sheared and the fuel dissolved from the cladding in 7.3 M nitric acid at 90 to 95°C until the specific gravity of the dissolver solution became constant over a 1-hr period. The dissolver solution was cooled and transferred to a holding tank, and the remaining hulls were leached in the next batch of 7.3 M nitric acid before transfer to the hull rinse tanks. The air-drip-dried hulls were then transferred to a furnace for drying before storage in the barrels (Wheelwright et al. 1979). For the leach

test the hulls were melted into buttons with a tungsten inert gas welding torch. This melting required about 2 to 3 sec and decreased the surface area more than fourfold.

One of the 1/2-in. pieces and one melted button were dissolved to measure the radiochemical content. Gamma scan data (Nielson 1979) and direct measurement of a 1/2-in. sample indicate that the gamma activity is low. However, based on the work of Griggs (1975), the NWVP batch dissolution time of about 4 hr would have left leachable quantities of plutonium. The MCC-1 test allows the measurement of this leachability on a standard basis for comparison to other waste forms. The MCC-1 tests are under way at this time.

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2.0 PILOT-SCALE RADIOACTIVE LFCM

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2.1 OBJECTIVE

The Pilot-Scale Radioactive LFCM (Liquid-Fed Ceramic Melter) is one component of Pacific Northwest Laboratory's (PNL) Commercial Waste Treatment Program. The principal objective of the Pilot-Scale Radioactive LFCM is to operate an LFCM under radioactive conditions to verify it as a viable process for converting high-level nuclear waste to borosilicate glass.

2.2 SUMMARY

During FY 1983, the design and fabrication phase began. Design of equipment components to be installed in existing facilities was finished and fabrication was started. The four major process components include a melter, waste canister turntable, feed system, and primary off-gas scrubbing equipment racks.

In addition to equipment-related activities, several safety- and environmental-related documents were prepared to support this activity. These include an Environmental Evaluation, Safety Analysis Report, and an Operational Readiness Plan. Many calculations were also completed, confirming criticality safety aspects of selected equipment components.

The 324 Building hot-cell facility in which the Pilot-Scale Radioactive LFCM is to be installed currently houses equipment used for previous radioactive experiments. A significant effort was made to remove this contaminated equipment, much of it technically obsolete, from the facility. Special remote cutting techniques using a plasma torch and arc saw were developed. Equipment has been remotely removed, surveyed for levels of contamination, then cut up and placed in shielded disposal boxes for burial. More than 30 m³ of compacted equipment and hardware has been buried this year.

2.3 INTRODUCTION

Since 1975, the LFCM process has been under development and testing in the United States. Its early success in producing borosilicate glass from high-level wastes (HLW) and its inherent simplicity and ease of operation and maintenance led to its adoption as the reference U.S. process for converting high-level nuclear wastes to borosilicate glass. During the late 1970s, both the spray calciner/in-can melter (SC/ICM) and the LFCM were being considered for use in U.S. waste solidification plants. The rapid technological development of the LFCM process by U.S. defense waste management programs led to its adoption. Currently, it has been adopted as the reference process in major Department of Energy (DOE) demonstrations for defense and commercial nuclear waste solidification, and as part of a commercial fuel reprocessing plant.

The projects include:

- West Valley Demonstration (WVDP)
- Defense Waste Processing Facility (DWPF)
- Hanford Waste Vitrification (BIPP)
- Breeder Reprocessing Engineering Test (BRET).

Because of the LFCM's adoption, the DOE Commercial Waste Treatment Program elected to design, construct, and operate a prototype radioactive pilot-scale waste solidification facility using the LFCM process. The data obtained from its operation will help to remove uncertainties about the process before it is used in the projects and production facilities listed above. It will also provide a data base for design of commercial plants.

2.4 PROCESS FEATURES

The Pilot-Scale Radioactive LFCM comprises three basic subsystems: waste feed preparation and feeding system, waste vitrification system, and off-gas and condensate treatment systems.

New equipment components to be installed as part of the Pilot-Scale Radioactive LFCM are shown in Figure 2.1 and include the waste preparation and feed tanks (TK-130 and TK-131), the radioactive LFCM, canister handling turntable (TK-133), ejector venturi, scrub solution recirculation tank (TK-134), and a

FIGURE 2.1. Simplified Engineering Flow Diagram of the Waste Preparation and Waste Vitrification Systems

seal pot (TK-135). A silver zeolite bed for iodine removal will also be installed as part of the secondary vitrification off-gas treatment system.

The source of radioactive waste to be used for extended operations of the Pilot-Scale Radioactive LFCM is chemical solutions simulating reprocessing waste which are spiked with dissolved spent PWR fuel to achieve the desired fission-product distributions. This waste material will be supplemented with radiocesium and radiostrontium concentrates, when required, and other chemicals to simulate a variety of waste solidification flowsheets. The adequacy of spent fuel as a radionuclide source has been reviewed based on three basic factors: 1) resultant chemical composition of the waste glass including fission products, actinides, and nonradioactive chemical additives; 2) glass radioactivity levels; and 3) glass decay heat levels. Based upon this review, chemicals spiked with spent fuel were determined to provide an appropriate alternative to simulate the actual waste from many reprocessing flowsheets. When high-activity or high-heat borosilicate glass is required, radiocesium and radiostrontium additions to the simulated waste will provide representative chemical flowsheets.

The simulated radioactive waste will be fed from the feed makeup tank to the Pilot-Scale Radioactive LFCM using a slurry feed and metering system. In the Pilot-Scale Radioactive LFCM, the liquid waste will be dried and melted into a vitreous form. Off gas from the vitrification process, which consists of air inleakage, water vapor, chemical decomposition products (e.g., NO, NO₂, CO, CO₂, H₂), entrained particulate, and volatile and semivolatile radiochemical contaminants, will be treated through successive stages of scrubbing, quenching, filtration, and absorption. The decontaminated off gas will be discharged to the existing cell process off-gas (POG) system, and eventually to the building stack.

The molten glass product formed in the LFCM overflows into a stainless steel canister where it cools into the solidified borosilicate glass product. The waste canister will be positioned underneath the LFCM by a rotating turntable. The turntable has positions for three canisters. Once filled, the canister will be allowed to cool, a dust cover will be placed on the canister, and the canister transferred to another part of the process cell for sealing

and nondestructive and/or destructive examination. The canister will be sealed by welding on a lid and then stored in an adjacent cell (A-Cell).

Waste Preparation System

The waste preparation and feed system comprises two 1250-L, pulse-agitated feed tanks and a feed pump for transferring radioactive slurry to the LFCM.

The pulse-agitated feed tank was chosen because of its greater flexibility and its ability to homogenize and suspend solids in HLW waste slurries as compared to a mechanically agitated feed tank. Its principal advantage is the degree to which agitation can be controlled by varying the pulsing frequency and intensity. This system has performed better than mechanically agitated tanks in homogenizing both simulated acidic and alkaline waste slurries in tests at PNL. This tank agitation concept was initially perfected for, and will be used in, the Federal Republic of Germany's PAMELA Project, Mol, Belgium.

Waste Vitrification System

The waste vitrification system comprises the melter, canister-handling turntable, and glass-level detection system.

The slurry-fed, joule-heated glass melter (Figure 2.2) operates on the same basic principle as commercial electric melters used in the glass industry. Molten glass is contained within a cavity made of highly corrosion-resistant, glass-contact refractory. Behind the glass-contact refractory are additional layers of lower density backup and insulating refractories. These backup materials provide secondary glass containment and added thermal insulation. The glass is joule-heated by passage of an alternating current between electrodes in contact with the molten glass. For the LFCM melter, the electrodes are composed of a nickel and chromium alloy known as Inconel-690®.

The canisters into which the glass is discharged from the LFCM are contained in and positioned by the canister-handling turntable, shown schematically in Figure 2.3. The turntable holds three canisters up to 40.6-cm dia and

® Inconel-690 is a trade name of the International Nickel Corporation.

FIGURE 2.2. Cutaway View of the Radioactive Liquid-Fed Ceramic Melter (RLFCM)

2.65-m long. It was designed for optimal cooling of the canister and can be adjusted by adding or removing insulating material from the removable liners.

The glass level in the canister will be monitored during pouring to prevent overfilling the canister. The level will be monitored using a gamma source (^{60}Co) and a series of eleven fixed NaI scintillation detectors mounted in the cell wall. The ^{60}Co source travels up and down the length of the canister. The gamma beam will be attenuated where the glass covers the beam, resulting in a significantly decreased detector response. The gamma detection system also has the flexibility to use radioactive sources (^{137}Cs , ^{90}Sr) present in the glass to monitor the glass level directly.

Primary Off-Gas Treatment

As part of the Pilot-Scale Radioactive LFCM, a new primary off-gas scrubber rack will be installed in B-Cell. This system will contain an ejector venturi, scrub solution recirculation tank, and seal pot.

The first off-gas treatment device is the ejector venturi. Its purpose is to condense 95% of the steam from the off gas, quench the off gases, and remove 90% of the particulate having a mean diameter below 1 micron, and essentially all particulate above 1 micron mean diameter. At the normal flows anticipated in the Pilot-Scale Radioactive LFCM, vitrification off gas will be cooled from 350 to 60°C; in the process steam will be removed from the gas at a rate of ~19 kg/hr.

2.5 EQUIPMENT DESIGN

A major milestone was completed during FY 1983, which was to complete the design of the system components. This included the melter, canister turntable, feed system rack, and off-gas scrubbing rack.

The LFCM is the heart of the vitrification system. Its function is to vitrify a radioactive waste-glass-former slurry and to discharge the resultant molten product into a receiving canister. The LFCM was designed so it can also accept and vitrify a dry solid feed, such as a loaded mix of inorganic ion-exchange mineral and glass former, such as zeolite.

The LFCM is an electrically heated (joule-heated), ceramic-lined melting device with a nominal surface area of 0.5 m^2 . The melter was designed for a maximum slurry feed rate of 40 L/hr (80 L/hr/m^2) and a normal operating feed rate of 25 L/hr (50 L/hr/m^2). The melter tank refractory arrangement was designed for a maximum glass temperature of 1300°C and a glass viscosity of 100 poise at this temperature. The melter was designed to operate with maximum pressure differential spikes of +12 cm of water or -50 cm of water between the melter plenum and the ambient cell atmosphere, and a normal operating differential of ~25 cm of water.

The general configuration of the LFCM as shown in Figure 2.2 includes a ceramic-lined melter tank with air-cooled Inconel-690 plate electrodes, a

monolithic ceramic submerged discharge throat and vertical airlift riser tube, an Inconel-690 discharge trough, an electrically heated discharge section, and the tapered outer discharge tube through which the molten glass passes as it free falls from the discharge trough lip to the receiving canister. The unit is contained in an Inconel-lined containment vessel. The top of the containment vessel is flanged, with a removable melter tank lid and removable discharge section lid attached. The containment vessel is positioned over the back edge of the receiving canister turntable, and a liquid-metal seal below the melter outer discharge tube forms a gas-tight connector between the containment vessel and the turntable.

The containment vessel is essentially a rectangular box 1.52 m wide x 2.16 m long x 1.19 m tall. The structural members, except for the upper flange, are fabricated with stainless steel. The floor of the containment vessel is fabricated from 0.48-cm Inconel-690, as is the tapered outer discharge tube in the discharge section, the outer discharge tube guide skirt, and the liquid-metal seal diaphragm attached to the containment vessel below the outer discharge tube. These pieces are exposed to the highest operating temperatures and potentially to the corrosive molten glass, and thus require the protection afforded by the Inconel-690 composition.

The containment vessel walls will be exposed to a much less hostile environment and are fabricated from 0.65-cm Inconel-601 plate. The walls and floors are seal-welded in the corners to provide an air-tight containment vessel.

The flange at the top of the containment vessel is fabricated of Inconel-690 plate 2.54 cm thick. This size plate was used to minimize bowing and subsequent air leakage when the lid section was bolted down to this containment vessel flange.

The rectangular melter tank is 0.61 m wide and 0.99 m long. Electrodes 7.6 cm thick are positioned at each end. The effective length of the tank is 0.84 m, and the effective glass surface is 0.51 m^2 . The low point in the discharge throat weir is 0.36 m above the melter floor. Taking into account the electrodes and the troughed floor bottom, the maximum static glass volume in the melter tank is 180 L.

The melter tank refractory design utilizes multiple refractory types to resist the corrosive action of the anticipated glass formulations.

The following six refractory types were used in the melter design:

- fuse-cast, chrome/alumina Monofrax K-3 (Carborundum Co.)
- fuse-cast, high-chrome Monofrax E (Carborundum Co.)
- machine-pressed and sintered AZS Zedmul-20 (Zedmark Co.)
- high-alumina, castable Alfrax-66 (Carborundum Co.)
- fused-alumina, bubble-castable Alfrax-57 (Carborundum Co.)
- high-density, alumina-silica Fiberfrax duraboard (Carborundum Co.).

Waste Preparation Tank Design

The waste preparation system consists of two pulse-agitated feed tanks and component parts. The pulse-agitated feed tank comprises three basic parts: tank, pulser tube, and air-displacement cylinders for moving the waste slurry. Both tanks will be installed as an integral part of a new 3B equipment rack.

Two conical-bottom, pulse-agitated feed tanks will be used to prepare and contain the simulated HLW waste slurries for feeding to the LFCM. Each tank, fabricated from 304-L stainless steel, will have a nominal diameter of 0.91 m and overall height of 2.36 m. Cooling jackets will be positioned around the cylindrical portion of the tanks to provide a heat-transfer surface. Each tank will have a 45.7-cm penetration for inserting the pulser tube and a 15.2-cm penetration for inserting a feed-transfer system. The total capacity of each tank will be 1250 L, allowing for freeboard. The active volume of the tank will be limited to 1000 L.

A pulser tube will be inserted in each tank. A piston assembly that uses air to displace a fixed volume of fluid will be mounted to the top of the pulser tube. The pulser tube will be fabricated from a pipe 2.4 m long and 40.6 cm in diameter. A conical reducer welded to the bottom of this tube will have a 5-cm opening. The cylinder drive system will be composed of a slave cylinder with a drive cylinder on opposing sides.

The synchronous operation of the piston system will create the pulsing action of the waste tank. The pulse system operates in two basic steps:
1) the drive cylinders force air into the slave cylinder above the piston, and

2) the piston is forced down, displacing a volume of waste slurry from the pulser tube. The total volume of fluid displaced is 60 L over a 15-sec period. Waste slurry is displaced from the pulser tube and accelerated towards the bottom of the tank as it passes through the 5-cm opening into the bottom of the pulser tube. Next, the drive cylinders are retracted by forcing air under the drive-cylinder pistons, creating a vacuum above the slave cylinder piston and pulling it up. Repositioning of the slave piston takes 45 sec. The waste slurry is agitated through a continual operation of the pulse system. The degree of agitation is adjusted by varying the air pressure to the drive pistons and the cycle time for the slave piston. Greater agitation is achieved by increasing the air pressure (volume flow) of air to the drive piston or by decreasing the cycle time for retraction of the slave cylinder.

Turntable Design

The canister turntable, shown in Figure 2.3, consists of a three-position, motor-driven carousel located inside a containment vessel. The carousel consists of three containment pods equally spaced around a central axis. It rotates around the center shaft supported by two bearings located at the top and bottom of the shaft. The turntable is normally rotated counterclockwise, although it can be rotated in either direction. The top of the shaft extends out of the containment vessel through a bearing seal retainer.

Each of the three containment vessel pods will contain removable thimbles for positioning various canister sizes. The thimble system can accept three canisters. In addition to providing containment of the canister, these thimbles will collect any glass shards that fall from the discharge trough.

The turntable containment vessel is fabricated from 304-L stainless steel plate. The walls are 0.5 cm thick, the floor is 1 cm thick, and the overall dimensions of the tank are 2.8 m tall, and 1.9 m in diameter.

The turntable containment vessel is equipped with: 1) dip legs for measuring any liquid that could collect in the tank, 2) a dip leg for jetting out that solution, and 3) six thermocouples. The thermocouples, arranged three to a set, are located at opposite sides of the turntable. Three are located near the canister filling position and three near the canister cooling position.

The thermocouples in each set are positioned near the top, bottom, and midway along the turntable wall. Each set of thermocouples is located within a blister connected to the tank. At the bottom of each thermowell is a window that allows contact of the thermowell with the inside of the vessel.

Two methods are used for centering the carousel underneath the melter overflow. The primary positioning method is to use a potentiometer attached to the carousel drive system. This system, once calibrated, limits the movement of the carousel to 120° with each activation of the drive motor. The second method is radioactive source tracing of the position of the carousel.

Glass-Level Detection System

A detecting system will be installed to monitor the accumulation of glass in the receiving canisters to preclude overfilling. Briefly, the system consists of 11 gamma-activity detectors positioned within the concrete shielding wall of the B-Cell facility. These detectors will be oriented and collimated so that the line-of-sight of each detector views a 5-cm-dia cylindrical segment of the receiving canister, passing horizontally through the canister's vertical centerline. A single, movable ^{60}Co source will be positioned on the opposite side of the canister from the gamma detectors sequentially in the line-of-sight of each detector. As glass accumulates at the line-of-sight level of a detector, the ^{60}Co counting rate for that particular detector will decrease. The degree to which the counting rate has reduced at any particular detector level will indicate the total accumulation of glass at that level. Due to the narrow collimation of the gamma sensor field of view, glass accumulation to either side above or below the detector line-of-sight cannot be determined. A redundant system utilizing the same 11 gamma detectors monitors the ^{137}Cs gamma activity at each detector level, and, since the glass contains ^{137}Cs , the degree to which that counting rate increases will indicate the accumulation of glass at that level.

Primary Off-Gas (POG) Scrubber System

The off-gas treatment equipment is designed to remove chemical and radiochemical contaminants and particulates from the off gas exiting the LFCM. The primary components include an ejector venturi scrubber and associated scrub

solution recirculation tank, a packed-tower quench scrubber, and a steam jet/condenser. After initial cleanup, the off gas will pass through several secondary pieces of equipment already in place in the hot cells, through a silver zeolite bed and HEPA filter, and finally to the 324 Building's POG system.

The ejector venturi scrubber is located on a jumper between the LFCM and the scrub solution tank (TK-134). Its function is to condense 95% of the condensible phase, cool the air, and remove 90% of the particulate including all particulates above a mean diameter of 1 micron. At normal flows, the venturi scrubber cools the off gas from 350 to 60°C. In the process, 19 kg/hr of steam is condensed. The remainder of the steam leaves as saturated air at 60°C. The cooling fluid to the scrubber is water at 40°C, which is recirculated from the scrub solution tank (TK-134).

The ejector venturi scrubber is a commercially available scrubber modified for this particular application. Corrosion potential dictates the use of Inconel-625 as the construction material for the entire jumper. For the venturi scrubber itself, 0.64-cm wall thickness was specified. The scrub solution connection is made via a PUREX connector with the spray nozzle attached to a female PUREX-type nozzle.

The scrub solution tank is located in the 3A rack. Its function is to contain, cool, and recirculate a water scrub solution to the ejector venturi scrubber.

Because of space limitations, TK-134 is oval shaped with a flat top and bottom 86 cm x 147 cm x 183 cm high. TK-134 has an overall volume of 2000 L, with an active liquid volume of 1700 L. The tank has 61 m of 2.54-cm Hastelloy C-276 pipe installed for cooling coils (heat transfer area 6.4 m²). The tank is designed to be replaceable in the cell without replacing the entire 3A rack. Corrosion potentials dictate that Inconel-625 be the construction material for the walls and to support the tank. As pipe and tubing fabricated from Inconel-625 were not available, Hastelloy C-276 was used for construction of the cooling coils and process piping.

2.6 SAFETY AND ENVIRONMENTAL CONSIDERATIONS

An Environmental Evaluation was prepared and approved for the Pilot-Scale Radioactive LFCM. The following conclusions were reached from the following assessments.

- The solid waste generated by the program will have negligible impact on existing solid waste operations at Hanford.
- Process operations will have no significant impact on the 300 Area liquid waste treatment system.
- Estimated gaseous emissions from operations will be in compliance with the maximum permissible concentration values specified in DOE Order 5480.1A, Chapter XI, Table II concentrations. These projected concentrations could potentially be exceeded for short periods; however, Table II concentrations were established for continuous exposure averaged over a year.
- A criticality event for the Pilot-Scale Radioactive LFCM was determined to be incredible due to design considerations that prevent attainment of a critical geometry or critical concentrations.

A 324 Building SAR Supplement for the Pilot-Scale Radioactive LFCM was also prepared for transmittal to DOE-RL. This SAR supplement documents potential hazards associated with its operation in B-Cell, 324 Building. Potential hazards were systematically identified and their impacts examined. All activities new to this facility were analyzed and determined to be less significant or no more significant than previous activities that have been conducted in B-Cell.

PNL requires that all projects involving the original startup or restart of a facility, complex operation, or sophisticated equipment be subjected to an Operational Readiness Review (ORR). The ORR process consists of evaluating the need for an ORR, appointing an ORR Board, reviewing and approving an Operational Readiness Plan (ORP), and final review of the implemented ORP and the facility before startup. It was determined that the Pilot-Scale Radioactive LFCM met the criteria for needing an ORR, an ORR Board was appointed, and an ORP was prepared and approved. The ORP identifies in checklist format all

applicable health, safety, and other requirements that must be met before startup. When all checklist items are completed, the ORR Board will review the project and recommend whether the facility is ready for radioactive operations.

Some of the Pilot-Scale Radioactive LFCM components had been used previously, and criticality safety calculations had already been completed (dissolver system). It was necessary to complete calculations for new equipment that will contain dissolved fuel, including the melter and two feed preparation tanks. It was concluded that these components would be subcritical for the fuel to be used for this program.

2.7 B-CELL EQUIPMENT REMOVAL

Test and Operation of Plasma Torch and Arc Saw

An effective cutting technique was needed to rapidly section obsolete equipment in B-Cell, 324 Building, into sizes that would fit into shielded burial boxes. In the past, in-cell cutting has been a time-consuming operation accomplished by an abrasive saw. A small, hand-held arc saw (Figure 2.4) and a commercially available plasma torch (Figure 2.5) (PAK-10 cutting system manufactured by the Thermal Dynamic Co.) were acquired for cutting tests in which manipulators are used to handle the cutting tool. The arc saw, which weighs ~7 kg, was supplied by Rockwell Hanford Operations.

Both the arc saw and plasma torch cut various diameters of stainless-steel pipe (up to 12 cm) and various thicknesses of stainless-steel plate (up to 2.5 cm) in both horizontal and vertical positions. After out-of-cell testing, the plasma torch was moved into B-Cell, where it was used to cut stainless steel support plates on the spray calciner. Other cuts in B-Cell with the plasma torch were on the TMI liner dryer, where cuts were performed on 10-cm channel, 2.5-cm plate, and light sheet metal. Hardened dowels and bolts were also cut off various pieces of equipment.

Cutting laminated steel components with an air gap between the pieces of metal is outside the capability of the PAK-10 plasma torch. Attempts to cut laminated steel, such as a pipe nested in a corner of sheet metal or angle, damaged the tip and necessitated its replacement. When laminated pieces of

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FIGURE 2.4. Arc Saw

steel are being cut, the slag does not blow through the steel backing, but is deflected back to the tip of the torch, which plugs or erodes the gas distributor or electrode.

Based on initial cutting in B-Cell with the plasma torch, the consensus is that the arc saw could effectively complement the plasma torch. Plans are to make an arc saw available for in-cell cutting after a larger power supply is received from a Hanford contractor. The arc saw was found to draw 1100 amperes at 20 V(dc), which is greater than the test power supply. A Linde-650 constant voltage power supply can supply continuous power without failing during the extensive cutting planned in B-Cell.

The arc saw exceeded expectations by cutting 2.5-cm stainless-steel plate. The cutting requirement imposed on the arc saw was to cut 1.25-cm stainless

FIGURE 2.5. Plasma Torch System

steel plate and cut 15-cm stainless-steel pipe in a single pass. The 2.5-cm stainless plate had proved impossible to cut with the original 30-cm mild steel, slotted blade furnished by Rockwell. After replacing the mild steel with an Inconel-690 blade, the cutting rate was roughly equivalent to that of the plasma torch on the 2.5-cm stainless plate. Although heat from the cutting operation bent the blade into a shallow cup, this warping failed to inhibit the cutting action.

Pipe cutting with the arc saw was reported to be much easier and faster than with the plasma torch. A 3.7-cm stainless steel pipe was cut in 10 sec with an arc saw fitted with an Inconel-690 blade. It was found that restricting the motion of the manipulator to act as swing arm was helpful.

When cutting with the plasma torch, the tip of the torch should be kept ~0.5 cm from the piece being cut. It is difficult to follow the curvature of a pipe on the side away from the manipulator. The pipe-cutting technique for the plasma torch was to cut a window out of the near side of the pipe and then

stick the plasma torch through the window and cut the far wall. A straight machine was found easier to use than the hand torch, on which the tip is at almost a 90° angle to the handle.

The preferred unit for in-cell remote cutting is the plasma torch, although our experience indicates that the two tools are complementary. The plasma torch is lighter and easier to handle than the arc saw; however, it is important to make sure that slag is blowing through the metal and away from the torch tip. Moving the torch too rapidly will prevent the complete penetration of the metal and cause the slag to "blow back" into the torch tip. Replacing a torch tip each shift is not unusual. Remote replacement can be done in a half-hour.

The operator of the arc saw feels a lot of vibration as the blade touches the material. Cutting does not begin until the material heats up; then the cut can begin but can progress only as rapidly as the heating zone. Cutting ahead of the heat zone can cause the blade to seize and the saw to buck. Forcing the blade into a cold metal without allowing sufficient time for heating can bend the blade, particularly the slotted mild steel blades, necessitating a replacement. More technique is required to use the arc saw than the plasma torch, and those with some welding experience acquire this technique most rapidly.

Dusting produced by the plasma torch was measured during tests to be 4.24 mg/m³. Samples were collected on 0.8-μm membrane filters. Particulate concentration in the air from arc saw operation was not measured.

3.0 WEST VALLEY SUPPORT (WSVP)

J. R. Carrell - Manager

3.1 OBJECTIVES

The overall objective of the WVSP is to provide technical support required by the site contractor at West Valley. Liaison with West Valley Nuclear Services, Inc. (WVNS) and the Commercial Waste Treatment Program (CWTP) has identified the following objectives:

1. Demonstrate through large-scale melter runs the application of liquid-fed ceramic melter (LFCM) technology for West Valley high-level waste (HLW).
2. Evaluate canister filling and cooling techniques for producing an acceptable glass/canister product.
3. Develop prototypic melter off-gas and feed systems compatible with West Valley needs.
4. As part of Item 3 above, continue tests on a submerged bed scrubber (SBS) as the first off-gas system component.
5. Coordinate the establishment of product (e.g., leach rate, impact resistance, etc.) and package requirements (e.g., canister closure specifications, surface contamination, transportation criteria, etc.).
6. Develop the glass composition for the reference waste feed.
7. Identify processing control parameters and/or measurements that will show product conformance and integrate into large-scale on-line testing for verification, including analyses of product from Item 1 above.
8. Provide process review and assistance.
9. Complete design verification of the development components. Provide the design of the Component Test Stand (CTS) equipment in accordance

with the approved Component Test Stand Equipment Design and Fabrication Plan. Begin preparation of the operating principle procedures. Conduct a design review of the EBASCO drawings of the CTS facility.

3.2 WASTE VITRIFICATION DEMONSTRATION - Major Contributors:

R. A. Brouns, W. J. Bjorklund, D. W. Brite, R. W. Goles, R. D. Peters, J. M. Perez, Jr., N. L. Scharnhorst, G. J. Seigny.

The Waste Vitrification Demonstration activity of the West Valley Demonstration Task (WVD) provides development and verification testing of the waste vitrification process equipment. This includes the slurry feed system, glass melting furnace and primary effluent treatment system. During FY 1983 the reference vitrification approach was defined and verified. Additionally, development needs and waste specific processing problems were identified.

Initially a melter feed formulation was selected on the basis of laboratory- and engineering-scale tests. Other work included several modifications to the nonradioactive pilot-scale vitrification system that were designed and installed early on in order to make the system more prototypical of the WVDP reference design. These included:

- an airlift feed metering system
- a submerged bed primary scrubber (SBS)
- a secondary particulate removal system
- a venturi off-gas flow meter
- a condensate recycle evaporator.

Three major experiments were conducted to test the selected melter feed formulation and upgraded equipment in the pilot-scale ceramic-lined melter (PSCM). The major confirming conclusions of the FY 1983 studies are presented below. The test results are described in the text that follows.

- Continuous glass pour rates as low as ~20 kg/hr are practical.
- The reference 45 kg/hr glass pour rate into an uninsulated canister produces a satisfactory casting.
- Unreacted mineral glass formers are preferred over premelted frits.

- The tendency of simulated West Valley glass to foam precluded achieving the desired process rate.
- Up to ~0.9 wt% $\text{SO}_4^{=}$ can be incorporated in West Valley waste glass.
- Airlift feed metering is a suitable approach for the acidified waste slurry.
- The reference submerged bed scrubber and the high-efficiency mist eliminator appear to be a viable approach.
- Off-gas line plugging between the melter and first scrubber under non-heated plenum conditions remains a potential problem.

Studies of Melter Feed Formulation

The objective of the feed formulation studies was to identify the appropriate waste slurry pretreatment and form of glass-forming additives for acceptable slurry transfer and melting characteristics. Laboratory- and engineering-scale melter tests were conducted to evaluate various formulations for differences in melting behavior and slurry rheology. Three methods for adding the glass formers to the waste slurry were studied: 1) as premelted frit, 2) as various combinations of unreacted minerals and 3) as an alkoxide derivative (Pope and Harrison 1982). In addition, waste acidification with both nitric and formic acid was evaluated for the waste-plus-premelted-frit formulation. For all tests the same base waste and glass-former composition was used. Table 3.1 lists the composition of the five unreacted mineral-type glass formers studied. Formulations 3 and 5 were used in engineering-scale tests.

The laboratory studies consisted of melting the various feed formulations, observing the waste decomposition and melting behavior by hot-stage microscopy, measuring the relative height of foam after melting in a crucible, and determining the decomposition gas composition as a function of temperature by quadrupole mass spectrographic gas analyses. In most cases the results of the laboratory tests either showed no significant difference in melting behavior between the various feed formulations or the observed differences did not correlate well with behavior observed in the engineering-scale tests.

TABLE 3.1. Unreacted Mineral Glass-Former Composition, wt%

Compound	Formulations				
	1	2	3	4	5
SiO ₂ (-200 mesh)	55.6	46.0	59.1	13.2	51.2
H ₃ BO ₃	--	--	--	14.8	--
B ₂ O ₃	--	9.1	11.7	--	--
Na ₂ B ₂ O ₄	22.0	--	--	--	--
Na ₂ B ₄ O ₇	--	--	--	--	15.4
Na ₂ SiO ₃	7.3	--	--	--	7.2
Na ₂ O·Si ₂ O ₅ (solution)	--	--	--	57.3	--
NaNO ₃	--	30.0	--	--	--
NaCO ₃	--	--	--	--	12.8
NaOH	--	--	18.1	--	--
MgO	1.6	--	1.6	1.6	1.5
Mg(NO ₃) ₂	--	4.6	--	--	--
La(NO ₃) ₃	0.4	0.3	0.5	0.4	0.3
Zr(NO ₃) ₄	1.1	0.9	1.1	1.1	1.0
Li ₂ CO ₃	11.2	8.7	--	10.8	10.2
LiOH	--	--	7.2	--	--
TiO ₂	0.8	0.6	0.8	0.8	0.7
	100	100	100	100	100

The experimental ceramic melter (ECM) was used to conduct the engineering scale tests. The ECM (Figure 3.1) is a joule-heated, ceramic-lined melter with an exposed glass surface area of 0.054 m² and a slurry processing capacity of up to about 4.5 L/hr. The simulated waste slurry was metered to the melter with a variable speed peristaltic pump.

Eight nominal 24-hr tests were conducted with a simulated West Valley waste composition. The various feed formulations were evaluated primarily on the foaming tendency of the glass melt, the processing capacity, the cold-cap venting behavior, and the slurry's tendency to settle and plug the feed system. Table 3.2 summarizes the results of these eight experiments. The evaluation relied chiefly on qualitative data; nevertheless, the study found

FIGURE 3.1. Experimental Ceramic Melter (ECM)

TABLE 3.2. Results of the ECM Feed-Formulation Studies

	West Valley Waste Frit-131S MV-2	West Valley Waste Frit-131S Formic Acid MV-3	West Valley Waste Frit-131S MV-4A	West Valley Waste Frit-131S Nitric Acid MV-4B	West Valley Waste Mineral Glass Former #5 MV-5	West Valley Waste Mineral Glass Former #3 MV-6	West Valley Waste Frit-131S MV-7	West Valley Waste Mineral Glass Former #3 MV-8	West Valley Waste Alkoxide Glass Former MV-9
Run length, hr	23.9	18.6	10.7	14.8	23.8	25.5	22.2	26.6	26
Down time, hr	--	--	--	--	--	~3	1.3	--	1.8
Feed used, L	62.2	58	34.7	38.9	82	83.2	73.4	107	103
Feed concentration, g oxide/L	360	171	420	420	480	480	480	480	200
Average feed rate, L/hr	2.6	3.1	3.1	2.6	3.45	3.7	3.5	4.0	3.97
Steady-state feed rate, L/hr/m ²	3.0(56)	3.8(70)	3.4(63)	3.0(56)	3.55(66)	4.1(76)	4.4 ^(d) (81)	4.5(83)	5.1(94)
Steady-state glass rate, kg/hr/m ²	(20 kg/hr-m ²) 1.08	(12 kg/hr-m ²) 0.65	26 kg/hr-m ² 1.43	(23 kg/hr-m ²) 1.26	(31 kg/hr-m ²) 1.70	(36 kg/hr-m ²) 1.97	(39 kg/hr-m ²) 2.11	(40 kg/hr-m ²) 2.16	(19 kg/hr-m ²) 1.02
Electrode power, kW	8.8	9.0	7.8	7.2	7.6	8.8	8.2	8.4	8.4
Melt resistance, ohms	0.35	0.35	0.36	0.36	0.37	0.42	0.39	0.37	0.36
Glass temp., °C	1125	1125	1140	1150	1150	1160	1130	1150	1150
Off-gas temp., °C	370	380	340	320	(b)	(b)	(b)	--	--
Comments ^(c)	Moderate foaming. Active cold cap.	Foamed, but the foam dissipated rapidly. Very active cold cap.	Moderate foaming. Active cold cap. Feed rate limited by foaming.	Excessive foaming. Some bridging. Moderately active cold cap. Plugged feed line because of settling.	Very little foam. Active cold cap. Slow feed set- tling rate.	No foam. Active cold cap. Slow feed settling rate.	Initially exces- sive foaming. Very little foam after startup. Active cap. Sev- eral feed line plugging problems as a result of settling.	Very little foam. Active cold cap. Slow feed set- tling rate.	Very little foam- ing. Several feed line plugs. Erratic off-gas flow.

(a) Inner refractory cooler off due to problems with low riser temperatures.

(b) Air cooling of off-gas exit port.

(c) All runs had salt layer on melter surface after run.

(d) Erratic feed rate due to feed system problems.

(e) Calculated from average feed concentration.

that the unreacted mineral glass formers consistently demonstrated stable melting behavior and good slurry transport properties.

In comparison, the formulation with premelted frit occasionally displayed glass melt foaming tendencies and difficulty feeding. Acidification with nitric acid of the premelted frit formulation seemed to increase foaming and to adversely affect slurry rheology. Rapid settling and subsequent feed system plugging was observed with this formulation. Acidification with formic acid, on the other hand, reduced foaming and did not increase settling of feed solids. The formic acid-treated formulation was not, however, noticeably better than those with unreacted mineral glass formers. The use of the alkoxide glass formers slightly improved the liquid processing rate of the waste slurry over that observed with the mineral glass formers. The alkoxide-based feed formulation, however, could not be concentrated to as high a solids loading as either the frit or mineral glass-former feed formulations, and thus a lower glass production rate resulted. The alkoxide feed was also more difficult to feed to the melter. Based on the favorable results with unreacted mineral glass formers, the formulation 3 composition shown in Table 3.2 was selected for use in the first pilot-scale test.

Testing of Pilot-Scale Equipment

The pilot-scale vitrification system consists of the pilot-scale ceramic melter (PSCM) and canister-handling system, a slurry feed system, and a primary effluent treatment system. The PSCM has a melting surface area of 0.73 m^2 and a slurry processing capacity of $\sim 60 \text{ L/hr}$. Figure 3.2, a photograph of the PSCM, shows a typical 24-in.-dia canister below. Figure 3.3 is a flow diagram for the pilot-scale off-gas equipment.

The three major experiments completed in FY 1983 used the PSCM. The first experiment (PSCM-14) was primarily designed to investigate the performance of the airlift in glass discharge, the canister filling as a function of fill rate, and the effects of discharge section inleakage on the pour stream. The experiment was nominally of 5 days duration and processed a dry simulated West Valley waste glass frit to effectively control the glass pouring at the target rate and allow continuous pouring at rates greater than practical while liquid feeding.

FIGURE 3.2. Pilot-Scale
Ceramic Melter (PSCM)

FIGURE 3.3. Flow Diagram of Pilot-Scale Developmental Off-Gas Equipment

The other two tests (PSCM-15 and PSCM-16) were nominal 10-day slurry-fed experiments to observe the processing behavior of the washed and the unwashed sludge flowsheets with unreacted mineral glass formers, respectively. The flowsheet for the second test did not assume any addition of nitric acid to the waste slurry from the condensate recycle or the supernate decontamination streams, and therefore the simulated waste was alkaline. The flowsheet for the third test was modified to assume acidification of the waste by nitric acid. The performance of the airlift feed metering system, a submerged bed scrubber, a high-efficiency mist eliminator, and a venturi off-gas flowmeter was evaluated during both tests. A Hydro Sonic Scrubber® was also installed and tested during the third experiment.

Results of these three tests are summarized below. Additional results on the canister filling results are presented in Section 3.3.

Glass Pouring and Airlift Drain System Performance

Continuous glass pouring rates as low as ~20 kg/hr were demonstrated to be practical. No nesting of glass was observed in the 48-in.-long discharge pipe between the pour tip and the neck of the canister. During one test, part of a canister was filled with glass at a rate of about 20.4 kg/hr. This resulted in the formation of a short pillar of glass ~8 in. in diameter. During another experiment an entire canister was filled at a glass rate of about 19 kg/hr. The glass completely filled the canister out to the walls in a characteristic lobing fashion. A visual observation of the quality of the glass fill indicated that no large voids formed and that the canister fill was greater than 95%. The difference in the can fill quality between these two tests was attributed to differences in glass viscosity. Tests performed at glass fill rates of 30, 40 and 44 kg/hr indicated that the quality of glass fill at rates greater than 30 kg/hr in an uninsulated, 24-in.-dia canister was acceptable.

Canister inleakage tests at air flows of 8 and 15 scfm were performed to determine the extent of interaction between the air and glass as the air passed out of the canister and up the discharge pipe into the overflow discharge section. This test was intended to simulate the effect of a poor canister flange

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seal that might occur in a remote facility. The pour stream left from the overflow section viewport via the pour tip of the overflow trough block and entered the canister from the canister viewport. At a glass pour rate of 28 kg/hr, a wave with an amplitude of about 0.25 in. traveled the length of the glass stream when the airflow was started. Very little movement of the glass stream in the melter discharge pipe was observed after the initial movement. The deflection of the stream viewed in the canister was a maximum of 2 in. from the axis. The effect of the inleakage on the glass pour stream was determined to be tolerable based on the visual observations.

Glass airlift tests were conducted in the PSCM at four bulk glass temperatures to study the efficiency of the glass airlift in lowering the glass level in the melter tank. The results of the test are summarized in Table 3.3. The level to which the glass could be lowered increased with increasing temperature and decreasing glass viscosity.

Another very important parameter was the glass-riser temperature. In the PSCM the glass riser block is flanked on each side with inner-refractory air coolers that prevent glass migrating from the melter tank into the overflow discharge section. These coolers draw considerable heat from the glass in the riser block as shown in Table 3.3. The temperature of the glass in the riser section was 200 to 300°C colder than the tank glass before the start of air-lifting. Even after glass had started through the riser, its temperature was 100 to 200°C colder than the tank glass.

Airlift Feed System Performance

The pilot-scale airlift feed system is shown schematically in Figure 3.4. Two stages in the airlift are used to transfer feed slurry from the feed makeup

TABLE 3.3. PSCM Glass Airlift Test Results

Test No.	Tank Level, In.		Bulk Glass Temp, °C			Riser Temperature, °C			Approx. Glass Viscosity/Avg. Temp., Poise	
	Initial	Final	Initial	Final	Avg.	Initial	Final	Avg.	Melter	Riser
1	13.75	13.5	960	992	976	740	870	805	871	>2000
2	13.5	12.75	1043	1001	1022	802	886	844	457	>2000
3	12.75	11.0	1128	1066	1097	827	998	913	151	1905
4	15	9.5	1140	1110	1125	860	905	883	35	910

Before the first PSCM experiment, the airlift was tested for a total of 406 hr with a simulated West Valley feed slurry during eight different tests. The longest period of continuous separation was achieved during test 8, lasting 142 hr. While the first seven tests were terminated due to plug formations, test 8 was terminated to enable preparation of the feed system for PSCM-15. The success of this test, about twice the length of any previous ones, was attributed to modifications in the second-stage footpiece and the use of periodic water flushes to this footpiece.

The airlift was operated for an 80-hr period of PSCM-15 with an alkaline waste slurry. The airlift plugged twice during this period. One of these feed system failures occurred in the gravity feed line between the air disengagement pot and the melter. The other plug formed in the second-stage footpiece near the air-injection point. Dilution of the feed slurry by ~20 vol% (from ~470 to ~390 g oxide/L) appeared to help improve the airlift's performance. The test period with diluted feed lasted only about 1.5 days, however, and consequently the results are inconclusive.

The simulated waste for PSCM-16 was acidic, with a free nitric acid concentration of 2 M. The feed concentration (~300 g oxides/L) was also lower than in PSCM-15. During the initial 91 hr of the test several plugs formed in the gravity feed line to the melter. Minor modifications to this line allowed the feed system to operate without problems for the remaining 131 hr of the test.

Variations of $\pm 20\%$ feed flow rate between the hourly averages were common during both PSCM tests. The primary cause appeared to be poor air disengagement in the first-stage headpot, which varied the submergence of the metering stage. The stability of the airlift flow rate with the acidified feed used in PSCM-16 was only slightly better than with the alkaline feed of PSCM-15.

Slurry rheology modification, such as addition of surfactants, is under investigation as a possible solution to the erratic flow rate problem. Scaleup of the airlift to a full-scale (150 L/hr) system is also expected to help stabilize the flow rate.

Waste Melting Performance

Attempts to operate at the specific design basis processing rate of 80 L/hr-m² of melting surface were compromised by glass melt foaming problems during both PSCM-15 and PSCM-16. Causes and control methods for foaming are currently under investigation; however, results to date suggest foaming is associated with reboiling of the glass triggered by relatively minor melter operational changes such as glass airlifting, power increases, or interruption of slurry feeding. Decomposition reactions during melting show no evidence of contributing to the foaming problem.

During PSCM-16 the operation of the melter was reasonably stable provided that the bulk glass temperatures were maintained at 1100 ± 25°C instead of 1150 ± 25°C as had been used in PSCM-15. The maximum stable processing rate demonstrated was ~65 to 70 L/hr-m² of glass surface for both the PSCM-15 and PSCM-16 feed formulations.

No detectable sodium sulfate salt layer was present on the melter glass surface at the end of PSCM-15. Chemical analysis of the melter feed slurry, glass, and off gas confirmed that essentially all the sulfur in the feed was dissolved in glass, except for ~4%, which escaped in the off gas. The average elemental sulfur content of the two PSCM-15 glass samples collected during the latter part of the experiment was 0.32 wt% (1.4 wt% as Na₂SO₄). Detailed analyses of a glass sample from PSCM-15 which contained 0.31 wt% sulfur showed no evidence of elemental or sulfur compounds in the form of entrained particles.

PSCM-16 feed slurry contained 0.38% average sulfur content, which is 27% more than in PSCM-15. The glass analysis shows only 76% of this was absorbed in the glass, with 6% escaping in the off gas. Consequently, a relatively large accumulation of sulfate salt was observed on the glass surface at the end of the experiment.

Off-Gas System Performance

The reference device for primary particulate removal for the West Valley Demonstration Task is the submerged bed scrubber (SBS). The SBS is a self-cleaning, wet-particle-bed filter which requires no pumps. A schematic of the pilot-scale developmental unit is shown in Figure 3.5. The SBS can be operated

FIGURE 3.5. Developmental Pilot-Scale Submerged Bed Scrubber (SBS)

as a quencher for condensing the off-gas steam or as an adiabatic scrubber which cools the incoming gas without condensing and removes gross particulate. During FY 1983 the primary testing was in the quencher mode.

The SBS performed well for both PSCM-15 and PSCM-16. No plugging or unstable off-gas flow behavior was observed. The pressure drop across the scrubber was nominally 30 in. of water column.

The average decontamination factor (DF) across the SBS was 31 for PSCM-15 and 39 for PSCM-16 when operating as a quencher. No deterioration of the SBS DF was observed when operated semi-adiabatically.

The melter steam and noncondensable gas emissions were effectively quenched from between 300 and 450°C to about 30°C when the alkaline waste slurry was processed. The resulting heat-transfer coefficient of the cooling coils ranged from 150 to 210 Btu/hr ft² °F, which is two to three times the value. When the 2-M nitric acid waste slurry was processed, the scrubber solution temperatures stabilized near 35 to 40°C, while outlet gas temperatures ran 60°C. This higher temperature is apparently due to an exothermic reaction between NO_x and H₂O. Operation without cooling coils resulted in fluid and outlet gas temperatures stabilizing at about 83°C. No temperature differential existed between gas and fluid, as happened when cooling coils were used.

A high-efficiency mist eliminator (HEME) is proposed as the secondary particulate removal device for the WVDP. Testing of the design shown schematically in Figure 3.6 was conducted during both PSCM tests. The pressure drop across the HEME remained at 1 in. of water column (WC) throughout PSCM-15. The average calculated DF during this test was 15. For PSCM-16 the pressure drop across the HEME started at about 3 to 4 in. WC due to a higher melter leakage and increased to between 5 to 6 in. WC by the end of the nominal 10-day experiment. A washdown for 5 min at 2 gpm did not lower the pressure drop. This suggests a possible irreversible load-up of solids that could require frequent replacement. Further investigation is under way.

A venturi flowmeter was installed in the off-gas jumper between the melter and first scrubber to continuously monitor the flow pattern of the noncondensable off gas. During liquid feeding tests, the flowmeter tended to plug after

FIGURE 3.6. High-Efficiency Mist Eliminator

about 2 days of operation. Solids deposited relatively uniformly at the 1.5-in.-dia throat but did not appear to deposit in the transition section leading to the throat. Periodic reaming of the flowmeter allowed operation to continue for the entire test.

After 10 days of operation, heavy deposits of solids were observed also in approximately the first meter of off-gas pipe from the melter and near the bottom of the submerged inlet of the SBS.

3.3 PRODUCT DEVELOPMENT AND EVALUATION- G. B. Mellinger

A glass composition was recommended to West Valley for use with their combined PUREX sludge-acid THOREX waste in the report entitled Recommended Composition for West Valley Waste Glass. This glass was developed by doing the following: 1) characterizing 85 glass compositions statistically chosen from rather wide study ranges for seven key performance-determining waste-form constituents, 2) deriving mathematical models of leaching rate, viscosity, electrical conductivity, and devitrification resistance from the data, 3) evaluating over 1,000,000 different glasses by computer simulation using these models to select the best 1000 glass compositions, and 4) manually evaluating the best 1000 to select the optimum composition.

The composition of glass formers used to make this glass is shown in Table 3.4. Also shown is the glass-former composition of the interim glass currently in use. The primary differences in the recommended glass are its higher Na_2O and CaO content and its lower B_2O_3 level. Also it does not contain the MgO and Li_2O present in the interim glass. The composition of the recommended glass was based, primarily, on achieving the lowest possible leach rate while maintaining a 1150°C processing temperature. The Al_2O_3 , B_2O_3 , and CaO levels resulted from a need to minimize both leaching and crystal formation.

A report, Draft Acceptability Specifications for Disposal of High Level Waste Solidified as Borosilicate Glass, was prepared and issued as a joint effort of the WVSP and Commercial Waste Treatment Program (CWTP). It contained specifications covering the following areas:

- Heat Generation Rate
- Maximum Sustained Glass Temperature
- Maximum Canister Temperature
- Maximum Radionuclide Content
- Release Rate from Failed Canister in Water
- Impact Resistance of Canister
- Particle Size After Impact
- Fire Resistance
- Volatility Limit

TABLE 3.4. Glass-Former Compositions of West Valley Recommended and Interim Glasses, wt%

<u>Oxide</u>	<u>Glass Formers for Recommended Glass^(a)</u>	<u>Glass Formers for Interim Glass^(a)</u>
SiO ₂	63.10	63.91
B ₂ O ₃	3.30	12.60
Na ₂	18.60	15.17
CaO	14.20	-
Al ₂ O ₃	0.80	-
Li ₂	-	4.89
MgO	-	1.71
ZrO ₂	-	0.43
La ₂ O	-	0.43
TiO ₂	-	0.86
	100.00	100.00

(a) Glass contains 28 wt% oxide, 72 wt% oxide glass formers.

- Standard Dimensions, Geometry and Weight
- Gas Generation and Pressure Buildup Within Canister
- Criticality Safety
- Package Identification and Data
- Surface Contamination Limits
- Canister Leak Tightness
- Canister Lifetime
- Maximum Radiation Field.

The document was not intended as a final set of specifications. Rather it was intended to be a starting point from which a set of specifications will evolve based on discussions with WVNS, other producers, waste transporters, and National Waste Terminal Storage (NWTs) sites. The document also does not specify how criteria are to be met and what test methods will be applied. These

will be determined when the needed specifications are agreed upon. The specifications as written, however, should be able to be met by current glass compositions contained within current canister designs. They are also written such that only minimal checking of production canisters may be needed for confirmation that certain specifications are being met.

A major activity of the process/product correlation subtests was the characterization of canisters of glass produced during PSCM tests. During PSCM-14 an insulated canister was filled with 1514 kg of glass at an average pour rate of 44 kg/hr. The run plans target rate of 45 kg/hr was the design basis pour rate for the WVDP. Throughout the uninterrupted pouring period, thermocouples placed in and on the canister recorded the fill. After the pour, the canister was moved from beneath the melter and allowed to cool by natural convection, and the thermocouples continued to monitor the glass and canister temperature until centerline thermocouple points reported $<100^{\circ}\text{C}$ temperatures.

After removing a 120° -section of the canister sidewall, it was evident that the glass formed numerous "lobes" as it poured (see photograph in Figure 3.7). Hence, there was not a radial symmetry to the flow of glass onto the surface, which will have to be accounted for in computer thermal calculations through some kind of averaging process. As a result of the lobes, there were numerous small voids between the glass and the sidewall, but no cracks entering the glass between the lobes were apparent. No "nesting" was seen. Horizontal core samples were taken at several locations within the canister. There was no apparent devitrification. Some discoloration of the glass is seen in thin bands or on exposed surfaces. The cores tended to be solid until broken on removal during drilling, suggesting that microcracking and perhaps macrocracking were absent or limited to horizontal planes throughout the canister.

The thermocouple measurements showed that for the uninsulated PSCM-14 canister the outside temperature peaked at about 450°C , decreased rapidly to about 300°C , and then cooled at about 10°C/hr . The centerline temperatures peaked at 1000 to 1050°C . The lowest temperature was recorded near the bottom of the glass fill, which presumably reflects heat lost at the start of the fill

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FIGURE 3.7. Filled PSCM-15 Canister with 120° Wall Section Removed

to heat the canister itself. The cooling rate was greatest at the top of the glass fill, reflecting heat transfer out the top of the canister as well as the sides.

At the middle and lower thermocouple centerline positions, after a rapid cooling from $\sim 1000^{\circ}\text{C}$ to 800 to 900°C , the cooling rate became logarithmic, with the $\log_e$ of the temperature decreasing at 0.0285/hr. This was found to correspond well with the theoretically predicted cooling rate using a side wall heat-transfer coefficient based on radiation, and considering the effect of simultaneous filling and cooling.

A report Performance of On-Line Test Techniques - 1st and 2nd FY 1983 PSCM Runs, was sent to WVNS. The report, covering feed and glass analyses during the first two FY 1983 West Valley melter runs, PSCM-14 and -15, states the following primary conclusions:

- The cooling rate of the canisters agreed well with heat-transfer theory and the assumption that cooling was mainly by radiation. For the expected WVNS melter pouring rate of ~45 kg/hr, the cooling should be an exponential decay to the ambient temperature, once the temperature reaches 900°C, with a decay time constant of 35 hr. This presumes unrestricted radiant heat transfer to cool surroundings.
- Because the cooling in the devitrification temperature range is primarily by radiation loss, devitrification can be minimized by increasing the canister's emissivity to increase its cooling rate. This could be done through the use of a pre-oxidation step or by some other means of darkening the can's exterior.
- About 10 to 15% devitrification (spinel) occurred at the pour rate of 44 kg/hr for the interim glass composition used. The WVDP design basis pour rate is 45 kg/hr. The extent of devitrification agreed qualitatively with the temperature histories.
- There was no evidence that separation of solids from supernate occurred in the feed system, based on the quality of the glass product.
- There was no evidence that precipitation of spinels, etc., occurred in the melter, based on the quality of the glass product.
- In general, there were no significant variations in the measured compositions of the feed, glass pour stream, or glass in the canisters for either PSCM run during the period of filling the instrumented canisters.

3.4 PROCESS SUPPORT- L. K. Holton

The Process Support Activity provides technical support through engineering review and experimentation to support the definition of the Conceptual Design Flowsheet for the West Valley Demonstration. Four activities were funded in FY 1983: Process Review, Sludge Wash Test, Sodium Removal Process, and Safety and Environmental Compliance Study.

Two major letter reports on process chemistry were completed: "Experimental Data Developed in Support of the Selection of a Treatment Process for the West Valley Alkaline Supernatant," Bray et al., WVSP 83/101 JRC (1983), which summarizes the laboratory studies and provides the technical data based from which the preliminary conceptual engineering of these processes was completed, and "Assessment of Four Processes for Treatment of the West Valley Alkaline Supernatant," Holton et al., WVSP 83/77 JRC (1983). Information on Rockwell Hanford experience with sludge mobilization was provided to WVNS. Preliminary accident analyses for the Safety Analysis Report (SAR) were completed. The Mott® cross-flow filter was evaluated in engineering-scale washing tests for separation of the sludge-supernatant and for the separation of precipitants that recover strontium, plutonium and cesium.

Process chemistry data were developed to evaluate a front-end process to be used in removing sodium from the neutralized HLW at West Valley. An engineering examination of four supernatant treatment processes was completed, including the generation of preliminary engineering flow diagrams and material flows based on 1) the experimental data (the four supernatant treatment processes were compared based on their ability to provide minimum decontamination performance for cesium, strontium, plutonium and technetium; 2) relative process and equipment complexity; 3) process safety and environmental considerations; and 4) impact of the process on the waste vitrification system and/or Low-Level Waste Treatment Facility (LLWTF). The methods developed for supernatant decontamination included inorganic ion exchange, organic ion exchange and precipitation.

The Sodium Removal Process Activity has developed the experimental data required to examine four processes that could be used for decontaminating the alkaline waste presently stored in Tank 8D2. Five areas of laboratory development were completed as follows:

1. Simulation and characterization of alkaline supernatant and sludge, which includes the determination of the radiochemical and chemical distribution between the aqueous and solid phase; and the investigation of sludge washing (H_2O) efficiencies, with emphasis on Na^+ and $SO_4^{=}$ ions.

2. Evaluation of the performance of a sodium tetraphenylboron (Na-TPB) precipitation process for recovery of cesium and a sodium titanate (Na-TiA) sorption process for recovery of strontium and plutonium, previously developed and tested at the Savannah River Plant (DOE).
3. Evaluation of the WVDP reference process which consists of the decontamination of the alkaline supernatant from Cs and Pu using an organic ion-exchange resin (CS-100) followed by an organic macro-reticular cation exchange resin (IRC-718) to remove Sr.
4. Evaluation of the performance of an inorganic ion exchanger (IE-95) to recover Cs, Sr, and Pu from alkaline supernatant.
5. Evaluation of the recovery of technetium (Tc) from alkaline supernatant using Dowex-1, X8 anion exchange resin.

West Valley alkaline waste was simulated to determine the distribution of key radionuclide species between the supernatant and sludge phases prior to sludge washing. A decrease of a hundredfold in the solubility of plutonium, tenfold for neptunium, and fourfold for americium and rare earths were observed when the pH was raised from ~10 to ~13. Cesium, strontium, and technetium solubilities were not greatly affected by the change in pH, and were about as expected at ~99, ~0.005, and ~90%, respectively.

The current process approach for treating Tank 8D2 sludge involves separating the sludge and supernatant and washing the resultant sludge to remove soluble salts. Major findings were that the $\text{SO}_4^{=}$ level in the sludge phase was reduced to 1 wt% equivalent of Na_2SO_4 in the waste glass (equivalent to 4% of the original $\text{SO}_4^{=}$ in Tank 8D2) after four washes. Na^+ ion levels were reduced to an equivalent loading of <7% Na_2O in the waste glass after four washes. Cs and Tc washed out of the sludge similarly to Na (3 to 9% remained in the sludge after four H_2O washes).

The Na-TPB process performance for recovery of Cs was found to be independent of pH from 10.4 to 12.8 or of temperatures between 25 and 50°C. The recovery of cesium is dependent upon the molar ratio of Na-TPB/Cs+K+Rb. To achieve a Cs DF of >10,000, this ratio must be at least 1.4. Not addressed

were the complex processing of the resulting organic precipitate, the loss of Na-TPB to the decontaminated supernatant, and the impact that this process would have on the vitrification system and LLWTF.

The Na-TiA process showed enhanced recovery of Sr and Pu at a pH level of 13.7 compared to 10.4, and at a temperature of 50°C compared to 25°C. Recovery of Sr was found to be independent of Sr concentration, indicating that it is not the controlling factor. To achieve DFs of ~225 for Sr and >6 for Pu, the weight of Na-TiA required was estimated to be 1.2×10^5 kg to process Tank 8D2 supernatant. No adverse effects were noted when Na-TPB and Na-TiA were combined in the experimental studies. However, the precipitant chemicals should be added to supernatant separated from the sludge.

To select ion-exchange materials for the recovery of Cs, Sr, Pu, and Tc from alkaline supernatant, a batch sorption screening test was completed. The results showed that the organic ion-exchange resins CS-100 and IRC-718 and an inorganic ion exchanger such as IE-95 were viable candidates for the removal of Cs, Sr, and Pu from alkaline waste. Removal of Tc using an anion resin such as Dowex-1 also appeared feasible.

Duolite® CS-100 performance for Cs was found to be dependent upon the resin particle size, temperature, and feed pH. Higher Cs loadings were achieved at lower resin size classifications. Cs loadings improved by a factor of 3.5 as the feed temperature was lowered from 50 to 6°C.

When the alkaline supernatant feed pH was increased from 10.4 to 13.6 (the major difference between the West Valley pH and Savannah River's), the column volumes (cv) of feed to the column increased from 1 to 6 at a C/Co (ratio of the effluent concentration [C] to the feed concentration [Co] of 0.1:Cs breakthrough). At a feed pH of 13.8, the highest Cs decontamination performance that the CS-100 ion-exchange resin achieved was ~1600. No Pu decontamination was found. Elution was achieved using 0.1 M formic acid.

Amberlite® IRC-718 performance for Sr was found to be dependent upon feed pH. Sr decontamination factors (DFs) of 100 and 1000 were achieved after 10 cv

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of feed were loaded at alkaline supernatant pH values of 10.8 and 13.3, respectively. Elution was achieved using 2 M formic acid.

The performance of the zeolite ion exchanger Linde Ionsiv® IE-95 in decontaminating West Valley alkaline supernatant was found to be dependent on temperature, flow rate, Na/Cs feed ratio, and pH. Loadings for Cs improved by a factor of 1.5 as the temperature was lowered from 50 to 6°C at 0.01 C/Co. Cs loadings increased by a factor of 1.4 as the feed pH decreased from 13.8 to 10.4 (the West Valley supernatant at pH 10 is more compatible with IE-95 than is the SRP waste at pH 13.8). DFs for Cs ($>10^4$), Sr ($\sim 10^3$), and Pu (~ 10) were achieved at the following column conditions: 0.6 cv/hr, pH 10.4, 8 cv, and 25°C. The Cs loading capacity on IE-95 (pH 10.4) was found to be three times greater than on CS-100 (pH 13.8).

Based on the laboratory data, four processes were evaluated for the removal of Cs, Sr, Pu and Tc to decontaminate the alkaline waste supernatant presently stored in Tank 8D2. These four processes are as follows:

1. Inorganic ion-exchange process (single-loading process) that uses a zeolite ion exchanger (Linde IE-95) to remove Cs, Sr, and Pu from the alkaline supernatant. The loaded ion exchanger is blended with other waste streams and converted to a borosilicate glass.
2. Inorganic ion-exchange process (eluted ion exchanger) similar to the first process except that the ion-exchanger is eluted to recover the radiochemical activity. The recovered radiochemical activity is blended with other waste streams and converted to a borosilicate glass. The eluted ion exchanger is disposed of as a low-level waste.
3. Organic ion-exchange process that uses regenerable ion exchangers selective to Cs (such as Duolite® CS-100) and Sr and Pu (Amberlite IRC-718) to decontaminate the alkaline supernatant.
4. Precipitation process which uses sodium tetraphenylboron (Na-TPB) to precipitate Cs and sodium titanate (Na-TiA) to adsorb Sr and Pu from the alkaline waste.

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These four processes would each be combined with a Tc removal process to comprise a complete supernatant decontamination system.

A preliminary engineering examination of each of the four supernatant treatment processes was completed to provide a basis for comparison. Process requirements and bases were defined based on the technical and schedular objectives of the West Valley Demonstration Program. In general, these bases specified that: 1) the Tank 8D2 supernatant be treated in a 9-month processing period assuming a process operating efficiency of 0.60 and 2) the supernatant treatment process be engineered, if possible, to provide the following minimum decontamination factors of 10^4 for Cs, 215 for Sr, and 6 for Pu.

The engineering examination of the four supernatant treatment processes included the generation of preliminary engineering flow diagrams and material flows based on experimental data developed during the testing of these processes with simulated West Valley waste. From these engineering diagrams, total material requirements, process cycle times, and equipment sizes were estimated.

Once characterized, the four supernatant treatment processes were compared based on their ability to provide minimum decontamination performance for Cs, Sr, and Pu; relative process and equipment complexity; process safety and environmental considerations; impact of the process on the waste vitrification system and/or the LLWTF.

The processes were then ranked according to technical preference based on the following attributes in order of importance.

- safety and environmental considerations
- process and equipment complexity
- impact on supernatant decontamination process on the waste vitrification and LLWTF
- process performance.

Based on these criteria, the supernatant treatment processes were ranked as follows:

1. Inorganic ion-exchange process (single loading process).
2. Inorganic ion-exchange process (eluted exchanger process).
3. Organic ion-exchange process.
4. Precipitation process.

While the two inorganic processes outranked the organic and precipitation processes, the two inorganic processes were viewed as essentially equal. Both inorganic ion-exchange processes provide more than adequate decontamination performance for Cs, Sr, and Pu, are uncomplicated as to process and equipment, pose no significant impacts on waste vitrification or the LLWTF, and no significant safety or environmental concerns.

The organic ion-exchange process does not provide sufficient decontamination performance, as defined by this study, for Cs and Sr. Moreover, this process is the most complex alternative under consideration and would have a significant impact on both the waste vitrification system and the LLWTF.

The precipitation process ranked lowest technically because of safety and environmental concerns associated with its operation, the rather complex processing required to treat the resulting organic precipitate, and the significant impact the process would have on both the waste vitrification system and the LLWTF.

3.5 DESIGN SUPPORT- D. H. Siemens

CTS Equipment Design

Design of the Component Test Stand (CTS) vitrification equipment is in progress. A comprehensive design and fabrication plan was prepared and submitted to WVNS for review. Comments received from WVNS were incorporated, and the plan was resubmitted and approved. Significant events since then, however, have necessitated the plan's revision.

Development Component Testing

A schematic of the WVSP vitrification system is shown in Figure 3.8. A mock cell wall is available in the 324 Building High Bay Extension (HBE). This wall provides a simulation of remote conditions for evaluation of component remotability in the CTS.

FIGURE 3.8. West Valley Vitrification System

The HBE crane has a rotating cell-type hook. All crane operations, including crane-held impact wrench, were capable of radio-controlled operation. Remote operation can be viewed through a television system to simulate cell conditions.

A full-scale operational turntable, designed, fabricated and installed in the HBE, is discussed here. A melter box having the dimensions and remote flanges similar to the reference melter design was constructed, fabricated and installed in the HBE. Support structures were designed, fabricated, and installed for supporting the melter box and turntable at the reference cell elevations with respect to the mock cell wall, floor, and gallery.

Turntable

The turntable superstructure and body was designed, fabricated and installed in the HBE facility.

Two melter/turntable connections were designed. A liquid metal-based seal concept was designed but discarded prior to fabrication in favor of an air-activated metal-bellows seal concept. Tests to evaluate candidate low-melting-point metals were completed in support of the nonreference design. Fabrication of the metal bellows offsite has proceeded more slowly than anticipated, and testing will be postponed until the bellows assembly and bellows flange/turntable E-ring arrive from offsite. Testing will evaluate the remote feasibility of the bellows seal method.

Canister Weighing

A strain-gauge load cell was adapted for use as a remote canister-weighing device. The load cell will be used to weigh the contents of the canister during filling. Remotization of the device has involved design of a jumper to connect the load cell with operating gallery instrumentation and a swing-arm to transfer the canister weight (force) the load-cell pad, located on the deck of the turntable. The load cell will provide an additional means of measuring the amount (mass) of product in the canister besides the level-detection system, which determines product volume. Both systems provide important parts of process quality control. The load cell and swing-arm mechanism have been fabricated, the remote jumper is being fabricated (at J. A. Jones Company), and the gallery instrumentation has been procured.

Canister-Level Detection

Design and testing of a ^{60}Co source-mobilizing device were completed (see Figure 3.9). The device consists of a source housing that is linked to an actuator shaft turned by a motor. As the shaft is rotated, the source travels downward and is made visible, for a discrete period of time, to each of a series of NaI gamma-ray detectors. In the proposed configuration, the array of detectors mounted in the cell wall view the mobile ^{60}Co source through the canister being filled. The actuator shaft is designed to cycle the mobile source upward and then downward along a travel distance that corresponds to the product stream path (descending from the trough pour spout to the bottom of the canister being filled). As the interposed canister is filled, the vitrified waste product reduces the intensity of the gamma rays that pass through it from the ^{60}Co source to the detectors. This source attenuation can be detected to establish whether the canister contains glass. The vertical array of detectors allows the presence of glass to be verified at several discrete levels within the canister. With this information, the volume of glass within the canister at a given time can be calculated. Testing verified the device's remotability and operability once installed.

Melter Overflow Discharge Insert

A remotely removable insert has been designed for the melter overflow discharge and is being fabricated for testing. The metal insert, in the shape of an inverted cone, is to provide a means to remove any possible glass plug that might form in the bottom of the melter discharge section if the canister were inadvertently overfilled or if bird nesting occurred. Its remotability is being tested in addition to how well it withstands operating temperatures.

Melter Discharge Thermal Mock-Up

A full-scale mock-up of a discharge section has been fabricated and installed and is undergoing tests. The mock-up incorporates the current reference lid, trough and air-cooled dam designs. Refractory materials are similar to those of the current reference melter design (from the standpoint of

FIGURE 3.9. In-Cell ^{60}Co Source Mobilizing Device

heat-transfer). The mock-up is completely operational and contains eight heating elements suspended from the removable lid. Plate heaters located at the rear of the mock-up are used to simulate the heat of molten glass within a melting cavity. The heat-sink effect of glass product within a canister (located in the turntable below the trough opening) is simulated using a steam coil. The steam coil is located within a mock removable discharge insert located on the interior floor of the mock-up. During testing, a nozzle on the

discharge lid is connected to a building vacuum system and air is let in at the base of the assembly through the mock insert. This flow of air simulates a hypothetical inleakage through the reference melter/turntable seal.

The testing will be done to measure the temperature distribution along the trough, warpage and temperature distribution of the dam, and integrity of refractory materials. The effect on dam and trough temperature distribution of hypothetical air inleakage (through the melter turntable connection), the presence of cold product, variations in dam cooling rate, and loss of lid-heating elements will be measured.

Instrumentation includes over 50 type-K thermocouples for measuring temperature distribution, a voltage-selector panel and digital multimeter for live amperage, and voltage measurement to enable evaluation of the performance of the heating elements. Photographs of the mock-up assembly interior taken between periods of operation will assist in evaluating material integrity.

Melter-Discharge Section Lid

An evaluation of a previous reference lid design indicated that further design development was required to provide more protection for the heating elements during remote installation. In that design, no provisions had been made for preventing the heating elements from contacting the melter or other cell equipment during remote installation of the lid. Such contact, made while lowering the section heater, could easily damage the elements and put the discharge section out of commission.

Two methods for protecting the heaters were considered. The first (and current reference) consists of two remote dowels suspended from the periphery of the lid flange. The dowels extend lower than the heaters and thus make the initial physical contact with the melter during lid installation. The lid is aligned with the melter using the dowels; alignment is achieved while the heating elements remain safely above the surface of the melter.

The second method involved a protective shield surrounding the element assembly. The shield, attached to the underside of the lid flange, would be lowered, with the elements, into the melter discharge section. Due to concern

that the protective shield would warp during operation of the discharge section and damage the elements, the shield design was shelved in favor of the remote dowel method.

A reference lid that incorporates the two remote dowels was fabricated as a component in the melter discharge thermal mock-up (described elsewhere) and will be remote-tested using the HBE remote testing facility.

During evaluation of the previous lid design, it was noted that air inleakage attributable to the discharge lid may not be enough, i.e., over 10 scfm at a vacuum of 10 in. water, to present a burden to melter operation. The primary source of inleakage has been found to be the relatively low pressure drop through the porous heaters. (Leakage through the lid to melter seal was found to be negligible.) To minimize inleakage, two airtight covers have been specified and are being fabricated for testing. The covers are rectangular boxes that are seal-welded to the lid and are sized to enclose four heating elements each. The sides of the covers are air-cooled, with a capability to remove up to 8 kW each and maintain an internal temperature of $\sim 400^{\circ}\text{C}$. (The cooling is required to prevent failure of the element electrical contacts at temperatures $>500^{\circ}\text{C}$.) The electrical leads extend through airtight fittings on the top of the covers. Cooling air will be provided using conventional remote cell techniques.

Melter-Discharge Electrical Services

The current reference concept is to provide separate electrical service input and output (I/O) lines to each of the eight heating elements, for a total requirement of 16 through cell wall lines. A remote 20-pin, 90-amp/pin connector is about 80% fabricated and will be evaluated as the electrical service connector. Sixteen of the 20 pins will be used. The capability to remotely connect the 16 I/O lines will result in the ability to wire and reconfigure the heating element electrical circuit(s) in the operating gallery for tighter element control. In addition, if a heating element should fail, this remote wiring capability will enable the remaining seven heaters to be reconfigured into their optimum circuit, thus avoiding a possible "domino effect" loss of the remaining elements.

A high-temperature (400 to 550°C) electrical contacting clamp has been designed, fabricated offsite, and is now being tested. The new clamps replace low-contact pressure clips that have tended to fail during nonremote testing due to their poor contacting, and thus generate high heat at the point of contact. Thus far, the clamps have been installed on the heating elements being used in the discharge thermal mock-up. With the discharge section interior at 1000°C and with an ampere load of 115, the exterior surface temperature of one of the clamps remained at a constant 400°C (in 70° to 90°C air with natural convection only). The clamps are silver-plated (0.005 in.) for extended life in a potentially corrosive environment.

Instrument Connectors

Two remotely installable multi-pin instrument connectors will be tested using the HBE facility. Testing will involve remote installation and removal, and verification of contact performance.

The reference connector contains 40 pins and was designed and prototype-tested at Savannah River Laboratory (SRL). During fabrication of the connector at PNL (80% complete), several minor revisions have been made to the SRL prints. Testing will include measurement of electrical resistances across connector pins to verify previously collected (SRL) data and remote installation by crane and impact wrench.

The alternate connector contains fewer pins but has the advantage of being installable using the crane only (no impact wrench).

Glass-Product-Sampling Device

A revision to the melt sampler (previously tested) was designed that will allow it to interface with the revised canister neck and canister grapppler and to fit within the canister-to-turntable clearances and will be tested pending design approval. Remote demonstration will be accomplished using the HBE facility.

Melter Electrode Power Bus

A direct through-wall power bus with high-ampere capacity (~2000 A) is being designed and will be mocked up and tested. The power line extends from

the operating gallery, through the cell wall and into the melter, where it attaches directly to an electrode. One power line (bus box) is required for each electrode. The buss bars will tentatively be made of Inconel 690 and stainless steel type 316. The Inconel 690 will constitute the portion of the bus extending from the cell wall to the electrode, while the stainless steel will be used for the part of the bar passing through the cell wall to the operating gallery. The bar material has been sized as stated in an earlier report. The bus bar will be equipped with ducts through which electrode-cooling air will be routed and a thermocouple access duct to the melter electrode. The electrode temperature-monitoring thermocouples will be installable from the operating gallery. Design criteria include prevention of gallery contamination and of degradation of cell walls by heat.

Testing will involve verification of ampere capacity using a 2000-A power system. Heat transfer will be simulated and evaluated, and thermocouple deployment from the gallery will be demonstrated.

3.6 MODEL MELTER SLURRY-FED CERAMIC MELTER (SFCM)

Two one-fourth-scale plexiglass models of ceramic melters were constructed and operated to gain design information on shape factors and melting cavity geometry. One model is of the current reference design and the other simulates an increase in melting-cavity floor depth and wall slope to potentially improve the power skewing abilities.

The Engineering Development Laboratory (EDL) test apparatus consists of two operational-scale models of the slurry-fed ceramic melter (SFCM) melting cavity, a three-phase delta-configuration power system, a simulated cold cap, controlled boundary conditions for wall and floor temperatures, and an LiCl-in-glycerine modeling fluid. Figure 3.10 is a photograph of the test apparatus during operation.

In designing and conducting the investigation, the following parameters that contribute to the thermal conditions within the melter were simulated as closely as possible (on a scale basis):

- SFCM melting-cavity geometry

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FIGURE 3.10. Electric Model of West Valley Slurry-Fed Ceramic Melter

- molten glass (hydrodynamic, thermal and electrical) transport properties
- presence of cold cap (thermal and hydrodynamic boundary condition)
- temperature gradients near melting-cavity floor and walls
- energy throughput (20% through walls, 80% through cold cap).

Four alternate power distribution modes were studied, and, over all variations in system parameters, a one-to-one correspondence was observed between the mode of power distribution and the pattern of fluid flow. Changing the geometry of the melting cavity walls and floor was not observed to significantly affect fluid motion. Finally, varying the wall and floor temperatures was not observed to have a pronounced effect on fluid motion.

This information suggests that the currently proposed SFCM design is adequate with respect to wall and floor geometry, and that the dependence of fluid motion on power distribution may be predictable enough to enable control of molten glass motion during feed processing.

Measurements of melting-cavity resistance over six different single- and three-phase power systems provided data for calculating shape factors.

REFERENCE

Pope, J. M. and D. E. Harrison. 1982. "Alkoxide Derived Vitreous Waste Forms." Proceedings of the Symposium on High Temperature Materials Chemistry, Denver, Colorado, October 11-16, 1981, pp. 186-200. Electrochemical Society, Inc.

4.0 THREE MILE ISLAND (TMI) COORDINATION

D. E. Knowlton - Manager

4.1 OBJECTIVE

The objective is to coordinate all PNL activities in support of the cleanup of the TMI-2 reactor and to provide waste treatment in those areas where the Department of Energy (DOE) can benefit by carrying out research and development of demonstration of technology.

4.2 BACKGROUND

The accident at the Three Mile Island Unit 2 (TMI-2) Nuclear Power Station was a loss-of-coolant incident, which resulted in damage to the core and subsequent flooding of the Reactor Containment and Auxiliary Buildings with contaminated water.

The safe cleanup of the reactor systems and associated buildings, and disposal of the wastes generated as a result of the accident at TMI, provides opportunity to demonstrate the reliability and versatility of waste treatment and disposal technologies for handling commercial nuclear wastes. The incident also provides a unique opportunity to evaluate the mechanisms and kinetics of core damage, develop analytical capabilities for assessing that damage, and develop analytical techniques that will improve assessment of, and response time to, unusual occurrences at nuclear reactors.

The scope of the activities within the TMI Coordination Task is multiphase and unrelated to each other except that they are all effectively providing assistance to the safe cleanup of TMI-2; thus, each activity within the TMI Coordination Program will be discussed separately.

4.3 ZEOLITE VITRIFICATION DEMONSTRATION - D. H. Siemens and G. H. Bryan

The cleanup of the high-activity water at TMI-2 provided an opportunity to further develop radioactive waste management technology. About 3.6×10^6 L of high-activity water was decontaminated using the Submerged Demineralizer System (SDS). In this process, the cesium and strontium in the water are sorbed onto

a blend of zeolites contained within metal liners. One disposal option for this zeolite is to mix it with glass formers and vitrify it to a borosilicate glass product. Under the Zeolite Vitrification Demonstration Program (ZVDP), DOE authorized the Pacific Northwest Laboratory (PNL) to take a portion of the zeolites from the SDS and demonstrate on a full scale^(a) that these zeolites can be vitrified with the use of the in-can melter (ICM) process.

Both nonradioactive and radioactive production-scale demonstrations have been conducted under the ZVDP. The nonradioactive and radioactive operations have been summarized (Bryan et al. 1982 and 1983). The radioactive demonstration consisted of the vitrification of the zeolite from one low-activity and two high-activity SDS liners. The objectives of the radioactive demonstration were to: 1) demonstrate the ZVDP process using actual SDS zeolites, 2) sample and analyze airborne effluents to determine their concentration and composition, and 3) analyze the glass product.

Process Development for Hot-Cell Operations

The process equipment placed in the hot cell for vitrification of radioactive SDS zeolites, as shown in Figure 4.1, was basically of the same design as that used during the nonradioactive process. Some minor modifications, however, were necessary to make the equipment compatible with requirements for hot-cell remote operation.

Zeolite Preparation

Three liners of zeolite were received from the Three Mile Island (TMI) SDS system for vitrification. The first liner (D-10015) was received at PNL in May 1982, and contained about 12,900 Ci of activity, of which 5,767 Ci were cesium and 1,012 Ci were strontium (the remainder was various daughter products). The two high-activity liners were received in January 1983. Liner D-10012 contained about 112,635 Ci of activity (53,046 Ci of cesium and 2,003 Ci of strontium) and liner D-10016 contained about 112,622 Ci of activity (52,358 Ci of cesium and 1,869 Ci of strontium).

(a) Full scale is defined as a 0.2-m-dia canister filled with 2 m of glass.

FIGURE 4.1. Zeolite Vitrification System and Off-Gas Sampling Site Location

After the liners were removed from their shipping cask and placed in the hot cell, they were sampled for gas content and then purged with nitrogen as a safety measure because of the possibility that hydrogen had built up from the radiolysis of water.

As received, these liners had a water content ranging from about 8 to 19 wt%. The water content had to be lowered sufficiently to make the zeolite dry and pourable. This was done to prevent plugging in the connecting piping and reduce the volume of gaseous effluents generated when the zeolite/glass former mixture was vitrified.

The zeolite was dried by a resistance-heated furnace. Two thermocouples were inserted through a liner flange and into the zeolite, one to a depth of about 6 in. and the other to about 24 in. The liner was then heated until both thermocouples reached a minimum temperature of 250°C.

After the zeolite in the two high-activity canisters cooled, it was sampled to determine the water content. This analysis is performed in the hot cell by heating a weighted zeolite sample to 1000°C and assuming the entire weight loss was due to water.

The weight of the dried zeolite was determined by pouring the entire contents of the liner into a mixer/feeder vessel and reweighing. From this weight and the water content, the correct amount of glass formers and silica to be added to the zeolite was determined. The glass formers and silica to be added to the bulk of the zeolite were placed in a hopper in the airlock of the hot-cell complex and then transferred to the hot cell, where they were added to the mixer/feeder vessel containing the zeolite.

The mixture was homogenized by tumbling the mixer/feeder vessel end-over-end for 1 hr using the handling fixture. At this point, the preparation of zeolite for vitrification was complete.

Operations Summary

After the zeolite was dried and blended with glass-forming chemicals, the mixer/feeder was inverted and connected to the feed and off-gas piping (tree) as shown in Figure 4.1. A stainless steel canister, 0.2 m in diameter by 2.5 m, was inserted in the ICM furnace and connected to the bottom of the tree.

Connections were tightened until there was a 0.13-m to 0.25-m mercury vacuum at the tree provided by the building's radiochemical ventilation system blower. Process effluents were drawn from the ZVDP system sintered metal filters through two condensers, a HEPA filter, a packed scrubber, another condenser, and two more HEPA filters before being vented to the building stack.

The feed rate was to be controlled at ~20 kg/hr or a minimum temperature of 900°C in the zone where melting was occurring. The canister had six zones, with thermocouples installed in each to monitor the temperature. As a zone filled with feed, additional power was required to melt this material. As a result, the canister zone temperature would start to fall. Increasing or decreasing the feed rate would increase or decrease this temperature drop. Because of heat losses, the feed rate would be reduced to only 1 to 2 kg/hr to maintain the 900°C temperatures near the top of the container. The radioactive SDS zeolite from the three liners was vitrified in four canisters. A summary of the operations is shown in Table 4.1.

Effluent and Analytical Studies - R. W. Goles

Effluent characterization studies have been established to support the TMI ZVDP. Their purpose is to provide basic off-gas engineering data around which

TABLE 4.1. Operations Summary

<u>Canister</u>	<u>Feed, kg</u>	<u>Maximum Feed Rate, kg/hr</u>	<u>Annealing Time, hr</u>	<u>Canister Fill Height, m</u>	<u>Glass, kg</u>	<u>Description</u>
Z-2	191	12.3	6	2.0	167	First high-level liner
Z-3	209	23	6	1.9	177	Low-level liner
Z-4	194	13.6	4	2.0	164	Remainder first high-level liner
						Start of second high-level liner
Z-5	180.5	10	8	1.9	161	Second high-level liner

an effective off-gas processing system can be designed for any future solidification facility utilizing ZVDP technology. The scope of these studies includes: 1) establishing the gaseous composition of melter-generated exhaust, 2) identifying the pathways for effluent escape, 3) quantifying the degree to which melter effluent losses occur, 4) characterizing the cesium distribution in zeolite liners and resultant canisters, and 5) establishing the influence of radiolysis upon liner cover gas composition and pressure.

The effluent characterization studies conducted during vitrification of TMI zeolite waste were primarily concerned with the radiologically important isotopes ^{134}Cs , ^{137}Cs , ^{90}Sr , ^{129}I , ^{14}C , and ^3H . The results of these studies are, however, generic to other ICM systems in that all classes of effluents, including volatile, semivolatile, and nonvolatile matter, are dealt with in these investigations.

Effluent generated in solidification of TMI zeolite waste was sampled by five discrete collection devices: 1) a filter, 2) a charcoal trap, 3) a condenser, 4) gas scrubbers, and 5) gas cylinders.

Filter Samples

Aerosol generation was found to be the predominant mechanism responsible for the losses of ^{134}Cs , ^{137}Cs , and ^{90}Sr during solidification. Table 4.2 summarizes melter system decontamination factors (DF) for ^{134}Cs , ^{137}Cs , ^{90}Sr , and total gross melter entrainment. These measurements are quite different from those obtained during cold testing of the vitrification equipment (Bryan et al. 1982). This strongly suggests a breached or malfunctioning filter housing. The sample collected from the D-10015 liner most strongly supports this notion. Calculated emission parameters associated with this liner were deliberately excluded from Table 4.2 due to the unrealistically high filter loading observed for this sample. Apparently, the sample nozzle had accumulated particulate matter during the processing of the D-10015 liner. When sampling was started toward the end of this processing campaign, the integrated sample was collected by the sampling filter. This was evidenced by a sharp decrease in the sample stream pressure drop that occurred soon after sampling began. Such an accumulation of matter could not have occurred had the process filter housing been

TABLE 4.2. Characteristics of Melter System Particulate Emissions

Zeolite Liner	Processing Date	Sampling Period	Feeding, kg/hr	Quenched Off-Gas Loading ^(a)					
				¹³⁴ Cs, ¹³⁷ Cs, μCi/L	⁹⁰ Sr, μCi/L	Partic- ulate, mg/L	¹³⁴ Cs, ¹³⁷ Cs	⁹⁰ Sr	Partic- ulate
D-10015	09/22/83	105 min	5.0	--	--	10.0	--	--	--
D-10012	01/18/83	79 min	7.0	19.0	0.99	0.26	23,000	31,000	9,400
D-10016	03/06/83	60 min	7.7	9.8	0.95	0.36	69,000	49,000	12,000

(a) Temperature/dew point: 20°C.

functioning according to design. This accumulation did not influence the data obtained from the two high-level liners because the sampling nozzle was cleaned before they were sampled.

Charcoal Trap

Although there is no reason to believe that ¹²⁹I would be present on cation exchangers, the potential for physical adsorption always exists. Consequently, charcoal sampling for the ¹²⁹I isotope was conducted. The results of this study suggest that ¹²⁹I is not a significant process-related effluent and thus, would not require off-gas emission control. This conclusion is, however, highly specific to the particular waste form being processed in this study.

Condensate

SDS liners were predried before shipment to PNL to reduce production rates of radiolytic gases. However, significant quantities of water remained in the zeolite liners after this drying process, thus presenting a radiological tritium burden to the off-gas system. In order to measure the impact of this isotope upon melter processing equipment, water vapor generated by the solidification process was sampled, condensed, collected, and analyzed for its tritium content. The results of these analyses appear in Table 4.3. Since the vitrification process has no capacity for water (DF = 1), the radiological impact of this isotope upon the off-gas system of any future solidification process will be dependent upon both the water loading of the melter feed and the specific activity of this water.

TABLE 4.3. Tritium Emission Associated with TMI Zeolite Vittrification

<u>Zeolite Liner</u>	<u>Tritium Loading, μCi/kg</u>		<u>Condensate Specific Activity, nCi/g</u>
	<u>Feed</u>	<u>Zeolite</u>	
D-10015	0.075	0.14	1.3
D-10012	0.99	1.9	17.0
D-10016	0.011	0.20	2.5

Gas Scrubbers

Since conversion of ^{14}C to CO_2 is most probable, gas scrubbing techniques were used to sample for this acidic gas. Analysis of these scrubbers failed to detect any significant quantities of this isotope in the off-gas stream.

Gas Samples

The composition of the noncondensable melter exhaust gas composition was routinely analyzed with a mass spectrometer. The results generated by the instrument characterize the process exhaust gas composition as being little more than wet, CO_2 -enriched inleakage, which presents no significant demands upon the design of a process-related off-gas system.

Result of Cask/Liner/Canister Analysis

Vessel pressure and gas composition were measured on both shipping casks and zeolite liners upon arrival at PNL. These results were compared with the initial conditions of the vessels as established at TMI before shipment (see Table 4.4. Significant differences in the way the low-activity and the two high-activity liners were shipped are responsible for the large differences in their final gas compositions. The high-activity liners were shipped with a palladium recombiner (H_2) and a rarified argon atmosphere.

Cesium-137 Profiles

The distribution of cesium in TMI zeolite liners and in product glass canisters was established using remote γ -ray scanning equipment. In this approach, the 662-keV γ -ray activity of ^{137}Cs emanating from a small volume element of the canister was used as a direct measure of the cesium concentration in that element. By mapping the γ -ray activity along the central axis

TABLE 4.4. Measurements of Cask/Liner Pressure Composition

Shipment	Vessel	Condition	Absolute Pressure Hg ^(a) , m	Average Molar % Gas Composition (Dry)					
				CO ₂	CO	O ₂	N ₂	H ₂	Ar
D-10015	Liner	Initial	(0.86)	--	--	--	100.0	--	--
	Liner	Final	0.93	0.55	<0.1	0.05	92.8	5.6	--
D-10012	Cask	Initial	(0.76)	--	--	--	100.0	--	--
	Cask	Final	0.76	0.03	<0.1	1.6	98.3	<0.01	0.08
	Liner	Initial	(0.10)	--	--	3.2	15.4	0.4	81.0
	Liner	Final	0.09	1.3	<0.1	12.3	83.2	2.1	1.1
D-10016	Cask	Initial	(0.76)	--	--	--	100.0	--	--
	Cask	Final	0.67	0.02	<0.1	1.4	98.4	<0.01	0.07
	Liner	Initial	(0.05)	--	--	0.6	3.7	0.1	95.6
	Liner	Final	0.17	3.3	<0.1	4.3	90.8	1.5	0.05

(a) Values in parentheses were calculated from gauge pressures assuming 0.76 m Hg ambient conditions.

of the liners and/or canisters, the distribution of cesium within these vessels was established. All three liners processed well-defined cesium-band structures totally confined to the top two-thirds of the bed. On the other hand, the product glass canisters exhibited uniform cesium distribution throughout.

Glass Product

Each canister of high-activity glass was core-drilled and the glass subjected to analysis by the Materials Characterization Center (MCC). Results of this study will be presented in a separate report.

4.4 MOBILE LABORATORY OPERATIONS AT TMI - C. W. Thomas

Summary

Two PNL trailers were assembled at TMI to perform onsite analysis activities to characterize the radiochemical and physical content of samples collected during the cleanup operation at TMI-2. These trailers are a mobile radiochemical laboratory complete with analytical equipment necessary to perform a variety of analytical procedures and a mobile radioactivity measurement

laboratory with state-of-the-art counting equipment including computer analysis. Samples analyzed consisted of material from the damaged core, sludge from the basement of the containment building, and water from the reactor building, as well as structural material from the reactor building.

Introduction

The reactor accident at TMI is probably typical of what may happen in any serious loss-of-coolant accident. Therefore, it is important that radiochemical and physical contents of the material released to the containment vessel be characterized and documented so that these data can be used in determining how to proceed with cleanup operations and can be used to assess any future reactor accident of this kind.

PNL placed inside the controlled area at TMI-2 two mobile laboratories that were designed for use in related type work. A mobile radiochemistry laboratory (Figure 4.2) was placed in the model room next to the Unit 2 containment vessel. This laboratory is a fully modern chemical laboratory with adequate shielding to handle samples with dose rates up to 5000 MR/hr. Analytical equipment installed allowed a variety of procedures to be performed, including ion exchange chromatography, solvent extraction, gravimetric analysis, and electroplating. The laboratory contains ventilated hoods, fume hoods, gas chromatograph, ion chromatograph, negative-pressure shielded glove box, macro and micro balances, air conditioning, and radioactive waste disposal and water facilities.

A mobile measurement laboratory was placed in the Unit 2 turbine building (Figure 4.3). This laboratory is equipped with the most modern, sensitive, and selective analytical equipment available for the direct counting of radioactivity. All detectors were placed in shielded lead caves for reduction of background radiation. An intrinsic gamma-ray spectrometer is used to measure photons from gamma emitters ranging in energy from 100 keV to 2 MeV. The gamma-ray spectrometer system is composed of a 25% efficiency detector, high-voltage power supplies, preamp power supplies, preamp-amplifier, analog-to-digital converter, and 4096 channel memory. The gamma-ray spectra are stored in memory and readout in hard copy. The data are also transferred by telephone modem link to the Pacific Northwest Laboratory for computer manipulation.

FIGURE 4.2. Mobile Radiochemical Laboratory Trailer
MO-949

FIGURE 4.3. Mobile Radioactivity Measurements Trailer
MO-4-51573

A thin window spectrometer is used to measure low-energy photons and x rays from the radionuclides of interest. This low-energy spectrometer contains the same electronics as the intrinsic germanium coaxial gamma-ray spectrometer. It is used to measure x rays and photons above from 5.9 keV up to 122 keV, especially those of ^{55}Fe and ^{129}I .

Many of the decontamination samples at TMI-2 require an analysis of their uranium and plutonium contents. In general, these alpha-emitting species are isolated in the radiochemistry trailer and prepared for alpha spectroscopy by electroplating procedures. The electronics components described earlier for the gamma-ray spectrometer are also required for this alpha spectroscopy system. At TMI-2, eight of this type of detector systems are in routine operation. A gas flow proportional counter (windowless) has been installed for measuring the extremely soft beta energy of ^{63}Ni . A gas flow proportional counting system is used to analyze beta emitters following their radiochemical isolation in the radiochemistry trailer. Radioisotopes such as ^{90}Sr and ^{99}Tc from the decontamination samples are analyzed in this way. A ZnS gross alpha detector composed of a ZnS matrix on a photomultiplier tube is used to detect gross alphas on the decontamination samples submitted for analysis. Using this gross alpha detection technique, the radioanalyst is determining the necessary radiological techniques which must be applied to sample analysis. An x-ray fluorescence system, using ^{109}Cd as excitation source, is used to identify trace element compositions of water and sediments at the ppm trace element concentration levels. This system is allowing the various elements to be identified by their characteristic x rays. The electronic requirements of the x-ray fluorescence analysis system are the same as those of the gamma-ray spectrometer. This system allows the determination of the trace element compositions of liquids and solids in the decontamination effort. An ion chromatograph^(a) (Dionex Corporation) is used to determine the ionic concentrations of specific anionic species. A gas chromatograph^(a) is used to analyze gas samples for their content, including hydrogen. A dedicated PDP 11/35 computer system with modem and large auxiliary disc was installed in late FY 1983 to handle data at TMI-2. It will result in much faster turnaround of samples.

(a) Housed in the Radiochemistry Laboratory.

Accomplishments

The analytical program initiated in FY 1982 was extended to include samples other than from the SDS zeolite liquid cleanup system. FY 1983, a section of the leadscrew (whose position in the core facility was in the vicinity associated with the gas bubble that formed in the reactor vessel during the accident) was received and leached consecutively with H_2O , borated H_2O , H_2O_2 - Na_2CO_3 , permanganate, citrate-oxalate, and nitric acid. These leachates were analyzed to determine the effectiveness of decontamination and elemental removal of the film associated with this type of surface. Several samples of solid material were received for complete radiochemical and elemental analysis. There was considerable interest in the long-lived ^{129}I associated with these samples because the concentration and position of this radionuclide would act as an indicator of the ^{131}I deposition during the accident. About 120 samples of influent and effluent from the SDS system were received, and a thorough radiochemical analysis was completed. These samples were analyzed for ^{54}Mn , ^{55}Fe , ^{60}Co , ^{63}Ni , ^{90}Sr , ^{99}Tc , ^{125}Sb , ^{129}I , ^{134}Cs , ^{137}Cs , ^{144}Ce , ^{234}U , ^{235}U , ^{238}U , ^{238}Pu , $^{239/240}Pu$, ^{241}Am , ^{242}Cm , and ^{244}Cm .

The samples were used also to generate appropriate chemical procedures to handle radionuclide contamination problems and interferences specific to TMI-2. Several underhead plenum residue samples were received, and pyrophoric tendencies were documented using General Public Utility (GPU) video cameras. Spark tests, flame tests, and strike tests were conducted on the plenum samples and compared to the results of the same tests on zirconium dust, zirconium oxide, and steel wool. The plenum residue samples, unlike zirconium dust, showed no pyrophoric characterizations. In attendance during the tests were representatives from GPU, EG&G, NRC, and DOE. The tests were necessary prior to removing the lid of the reactor vessel.

4.5 BETA DOSIMETRY - R. I. Scherpelz

This project has been assisting in the cleanup effort at TMI Unit 2 by determining beta and gamma dose rates inside the containment building using passive dosimeters. A new multi-element beta dosimeter has been developed at PNL, and this dosimeter has been well-suited to the measurement of dose rates

on contaminated surfaces such as those found in the TMI-2 containment building. To date, 176 multi-element beta dosimeters have been used at TMI-2 in five sets of exposures. The first three sets of exposures were performed in FY 1982; the fourth and fifth were performed in FY-1983. During this project a number of improvements have been made to the design of the dosimeter and the algorithms used for dosimeter analysis.

Technical Accomplishments in FY 1983

Table 4.5 summarizes the sets of exposures that have been made at TMI-2 using the PNL multi-element beta dosimeters. The "number of dosimeters" listed in Table 4.5 represents the number of dosimeters prepared by PNL, exposed at TMI, and analyzed by PNL. In some cases one or two dosimeters were lost or became contaminated by radioactive material and could not be analyzed; the lost dosimeters were not included in the table. All dosimeters listed in Table 4.5 have been analyzed to determine beta and gamma dose rates, and the results have been communicated to EG&G personnel at TMI.

An ongoing effort of the Beta Dosimetry project has been the continual improvement of the dosimeter system. Since the first experiment, the dosimeter has been upgraded from four elements to seven elements, and for the two experiments in FY 1983, eight-element versions have been used. The algorithm for converting thermal luminescent dosimeter (TLD) readings into dose has also been improved. Two different algorithms are thus available for use for the beta dose determination, allowing necessary flexibility for analysis.

TABLE 4.5. Dosimeter Exposures at TMI-2

<u>Experiment</u>	<u>Date Exposed</u>	<u>Number of Dosimeters</u>
Pre-gross decontamination experiment	Dec. 1981	38
Post-gross decontamination experiment	Mar.-Apr. 1982	33
Pre-flushing TLD tree experiment	June 1982	16
Exposures during basement sludge sampling	Feb. 1983	11
Basement walls characterization experiment	June 1983	78

During FY 1983 a report was published documenting the dosimeter design, calibration procedures, and the first analysis algorithm. It also reported the results of the three sets of exposures performed in FY 1982. The report was published as PNL-4714 and is also due to be published as a GEND document.

The measurements performed during this project have been useful in characterizing the dose rates due to high-activity contaminants on various surfaces in the TMI-2 containment building during different phases of the reactor cleanup effort. As the cleanup effort continues, such dose rate characterizations should continue to be important for guiding and assessing the cleanup operations.

4.6 ANOMALIES IN O_2/H_2 RATIO IN RADIOLYTIC GAS PRODUCTION - E. C. Martin

During cleanup after the TMI incident, it was decided to remove the radioactive contamination from the sump water in the TMI-2 Containment Building, by the use of Linde Zeolite Resin 1E-96 and A51. It was recognized that radiolytic gases, principally O_2 and H_2 , would be produced by radiolysis of water in the liners containing the zeolite with the sorbed radioactive ions. Efforts to avoid producing explosive mixtures of hydrogen and oxygen led to the use of platinum/palladium catalyst O_2-H_2 "recombiners" to serve as oxygen and hydrogen "getters." Considerable speculation has focused on the observation that the oxygen-hydrogen ratio found in the radiolytic gases has not been stoichiometric. That is, the oxygen-hydrogen ratio has not been 1:2, as would be the case if water were broken down to its elemental constituents without the occurrence of additional reactions. The oxygen concentration has proved consistently lower than the stoichiometric value. The purpose of this study was to examine the literature to determine the reasons for this behavior.

Discussion

The potential for explosive reaction of hydrogen with oxygen is an ever-present concern among persons who deal with gaseous reactions involving those elements. When these explosive mixtures are associated with radioactive elements, the concern greatly increases.

The lower flammability limit for hydrogen in oxygen has been reported to be 4.65%; for oxygen in hydrogen the value is 6.10% (Handbook of Chemistry and Physics). A constant concern that these conditions do not occur is paramount for workers in this field.

This situation is possible whenever water or aqueous solutions are subjected to radiant energy from radioactive sources. Thus, zeolite in exchange columns on which radioactive ions have been sorbed potentially can generate the required O_2-H_2 mixture. The problem then complicates the TMI cleanup operation.

The yield of hydrogen and oxygen from the gamma irradiation of the type of material present in a TMI liner is difficult to predict since the decomposition of water depends on so many variables.

First, several factors are concerned with establishment of an equilibrium between hydrogen and hydrogen peroxide, the primary molecular products. Is the system a closed or an open one? In a closed system with no head space (excluding catalytic effects), negligible hydrogen and hydrogen peroxide will be produced. Under these conditions only traces of oxygen should form. In a system completely open to the atmosphere, the hydrogen peroxide will gradually decompose to water and oxygen, and eventually all the water will be converted to these gases. The presence of head space in the system should produce intermediate concentrations of oxygen.

Second, the presence of certain metallic catalysts may participate in the decomposition of hydrogen peroxide, thus upsetting the equilibrium process. The participation may proceed either homogeneously, by dissolved ions, or heterogeneously by interaction with undissolved compounds and with the container walls. Scratches, scale, weld splatter, etc., will all participate by providing sites for the decomposition of hydrogen peroxide. The yield of oxygen will be further dependent on the nature of the metal ions present to consume oxygen by forming insoluble oxides or hydroxides. Thus, the yield of oxygen will depend on the nature and amount of participating ions that have contaminated the system.

Under many conditions the gaseous product will be only hydrogen since the oxygen will be retained in solution as hydrogen peroxide. However, if

catalysts for decomposition of hydrogen peroxide are present in solution, the gaseous products in a closed system may tend to a stoichiometric mixture of hydrogen and oxygen. In an open system, hydrogen gas can escape and hydrogen peroxide can accumulate in solution. If this system is then closed so that hydrogen no longer escapes, and the hydrogen peroxide is decomposed by catalysis or elevated temperature, the gas phase could contain oxygen at levels in excess of stoichiometric. In any event, reaction of the gaseous products with radicals in solution will cause an equilibrium to be established.

Possible Techniques To Minimize H₂ and O₂ Resulting from Gamma Radiolysis of Water

Temperature has a significant effect on the yields of radiolytic gases from aqueous solutions. As the temperature is reduced, the quantity of water decomposed is reduced. It has been reported that G_{-H_2O} falls from 4.5 in neutral water at 20°C, to 3.4 in ice at -10°C, 1.0 at -78°C and 0.5 at -200°C (Ghormley and Stewart 1956).^(a) It is presumed that at these progressively lower temperatures the movement of the hydrogen and hydroxide radicals becomes more restricted by a cage of ice molecules. Virtually all of the radicals must combine to reform water molecules.

Pressurizing a vessel with hydrogen will reduce the release of oxygen. The following equations illustrate the reactions that reduce hydrogen peroxide and the hydroxyl radical to water:

(a) The "G" value identifies the number of molecules transformed per 100 eV absorbed.

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5.0 COMMERCIAL REPROCESSING PLANT TASK

S. C. Slate - Manager

The U.S. government has had the policy that private industry should participate in the closing of the back end of the nuclear fuel cycle by operating a commercial reprocessing plant (CRP) for spent nuclear fuel. To operate such a plant, a facility would be needed to treat liquid high-level waste (HLW) and transuranic wastes (TRU). The technology to support the design of such a facility is currently being developed and applied by the CWTP for several DOE demonstration projects.

The mission of this task was to assist in deploying this treatment technology at a commercial facility. Emphasized were the implementation aspects of particular concern to a commercial operation, especially licensing the facility, minimizing radiation exposure and costs, and producing waste forms acceptable to commercial repositories.

5.1 OBJECTIVES

Four specific objectives were identified to guide the activities supporting the program's mission. These objectives were concerned with establishing the technical base to support the future studies needed to actually deploy the technology at a CRP. The objectives were as follows:

1. To specify reference definitions of CRP waste streams and then develop an overall strategy on how to treat them.
2. To obtain commercial operator input on specific CWTP research areas.
3. To assess HLW process options and then prepare design criteria and basic facility concepts for a HLW treatment system.
4. To prepare a plan to acquire process and waste form data that can be used to support licensing of waste treatment facilities and repositories.

The activities conducted to support these objectives were performed by both PNL and Allied-General Nuclear Services (AGNS). The AGNS staff was included in this project because of their particular expertise in waste

flowsheet development, economic analyses, and facility design. Their involvement was particularly useful because of their actual commercial experience with a fuel reprocessing plant.

The activities in this project were organized into four areas that parallel the specific objectives listed above. The results and major accomplishments for each area are described in the following sections. Discussions of the future applications of the results are also included.

5.2 WASTE FLOWSHEET ANALYSIS

The primary focus of the activities in this area was on gaining accurate information on the wastes created at the CRP and on developing a strategy for treating them. The data on commercial HLW liquids and glass will be used as a reference in designing a commercial vitrification process. The results supporting the strategy will be used to set CWTP research priorities. The four major studies completed in this area last year are described below.

High-Level Liquid Waste Description - J. A. Swanson

A report titled Properties of the Reference Liquid High-Level Waste was prepared by PNL staff. It contains a compilation of the engineering properties of the liquid HLW (HLLW) and an experimental plan to obtain the necessary data that do not exist. Reference compositions of the HLLW and liquid intermediate-level waste (ILLW) were developed. The variabilities and uncertainties associated with these compositions were also identified.

The major concern regarding properties of the HLLW and ILLW streams, when being combined for vitrification, is the presence of solids. The amount of solids varies with concentration, temperature, age (time after dissolution), and actual chemical composition. The solids will primarily be zirconium molybdate, barium-strontium nitrate, cesium double salts, tellurium and other metal fines. The percentage of solids at the reference concentration of 200 gal/MTU will probably range from 1 to 4%, which should not cause significant handling or processing problems. The primary sources of experimental data were ORNL and INEL reports.

An experimental program was outlined to provide the missing data on HLLW properties. The major data needed concern the effects on HLLW properties of denitration, waste concentration, phosphate content and radiolysis. The level of effort to provide the data was estimated to be 2 to 4 man-years.

Reference High-Level Waste Glass - L. A. Chick

A major accomplishment of the project in FY 1983 was the development of a new reference HLW glass composition for a CRP. Before this fiscal year, the reference composition was a PNL glass designated 77-260. The composition and properties of that glass have been detailed by Slate, Ross, and Partain (1981). The new reference glass will be used by the CWTP in design studies and by the repositories in performance assessment studies.

The new composition was developed to reflect new information on glass formulation and changes in the HLLW composition from earlier estimates. The two compositions are shown in Table 5.1 along with some sample leaching results. The new reference, labeled 83-B-15, is a simpler composition with improved leaching performance. The new glass has a much improved devitrification performance over 77-260 and does not form an alkali molybdate phase during melting. Characterization of the glass did reveal, though, that RuO_2 crystals will settle out in quiescent molten glass. Convection in the melter, however, should minimize this settling during processing. Additional details on the performance of 83-B-15 are being developed in the CWTP.

CRP Waste Descriptions

An AGNS report (Anderson, Carr, and Mitchell 1982) was prepared at the end of FY 1982, and revised and issued in FY 1983, that presents data on the wastes and their treatment options for the Barnwell Nuclear Fuel Plant. The waste definitions include where possible: sources, flowrates, compositions, activity levels, storage capacities, and expected variations. A large number of waste streams (40 to 50) are identified from all parts of the plant. The wastes are in solid, liquid, or gaseous forms and are classed as low- and high-level general process trash, non-TRU wastes, hulls, and intermediate- and high-level wastes. Descriptions and cost estimates were also prepared for the various waste treatment options that were available.

TABLE 5.1. Reference HLW Glass Composition and Sample Leaching Results

<u>Glass Composition</u>	<u>77-260 wt%</u>	<u>83-B-15 wt%</u>
SiO ₂	36.0	48.0
B ₂ O ₃	9.0	9.0
Na ₂ O	8.0	3.5
K ₂ O	2.0	--
Li ₂ O	--	4.5
CaO	1.0	--
TiO ₂	6.0	--
Al ₂ O ₃	2.0	5.0
CuO	3.0	--
Fe ₂ O ₃	--	--
Waste	<u>33.0</u>	<u>30.0</u>
	100.00	100.00

Leaching Results^(a)
Normalized Release, g/m²

	<u>77-260</u>	<u>83-B-15</u>
Distilled water	13	4.0
Buffered pH3 solution	26	5.4

(a) 7-day; 90°C SA/V = 10 m⁻¹; Si, Na, B, Mo, La

A separate study was also completed by AGNS on determining the feasibility and incentives for recovering noble metals from the dissolver fines. The metals of interest are ruthenium, rhodium, and palladium. After a 100-yr storage, the trace levels of radioactivity in these metals would be essentially zero. At current prices the value of these metals would be near \$30 million per year at the expected production rate of the Barnwell Plant. A technique for removing these metals from the dissolver and separating them from the fines was described. The technique appears feasible but should be tested before inclusion in the plant flowsheet.

Waste Treatment Strategy

The above information on the wastes was to be used with a detailed AGNS economic study to develop a CRP waste treatment strategy. The strategy will be the most cost-effective scenario for treating and disposing of CRP wastes and will still meet safety, operational and regulatory requirements. This strategy will be very important to the CWTP in formulating plans and establishing priorities for waste form and process development activities. The actual preparation of the strategy had to be delayed to FY 1984 because of the late delivery of the AGNS cost analysis.

The AGNS-developed Waste Management Economic Model (WMEM) was used to evaluate all the costs associated with all major waste streams from their generation point to final disposal. The model considers a very large set of variables that affect costs. These variables and the model itself are described in detail by Godfrey and Cholister (1978).

The results of the study showed the primary cost centers for the reference CRP to be treatment of general process trash, hulls and HLW and the liquid waste storage facility. The major variables for each cost center were also identified: such items as interest rates, start-up dates, shipping parameters, capital costs, and treatment methods. These important variables have now been included in a simplified waste management economic model that provides for parametric cost analyses of CRP waste treatment without the complexity of using all variables. The results of the cost analyses will be coupled with the information on waste streams and on other factors such as waste form specifications to develop a waste treatment strategy in FY 1984.

5.3 HLW TREATMENT SYSTEM DESIGN

The activities in this area were concerned with the evaluation of HLW treatment options and the development of a package of detailed design criteria for a HLW solidification facility. The criteria package will provide important guidance to the CWTP because it identifies a number of data requirements that must be met before a commercial HLW facility can be built and operated.

The AGNS staff produced a very comprehensive document that contains a description of the HLW process and facility, a set of preconceptual design drawings, a facility cost estimate, and a very detailed listing of design criteria. A discussion was also included on facility licensing which was used as a basis for development of the plan to acquire licensing data. The preconceptual design was used to prepare a cost estimate of \$162 million 1983 dollars for a HLW facility. The detailed disclosure of the contents of this document is currently limited by Applied Technology controls.

5.4 TRU TECHNOLOGY ASSESSMENT

A major research area in the Technology Development Task is concerned with the development of processes to treat TRU wastes. Two of the studies under way, hulls decontamination and consolidation of metallic TRU wastes, were reviewed and supplemented by AGNS.

Economics of Hulls Decontamination

A CWTP study was made to determine the technical feasibility of decontaminating hulls to the extent that they would be non-TRU. This would potentially allow cost savings at disposal. The AGNS Waste Management Economic Model was used to determine what cost savings could be realized by evaluating the costs associated with five different hulls-handling options. The model included costs for the facility, operations, transportation, and disposal. The analysis showed that there is a very strong economic incentive (on the order of \$1 billion over the life of the plant) to decontaminate the hulls sufficiently that they can go to a nearby disposal site. The personnel dose commitment for each option should be evaluated before a final course of action can be considered.

Review of Metallic TRU Consolidation Technologies

A study of potential technologies for consolidating metallic TRU wastes was made in the Technology Development Task (Nesbitt and Montgomery 1983). AGNS reviewed the draft report for this study from an engineering and operational viewpoint to provide input to final selection of the reference consolidation process. The results of this review are included in the final version of the Nesbitt document.

5.5 LICENSING-DATA ACQUISITION - W. L. Kuhn

The objective of this activity was to prepare a plan to ensure that the necessary process and waste-form data are available to support licensing of commercial treatment facilities and repositories. The guiding philosophy for this plan was taken from 10 CFR 50, which will be the primary basis for licensing nuclear waste facilities. Specifically, provisions in 10 CFR 50 determine the data and the supporting information that must be used in preparing a PSAR and FSAR. The three major areas that must be documented are:

- technical feasibility of the solidification process
- safety of the solidification process
- acceptability of the waste form for final disposal.

The plan identifies the types and quantities of data, the subject areas, the extent of experimentation, and the necessary quality provisions for assurance. Specific documents to be produced are also described.

The plan is currently in preliminary form. Specific activities will be included later as technical projects within the CWTP begin to structure their activities around the plan. The plan will evolve over time as old issues are resolved and new ones are uncovered. External influences such as regulations or performance requirements may also change, requiring modification of the plan.

5.6 CONCLUSIONS

The Commercial Reprocessing Plant Task established a sound reference base from which to develop treatment technology for commercial operations. Studies to continue development of the key areas initiated in this program will be continued in the Technology Development Task. Future work should emphasize the completion of the waste treatment strategy and the implementation of the licensing data acquisition plan.

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6.0 BREEDER FUEL REPROCESSING PLANT WASTE TREATMENT

M. S. Hanson - Manager

6.1 OBJECTIVE

Pacific Northwest Laboratory (PNL) is providing technology for treating high-level liquid wastes (HLLW) from the Breeder Reactor Engineering Test (BRET). This test will be installed in the Fuels and Materials Examination Facility (FMEF) at Hanford to demonstrate the viability of the full fuel cycle for liquid metal fast breeder reactors (LMFBRs).

Reprocessing of the FFTF fuel will produce a HLLW stream typical of that expected from future breeder fuel reprocessing plants. The aqueous waste stream, which contains greater than 99% of the fission products from reprocessing, must be solidified and packaged in a manner which will enable its disposal in a geologic repository.

This task is to ensure the availability of waste treatment technology for use in the closure of the LMFBR fuel cycle. While the technology for treating waste from light water reactors (LWRs) has been developed and demonstrated, the difference between the LWR and the LMFBR is great enough to require research into treatment of the LMFBR waste stream. For example, because of the recycling of uranium and plutonium in the fuel cycle and the greater burnup planned for LMFBRs, the waste will be more radioactive and the concentrations of fission products and actinides higher than in LWR wastes.

6.2 ACCOMPLISHMENTS IN FY 1983

Vitrification Process - M. S. Hanson

Based on a review of state-of-the-art technology for immobilization of HLW in the U.S. and abroad, PNL studied three vitrification processes: 1) liquid-fed ceramic melting; 2) liquid-fed in-can melting; and 3) rotary kiln/metallic melting. After a thorough review of the attributes of these processes, the liquid-fed ceramic melter was selected as the reference solidification process because it:

- can operate at high temperatures
- has higher capacity than the other systems
- is undergoing development and design in other U.S. applications.

Waste Stream - M. K. W. Chan

The inclusion of BRET secondary wastes with HLLW was evaluated during FY 1983. Results of this evaluation indicate that the feed stream to the vitrification system can include high-activity waste (HAW), solvent wash waste, low-level waste (LLW) concentrator bottoms, and sodium waste from the fuel wash process. Inclusion of other wastes such as dissolver solids is being studied. Formulations for the waste glass, both with and without dissolver solids, were prepared. During this year's work, the glass formulation was improved: its leach rate is lower and its viscosity is 100 poise at 1140°C. To allow inclusion of the NaOH wash solution in the reference BRET HLLW, the sodium of the NaOH solution was submitted for sodium-based glass forming chemicals.

Preconceptual Design - J. M. Perez, Jr.

The preconceptual design of the high-level waste vitrification system has been completed. The scope of PNL's involvement included HLW preparation, glass melting, waste canister welding, and decontamination. PNL provided input to the BRET project design effort, from interim design reviews to preparation of the preconceptual design report.

A study was conducted in FY 1983 to determine which combinations of

- glass production rate
- canister diameter
- melter size
- decay heat loading
- waste loading in the glass

will satisfy constraints in design. The preconceptual design reflects equipment size and operating conditions.

Because the LFCM as currently designed is too heavy for the FMEF cranes to handle, it will be installed in two pieces: the lid and refractory box. Evaluation of design changes to circumvent the problems are under way.

The life of the melter is projected at 3 years. Methods for decommissioning the melter are being evaluated.

In designing the BRET vitrification process, the following constraints were considered:

- The joule-heated glass melter must produce at least 8 kg/hr glass (~20 L/hr slurry feed).
- The decay heat should not exceed 75% of the power requirement for the melter during idling.
- The canister should be at least 6 in. in diameter.
- The canister centerline temperature should not exceed 500°C during steady state to prevent glass devitrification.
- It must be possible to remove enough sensible and decay heat from the canister during glass pouring to avoid canister wall temperatures greater than 900°C.
- The decay heat in the canister should stay within the limits expected to be required for geologic repositories at the time of anticipated canister emplacement (about 5 to 10 years after reactor discharge).

Heat Effects - S. C. Slate

The power required for idling the melter during the part of the vitrification process when the waste is not being fed will be provided by decay heat and electric joule heating. Electric joule heating must contribute at least 25% to provide a margin for external control of the temperatures within the melter. The actual amount of heat required is dependent on refractory thickness and the size of the melter.

Removal of decay heat is one of the most significant design variables. There is a strong incentive to go to a longer fuel decay time prior to reprocessing if that is cost-effective for the complete fuel cycle. With a longer decay period, both the waste loadings and canister diameters could be increased. The reference waste age was changed from 180 days to 1 year to help alleviate heat problems such as waste loading limits and canister size limits.

The disposition of the waste canisters poses a particular problem due to the high heat loading of the waste. PNL generated data for BRET defining canister size limits, waste loadings, canister array, and shipping cask limitations. Although the waste canister will be stored in water, they will spend short periods in air during processing. Thus the canister was designed so that its centerline temperature is acceptable when at a steady state in an air environment.

Other Accomplishments

ORIGEN-II calculations were used to determine source terms, which were included in the flowsheets. Safety assessments, canister/melter shielding calculations, and analysis of helium buildup in a canister were conducted.

Input on the effects of the HLW treatment system was provided to the BRET environmental assessment.

6.3 FUTURE ACTIVITIES

A 48-hr small-scale test using simulated BRET waste is planned to observe:

- ruthenium volatility
- organic vapors in the off gas
- corrosive levels in the off gas
- 6-in.-diameter canister filling.

7.0 SPENT FUEL TASK

J. H. Jarrett - Manager

7.1 OBJECTIVE

The objective of this task is to analyze the adequacy of commercial spent fuel waste packages for possible repository disposal. This analysis will be qualitatively compared to existing adequacy analyses for defense and commercial HLW glass packages. The required spent fuel treatment technology for repository disposal will be established and the necessary NEPA documentation will be prepared.

7.2 EXECUTIVE SUMMARY

In mid-FY 1983 the Commercial Waste Treatment Program Office initiated a task at DOE's request to evaluate spent fuel as a commercial high-level waste form. Internal draft reports covering the following topics were prepared: the current status of applicable standards and regulations, comparison of the basic properties of HLW glass to those of spent fuel, survey of techniques for spent fuel repository performance assessment, available spent fuel waste package designs, and a review of spent fuel properties pertinent to repository disposal. This report summarizes these internal draft reports. These FY 1983 studies will provide a basis for a spent fuel performance report to be issued in FY 1984.

7.3 INTRODUCTION

It is increasingly likely that spent fuel from commercial power reactors will not be routinely reprocessed before the year 2000. Therefore, direct disposal of spent fuel in a deep geologic repository must be considered. This requires the evaluation of spent fuel itself as the primary waste form, and if such evaluation indicates the necessity, also requires developing technology for treatment (modifying physical and/or chemical properties) of as-discharged spent fuel prior to disposal.

In mid-FY 1983 the Commercial Waste Treatment Program Office (CWTP0) initiated the Spent Fuel Task, at DOE's request, to evaluate spent fuel as a commercial high-level waste form. The initial objective is to prepare a draft report, in FY 1984, entitled "Technical Evaluation of Spent Fuel as a Commercial High-Level Waste Form." The document will be a companion to a similar draft report evaluating borosilicate glass, which was prepared by the Technology Development Task of the CWTP0. Studies were conducted during the last half of FY 1983 to provide a technical basis for the FY 1984 work.

Five draft internal reports (summarized in Sections 7.4-7.8) were prepared covering the following topics:

1. An overview of regulations applicable to geologic disposal of spent fuel
2. A comparison of spent fuel and borosilicate glass waste form properties
3. A review of waste package designs for geologic disposal of spent fuel
4. A survey of performance assessments for spent fuel disposal analysis
5. Review of characteristics and behavior of spent fuel in repositories

7.4 REGULATIONS APPLICABLE TO SPENT FUEL DISPOSAL IN REPOSITORIES -

K. H. Rising

The government agencies authorized to regulate nuclear waste (including spent fuel) disposal include the Department of Energy (DOE), Environmental Protection Agency (EPA), Nuclear Regulatory Commission (NRC), Department of Transportation (DOT), Department of the Interior (DOI), and individual state governments.

There are five major areas of rule-making for the safe disposal of nuclear waste in repositories: 1) radiation protection standards, 2) environmental standards, 3) repository siting guidelines, 4) packaging and transportation requirements, and 5) repository disposal criteria. The regulations applicable to these areas are published in the U.S. Code of Federal Regulations (CFR). At present, most of the regulations have been established. The only two in the

proposal stage are EPA's Environmental Standards for Nuclear Waste Disposal (40 CFR 191) and DOE's Guidelines for Nuclear Waste Repository Siting (10 CFR 960) established in accordance with the requirements of the Nuclear Waste Policy Act of 1982. A summary of the pertinent regulations and their status (as of August 1983) is given in Table 7.1.

TABLE 7.1. Status of Major Regulations Applicable to Spent Fuel Disposal in Repositories

Code	Regulatory Agency	Applicability	Status
10 CFR 960	DOE	General Guidelines for Recommendations of Sites for Nuclear Waste Repositories	Proposed Rule (current draft 5/27/83)
10 CFR 20	NRC	Standards for Protection Against Radiation (at NRC Licensed Facilities)	Final
10 CFR 50	NRC	Domestic Licensing of Production and Utilization Facilities	Final
10 CFR 60	NRC	Disposal of High-Level Radioactive Wastes in Geologic Repositories, Technical Criteria	Final
10 CFR 71	NRC	Packaging of Radioactive Material for Transportation and Transportation of Radioactive Material Under Certain Conditions	Final
10 CFR 73	NRC	Physical Protection of Plants and Materials	Final
49 CFR 171-178	DOT	Hazardous Materials Regulations (for Transportation)	Final
40 CFR 190	EPA	Environmental Radiation Protection Standards for Nuclear Power Operations	Final
40 CFR 191	EPA	Environmental Standards for the Management and Disposal of Spent Nuclear Fuel, High-Level and Transuranic Radioactive Wastes	Proposed Rule (issued 12/19/82)

7.5 COMPARISON OF SPENT FUEL AND BOROSILICATE GLASS WASTE FORMS - K. H. Rising

Comparison of the properties of spent fuel and borosilicate glass waste forms indicates that there are substantial variations with regard to geologic disposal. The relevant properties under consideration are radionuclide inventory, physical properties, thermal and radiation properties and leaching behavior. A key difference in radionuclide inventory is the presence of ^{129}I and ^{14}C . These radionuclides are not present in borosilicate high-level waste forms. Geologic performance assessments indicate that these radionuclides are predominant dose contributors in spent fuel due to their low sorption and high solubility.

In general, the elemental release from spent fuel is higher than that from borosilicate waste glass. Spent fuel and waste glass exhibit different leaching behaviors, and their leach rates are affected by different factors. For example, the leach rate of waste glass is exponentially related to temperature over a wide range of temperatures, while the leach rate of spent fuel shows a much smaller temperature dependence between 25 and 150°C.

Apparently, long-term leaching from HLW glass is determined by the buildup of silica dissolution products in the boundary layer. Long-term leaching from spent fuel is controlled by the creation of uranyl gel layer, depleted in nuclides, and the dissolution of the UO_2 matrix, freeing other isotopes to diffuse through the gel to the free ground water. In both cases, corrosion of the primary matrix likely determines the actual long-term release behavior of the few soluble radionuclides (^{135}Cs , ^{129}I , ^{14}C , ^{99}Tc). Solubilities and transfer rates across the boundary layer will determine the release of most radionuclides.

7.6 REVIEW OF WASTE PACKAGE DESIGNS - K. H. Rising

The review of the current spent fuel package designs considers designs for various repositories, including salt, tuff, basalt, and granite. The review describes existing design concepts, compares the various components of each spent fuel package with the corresponding glass package design, and examines the different design concepts in terms of their system performances and costs.

The findings in this review indicated that there are two basic approaches to spent fuel package design: 1) the borehole package concept and 2) the self-shielded package concept. The choice of suitable package design for a specific repository would depend on the properties of the repository environment, the availability of resources, the package performance requirements, and a balance of the above features against economics.

7.7 SURVEY OF PERFORMANCE ASSESSMENT TECHNIQUES ANALYSIS FOR SPENT FUEL DISPOSAL - P. J. Mitchell

Eight recent performance assessment documents were surveyed; the scope of the effort prohibited an in-depth review. The variation in computational techniques, assumptions and measures of performance do not permit a rigorous comparison of results. The purpose is for the project to become familiar with the performance assessment literature. The transport analyses were done with one-dimensional, saturated ground-water models and generally assumed congruent radionuclide source terms. One analysis used estimated solubility-limited dissolution rates and, therefore, distinguished release rates between elements. The analyses also relied upon simple radionuclide retardation coefficients to estimate the more complex attenuation factors in the geologic system.

Several documents summarizing computer models relevant to geologic disposal in repositories were also surveyed. The U.S. Nuclear Regulatory Commission (NRC) is sponsoring an evaluation of codes used in repository performance assessment. A result of that effort is a report by Thomas et al. (1982) which summarizes repository siting models of saturated flow, unsaturated flow, surface-water flow, geochemistry, solute and/or heat transport, and geomechanics. Thirty-one codes are summarized to show how they might be applied. Mills and Vogt (1983) summarize radiological transport dose models for analyzing radionuclide source terms, radiation shielding, the concentration of radionuclides in the environment, resulting dose-to-man, and expected mortality rate. The NRC is planning to benchmark the codes after identifying and selecting appropriate data sets.

The Office of Nuclear Waste Isolation (ONWI) has compiled descriptions of waste isolation computer models (ONWI 1981) in categories of nuclide inventory and activity, transport, geochemistry, heat transport, mechanical stress, seismicity, geosphere biosphere transport, dose-to-man, risk assessment, etc. A more recent compilation of geosphere transport codes is included in ONWI's draft, Verification and Validation Plan (VVP) for Performance Assessment Technology for a Nuclear Waste Repository in Salt (ONWI 1983, p. iv).

The far-field transport codes identified for use in the spent fuel disposal evaluation are BAIRN, ALLDOS, PABLM and EXPOSE.

BAIRN is a group of four programs that simulates ground-water transport of radionuclides from the repository through the biosphere. This is part of the Simplified Codes for Performance Evaluation (SCOPE) under development at PNL (Petrie et al. 1983, p. 1.1). BAIRN uses analytical solutions to the equation for one-dimensional solute transport for up to a three-member decay chain.

The solute transport equation is that used in the UCBNE10.2 code developed at the University of California, Berkeley (Harada et al. 1980). The code provides two analytical solutions originating from the application of two different boundary conditions at the nuclide source: the volumetric source-term and the concentration boundary condition without a source-term. SCOPE also contains codes that use BAIRN results for further analysis:

- Program EXPOSE uses a given set of criteria to estimate the potential hazard to man from the transport of radionuclides from radioactive material to the biosphere. EXPOSE sums the curies passing through the boundary of an aquifer over time. These results are compared to given criteria.
- Programs ALLDOS and PABLM calculate internal radiation dose-to-man from radionuclides in food products and external radiation doses from radionuclides in the environment. Both programs use the results of BAIRN as well as input from the user for these calculations. The results from ALLDOS and PABLM are similar; they differ mostly in operational details.

7.8 CHARACTERISTICS AND BEHAVIOR OF SPENT FUEL IN REPOSITORIES -

R. J. Guenther and J. O. Barner

The review of spent fuel as a waste form in a repository environment (Guenther and Barner 1983) has compared the known and expected characteristics of spent fuel as it is discharged from reactor pools, dry interim storage, and/or monitored retrievable storage (MRS) to determine expected behavior of spent fuel after emplacement in a repository. Some characteristics of spent fuel are common regardless of the method of previous storage, while others may depend on storage methods. The repository environment affects the behavior of spent fuel in a repository most greatly through the thermal history to which the fuel is exposed.

Spent fuel, as it exists today, consists of a variety of fuel rod designs and burnups for both pressurized and boiling water reactors. Fission-gas pressures may reach as high as 6.6 MPa in some PWR rods, depending on their power history. The radioactive nuclide inventory and cladding characteristics will depend on the power history and water chemistry, respectively. In general, pool storage of the SF and its transport to repositories are not expected to degrade the fuel rods.

Stress rupture and fuel oxidation are the principal degradation concerns for SF in dry interim storage and MRS facilities. Previous analyses indicated that stress rupture in Zircaloy cladding should be prevented in dry storage if temperatures are held below about 400°C. Results using a cumulative damage method for calculating damage to the cladding indicate that temperature limits may be 300°C for ten-year-old fuel to prevent stress rupture for 100 years in dry storage. The 300°C temperature limit is near the 275°C peak temperature calculated for a basalt repository. In addition, the limits for dry storage assume a decreasing temperature history for dry storage, whereas the temperature in a repository will increase initially, then decrease more slowly than for dry storage. This could worsen cladding damage during the early stage in a repository environment.

There are very few defective fuel rods that result from effects of power operations, transport, or handling. However, a few defected or incipiently-defected fuel rods will probably reach a repository. Most of the cladding is

expected to eventually fail during the long disposal period. Oxidation of the fuel in these defected fuel rods can occur in a dry environment at sufficient temperatures, causing fuel swelling and additional degradation to the cladding. Fuel oxidation in dry storage is of importance because of its effect on retrievability. Fuel oxidation in a canister emplaced in a repository will be of importance when the canister fails because U_3O_8 is expected to leach more easily than unoxidized spent fuel.

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8.0 ACRONYMS

AGNS	Allied General Nuclear Services
AVH	French Rotary Calciner/Metallic Melter (at La Hague)
AVM	French Rotary Kiln Calciner/Continuous Melter (at Marcoule)
BNFP	Barnwell Nuclear Fuel Plant
BRET	Breeder Reprocessing Engineering Test
BWIP	Basalt Waste Isolation Project
CRP(P)	Commercial Reprocessing Plant (Program)
CTS	Component Test Stand
CWTP	Commercial Waste Treatment Program
DF	Decontamination Factor
DOE	Department of Energy
EPA	Environmental Protection Agency
GPU	General Public Utility
HEME	High-Efficiency Mist Eliminator
HLLW	High-Level Liquid Waste
HLW	High-Level Waste
ILLW	Intermediate-Level Liquid Waste
LFCM	Liquid-Fed Ceramic Melter
LLWTF	Low-Level Waste Treatment Facility
LWR	Light-Water Reactor
MCC	Materials Characterization Center
MTE	Metric Ton Equivalent
NRC	Nuclear Regulatory Commission
NWVP	Nuclear Waste Vitrification Project
PNL	Pacific Northwest Laboratory
RLFCM	Radioactive Liquid-Fed Ceramic Melter
SBS	Submerged Bed Scrubber
SDS	Submerged Demineralizer System
SF	Spent Fuel
SFCM	Slurry-Fed Ceramic Melter
TMI	Three Mile Island
TRU	Transuranic

WMEM	Waste Management Economic Model
WVNS	West Valley Nuclear Services
WVSP	West Valley Support Program
ZVD	Zeolite Vitrification Demonstration

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