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Nuclear Waste Treatment Program Annual Report for FY 1986

**Compiled by
H. C. Burkholder and R. A. Brouns**

September 1987

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

**Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
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NUCLEAR WASTE TREATMENT PROGRAM
ANNUAL REPORT FOR FY 1986

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Pacific Northwest Laboratory
Richland, Washington 99352

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EXECUTIVE SUMMARY

Two of the U.S. Department of Energy's (DOE) nuclear waste management-related goals are: 1) to ensure that waste management is not an obstacle to the further deployment of light-water reactors (LWR) and the closure of the nuclear fuel cycle and 2) to fulfill its institutional responsibility for providing safe storage and disposal of existing and future nuclear wastes. As part of its approach to achieving these goals, the Office of Remedial Action and Waste Technology of DOE established what is now called the Nuclear Waste Treatment Program (NWTP) at the Pacific Northwest Laboratory (PNL) during the second half of FY 1982. To support DOE's attainment of its goals, the NWTP is to provide 1) technology necessary for the design and operation of nuclear waste treatment facilities by commercial enterprises as part of a licensed waste management system and 2) problem-specific treatment approaches, waste form and treatment process adaptations, equipment designs, and trouble-shooting assistance, as required to treat existing wastes. This annual report describes progress during FY 1986 toward meeting these two objectives. The detailed presentation is organized according to the task structure of the program, but this Executive Summary is organized by program element.

In addition to this series of annual reports, progress in liquid-fed ceramic melter vitrification technology is reported quarterly (starting with the first quarter of fiscal year 1985).

FIRST-GENERATION HIGH-LEVEL WASTE TREATMENT

In the feed preparation area, topical reports on bench-scale mixing studies and feed-metering pump design (recommending selection of the air-displacement pump) were published. These data and results provided the basis for design of the large-scale prototype feed preparation system that was fabricated and installed.

The pilot-scale ceramic melter (nonradioactive) was rebuilt, and a topical report was prepared describing that work as well as design changes made to more closely resemble the pilot-scale radioactive melter. A laboratory-scale mini-melter was constructed and tested; it appears to be a useful tool for

predicting the performance of melter feeds in larger scale melters. Two engineering-scale melter experiments were performed as part of a study to determine scale-up factors for ceramic melters, and a report summarizing the status of this study was prepared.

An automatic temperature control algorithm was developed for liquid-fed ceramic melters and was successfully demonstrated. Tests were completed on the pilot-scale off-gas submerged bed scrubber, and two reports were written which describe the SBS design correlations and performance optimization studies. Significant design improvements were made to the in-melter infra-red viewing system.

A liquid-fed ceramic melter process model was developed that uses process control parameters to control and predict product quality, and a report was prepared describing this process control methodology. A report on a correlation developed between canister thermal history and degree of glass cracking was written, and improvements were made to the TEMPEST code, which is used to predict canister thermal history.

A reference commercial high-level waste (HLW) composition for future reprocessing operations was defined and documented. A report on the effect of feed composition and operating parameters on cesium losses from the melter was written.

SECOND-GENERATION HIGH-LEVEL WASTE TREATMENT

Tests were conducted on additional high-temperature glass compositions expected to provide improved chemical durability. A report comparing Synroc-C (for commercial waste) and PNL 76-68 glass was issued which concludes that Synroc-C performs approximately an order of magnitude better than the reference borosilicate glass for the test conditions employed.

TRANSURANIC WASTE TREATMENT

An evaluation of alternative treatment methods was documented for secondary wastes from spent fuel consolidation. Results of long-term leach testing of metal melted product from non-fuel-bearing hardware showed the metal

product to have good leach resistance. Low-speed shredders for volume reduction of high-efficiency particulate air (HEPA) filters were shown to be effective. Over 40 new HEPA filter designs were prepared and evaluated from a viewpoint of waste management. The problem of cementing incinerator ash containing aluminum metal (primarily from HEPA filters) was confirmed.

WEST VALLEY SUPPORT

Documentation of the design of the West Valley melter and support systems was completed. The design of an evaporator/concentrator to process mixtures of high-level waste and glass formers was provided. A hydraulic study was performed to determine the optimum pipe size for gravity flow in the component test stand waste header and transfer line. A mass balance simulation model is under development for the West Valley vitrification plant to predict the composition of, and the confidence limits for, nuclear waste glasses. A glass pour sampling plan was proposed to provide data for fitting to the model.

Cesium-loaded zeolite was tested for its storage stability prior to incorporation into the melter feed. Studies were conducted on resuspension, mixing, and removal of high-level wastes from tanks prior to vitrification. The valence state of trace plutonium in the supernatant phase was determined. Destruction of phosphate in the supernatant and sludge phases was also determined. The chemistry was developed to remove the crystalline formations in the THOREX waste storage tank.

HANFORD WASTE VITRIFICATION PLANT SUPPORT

The pilot-scale ceramic melter rebuild task and portions of the radioactive testing program were cooperative efforts with the HWVP program since the results are useful to both programs.

FEDERAL REPUBLIC OF GERMANY REPOSITORY TESTING SUPPORT

Production of the first ten FRG canisters was initiated. These are isotopic heat sources containing ^{90}Sr and ^{137}Cs isotopes in borosilicate glass. Feed preparation was conducted using sequential blending, denitration, and volume-reduction steps. During feeding of the melter, entrainment and

volatility losses were found to be much greater than anticipated based on past nonradioactive testing. An off-gas reamer was designed and tested to prevent off-gas plugging problems. The air-displacement slurry pump used for melter feeding performed excellently.

JAPAN TOKAI PILOT PLANT SUPPORT

The conceptual design of an off-gas submerged bed scrubber for the Japanese Tokai Mockup Facility was prepared under the DOE/PNC^(a) cooperative exchange agreement.

LOW-LEVEL WASTE COORDINATION

A comprehensive report was issued documenting all work performed to date under the Engineered Sorbent Barriers Program. Work included laboratory studies to determine materials effective for sorbing ^{137}Cs , ^{60}Co , and ^{90}Sr as well as engineering-scale column studies of barrier formulations. The most effective barrier tested comprised 20 wt% A-51 zeolite, 6 wt% activate charcoal, 1 wt% greensand, and 73 wt% local soil.

Performance of nuclear power reactor waste forms with matrices consisting of cement, Dow polymer, and bitumen were studied in a field-scale lysimeter facility that simulated an arid shallow-land burial site. A topical report summarizing laboratory and field studies was issued. Five of the ten lysimeters (those containing BWR waste forms) have shown breakthrough of ^{60}Co due to complexation with organic chelating agents. Laboratory experiments were conducted that predicted the ^{60}Co breakthrough experienced in the field-scale facility.

(a) Power Reactor and Nuclear Fuel Development Corporation.

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1.0 TECHNOLOGY DEVELOPMENT

W. A. Ross - Manager

1.1 OBJECTIVES

The original objectives of this task for FY 1986 were to: 1) define the documentation necessary for potential users of nuclear waste treatment technology to design and operate full-scale waste treatment facilities with both efficiency and confidence, 2) establish specifications and requirements for high-level waste (HLW) and transuranic waste (TRUW) waste forms, 3) develop technology for treatment of commercial TRUW, 4) monitor the needs for the treatment of spent fuel, and 5) develop and monitor alternative technology for the treatment of HLW.

During the first quarter it was determined that the task work should be closed out in an orderly manner. Therefore the work was limited to completion of existing activities and contracts. The activities in the task were grouped into the following subtasks: Strategy, Performance, and Product Requirements; TRU Waste Treatment; Second Generation HLW Technology; and Technology Documentation.

1.2 SUMMARY

In the Strategy, Performance, and Product Requirements subtask, an evaluation of alternative treatment methods for secondary wastes from the consolidation of spent fuel was reported and is summarized in Section 1.3.

In the TRU Waste Treatment subtask, the potential for using the coreless induction melting furnace for treating non-fuel-bearing hardware was evaluated along with that for treating a wide variety of wastes in a single process (Section 1.4). Longer-term leach testing of a metal melted product was conducted, and the melted product was shown to be leach-resistant (Section 1.5). Further testing of low-speed shredders for treating high-efficiency particulate air (HEPA) filters was evaluated (Section 1.6) and shown generally effective. Testing also confirmed the potential problem of cementing incineration ash with

residual aluminum metal (Section 1.7). Over 40 new designs for HEPA filters were prepared, and an evaluation was begun on their potential advantages (Section 1.8).

As part of the Second Generation HLW Technology, additional high-temperature glass compositions were tested; the best was evaluated (Section 1.9); and a comparison of Synroc-C and 76-68 glass was completed and reported on (Section 1.10).

Documentation of the design of the West Valley Melter and support systems was completed and is reported as part of the Technology Documentation subtask (Section 1.11).

1.3 EVALUATION OF ALTERNATIVE TREATMENTS FOR SPENT FUEL ROD CONSOLIDATION WASTES AND OTHER MISCELLANEOUS COMMERCIAL TRANSURANIC WASTES - W. A. Ross, K. J. Schneider, K. H. Oma, R. I. Smith, and L. R. Bunnell

This evaluation compares eight major alternatives and four subalternatives for treatment of commercial transuranic waste (TRUW) and high-activity waste (HAW) based on their product characteristics, process characteristics, and total system economics. The study recommended further consideration of the supercompaction, arc pyrolysis and melting, and maximum volume reduction (MVR) alternatives and also recommended testing and demonstration of the last two alternatives. The detailed study has been published (Ross et al. 1986).

The wastes studied include all commercial TRUWs that have been and are expected to be generated. The major wastes may originate from a central treatment facility for spent fuel rod consolidation, either a Monitored Retrievable Storage (MRS) facility (if approved by Congress) or a similar facility at a future selected repository. The conceptual MRS facility design was used as the reference to define information about waste generation. An estimated 1,300 m³/yr of untreated wastes are to be generated from spent fuel rod consolidation activities. All other TRUW from non-spent fuel rod consolidation activities at other commercial sites can be processed at a rate of 500 m³/yr. The MRS facility wastes are mostly the spent fuel hardware and contaminated high-efficiency particulate air (HEPA) filters from the central treatment facility. Cemented wastes are expected to be the largest volume of non-MRS civilian

wastes. The HEPA filters are a challenging treatment problem as they contain mixed organic, metallic, and ceramic materials. Additional types of waste include failed equipment, ion-exchange resins, solutions and sludges, mixed combustibles, and filters.

Each alternative provides a treatment method for each of the various wastes. Most alternatives would produce several different waste forms and use several processes. These alternatives cover a wide spectrum of choices both in process complexity and in waste-form quality. Most were not optimized before their selection and evaluation, and thus serve only as general guidance for decision-making. However, maximum volume reduction (MVR) subalternatives (4A, 4B, 4C, and 4D in Table 1.1) were subsequently evaluated to optimize Alternative 4 and provide better direction to demonstration activities for these technologies.

Although the disposal method for these wastes has not been selected, it has generally been assumed that they would go to a combined defense/commercial repository. This assumption was used in this study to evaluate costs and potential requirements. It is understood that the MRS facility and geologic repository are currently being evaluated by the DOE as potential nuclear waste treatment and long-term waste storage and disposal facilities.

Because the waste-form characteristics required for disposal have not been established, no minimum requirements were used to eliminate any treatment alternative. The major concerns about waste-form quality relate to the following potential requirements:

- low release rate to meet the Nuclear Regulatory Commission limit of less than 1 part in 100,000/yr released from engineered barriers
- no organics or combustible materials
- immobilized particulates
- no pyrophoric potential
- structural stability
- radiation resistance.

TABLE 1.1. Final Waste Volumes and Total Life-Cycle Costs for Management of TRUW and HAW from 70,000 MTU^(a)

Alternatives		Final Waste Volume, m ³	Treatment Costs: Capital, Operating, & Decommis- sioning, \$M	Transportation Costs: Capital & Operating, \$M	Disposal Costs, \$M	Totals, \$M	Comparison with MRS Reference, \$M
1.	No Treatment	2,900	210	971	2,055	3,236	+1,460
2.	MRS Reference	1,090	123	326	1,327	1,776	--
3.	Supercompaction	385	84	116	743	943	-833
4.	MVR with Decontamination	181	172	84	531	787	-989
4A.	MVR with Decontamination and Melting	267	128	113	622	863	-913
1.4 4B.	MVR with Melting Only	294	121	104	631	856	-920
4C.	MVR with Decontamination and Cementing	338	123	129	731	983	-793
4D.	MVR with Cementing Only	378	113	119	736	968	-808
5.	Cementation	1,345	145	387	1,437	1,969	+193
6.	Arc Pyrolysis and Melting	212	151	89	562	802	-947
7.	Sulfur-Bonded Graphite	400	142	122	732	996	-780
8.	Highest-Quality Waste Form	250	210	108	619	937	-839

(a) Values are shown in more significant figures than accuracy of the data warrants in order to maintain consistency of the calculations.

Using a numerical ranking method and the above potential requirements, the various waste products were ranked. The processes in each alternative were also ranked numerically by combining the value for each process for both the contact-handled and the remote-handled wastes based on their processing characteristics of operational safety, processing simplicity, and status of technology. Based on waste composition and expected product characteristics, the volumes of treated waste were calculated for each alternative. These volumes can significantly affect the costs of transportation and repository disposal which are shown in Table 1.1.

Treatment costs include those for equipment, facility, certification, canisters, emplacement of waste in canisters, 4-month interim storage capability for the treated wastes, and decommissioning. Transportation costs are based on shipping the wastes 2,000 miles by train. Disposal costs are based on disposal of the wastes in a postulated basalt repository in heavy overpacks with the spent fuel. All costs are based on 70,000 MTU of spent fuel.

The disposal costs dominate the total system costs, followed by transportation costs, and then treatment costs. Savings in transportation costs (assuming MRS) alone justify more extensive treatment of the wastes to reduce the volume. Treatment costs account for only 7 to 22% of the total system cost, depending on the alternatives considered. Furthermore, there were additional potential large savings when comparing the more extensive treatment alternatives to the MRS facility alternative. These savings appear to justify a significant effort to develop, demonstrate, and implement volume reduction technology for these wastes.

Based on this evaluation, supercompaction, MVR, and arc pyrolysis and melting are the best alternatives. Supercompaction is a developed technology commercially available; however, its products would not meet some of the potential disposal requirements already noted. The arc pyrolysis and melting process is untested, but designs have been prepared for treatment of capacitors containing polychlorinated biphenyls (PCBs) and for treatment of municipal garbage. It is an attractive alternative, but considerable testing and demonstration would be required for TRUW treatment needs. The MVR alternative had the lowest potential cost but requires numerous processes, many of which have

been used previously for nuclear waste treatment. The evaluation of MVR sub-alternatives (4A, 4B, 4C, and 4D) indicates that an optimized strategy would not treat the previously cemented wastes, nor would it decontaminate the non-activated metals. Both of these process simplifications would come at the expense of slightly higher total costs.

1.4 TREATMENT OF SECONDARY WASTES FROM SPENT FUEL ROD CONSOLIDATION -

K. H. Oma, W. A. Ross, C. E. Bigelow, D. R. Montgomery, and W. C. Morgan

Projections are that large volumes of waste in the future will be generated during commercial activities involving consolidation of spent fuel assemblies. About 98% of the secondary waste volume from spent fuel consolidation is projected to be non-fuel-bearing hardware (NFBH) and contaminated HEPA filters. The NFBH is all metallic, is highly radioactive with activation products, and requires remote handling. The HEPA filters, however, are typically a composite of organic binders and sealants, fiberglass media, and wood or metal frames. Contaminated during hot-cell operation, most filters will require remote handling.

Experimental work at PNL from previous years has shown that melting in a graphite crucible with induction heating has the potential for consolidating the metal wastes (Westsik et al. 1986). Melting tests this year investigated corrosion of crucible material as it relates to the expected variation in waste compositions.

Evaluation of alternative treatment methods for the TRU and high-activity wastes has shown that a single process which can treat NFBH, HEPA filters, and other composite wastes is very attractive, and development of such a process is warranted from the viewpoint of both waste-form quality and system economics (Ross et al. 1986). The remainder of this section contains results of the induction melter crucible corrosion tests and a preliminary evaluation of alternative treatment methods.

1.4.1 Crucible Corrosion Tests

The anticipated compositions of materials which may be fed to the metal melting furnace were investigated by reviewing non-fuel-bearing hardware from

the various fuel assembly manufacturers (Luksic et al. 1986). Table 1.2 lists the anticipated waste compositions for five different manufacturers. The compositional ranges are 19 to 50% Zircaloy, 33 to 79% stainless steel, and 1 to 27% Inconel. BWR fuel channels are made primarily of Zircaloy; melting could drive the Zircaloy concentration as high as 83%. If wastes other than NFBH are melted (such as failed equipment), the stainless steel composition could go as high as 100%. These compositional variations were used to determine the experimental region of interest on a three-phase diagram of Zircaloy, stainless steel, and Inconel.

A series of ten experiments was conducted using a statistical mixture design in an effort to determine the applicability of graphite crucibles for the different waste compositions. For each test, a graphite coupon was attached to the side of the crucible with its bottom extended to near the bottom of the crucible. The different metal compositions were then melted using a pilot-scale vacuum coreless induction furnace. Compositional ranges and the metal alloys used for the tests were 0 to 85% Zircaloy-4, 15 to 100% 304 stainless steel, and 0 to 30% Inconel-722. Once melted, the metal was

TABLE 1.2. Compositions of Anticipated Non-Fuel-Bearing Hardware, wt%

<u>Fuel Assembly Manufacture</u>	<u>Zircaloy</u>	<u>Stainless</u>	<u>Inconel</u>
Babcock & Wilcox (a)	23-27	40-45	24-27
Westinghouse (a)	23-39	33-60	4-17
Combustion Engineering (a)	45-50	37-46	6-14
Exxon (a)	36-48	52-63	1
General Electric (b)	19-27	58-79	3-10
Exxon (b)	20	76	3
Compositional variance	19-50	33-79	1-27

(a) Pressurized water reactor (PWR)

(b) Boiling water reactor (BWR)

poured through an inductively heated bottom drain into a canister. The average and the maximum corrosion rates of the graphite coupons were measured after each heat.

Figure 1.1 shows the test compositions on a three-component mixture diagram. Below each composition are the average and the maximum corrosion rates for the graphite coupons. Data for the lower left-hand corner of the diagram (100% stainless steel) was from a test in which incinerator residue was melted. The incinerator residue actually contained only 54% stainless steel; that is probably why the corrosion rate is lower than for the other alloys near 100% stainless steel.

FIGURE 1.1. Compositions and Graphite Corrosion Rates for Three-Phase Mixture Experiments

Attempts have been made to correlate the corrosion data with zirconium concentration, stainless steel concentration, Inconel concentration, metal melting point, melt pouring temperature, and melt alloy temperature. The alloy temperature is that at which the metal is all melted and the crucible thermocouples indicate a uniform bottom-to-top temperature distribution.

The major correlations found were due to the zirconium and stainless steel concentrations. Figure 1.2 shows a plot of graphite corrosion rate versus the zirconium concentration. Graphite corrosion rates are essentially zero for metal compositions containing greater than 40% zirconium. Corrosion rates are less than 3 mm/hr for greater than 25% zirconium.

FIGURE 1.2. Graphite Corrosion Rate as a Function of Zirconium Concentration

The increased graphite corrosion rates at lower concentrations of zirconium are due primarily to increased stainless steel; however, the addition of Inconel has a slight additive effect on the corrosion rate. If the stainless steel component is minimized, the corrosion rate can be controlled to a low level. Pure iron can dissolve up to 4.5 wt% carbon, and if chromium, manganese, or certain other elements are present, even higher amounts of carbon can be dissolved. Type 304 stainless steel contains up to 20 wt% chromium, up to 2 wt% manganese, and only 0.08 wt% carbon. Thus, the stainless steel has a large capacity to dissolve additional carbon.

These corrosion-test results suggest that three possible options exist for operations: 1) maintain at least a 40% zirconium composition during melting, 2) use a water-cooled crucible, and 3) identify other crucible materials that perform well in the compositional region of interest. The first option requires that zirconium be added to certain melts (refer to Table 1.2), which raises the cost of "volume reduction." The second option, while standard technology, requires the use of a coolant fluid in the cell, which is undesirable. For these reasons, the third option has been pursued first.

Additional corrosion tests were conducted using refractory samples of a magnesite ramming mix, several magnesite/graphite composites, zirconia, and alumina all in a graphite crucible. All the test refractories are suitable for different types of steel production; however, their resistance to molten zirconium is not well known. The melt composition used was 60 wt% zirconium, 35 wt% stainless steel, and 5 wt% Inconel. The magnesite ramming mix was the only material that was not severely attacked by the melt during the test.

Further tests are needed to determine whether the magnesite ramming mix can be used for all compositions of interest. Use of a water-cooled crucible should also be evaluated further.

1.4.2 Alternative Treatment Methods

Arc furnaces and/or other associated technologies can potentially treat non-fuel-bearing hardware, HEPA filters, and all other expected waste types in one process unit with little or no pretreatment. This greatly simplifies the process and at the same time produces a durable waste form (Ross et al. 1986).

Arc melting units are used in the steel industry to melt specific metals. Direct current arc pyrolysis has been identified as a possible method to treat municipal garbage as well as large capacitors containing polychlorinated biphenyls (Wittle et al. 1984). The furnace is heated by an electric arc passing between a hollow graphite electrode and a molten pool of metal and slag. The organics and combustibles are pyrolyzed in the furnace and then exit through the arc and up the center of the electrode. The residual materials are melted and periodically tapped from the furnace. The waste form produced is a mixture of cast metal and ceramic.

Because other high-temperature concepts may be as effective as the direct current (DC) electric arc for the waste application, two independent surveys of potential concepts were made. One survey was performed by Retech, Inc., of Ukiah, California, and the second by the Mineral Resources Research Center at the University of Minnesota. Both organizations conducted literature searches and reviewed manufacturers' literature to identify possible heating methods. Heating methods identified include alternate current (AC) electric arc, DC electric arc (one and two electrodes), thermal plasma (transferred and nontransferred), coreless induction, cored induction, microwave plasma, electron beam, laser, combustion heater, and electrical resistance heater. A preliminary evaluation of these heating methods has led to selection of the following four most promising concepts for further consideration:

- transferred thermal plasma and nontransferred thermal plasma hybrid (using water-cooled electrodes)
- DC electric arc (using one graphite electrode)
- DC electric arc (using one graphite electrode) and nontransferred thermal plasma hybrid
- coreless induction and nontransferred thermal plasma hybrid.

1.5 CHARACTERIZATION OF METAL MELTING PRODUCT - J. H. Westsik, Jr., and K. M. Olson

Specimens cut from an ingot of Zircaloy-4 (82%) and 316 stainless steel (18%) have been exposed to deionized water, silicate water, and brine at 90°C

for 27 and 182 days in accordance with the MCC-1P leach test procedure. Preparation of the ingot was described earlier (Burkholder and Jarrett 1986). The results of the test are shown in Table 1.3. When the 27- and 182-day test results are compared, the leaching tests in deionized water show increased iron in the leachates and the presence of manganese and nickel. Very little leaching occurred in the silicate water leachates. The brine leachates showed the most leaching, and significantly increased leaching between 27 and 182 days.

After 182 days, the leachates of one deionized water replicate and all three brine replicates had turned orange; the orange color of the brine leachates was first noticed at about 4 months of testing. When the brine test containers were opened after the 182-day test, particles were floating in the leachate. This coloration is due probably to Fe_2O_3 released via corrosion of iron in the Zircaloy/stainless steel alloy.

The normalized elemental releases for the Zircaloy-stainless steel alloy in deionized water and silicate water leachates are generally about two orders of magnitude lower than are the releases from the reference ARM-1^(a) glass. The magnitudes of the normalized releases from the alloy in brine are comparable to those for the glass in brine.

TABLE 1.3. Results of MCC-1P Leach Test on Zircaloy/Stainless Steel Waste Form

	<u>Deionized Water</u>		<u>Silicate Water</u>		<u>Brine</u>	
	<u>27 days</u>	<u>182 days</u>	<u>27 days</u>	<u>182 days</u>	<u>27 days</u>	<u>182 days</u>
pH Change	+0.3	+0.08	+1.9	+1.1	+1.7	+1.8
Normalized elemental mass loss, g/m^2						
Fe	0.02	0.044	ND	0.005	1.8	8.1
Mn	ND ^(a)	0.4	0.35	ND	ND	8
Ni	ND	0.78	ND	ND	2.3	17
Zr	ND	ND	ND	ND	0.33	2.3

(a) Not detected.

(a) ARM: approved reference material.

1.6 SHREDDER DEVELOPMENT - K. H. Oma, W. A. Ross, and R. P. Allen

Several development needs were identified for low-speed shredders during a previous study of shredder and incinerator technology for treating commercially generated TRU wastes (Oma et al. 1985). In that study, shredding was evaluated as a waste pretreatment step for the incineration process. The development needs identified concern three difficulties experienced in shredding HEPA filters. First, wood-framed HEPA filters were not easily gripped by the cutter hooks; they tended to ride on the cutter wheels and spacers without being shredded. Second, metal-framed HEPA filters were difficult to shred, causing the shredders to reach a high-torque limit (set by the motor current) and initiating an automatic reversal cycle. Lastly, loaded HEPA filters released particulates during shredding, which is undesirable in hot-cell operation.

These development needs were addressed by testing selected low-speed shredders at Shredding Systems, Inc., of Wilsonville, Oregon. The objectives of the shredder tests were as follows:

1. Test a ram device for feeding wood-framed HEPA filters.
2. Test a shredder capable of processing metal-framed HEPA filters by causing the shredder to jog-reverse. This is intended to prevent undue wear and tear on the equipment associated with high-torque limit-induced reversals.
3. Test fixatives to reduce dust released during shredding of loaded HEPA filters.

A 60-hp Model 1450-E shredder, manufactured for use at a nuclear power plant, was employed in the tests. The unit had a 1+1+1 (one cutter, one spacer, and one cutter) configuration. Cutter wheels had one hook on the fast shaft and two hooks on the slow shaft. Each cutter tooth was offset from the adjacent tooth in what is termed a "single-spiral" alignment. The tooth offset is such that it takes the full length of the cutter shaft to make one revolution in the cutter tooth positions. The rated hook force was 90,000 N on the fast shaft. The shredder was equipped also with an electromechanical ram to aid in the feeding of materials that are difficult to grip. The wastes expected

for this unit include plastics, paper, wood, and other general wastes loaded in 55-gal drums, and some wood-framed HEPA filters.

Three metal-framed and 17 wood-framed HEPA filters were shredded during the testing. Twelve of the wood-framed filters were shredded as part of an effort to evaluate fixatives for dust control. The metal-framed HEPA filters were processed first. It was intended to prevent high-torque reversals by manually jog-reversing the shredder after a predetermined time delay; however, the shredder experienced high-torque reversals before it could be manually reversed. The shredder experienced six such reversals with the first HEPA. The next two HEPAs were processed using manual reversing or high-torque shut-off and reversal (whichever occurred first). Although nine reversals occurred during shredding, these filters were eventually processed. The excessive number of reversals could be reduced by using a shredder with a higher tooth force rating and/or by using a coarser cutter configuration such as a 2+2+2.

A ram feeder was used to force-feed the wood-framed HEPA filters into the cutter chamber. The first filter was easily fed with one ram stroke and no cutter reversals. During processing of the second wood-framed HEPA, the ram force exceeded the rating of the shaft, causing the shaft to bend. Subsequent HEPA filters were shredded without use of the ram. After these filter tests, the ram was repaired and the rated force was reduced from 43,000 to 22,000 N to prevent future shaft damage.

Three different fixatives were applied to dust-coated HEPA filters. Details of the three fixatives tested are given in Table 1.4, but their compositions are all proprietary. All filters tested had plywood frames and aluminum separators. Particulate loading measurements were taken directly above and directly below the cutter wheels using sample pumps and particulate filters.

Table 1.5 shows the average particulate loading during shredding of both new (no loading) and used (loaded) HEPA filters. Airborne particulate in this use is reduced by about 48% with the Clear Coat, 88% with Coherex, and 82% with MicroFoam compared with the untreated loaded filters. Both the Coherex and the MicroFoam reduce the dust loading to the level observed for the new (no loading) filters.

TABLE 1.4. Fixatives Used During HEPA Filter Shredding Tests

Trade Name	Manufacturer	Application Method	Composition
Clear Coat	Oakite Products Berkeley Heights, NJ	Pretreatment by airless sprayer - no dilution	Proprietary - alkylene water soluble resins and inhibitors (PVA)
Cohrex	Witco Corp. Oildale, CA	Pretreatment by airless sprayer - diluted 10:1 with water	Proprietary - hydrocarbon in water emulsion
MicroFoam	DeTer Co., Inc. Burgin, KY	In situ treatment while shredding - generated by a foam metering unit and applied by spraying	Proprietary - DeTer #1010 MicroBond Surfactant

TABLE 1.5. Performance of HEPA Filter Dust Fixatives

Dust Fixative	Filter Loading	Average Particulate, mg/m ³		Reduction in Airborne Particulate, %
		Above Cutters	Below Cutters	
None	None	25.0	16.5	--
None	Loaded	No data	123	--
Clear Coat	Loaded	117	64.5	48
Cohrex	Loaded	19.5	15.0	88
MicroFoam	Loaded	19.3	22.7	82

In summary, the ram feeder permitted fast shredding of wood-framed HEPA filters without manual repositioning. Also, fixatives applied either before or during shredding can reduce airborne particulate by 80 to 90%. Other important observations were made from the shredding test data:

- The shredder hopper should be wider than the HEPA for effective shredding.
- A ram force of 22,000 N is sufficient for effectively feeding wood-framed HEPA filters through the shredder.

- Force by the ram can cause overfeeding of the shredder, resulting in unwanted reversals. To remedy this, the ram cycle could be interlocked with the shredder motor current such that the ram retracts when the current reaches a predetermined value.
- Despite the high tooth force, metal-framed HEPA filters still caused high-torque reversals of the shredder. Higher tooth forces will alleviate this condition. Also, the use of a coarser cutter pattern such as a 2+2+2 single-hook configuration will help eliminate the high-torque condition.

1.7 CEMENTING INCINERATOR ASH CONTAINING ALUMINUM METAL - R. O. Lokken

The ash resulting from incineration of shredded trash that contained HEPA filters has substantial amounts of residual aluminum metal foil and flakes. (Aluminum metal foil is used as separators in the HEPA filters.) The residual aluminum interferes with later cementing processes because aluminum metal reacts with calcium hydroxide released during cement hydration to form hydrogen gas. Resulting gas bubbles can create pressures that deform the cement-based paste and result in swelling, cracking, and increased porosity. The hydrogen released after setting of the concrete also creates a safety concern. The objectives of this study were to assess the magnitude of these reactions and to develop methods of reducing or eliminating the detrimental reactions.

The reference cement-based product was composed of 50% Type I/II Portland cement, 20 wt% water, 15 wt% sand, and 15 wt% incinerator ash. Also a small quantity of plasticizer was added to decrease the viscosity of the paste. After a few hours, reactions occurred that formed gas bubbles, causing the paste to expand and ultimately increase volume by about 20%.

Gas Generation Rates

Four mixes were prepared to determine gas pressure as a function of time. Their compositions are shown in Table 1.6. About 40 mL of freshly mixed paste was placed in a pressure vessel equipped with a pressure transducer. Figure 1.3 shows the curves for pressure versus time. The curve for the reference mix is characterized by two near-linear regions from 0 to 6 hr and from 6 to

TABLE 1.6. Composition of Cement-Based Pastes Used in Pressure-Generation Tests

Component	Amount, g			
	Mix 1 (Reference)	Mix 2	Mix 3	Mix 4
Type I/II Portland cement	1000	1000	1000	--
Type III Portland cement	--	--	--	1000
Incinerator ash	300	300	300	300
Alumina sand	300	300	300	300
Water	400	422	400	404
CaCl ₂	--	--	27	27
Al(NO ₃) ₃	--	75	--	--

FIGURE 1.3. Pressure Generation with Time for Four Cement-Based Mixes Containing Incinerator Ash

36 hr, and then a gradual decrease in slope from 48 hr and beyond. The pressure increased to 30 psi over the first 3 days, then remained relatively constant.

The use of $\text{Al}(\text{NO}_3)_3$ to delay the hydroxide-aluminum reaction and to hasten setting resulted in lower pressures during the first 24 hr, but after 4 days the pressure continually increased and was the highest of the modified samples. The substitution of Type III Portland cement for Type I-II (Mix 4 versus Mix 3) resulted in significantly lower pressures, particularly during the first 3 days. The total pressure generated with the reference sample was considerably greater than with the latter three, showing the effectiveness of the set accelerators in reducing gas generation and pressurization.

Reactions in the latter three mixes produced hydrogen and methane gas and depleted the oxygen. The hydrogen composition ranged from 15.8 vol% for Mix 4 to 39.8 vol% for Mix 2. The methane varied from 8.3 to 9.2 vol%.

1.8 HEPA FILTER DESIGNS FOR IMPROVED WASTE MANAGEMENT - K. H. Oma and W. A. Ross

The need to treat and dispose of used HEPA filters was highlighted in two recent waste treatment studies performed by PNL. The first study considered treatment of wastes from spent fuel reprocessing, and the second considered the wastes from spent fuel rod consolidation (Ross et al. 1985 and 1986). In both studies, HEPA filters were identified as a major waste stream by volume. The review of volume reduction for filters revealed that some treatments are not feasible because of present construction methods and materials used in making the filters. This study identified and evaluated methods to reduce waste generation and to facilitate volume reduction and packaging of used HEPA filters. The following specific concerns were identified:

- Most HEPA filters are composites of metallic, ceramic, and organic materials. Metal frames are difficult to process because of their high strength and bulky dimensions. Aluminum, used as separators in many HEPA filters, causes undesirable gas generation if the filters are cemented. Organic materials, present as gaskets, sealants,

binders, and frames, may prevent the waste from being certified for disposal with other high-level wastes.

- The rectangular shape of the filters makes for inefficient packaging within standard cylindrical containers (55- and 80-gal drums).
- Separation of the media from the frames to permit specialized treatments such as decontamination of frames is very difficult because of the organic glues used to bind the media to the frames.

These concerns prompted the selection of the Mine Safety Appliances Company of Evans City, Pennsylvania, to develop filter designs that will reduce waste generation and make waste treatment and packaging easier. Over 40 new filter designs were identified and were grouped according to the following features:

- HEPA frame designs that permit easy remote disassembly for disposal in a standard 55-gal drum.
- HEPA frame/media interface designs and methods that permit easy remote removal of the media for special treatment.
- HEPA designs that permit easy decontamination of the frame for disposal as low-level waste, even if the media itself is highly radioactive.
- Metal-framed HEPA filter designs that contain no organics.
- Wood-framed HEPA filter designs that contain no metals, only media and organics, and would be suitable for treatment by incineration.
- Other frame materials that lend themselves to easy decontamination, incineration, or recycle.
- High-flow HEPA filter designs that have an extended service life.

The technical merit of each filter concept has been determined by applying weights to several performance criteria for each filter. The performance criteria included: durability under rough handling, resistance to heated air, spot flame, moisture and overpressurization, and acid gases and other chemicals, flow capacity and rated pressure drop, plus filtration efficiency, and compatibility with standard filter housing designs.

Preliminary evaluation of the results indicates that performance and cost improvements are possible. The magnitude of these depend on the overall strategy selected for treatment.

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

Statistically designed studies of glass formulations, such as Chick et al. (1984), indicate clearly that an increase in processing temperature is associated with better chemical durability. It is reasonable to expect that, for glasses of the general borosilicate type, increasing processing temperature to 1400°C should result in an order-of-magnitude performance increase. During FY 1985, considerable experimentation was done on glass compositions (Burkholder and Jarrett 1986). Three approaches--an analog study, an empirical mixture study, and a substitution study--were all used so as to accomplish the most in the least time.

Work has continued on the empirical mixture study, which had produced encouraging initial results. The original study included six compositions chosen to contain different amounts of alkali, Al_2O_3 and B_2O_3 . The composition space was expanded in the direction indicated by the most encouraging initial results, and some intermediate compositions were added. Formulation, melting and leach testing continued, and the best final composition, EMS-11, released boron 45 times slower (MCC-3, deionized water, 90°C) than did PNL 76-68 glass and 10 to 12 times slower than did SRL-165 glass. Boron is chosen as a nonsolubility-limited indicator of general matrix dissolution. Figure 1.4 shows boron release contours produced by modeling the experimental results. Obviously, EMS-11 is the highest performer. Compositions even lower in alkali would probably perform even better, but would not have a sufficiently low viscosity (100 poise) for processing.

Although further work on high-temperature glasses has been terminated, the soundness of the basic thinking has been demonstrated, and the approach offers some clear directions should higher-performance glasses be needed.

FIGURE 1.4. Boron Release Contours for Empirical Mixture Study Composition Space

1.10 EVALUATION OF SYNROC-C - J. W. Shade

This study evaluated the leaching performance of an Australian-prepared Synroc-C-C (for commercial waste) by comparison with a well-documented borosilicate glass, PNL 76-68, using several test methods. The details of the study are contained in the report Evaluation of SYNROC-C as a Second-Generation Waste Form (PNL-5915). The leach tests were selected to focus on measurements, such as saturation values and initial leach rates, that can be applied to repository transport models as well as be used to compare waste forms.

The 76-68 glass used in this work contained 33 wt% PW-8a waste calcine and 4.16 wt% UO_2 , while the Synroc-C contained 10 wt% PW-4b calcine and 0.49 wt%

UO₂. Uranium was the only radioactive species in these tests. Two test procedures were used: a modified MCC-1 procedure using monolithic test specimens and the MCC-3 procedure using specimens crushed to -40/+80 mesh (-420/+177 μ m) to obtain an unreacted high surface area. The tests were conducted at 90°C and 150°C in silicate water (0.002M NaHCO₃, 0.001M SiO₂) with a pH of 8.67 and brine (0.65M KCl, 1.54M NaCl, 1.22M MgCl₂) with a pH of 4.43. The monolith tests were terminated at 28 days, but the MCC-3 powder tests were continued for up to 90 days. All leachate samples were filtered through 0.5- μ m filters, and samples from powder tests were also filtered through 1.8-nm filters to determine possible colloidal species. In addition to these tests, the temperature dependence on the initial leach rate was estimated between 90°C and 250°C in low surface area-to-volume (SA/V) tests conducted for 1 day.

The performance of Synroc-C relative to 76-68 glass in silicate water can be considered in terms of the release of barium, molybdenum, cesium, and uranium. In monolith tests for up to 28 days, barium concentrations found in solution from Synroc-C were less than 1 ppm at 90°C and increased by about a factor of three at 150°C. Barium is present in glass only as an impurity, and dissolution rates are consequently less than in Synroc-C. The concentrations of molybdenum, cesium, and uranium in these monolith tests were normalized to the amount present in the waste-form material. Normalized molybdenum released from Synroc-C (2.0 g/m²) was about an order of magnitude lower than from glass at 90°C. At 150°C, however, normalized molybdenum was more than an order of magnitude higher in glass systems than in Synroc-C, which indicated little temperature effect. Normalized cesium also showed very little temperature effect for Synroc-C, with values of about 0.3 g/m²; but cesium concentrations from glass systems were 20 g/m² at 90°C and 80 g/m² at 150°C. At 90°C, normalized uranium concentrations were about 5.0 g/m² from glass monoliths but were about 0.1 g/m² for Synroc-C. At 150°C, limited data suggest that normalized uranium concentrations for Synroc-C may approach those for glass.

Results from the powder leach tests are reported in terms of concentrations, not normalized. Uranium concentrations reached a maximum at 28 days and decreased to less than 10 ppb for both Synroc-C and glass at 90 days, suggesting that a similar uranium-bearing reaction product may be forming for

both materials. Comparisons of 0.5- μ m and 1.8-nm filtrates indicated that part of the uranium from glass may form colloids and that barium from Synroc-C also tends to form small particles. Concentrations of barium in silicate water at 90°C were near 5 ppm in 0.5- μ m filtrates but were about 1 ppm in 1.8-nm filtrates. Cesium concentrations approached a steady state of about 10 ppm in glass systems but were about an order of magnitude lower in Synroc-C systems, suggesting that two different cesium phases are controlling dissolution. The molybdenum concentration reached a steady-state value of 10 ppm in Synroc-C powder tests at 90 days, but molybdenum release from glass was about a factor of five higher and did not exhibit steady-state behavior.

The temperature dependence for the initial release rate of molybdenum and cesium was estimated for both waste forms between 90°C and 250°C by conducting 1-day dissolution tests at low SA/V ratios. In glass systems, initial release rates were one to three orders of magnitude higher than in Synroc-C. Activation energies determined from cesium release rates from glass were the same as those from molybdenum and had a value of 8.7 kcal/mol, ignoring some slight curvature in the data. Activation energies determined from cesium release rates from Synroc-C were 3.2 kcal/mol while those based on molybdenum release were about 1.3 kcal/mol, suggesting that cesium and molybdenum are associated with separate phases in Synroc-C.

In conclusion, Synroc-C appears to be a better waste form than a 76-68-type borosilicate glass by about an order of magnitude, based on general leach test performance. The concentrations of some radionuclides that typically form low-solubility reaction products, such as uranium, may be controlled more by the type of reaction product formed than by release from waste forms.

1.11 WEST VALLEY DESIGN DOCUMENTATION - C. A. Knox

The report Design and Operating Features of the High-Level Waste Vitri-fication System for the West Valley Demonstration Project (Siemens et al. 1986) was prepared and issued in FY 1986. This multi-author report describes the equipment designed in support of the high-level waste vitrification program at West Valley, New York. The liquid-fed, joule-heated ceramic melter system is the reference vitrification process for immobilization of high-level liquid

waste in the U.S. and several other countries. This system has been under development for over 10 years at PNL and other national laboratories operated for the Department of Energy. PNL contributed to this research through the Nuclear Waste Treatment Program and used applicable data to design and test melters and the related systems.

For this project, PNL worked closely with West Valley Nuclear Services Company to design a liquid-fed ceramic melter, a liquid waste preparation and feed tank, a feed pump, an off-gas treatment scrubber, and an enclosed turntable for positioning the waste canisters. This report details the final design of these components. In addition, the rationale for the design features is presented and the different alternatives that were considered are discussed. Thus the report documents the design process from inception to final product.

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2.0 TECHNOLOGY TESTING

R. A. Brouns - Manager

2.1 OBJECTIVES

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

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

Major FY 1986 objectives include the following:

1. Construct and install a large-scale prototype feed preparation system in order to establish correlations between feed mixing and sampling parameters and the feed homogeneity.
2. Establish a relationship between melter performance and scale through evaluation of laboratory, engineering, and pilot-scale melter test data.
3. Complete the development of a remote melter viewing system and documentation of a melter control algorithm to ensure safe, efficient operation.

4. Complete off-gas particulate removal tests under generic conditions for the submerged bed scrubber in order to develop the empirical performance models needed to design and operate such a device.
5. Prepare a preliminary waste-form qualification model using available correlations and data to illustrate the proposed approach based on process modeling and control.
6. Define a glass-cracking correlation that relates canister thermal history to the quality of the glass fill and a thermal model that relates canister filling parameters to thermal history of the glass.
7. Establish a relationship between laboratory- and large-scale melting phenomena so that laboratory tests can be used to develop acceptable melting waste glasses and to support radioactive operations.

2.2 SUMMARY

Major progress was made in FY 1986 toward meeting the task objectives. Summarized below are the highlights of this work. Sections that follow give details of specific activities.

- A topical report on the bench-scale feed mixing studies was published, which established the basis for selection and design of the large-scale system.
- A topical report on feed-metering pump design and testing was published. The air-displacement pump was shown to be more flexible and reliable than the air-lift pump for the range of feeds encountered.
- The large-scale prototype feed preparation system was fabricated and installed.
- The pilot-scale nonradioactive melter was rebuilt to be even more similar to the pilot-scale radioactive melter for future performance correlation development. A report was prepared describing the condition of the melter after 5 years of operation and the design changes made as a result of this inspection.

- An automatic LFCM temperature control algorithm was successfully developed and demonstrated.
- Two engineering-scale melter experiments were completed, which provided additional data for establishing melter scale-up correlations.
- The conceptual design of a submerged bed scrubber (SBS) for the Japanese Tokai Mockup Facility was prepared under the DOE/PNC cooperative agreement.
- Pilot-scale submerged bed scrubber performance tests were completed, providing data for SBS design correlations and performance optimization. Two topical reports were prepared, and a presentation was made at a national conference.
- A correlation between canister thermal history and degree of glass cracking was developed and documented.
- International technology on fuel reprocessing was reviewed and a reference commercial HLW composition defined. This composition was a best estimate of the most likely wastes resulting from future reprocessing operation and provides a basis for LFCM process testing with high fission-product-containing wastes that are typical of commercial reactor fuel reprocessing operations.
- Studies on the resuspension of melter feed solids that settle in pipes during transfer equipment failures were completed. Settling rates and pumping requirements to resuspend the solids were defined for a West Valley-type slurry.
- The in-melter IR viewing system was redesigned based on improvements that evolved from operation of the first camera.
- A paper was prepared concerning the relationship between melter cesium losses and both the feed composition and the operating parameters.
- An LFCM process model was developed for a hypothetical vitrification system using available data and correlations to illustrate the use of

process control parameters to control and predict product quality. The model helped to identify needed data and correlations for focusing follow-on work.

- Further improvements were made in the predictive capability of the TEMPEST code, which is used to predict canister thermal history, and were documented.
- A report was prepared on applying statistical process control methodology for LFCM process and product quality control.
- A laboratory-scale mini-melter was developed and tested with several feeds that had been previously processed through larger research melters in order to establish a correlation. Promising results were obtained, suggesting the mini-melter may be a useful tool in waste glass development with real waste and in trouble-shooting problems during actual production.

2.3 INTRODUCTION

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

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

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

2.4 FEED PREPARATION AND TRANSFER SYSTEMS - M. E. Peterson and R. K. Nakaoka

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

During FY 1986, specific activities concerning feed preparation and transfer systems included:

- Documentation of mixing studies and feed pump evaluations that were conducted during FY 1985.
- Installation and functional testing of a large-scale mixing tank complete with agitator.
- Evaluation of the resuspension of simulated melter feed slurries in pipes.
- Evaluation of the heat transfer equipment required to concentrate the HLLW in the feed makeup tanks.

2.4.1 Documentation of Feed Makeup and Transfer Systems Development Activities in FY 1985

The transfer of information among the various HLW treatment programs, including nonradioactive and radioactive testing, requires that the work conducted and results obtained by each program be well documented. Two topical reports were published to document the FY 1985 Feed Preparation and Transfer Systems activity. The topical report Design of a Mixing System for Simulated High-Level Nuclear Waste Melter Feed Slurries (PNL-5745) documents the results of bench-scale experiments used to assess the effects of a number of independent variables on the degree of homogeneity in the mixing tank. These results were scaled up and used in the design of the large-scale mixing tank. The topical report Evaluation and Testing of Metering Pumps for High-Level Nuclear Waste Slurries (PNL-5851) documents the results of an evaluation of commercially available metering pumps and the results of testing two candidate pumps: the air-displacement slurry pump and the air-lift pump.

2.4.2 Installation of a Large-Scale Mixing Tank

During FY 1985, bench-scale mixing experiments were conducted (Peterson, McCarthy and Muhlstein 1986). One goal of the experiments was to select a reference prototype mixing system for large-scale verification tests. After the reference system was selected, the fabrication drawings were prepared for a large-scale mixing tank that incorporates the geometric features necessary to properly mix simulated melter feed slurries.

Fabrication and installation of this tank have been completed. The tank is 9 ft in diameter and 11 ft high. The maximum liquid level is 9 ft, or 4300 gal of liquid. The total height of the mixing tank was set at 11 ft to allow for 2 ft of freeboard above the maximum liquid level. The tank has a flat bottom and is equipped with four equally spaced wall baffles. The agitator has a 10-hp motor with a 0- to 84-rpm variable-speed drive. Different slurries will need different power levels to maintain homogeneity, necessitating the use of a variable-speed drive. The agitator contains two impellers: a flat-blade turbine is located 6 in. off the tank bottom, and a pitch-blade turbine is located 4.5 ft from the tank bottom. This tank, shown in Figure 2.1, will be used as the melter feed makeup tank for the pilot-scale ceramic melter

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FIGURE 2.1. Large-Scale Mixing System

(PSCM) experiments. Researchers will verify the ability to achieve and maintain slurry homogeneity with this tank configuration and agitator.

2.4.3 Evaluation of Resuspension of Simulated Melter Feed Slurries in Pipes

Experience with melter feeds at PNL has shown that these slurries tend to settle and form deposits that are difficult to resuspend. This settling of solids may occur in transfer lines and processing equipment. The ability to resuspend settled solids is important to the vitrification process and to product quality. As a starting point for understanding the resuspension phenomenon, an experimental study was conducted by PNL and the Department of Chemical Engineering at the University of Idaho. The scope of these studies was to evaluate resuspension of a West Valley melter feed slurry (WV-205 composition) in horizontal pipes. The process equipment must be designed to deliver a slurry at the required velocity and pressure to resuspend settled solids.

The specific objectives of this evaluation were to 1) determine the pressure drop and velocity required to resuspend settled solids; 2) evaluate the rheological behavior of a slurry using a rotary viscometer, capillary tube viscometer, and data obtained during pipe-loop experiments; 3) identify the pressure drop and velocity relationship for transporting fully suspended slurry through the pipe loop; and 4) compare the experimental results with theoretical and empirical models identified in the literature.

To evaluate the pressure drop and critical velocity, data was needed on the physical and rheological characteristics of the slurry. The WV-205 slurry used in this study contained metal nitrates, ground silica, and ground ion-exchange resin. Standard laboratory procedures were used to characterize the slurry. The slurry had a density of 1.3 g/mL and contained 36 wt% total solids with 25 wt% suspended solids. The solids had a median volume diameter of 5-9 microns. The slurry had a slow settling rate of 0.0012 cm/min at 24°C. The slurry exhibited primarily homogeneous slurry properties due to the small particle size and the slow settling rate.

The rheological evaluations determined that the slurry could be classified as a yield-pseudoplastic, or in some cases as a Bingham plastic fluid. The data on shear stress versus shear rate were analyzed using both a linear regression and a nonlinear curve fit method. The parameters used in the rheological model varied depending on the method used. The nonlinear curve fit produced parameters that statistics indicated were more correct. The yield stress of the slurry was 1.59 Pa, the consistency index was 0.00116 Pa s, and the flow behavior index was 0.883. The physical and rheological data were used in evaluating the results of the pipe-loop experiments.

Comparison of rheological data from the rotary viscometer, capillary viscometer, and pipe loop is continuing into FY 1987. The evaluation of these data identified the need to apply correction factors to the rotary viscometer data. These correction factors do not exist in the literature and must be mathematically developed. The mathematical relationships for the correction factors will be determined in FY 1987 and applied to these data.

The pipe-flow test loop shown in Figure 2.2 was used to evaluate the resuspension phenomenon. The test loop was 24 ft long and comprised three different pipe diameters: 1/4 in., 3/8 in., and 1/2 in. Three diameters were used to permit scale-up of the data and to allow prediction of the critical

FIGURE 2.2. Schematic of the Pipe-Flow Test Loop

velocity for other pipe diameters. First, experiments were conducted to measure the pressure drop for fully suspended WV-205 slurry at varying velocities. Then slurry was allowed to settle in the test sections for 20 and 44 hr. The depth of the sludge layer was measured. Fully suspended slurry was then pumped through the test section across the sediment bed at a set flow rate. The differential pressure across the test section was measured as a function of time. The sludge layer represents a restriction of the normal flow area, and hence a greater differential pressure drop will be measured for a given flow rate. The flow rates were increased from the laminar flow regime to the turbulent flow regime. The flow rate at which the differential pressure decreased with time is the necessary flow rate or velocity to resuspend the sediment bed. When the differential pressure decreases to the already known steady-state fully suspended slurry pressure drop, the sediment bed is fully resuspended. The pressure drop versus time is shown in Figure 2.3 for the 1/2-in.-diameter pipe test section at a flow rate of 40.0 mL/s and after a settling time of 44 hr.

FIGURE 2.3. Pressure Drop Versus Time Using a 1/2-in.-Dia Test Section at a Flow Rate of 40 mL/s and After a Settling Time of 44 hr

The laminar-to-turbulent transition point for the transport of fully suspended slurry ranged from Reynolds numbers of 2700 for the 1/2-in.-dia pipe to 3600 for the 1/4-in.-dia pipe. The transition Reynolds numbers and the laminar data when plotted as the friction factor versus Reynolds number agreed with predictions using Hanks' model (Hanks 1984). The turbulent data did not agree with the predictions from Hanks' model. Evaluations are continuing to correct Hanks' model to obtain better predictions.

The resuspension of the settled solids of WV-205 slurry occurred at flow rates of 10 to 30 mL/s, which corresponded to Reynolds numbers in the theoretical laminar region. This was an unexpected result. The WV-205 slurry contained small particles that created a homogeneous slurry. The lift and drag forces on these particles can easily overcome the gravity forces, enabling resuspension at low flow rates and in the laminar region. Therefore, a conservative approach would be to design the pumping system to transport the slurry at flow rates above the laminar and transition regions. This approach would permit the resuspension of a sediment bed.

2.4.4 Evaluation of the Heat-Transfer Equipment Required To Concentrate the HLLW in the Feed Preparation Tanks

The HLLW slurries are typically stored as dilute solutions (<10 wt% solids) to reduce the heat loading caused by radioactive components. To reduce the costs of vitrification, the first step in preparing melter feed is to concentrate the waste fraction. A bench-scale evaluation of simulated HLW heat-transfer properties in an agitated vessel was begun in FY 1986.

The objective of this evaluation is to conduct bench-scale experiments to establish the heat-transfer properties and time cycles for a simulated West Valley waste. The experiments will be performed at various impeller speeds and solids concentrations to evaluate their effects on heat-transfer efficiency, using both an internal steam coil and an external heating jacket. Experimental results will be used to generate empirical correlations that relate fluid properties and mixing conditions to heat-transfer efficiency. These correlations will then be coupled with desired scale-up criteria (such as equal heat transfer per unit heat-transfer area or equal heat transfer per unit fluid volume) to predict operating conditions for full-scale application.

The specific objectives are 1) to establish the reliability of the bench-scale test equipment, including the agitation, steam condensate collection, and data acquisition systems; 2) to determine the effects of impeller speed on heat-transfer efficiency for both Newtonian and non-Newtonian fluids; 3) to establish a relationship between fluid rheological properties and heat-transfer characteristics; 4) to identify empirical correlations between fluid properties, mixing parameters, and heat-transfer characteristics for the Newtonian fluid and the bench-scale test equipment; 5) to develop an expression for bulk fluid viscosity as a function of impeller speed and fluid properties; 6) to identify an empirical correlation for non-Newtonian HLW heat transfer in an agitated vessel; and 7) to predict the operating conditions needed in a full-scale mixing tank from results of bench-scale testing.

During FY 1986, the heating experiments were initiated using the steam coils. Testing with the heating jacket will begin in FY 1987. The bench-scale test equipment with the steam coils worked well; data analysis is under way. The results of this study will be reported in FY 1987.

2.4.5 Conclusions

Conclusions of the Feed Preparation and Transfer Systems activity follow.

- The air-displacement slurry pump is preferred over the air-lift pump for metering the mixture of HLW and glass-formers to the ceramic melter because of its superior operation in both acidic and alkaline slurries and its minimal flushing requirement.
- The large-scale mixing tank that has been fabricated and installed incorporates the geometric features necessary to properly mix simulated melter feed slurries and will be used for the pilot-scale ceramic melter experiments.
- The slurry used in evaluating the resuspension of a simulated melter feed slurry was a non-Newtonian fluid classified as a yield-pseudoplastic, or in some cases a Bingham plastic fluid. The parameters in the rheological models were determined from a rotary

viscometer, a capillary viscometer, and the pipe-loop experiments. After correction factors are developed, comparison of the data will be completed.

- Resuspension of the settled slurry occurred at flow rates of 10 to 30 mL/s, which corresponds to the laminar flow regime. This was an unexpected result. Further evaluation, however, indicated that the lift and drag forces on the particles easily overcome the gravity forces to permit resuspension in the laminar region.
- Testing completed in FY 1986 to evaluate the heat transfer to concentrate HLLW has successfully demonstrated the use of steam coils with the bench-scale test equipment.

2.5 MELTER DESIGN AND OPERATION - S. S. Koegler, J. H. Westsik, Jr., B. B. Brenden, and S. J. Mitchell

2.5.1 Pilot-Scale Ceramic Melter Rebuild

The pilot scale ceramic melter is one of several prototype waste vitrification systems developed and tested by PNL. The PSCM is a joule-heated glass melter that is directly fed a slurry of glass formers and simulated HLW. In 1985 the PSCM was dismantled and inspected. The melter tank walls, electrodes, and lid refractory had been damaged from corrosion caused by 5 years' exposure to molten glass and fumes at high temperature. The electrodes were replaced with electrodes of a similar design, improving the electrical bus connection. The melter tank refractories were replaced, and the melter lid was changed extensively to bring the melter up to state-of-the-art design and to correct marginal refractory support. The melter support structure was modified to correct marginal structural strength. No major changes were made to the off-gas system.

2.5.1.1 Melter Inspection

The PSCM operated from April 1978 through September 1985 with one major rebuild and rebricking in 1979 to 1980. Since 1980, there have been several

shutdowns during which the lid, electrodes, or other components were modified. Appendix A gives a brief chronology of the PSCM experiments and shutdowns from 1978 to 1985.

The melter was drained and inspected in September 1985. A layer of sludge and glass 1 or 2 in. thick remained on the floor of the melter after the glass had drained. The melter walls, lid and electrodes had corroded considerably, and the pour trough also required replacement.

Although the general condition of the electrodes, faces and feet appeared good, large vertical cracks had formed in the electrodes and significant corrosion was evident on the back sides of both electrodes (next to the wall) near the glass operating level. Also material accumulated behind the electrodes, possibly corrosion oxides, had pushed the electrodes away from the tank walls, causing failure of much of the bus weld connections at the top of the electrodes. Sand blasting removed the corrosion products and exposed the severe corrosion that had occurred to the electrodes. (Figure 2.4 shows the back side of the south electrode after sandblasting.) The most severe corrosion can be seen at the bus connections and on the rear of the electrodes at the glass interface level, about at the electrode midpoints.

The K-3® brick on the melter walls showed some corrosion consistent with the 5-year operating life of the melter refractory. Melter wall measurements indicated that the most severe corrosion of the brick occurred 10 to 12 in. above the melter floor, near the operating liquid level. About 1/2 in. of K-3 brick had corroded away near the north-south midpoint of both melter side walls. These measurements showed also that corrosion was more pronounced at the center of the tank than on the ends near the electrodes. Inspection of the melter confirmed also that a portion of the lid refractory material above the overflow section had fallen into the melter tank. Its failure was attributed to lack of structural support for this section of refractory. This problem was addressed by the use of ceramic hangers in the new lid design.

Width measurements indicated that the riser block was subject to the same erosion/corrosion as the rest of the east and west walls. The riser block also

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FIGURE 2.4. Back of PSCM South Electrode After Sandblasting

exhibited a 1/2-in. concave band about 4 in. below the glass level and about 6 in. high. The throat entrance had widened from an original 2.0 in. to 2.5 in. in 1982 and to 2.9 in. in 1985. In addition, the pour trough was removed to replace the corroded pour tip. Although the main K-3 portion of the pour trough was in good condition, the entire trough was removed to replace the pour tip.

2.5.1.2 Melter Rebuild

Although changes to the PSCM design were necessary to replace damaged components, the changes were oriented to correlate closely with the current melter design. Functional changes made to bring the PSCM design closer to the Hanford Waste Vitrification Plant (HWVP) and the B-cell RLFCM designs were as follows:

1. wall and floor insulation increase - This change allows the PSCM to better simulate the well-insulated HWVP melter and the RLFCM. Thermowells were installed behind the K-3 brick to monitor heat transfer.
2. lid height decrease - The plenum heaters were removed, and the lid was lowered to better match with the RLFCM and HWVP plenum heights. This will give more prototypic plenum and off-gas conditions in the PSCM.
3. dam and discharge trough - The Inconel-690 trough and dam are similar to the HWVP and RLFCM designs. The slope of the discharge trough was increased from 5° to 20° to match the HWVP and RLFCM designs.

Figure 2.5 is an east-west cross section of the melter tank looking north. The sketch shows the brick layout, overflow trough and riser block, and the north electrode. The major differences between this design and the previous one are that Zirmul® brick has been used to raise the floor 4 in. and an additional 1/2 in. of Duraboard® was added to the melter walls. In the melter floor, only the K-3® brick was replaced. A 4-in. layer of Zirmul brick was added on top of the existing Zirmul, and K-3 brick was installed on top of that. In the melter cavity walls, an additional 1/2-inch layer of Duraboard was added and the single layers of Zirmul, Alfrax-66®, and K-3 brick were replaced. No changes were made to the melter tank shell.

The overflow riser block was replaced because of corrosion. The design of the discharge throat is very similar to the previous riser block throat. The vertical riser hole was moved 1 in. closer to the melt cavity to slightly increase the temperature of the overflow glass, and the block was keyed to mate with the dam and overflow trough. The overflow trough was fabricated entirely

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FIGURE 2.5. Sketch of Melter Cross Section

from Inconel-690 instead of K-3 brick. The Inconel-690 trough/dam assembly (Figure 2.6) is expected to be more reliable than the previous design.

The electrode design (Figure 2.7) is similar to the previous design, but uses 2.5-in. Inconel-690 plate instead of 2 in. plate with a 5-in.-wide electrode foot. The 2.5 x 5-in. foot will give the same foot-to-face current density as the present 2 x 6 in. RLFCM electrodes. The new electrodes are

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FIGURE 2.6. Inconel-690 Trough/Dam Assembly

about 6 in. taller in the center to allow the power bus bar to be connected directly to the electrode instead of welded to an attaching plate as in the previous design. The electrode cables and thermocouples were also replaced.

The melter lid was modified to cover both the melter cavity and the overflow section. The one-piece lid design eliminates the need for a lid support flange that extended from north to south above the overflow section. Feed and off-gas ports were relocated on the new lid, and the height of the plenum space was decreased. The height of the plenum above the melt surface is now about 2 ft, similar to the RLFCM design. A large section in the center of the lid is removable to allow for better tank access and sampling, and the lid refractories are now supported by ceramic anchors. The anchors are attached to the lid shell by Inconel-690 clips. This modification will provide better support

FIGURE 2.7. Sketch of New Electrode Design

and corrosion resistance than did the Inconel hangers used in previous lids. Figure 2.8 shows the underside of the melter lid with the ceramic anchors and Duraboard in place before the castable refractories were poured.

No major changes were made to the off-gas system although the off-gas nozzle and the emergency-vent nozzles were changed from 4 in. to 6 in. for increased flexibility. It was necessary to modify the emergency-vent line and the jumper between the melter lid and the venturi scrubber because of the changes to the lid. The venturi scrubber and other off-gas equipment were not modified.

The melter support structure was modified by mounting the melter carriage on I-beams attached directly to the floor under the melter. This change was

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FIGURE 2.8. New Melter Lid

necessary to correct the marginal structural strength of the existing carriage assembly and accommodate the additional weight of the melter modifications. The change was a simple, low-cost means to correct this safety problem and also raised the melter high enough to permit the filling of full-size (10-ft-tall) canisters.

2.5.2 Instrumentation Development

2.5.2.1 Temperature Control Algorithm

Control of electrical power to the electrodes of liquid-fed ceramic melters is necessary to maintain optimum glass temperatures. This control helps to ensure that a product of acceptable quality is produced, processing rates are maintained, and the equipment is operated safely and efficiently. Previous control systems have relied upon current, power, or resistance feedback control schemes to control power to the melter. Melter operators functioned as process controllers by adjusting the current, power, or resistance set point to maintain the glass temperatures within an acceptable range. Frequent adjustments were required during startup, shutdown, changes in feed rate and feed composition, and during glass-foaming incidents.

Direct-temperature feedback has not been implemented previously because of concerns about the response to the failure of thermocouples used to measure glass temperatures, and to the normal temperature fluctuations associated with convective currents in the glass.

A temperature-feedback control system that overcomes these problems has been developed for controlling electrical power to the LFCM (Westsik 1986). Glass temperatures are processed by a microcomputer, and a power set point is sent to the power feedback process controller. This temperature-control algorithm effectively completes the control function previously performed by melter operators. The algorithm includes steps to 1) reject thermocouples that do not appear to be functioning, 2) average the glass temperatures measured at different locations in the melter, 3) smooth the spatially averaged glass temperature to reduce the magnitude of the temperature oscillations, and 4) determine whether the glass may be foaming and take corrective action if needed.

The temperature-control system has been tested during five melter experiments employing two different melters at PNL. Three control modes--proportional, proportional-integral, and proportional-integral-derivative were evaluated. All three control modes provided acceptable control during steady-state operation. The proportional-integral control mode provided the best control during all phases of melter operation, including startup, steady-state operation, intentional and unintentional feed stoppage, and idling. The control logic has been implemented on distributed control systems for radioactive melters at PNL and West Valley Nuclear Services.

2.5.2.2 Melter Viewing System

A new camera for viewing the interior of the pilot-scale ceramic melter (PSCM) has been designed incorporating improvements that evolved from operating experiences with the first camera. Most optical components have been moved out of the harsh environment of the melter plenum, resulting in a simpler, easier to repair camera housing. To reduce interference with other equipment on the melter, the camera housing is also more upright. In all previous camera designs for the PSCM, RLFCM, HWVP, and West Valley melters, the optical axis was vertical as it penetrated the melter but was deflected 30° from vertical in order to view as much of the molten glass surface as possible from one corner of the melter. This offset is not needed in the new PNL design because the PSCM has been fitted with a nozzle offset 30° from vertical. Therefore the camera design could be simplified (see Figure 2.9). Two mirrors and a complex structure to hold the mirrors are eliminated from the nose of the camera. The camera nose is thicker and more simply structured, which should decrease corrosion. To help keep the camera cool, it is designed to be recessed into the refractory. Any required servicing will be easier because the optical system is more readily removed from the outer enclosure.

2.5.3 Melter Scale-Up Study

This activity provides input to a melter scale-up model that can be used to design and operate a full-scale melter using smaller-scale melter data. During FY 1986, the major thrust was to develop an empirical correlation between the laboratory-, engineering-, and pilot-scale melters. Two experiments were conducted to fill gaps in the existing data base for the melters.

FIGURE 2.9. New PNL Camera Design

The data base was then examined to determine correlations between melter scale and processing conditions. The data were also compared with the output from a cold-cap heat transfer model of melter performance.

Data from applicable melter runs at PNL in the PSCM, the high-bay ceramic melter (HBCM), and the experimental ceramic melter (ECM), and from melter runs at Savannah River Laboratory (SRL) in the large slurry-fed melter were included in this study. Laboratory-scale experiment results from the ongoing mini-melter development work were also included. Two melter runs were made during FY 1986, a 4-day experiment in the HBCM with feed of SRL composition and a 3-day experiment in the ECM with feed of the HWVP composition. Both melter feeds were also run in the mini-melter for comparison. The HBCM experiment was completed in March, and the ECM experiment was completed in May, meeting two milestones established for this task. These experiments are summarized here.

A draft-form status summary report was prepared at the end of FY 1986. This report documented the melter scale-up activity progress and met the scheduled milestone for this task. The data from ten experiments in five different melters, using two different melter feed compositions, were included in the scale-up study. The feed-rate and temperature data were the most useful in comparing melter processing capacities. Nominal melter feed rate divided by melter surface area gave a fair estimate of melter capacity and was reasonably independent of melter size. Based on melter surface area, the nominal glass melt rate increased with melter size. Comparisons were also made between the actual melt rate data and melt rates predicted by a cold-cap heat-transfer model. The heat-transfer model takes into account glass and cold-cap properties and melter physical parameters. The heat-transfer model has the potential for use in scale-up calculations, but suffers from a lack of data on the cold-cap characteristics. The status report recommends that experiments specifically designed to determine heat-transfer parameters be conducted to further develop the model.

2.5.3.1 High-Bay Ceramic Melter Experiment (HBCM-86-1)

This experiment was completed in March 1986 and consisted of 5 days (93 hr) of melter operation. It was patterned after PSCM-4, a 107-hr experiment made in the PSCM in December 1981, using SRL-formated feed and frit 131

(SRL-TDSF-131). The feed for the experiment was prepared following the procedures for feed make-up used during PSCM-4. A primary objective of the experiment was to determine accurate feed rate data for comparison with PSCM-4 and other melter runs made using SRL-TDSF-131 feed. To make valid comparisons, the experimental constraints for PSCM-4 were followed, i.e., operating temperature and other operational variables.

The objective to obtain accurate feed rate data was accomplished. A nominal feed rate of 14.2 L/hr and a maximum feed rate of 15.5 L/hr were obtained using the SRL-TDSF-131 feed composition. These rates were obtained during a 27-hr period of continuous glass pouring, allowing very steady-state conditions. Continuous pouring was successfully accomplished in the high-bay melter for the first time.

Approximately 1147 L of feed was processed, producing 592 kg of glass. An early problem with feed-line blockage caused by agglomerated chemicals was resolved by the installation of a strainer prior to the feed pump. Because of the shutdowns necessary to clear the feed lines and to install the strainer, the experiment had on-line efficiency of 89%. Otherwise, the feed processed extremely well with no foaming, bridging, or other problems occurring in the melter. The glass composition generally converged toward the target composition as the experiment progressed, and the glass product looked good, with minimal crystallinity. Table 2.1 summarizes the data from HBCM-86-1.

TABLE 2.1. Summary of HBCM-86-1

Test Duration	93 hr 10 min
Unscheduled Downtime	10 hr 5 min
Process Efficiency	89.2%
Total Feed Used	1147 L
Nominal Feed Rate	14.2 L/hr
Maximum Feed Rate	15.5 L/hr
Total Glass Produced	592 kg

2.5.3.2 Experimental Ceramic Melter Experiment (ECM-86-1)

This experiment was completed during May 21 through 23, 1986, and consisted of 3 days (52 hr) of operation. It was made using a HWVP feed composition and was patterned after experiments HWVP-11/HBCM-85-1 and HWVP-12/PSCM-22, performed during April and July of 1985. Feed left from the PSCM-22 experiment was used during the initial portion of the run, and feed prepared for the HWVP-13/HBCM-86-2 experiment (very similar composition) was used during the second portion of the run (because of problems encountered with the aged PSCM-22 feed). A primary objective of this experiment was to determine accurate feed-rate data for comparison with HBCM-85-1, PSCM-22, and other melter runs made using the same HWVP feed composition. To make valid comparisons, the experimental constraints for HBCM-85-1 and PSCM-22 were followed, i.e., operating temperature and other operational variables.

The objective to obtain accurate feed-rate data was accomplished. A nominal feed rate of 2.9 L/hr and a maximum feed rate of 3.3 L/hr were obtained using the HWVP simulated waste composition. These feed rates were obtained during the second portion of the experiment using feed from HBCM-86-2 because problems were encountered with the initial feed, which had been left over from PSCM-22.

During the run a total of about 122 L of feed was processed, producing a total of 48.4 kg of glass. During the initial portion of the experiment, a problem with the feed from PSCM-22 was encountered: the feed did not spread out over the surface of the melter, but instead formed volcano-like formations that built up to the feed nozzle. This problem was apparently caused by feed rheology changes that occurred during aging (about 1 year); a decision was made to use instead feed from the HBCM-86-2 experiment, which was very similar in composition. Because of the feed problems encountered, the experiment had an overall on-line efficiency of 91%. The feed during the second portion of the experiment processed very well, with no major problems occurring in the melter. The glass composition generally converged toward the target composition as the experiment progressed, and the glass product was good in appearance. Table 2.2 gives a summary of the data from ECM-86-1.

TABLE 2.2. Summary of ECM-86-1

Test Duration	52.7 hr
Unscheduled Downtime	4.85 hr
Process Efficiency	90.8%
Total Feed Used	122 L
PSCM-22 Feed Used	58 L
HBCM-86-2 Feed Used	64 L
Nominal Feed Rate	2.9 L/hr
Maximum Feed Rate	3.3 L/hr
Total Glass Produced	48.4 kg

2.6 EFFLUENT TREATMENT SYSTEM DEVELOPMENT - C. M. Ruecker and P. A. Scott

Studies of the pilot-scale submerged-bed scrubber (SBS) were conducted this year using an aerosol generator to produce a controlled source of airborne particles. The SBS is one of several aerosol collection devices that can be used as the primary scrubber in an LFCM off-gas treatment system. This scrubber is especially attractive for use in remote locations because it is effective and does not depend on a pump or any other moving parts.

Figure 2.10 is a schematic of the SBS. The SBS consists of a bed of packing, usually ceramic spheres, submerged in an aqueous pool. The gas inlet pipe runs down through the center of the bed to the packing support plate. The bed-retaining wall extends below the support plate, creating a lower skirt to allow the formation of a gas bubble underneath the packing. A holddown screen is used to prevent the bed from becoming fluidized at high gas velocities. Captured aerosols are continuously removed from the SBS through an overflow line. The overflow rate is determined by the rate of steam condensation and the flow rate of makeup water. The entire bed is suspended off the floor of the SBS to allow the scrubbing solution to circulate freely through the bed.

Natural water circulation occurs as a result of the flow of off gas through the bed. The off gas bubbling up through the bed lowers the apparent density of the fluid within the bed, causing a small pressure difference between the water on the outside of the retaining wall and the two-phase fluid on the

FIGURE 2.10. Cross-Sectional View of the Submerged-Bed Scrubber

inside. This head difference causes water to be forced up through the packing and eliminates the need for any moving parts.

The influence of several parameters on the aerosol removal performance of the SBS was investigated during FY 1986 (Ruecker and Scott 1986a). These parameters included the off-gas flow rate, volumetric steam-to-air ratio, aerosol solubility, inlet concentration, bed diameter, packing size, and inlet gas temperature. All parameters except the inlet temperature were found to have a significant effect. A total of 112 experiments were conducted.

The aerosol scrubbing performance was related directly to the superficial velocity of the off gas, defined as the volumetric flow rate at standard conditions divided by the bed cross-sectional area. The aerosol scrubbing performance, or decontamination factor (DF), decreased with increasing velocity for insoluble titanium dioxide aerosols in the 0.3- to 0.7- μm size range as shown in Figure 2.11. The DF is defined as the aerosol mass flow rate into the SBS divided by the mass flow rate out. Part of the decrease occurs because the aerosol-capture mechanism of these particles is less efficient at higher velocities, and part is the result of increased losses because of particle re-entrainment. As the off-gas bubbles break the surface of the aqueous pool, droplets of scrubbing solution are ejected into the void space above the pool,

FIGURE 2.11. Influence of Steam on Removal of Insoluble Aerosols by the Submerged-Bed Scrubber

where they can become entrained in the exiting off gas. These droplets will contain previously captured aerosols; thus this mechanism lowers the overall performance of the SBS.

Also demonstrated in Figure 2.11 is the influence of steam on the capture performance. Steam significantly enhances the aerosol capture mechanism by condensing on the aerosols, making them effectively larger and easier to capture. Some of the steam will condense on the gas-liquid interface, causing an aerodynamic draft toward the interface that improves the transport of the particles to the collecting medium. Even greater improvements could be achieved by ensuring that the steam in the off gas condensed preferentially on the aerosols. For this experiment, steam was injected into a cool (20°C) inlet gas stream. The inlet gas cooled the steam below its dew point, causing the steam to condense on the aerosols. If the steam does not condense until it is in the bed, most of the condensation will occur at the scrubbing solution interface. Up to sixfold improvements in the DF, over the amount shown in Figure 2.11, were observed when the steam was condensed on the aerosols before entering the bed.

One of the most important parameters influencing the capture performance of the SBS is the solubility of the aerosols in the scrubbing solution. The ability of the scrubbing solution to capture soluble aerosols appears to be limited by re-entrainment. An experiment was conducted using soluble sodium chloride aerosols in which the inlet aerosol concentration was continuously increased. The outlet concentration remained essentially constant, indicating that all incoming aerosols were being captured and all aerosols leaving the SBS were particles that had been re-entrained. The DF for soluble aerosols is about an order of magnitude higher than those for insoluble aerosols (Figure 2.11). Because the outlet concentration is independent of the inlet concentration for soluble aerosols, the DF increases quickly with increasing inlet concentration.

The bed diameter had little influence on the aerosol scrubbing performance. Experiments involving two bed diameters showed that the smaller bed exhibited higher DFs at equivalent superficial velocities. This effect is apparently the result of differences in gas distribution within the beds. No

special equipment was used to distribute the off gas evenly across the bed to determine whether the packing itself would adequately distribute the off gas. If uniform gas distribution had been achieved for both bed diameters, it is likely that no effect would have been observed.

Increases in the aerosol removal performance were also observed for different packing sizes. Larger packing sizes were more efficient than smaller packing. Based on the classical aerosol-capture mechanisms, one would expect the smaller packing to be more effective because of the smaller particle-to-packing size ratio. However, as the packing size decreased, the ability of the off gas to form distinct bubbles diminished. This caused channeling of the gas through the bed, decreasing the residence time and the surface area of the off gas in the bed. As a result, the DF declined with smaller packing. This phenomenon was observed visually using a plexiglass model of the SBS and the two different packing sizes (0.3 and 1.0 cm).

The inlet temperature had no influence on the aerosol capture performance of the SBS over the range investigated (60° to 100°C). There would probably be a measurable effect if a larger temperature range were used. The limited temperature range was used because the off-gas measuring instruments were not designed for temperatures above 100°C. The aerosol capture performance of the SBS should be enhanced at the temperatures of actual melter off gas (200° to 600°C). The higher temperatures should lead to significant radial temperature profiles within the bubbles rising through the bed. The temperature gradient moves particles down the gradient toward the gas-liquid interface. Higher inlet temperatures are also advantageous because they allow larger steam-to-air ratios, which increases the potential amount of steam that can be condensed on the aerosols.

A separate experiment was conducted to determine the influence of re-entrainment on the aerosol capture performance. One experiment was repeated twice, first using sodium chloride and then using titanium dioxide. Large amounts of the compound of interest were added to the scrubbing solution to represent captured aerosols. Room air was then drawn through the SBS. The outlet concentration was monitored using a classical scattering aerosol spectrometer. The outlet concentration gave a measure of particles re-entrained in

the exit off gas because there were essentially no particles in the size range of interest (0.3 to 0.7 μm) entering the SBS. The outlet concentration, or re-entrainment, is shown as a function of the scrubbing solution concentration in Figure 2.12.

The curve for the insoluble material rises quickly. The curve for the soluble sodium chloride rises much more slowly. The difference for the shape of the two curves is discussed in Ruecker and Scott (1986b). The important result was that re-entrainment increased rapidly once a given concentration of captured aerosols was reached in the scrubbing solution. Re-entrainment also increased with increasing velocity. To limit re-entrainment, both the captured aerosol concentration in the scrubbing solution and the superficial velocity should be minimized. These results can be achieved by condensing more steam from the off gas, adding makeup water to the scrubbing solution, increasing the bed diameter, and limiting the flow rate of noncondensable gas. The first two modifications will increase the rate of purging, or overflow rate, of water out of the SBS. The second two modifications will reduce the superficial velocity, limiting the number of droplets ejected into the exiting off gas.

Re-entrainment can be controlled using a surface active agent. A small amount of Dow defoamer DB-110A® was added to the scrubbing solution at the end of the re-entrainment experiment involving sodium chloride. As seen in Figure 2.13, the outlet concentration quickly dropped to levels observed before any salt was added. The defoamer had essentially eliminated re-entrainment.

The key to improving the aerosol capture performance of the SBS lies in improving the ability to make small bubbles to minimize the transport distances, improving the ability of insoluble aerosols to penetrate the gas-liquid interface, and limiting the re-entrainment of material once it has been captured. Small bubbles can be achieved using a simple orifice distribution plate; however, the size of the resulting bubbles is more controlled by the properties of the gas and the liquid than by the size of the orifices below a certain size. Steam can be instrumental in producing still smaller bubbles. If high steam-to-air ratios are used, further reductions in the bubble size below that generated by the distribution plate can be achieved as a result of

®A registered trade name of Dow Corning Corporation, Midland, Michigan.

FIGURE 2.12. Outlet Aerosol Concentration as a Function of the Captured Aerosol Concentration in the Scrubbing Solution

FIGURE 2.13. Effect of Dow Defoamer DB-110A® on Re-Entrainment
(®Dow Corning Corporation, Midland, Michigan)

both the quenching of the off gas in the bubble due to temperature-related volume reductions and the loss of vapor mass as the steam condenses. The steam will also prewet insoluble particles, thus improving the ability of these particles to penetrate the gas-liquid interface. For collecting particulate, the ideal SBS would be sized so that the bed diameter is as large as reasonably possible, keeping in mind the distribution plate's capability to effectively distribute the gas.

The information gained from the characterization study of the SBS was used to generate design correlations (Ruecker and Scott 1986a). The SBS-sizing procedure outlined by Ruecker and Scott (1986a) was used to provide conceptual design information to the Japanese for an SBS to be used at the Power Reactor and Nuclear Fuel Development Corporation Tokai Mockup Facility.

2.7 PROCESS/PRODUCT MODELING - W. L. Kuhn, P. W. Reimus, R. K. Farnsworth, D. W. Faletti, and L. J. Ethridge

One objective of the NWTP is to demonstrate the application of modeling techniques to waste-form qualification activities. As the NWTP is not responsible for the design of a current vitrification facility, a hypothetical but representative process has been considered in illustrating the role of a mass balance model in controlling and predicting the composition of vitrified waste.

2.7.1 Process Simulation

A mass balance model has been implemented using the SIMAN simulation language (Pegden 1985) because SIMAN offers dynamic simulation modeling capabilities that enabled uncertainties (stochastic variables) and batch-wise processes (discrete events) to be incorporated into a model otherwise described by a system of differential and state equations. This feature is important because understanding the propagation of uncertainties through the batch-operated LFCM vitrification system is essential to developing and demonstrating waste-form qualification technology.

The hypothetical LFCM vitrification system, as described in the topical report Demonstration of an Approach to Waste Form Qualification Through Simulation of Liquid-Fed Ceramic Melter Process Operations (Reimus et al. 1986),

consists of: a waste batching tank, two evaporator tanks (glass formers are added to the second tank), a melter feed tank, and a melter. Seven components were considered in the system: heat-producing compounds in the waste, other constituents in the waste, sodium oxide (Na_2O), boron oxide (B_2O_3), silicon dioxide (SiO_2), other glass formers, and water. All components were considered to be oxides at every point in the system (i.e., conversion of hydroxides, nitrates, etc., to oxides was not taken into account). Melter decontamination factors for all components except water were assumed to be infinity (an off-gas system was not included in the model). All tanks in the system were considered to be ideally mixed.

An objective during operation of the hypothetical system was to achieve a target loading of both heat and boron in the glass (assuming that boron controls key glass properties related to quality and processing rate). To accomplish simultaneous control of these two parameters, two glass formers were used: one rich in boron, the other lean in boron. A control algorithm for determining how much of each glass former should be added to each batch of waste (based on upstream sampling of the waste) was developed and incorporated into the model. Addition of glass formers had to be controlled because of the inherent batch-to-batch fluctuations in incoming waste composition. Precise control was impossible, however, due to sampling error, error in measuring levels in tanks, and error in glass former make-up and addition.

Sampling error included two components: sample-to-sample variation (when duplicate samples are taken at the same time) and sample analytical error. These two sources of error allowed the user to investigate how well glass composition could be controlled or predicted based on the number of samples taken and/or the number of analytical determinations performed (on each sample).

All uncertainties in the mass balance model were treated stochastically. This was accomplished by taking advantage of internal subroutines in SIMAN that generated random numbers and used these to randomly sample distributions that the user defined. Only normal distributions were specified in the model. The following uncertainties were included in the model:

- 5% relative standard deviation (RSD) in batch-to-batch waste composition
- 5% RSD in sampling and analytical errors for waste constituents
- 4% RSD in sampling and analytical errors for glass-former constituents
- 1% RSD in tank level measurements (1% of full-scale reading)
- 2% RSD in the amount of glass formers added relative to what the control algorithm prescribed
- 2% RSD in the time between batch canister pours.

When the mass balance model was executed, the concentration of each constituent in each tank versus time was calculated by simultaneous solution of the differential and state equations that described the system (these were mass balance equations for ideally mixed tanks). The equations were solved using a Runge-Kutta-Fehlberg numerical differentiation algorithm that is part of the SIMAN subprogram library. The values obtained from solving these equations were taken to be the "true" concentrations in the system. Apparent concentrations differed from the true concentrations because they had sampling and analytical errors imposed on them. "Predicted" concentrations in the system were calculated by taking the apparent concentrations and plugging them into the same set of equations used to calculate the true concentrations. By doing this, the apparent concentrations at the sampling points were propagated through the system in the same way that the true concentrations were propagated.

2.7.2 Statistical Analysis of Simulated Results

The mass balance model was used to simulate 40,000 hr of operation of the hypothetical vitrification plant. The purpose of the runs was to investigate the effect of different strategies for sampling and analyzing samples of waste and feed on the ability to control and predict the composition of the glass being produced. The sampling strategies investigated were as follows:

- Case 1: 1 sample and 1 analysis of both the waste and the feed.
- Case 2: 1 sample and 1 analysis of the waste, 5 samples and 5 analyses of each sample of the feed.
- Case 3: 5 samples and 5 analyses of each sample of the waste, 1 sample and 1 analysis of the feed.
- Case 4: 5 samples and 5 analyses of each sample of both the waste and the feed.
- Case 5: Infinite number of samples and infinite number of analyses of each sample of both the waste and the feed (analogous to no sampling or analytical error).

The absolute differences between the true (simulated) and target glass compositions (ADTT) were used as a measure of the ability to control the process, and the absolute differences between the simulated true and predicted glass compositions (ADTP) were used as a measure of the ability to predict the glass composition. The spread of the absolute differences was examined by obtaining the 95th percentile point of all absolute differences from the simulation runs (95% of the differences are less than the 95th percentile point). In general, it was found that the glass composition was better controlled when more samples and analyses were taken of the waste, and the glass composition was better predicted when more samples and analyses were taken of the feed.

The values of the average ADTT varied from 0.6% of the target composition for the case of boron and sampling Case 1, to 5.2% for "other waste" and sampling Case 2, while the maximum ADTT varied from 2.3% for boron and sampling Case 2, to 23.5% for "other waste" and sampling Case 1. The values of the average ADTP varied from 0.5% of the target composition for silicon and sampling Case 2 and 3, to 3.1% for "heat producing constituents" and sampling Case 1, while the maximum varied from 2.1% of the target composition for silicon and sampling Case 2, to 16.4% for "heat producing constituents" and sampling Case 1.

The above work is detailed by Reimus et al. (1986) and was presented by W. L. Kuhn as a paper, "A Method For Qualifying Canisters Of Vitrified High-Level Waste For Disposal," at the ANS International Meeting in Niagara Falls, New York (Proceedings in press).

2.7.3 Statistical Process Control

One objective in repetitively exercising the mass balance model was to investigate the possibilities of applying process control charting to the operation of the vitrification system. Among other things, process control charting provides an objective, statistically based method to distinguish between normal process fluctuations and true process upsets. Control charting can be used to determine when the process has deviated enough from steady-state conditions to warrant corrective action. Part of the process modeling activity was to examine the application of the theory of statistical quality control to the melter process.

Statistical quality control (SQC) techniques are widely used in industry to monitor a product's quality level and to gain increased understanding of the variables influencing the process. As these techniques are standard industrial practice, they can be used to enhance public demonstration of glass quality.

The normal application of SQC assumes independent observations, but the melter process is unlike many processes where the observations over time are independent of one another. Sequential samples from the tanks along the melter process are correlated because of the heels left in each tank after completing a transfer. Appropriate methods for applying SQC to correlated data were examined and developed.

These methods were applied to data simulated from the mass balance model. SQC was applied to the simulated feed samples. The ability of these methods to detect shifts in the boron composition of the feed was examined for various feed and waste sampling schemes. We examined the average number of observations plotted on a control chart after a process shift and before detecting an out-of-control point. We found in this simulation that by using five replicates of feed samples and five replicates of analyses of samples, a 10% change in the boron concentration can be detected after ten points plotted on a

control chart. This work will be published during FY 1987 as the topical report, Statistical Process Control Applied to the Liquid-Fed Ceramic Melter.

A paper entitled "Statistical Process Control: An Approach to Quality Assurance in the Production of Vitrified Nuclear Waste" is being presented at the Waste Management '87 meeting and will appear in the Proceedings. The paper shows statistical process control (SPC) to be a widely applied method for quality control: numerous examples of applications in well-known industrial companies are referenced. SPC's main purpose is to provide for intelligent decisions in the midst of uncertainty. Changes should be made only when a change in the process beyond its expected, inherent variations is indicated. Studying these indications can increase understanding of the process and provide for continual process improvement.

One SPC tool, control charts, can be applied to monitor LFCM feed composition through use of results from a simulation of the LFCM system. The special nature of the LFCM system required that specific adaptations of control charting be developed. The control charts developed can detect changes in the process average as well as in the process variation.

The probability of detecting changes of a particular magnitude in the process average or variation depends on the sampling schemes of the waste and feed compositions. SPC can aid in determining the appropriate sampling schemes by examining the capability of the control charts to control product quality. This is accomplished by examining the average run length of the control charts.

Feed composition can be adjusted in the feed preparation tank after the sampled composition is examined. Use of control charts can determine whether adjustment is needed. If control charts are not used, the variability of the true composition could be increased rather than decreased under some conditions. The paper discusses control charting as a means for deciding to further adjust the feed composition.

2.7.4 Product Model

It has long been known that the chemical durability of glass is affected by its composition. Establishing this dependence for the purpose of quality control is important because waste-form manufacturers have primary control over

glass composition. An approach is presented here for correlating glass dissolution rate versus composition. The method is tested using leach rate data for several waste glass compositions in both fresh water and brines. With this information, a preliminary dependence of dissolution rate and composition is determined. Additionally, methods are developed for relating the uncertainty in predicted glass dissolution rate with the uncertainty in predicted composition of waste glass.

This approach is based on the work of A. Paul (1977), who correlated glass chemical durability with composition via thermodynamic stability of the glass constituents. Plodinec et al. (1983) applied this method to evaluating nuclear waste glasses and several simple glasses. Accordingly, glasses are treated as a composite solid of individual silicate and/or oxide phases. The free energies of aqueous dissolution reactions are calculated for these phases, and this provides an indicator of glass durability. It should be understood that this method has no rigorous thermodynamic or kinetic basis because 1) the thermodynamic state of a vitreous phase cannot be defined and 2) kinetic mechanisms are not identified. The procedure, however, is useful in correlating the effect of variation in composition on glass durability.

It is assumed that the driving force for these individual reactions is determined according to their free energy, which is calculated as follows:

$$G = RT \ln Q + G^\circ \quad (1)$$

where $Q = \prod_i a_i^{v_i}$ is the ratio of the activities of the products and reactants, where a_i is the activity of a product or reactant, and v_i is the associated stoichiometric coefficient.

The free energy data is to be correlated with glass dissolution rates. Most leach tests are performed in fixed volumes of water, and the dissolution rate generally is found to decrease with time. This trend is associated with "saturation" effects. In a repository, it is expected that slow mass transfer rates away from the waste package will result in similar saturation. Therefore, such leach tests provide useful information about the behavior of glass in repositories. The rates used for correlating the free energy data are those

obtained at "saturated" or near-saturated leachate conditions from these static tests. Grambow (1985) attributes this final rate to the residual affinity of the glass to dissolve in aqueous solutions. Table 2.3 presents the final dissolution rates for four glasses that have been studied at PNL. The rates are derived from changes in the concentration of soluble species dissolved from the glass, such as sodium, boron, and lithium.

The composite free energy of the glass dissolution reaction is assumed to be represented by the mole-fraction weighted sum of the individual free energies of reactions (Equation 1) of the glass constituents:

$$G = \sum v_i [RT \ln(Q_i) + G_i^\circ] \quad (2)$$

where v_i is the mole fraction of glass constituents. Grambow (1985) reported that dissolution rate should depend on free energy according to:

$$\ln(\text{Rate}) = A' - B G \quad (3)$$

where A' and B are constants at a fixed temperature, and G is obtained from Equation 2. It is difficult to rigorously calculate G in this case since the activities of the dissolved products and reactants are not known with sufficient accuracy. However, rearrangement of Equation 2 is possible such that the

TABLE 2.3. Dissolution Rates and Free Energies for Waste Glasses

	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Dissolution Rate at 90°C, g-glass/m ² day	0.016	0.035	0.25	0.01
Standard Free Energy of Glass at 90°C (G ₀), kcal/mole	-5.5	-6.4	-7.7	-4.9

dependent variable involves only the standard free energies. Expanding Equation 3 with Equation 2 results in:

$$\ln(\text{Rate}) = A' - B \sum v_i RT \ln(Q_i) - B \sum v_i G^\circ \quad (4)$$

Combining the terms A' and $B \sum v_i RT \ln(Q_i)$ into a new "constant" A results in:

$$\ln(\text{Rate}) = A - B G^\circ \quad (5)$$

where G° is the standard free energy of hydration of the glass and is given by $\sum v_i G_i^\circ$. By combining the solution activity term into a constant, Equation 5 implies that the free energy contribution of the aqueous solution activities for all glasses is the same. Although this is not rigorously correct, such an approximation may be reasonable, considering that the leach solutions are nearly saturated in many of the dissolved species.

The standard free energies for the glasses, calculated without the activity term, are shown in Table 2.3. The free energy data was taken from Plodinec et al. (1983) and extrapolated to 90°C using the Van't Hoff equation. Following Equation 5, a regression analysis was used to fit a straight line through the four data resulting in the following values ($\pm$ standard error) for the parameters A and B :

$$A = -10.43$$

$$B = 1.15$$

The variances and covariance for the fit are presented below. Equation 5, with these coefficients, is thus the resulting empirical correlation for the composition dependence of the final dissolution rate of nuclear waste glasses at 90°C.

With the above correlation, the glass composition can now be related to dissolution rate. The overall objective is to understand how changes in composition (due to vitrification process variations) will affect this dissolution rate. Uncertainties associated with the vitrification process can be propagated through to a variation in leach rate of the glass. Using statistical propagation-of-error methods, the error in Equation 5 is given by the following relation:

$$\sigma_{\ln R} = \left[\left(\frac{\partial \ln R}{\partial A} \sigma_A \right)^2 + \left(\frac{\partial \ln R}{\partial B} \sigma_B \right)^2 + \left(\frac{\partial \ln R}{\partial G} \sigma_G \right)^2 + 2 \operatorname{cov}(A, B) \frac{\partial \ln R}{\partial A} \frac{\partial \ln R}{\partial B} \right]^{1/2} \quad (6)$$

where σ_A^2 , σ_B^2 , σ_G^2 represent the variance in A, B, and G° , respectively. Carrying out the differentiation in Equation 6 yields:

$$\sigma_R = [\sigma_A^2 - 2G \operatorname{cov}(A, B) + (G^\circ \sigma_B)^2 + (B \sigma_G)^2]^{1/2} \quad (7)$$

The error in the free energy, σ_G , depends on errors in individual glass component free energies and also on errors in composition. Assuming that component free energies are known exactly and, further, that mole fractions can be varied independently, results in the following relation for σ_G :

$$\sigma_G = [\sum (G_i \sigma_{v_i})^2]^{1/2} \quad (8)$$

where σ_{v_i} is the error in mole fraction of individual components. If it is assumed that all mole fractions of glass constituents are known to within the same fractional limit f , then substituting $\sigma_{v_i} = f v_i$ into Equation 8 results in:

$$\sigma_G = f [\sum (v_i G_i^\circ)^2]^{1/2} \quad (9)$$

Of interest is the sensitivity of the error term for the predicted glass dissolution rate (Equation 6) on the composition error factor f . To carry out the analysis numerically, a value of $G^\circ = -6.4$ kcal/mole is selected, corresponding to the oxidized form of the glass No. 2 from Table 2.3. Using the available composition and standard free energy data, the term $[\sum(v_i G_i^\circ)^2]^{1/2}$ in Equation 9 becomes 6.89 kcal/mole. The regression analysis done above resulted in values of $\sigma_A = 0.8$, $\sigma_B = 0.13$, and $\text{cov}(A,B) = 0.102$. Equation 6 becomes:

$$\sigma_{\ln R} = (0.026 + 62.8 f^2)^{1/2} \quad (10)$$

According to Equation 10, $\sigma_{\ln R}$ is not significantly affected until f reaches values greater than 0.02. This means that relative uncertainties in composition of less than 2% will not have a statistically significant impact on glass dissolution rates, assuming that glass dissolves according to the correlation given by Equation 5. The results of the process simulations performed by the Technology Testing subtask indicate that process variations (excluding upsets) are expected to result in uncertainties in composition on the order of 1 to 5% (f values on the order of 0.01 to 0.05) if the assumed standard deviations for process operation are correct.

2.7.5 Canister Thermal Model

The TEMPEST heat-transfer numerical computer code is being applied to the problem of predicting the temperature of glass after it is poured into a canister and cools to its final temperature distribution.

The TEMPEST code has been successfully applied in numerous canister-filling and cooling situations. However, the code was unable to execute using input parameters specific to the case of one 24-in.-dia canister filled during a recent pilot-scale melter run (PSCM-21). The problem lies within the code itself. Several unsuccessful attempts were made to conduct thermal computations for comparison with temperatures measured during the filling and cooling of the 24-in. canister. Though a number of errors were uncovered and corrected, the problem remained unsolved by the end of the year. Efforts are under way to fully correct the code.

We are utilizing the implicit fluid mechanics option of the newest version of TEMPEST, and are developing a small test problem (analogous to the 24-in. canister problem). Installation, debugging, and successful testing of the implicit fluids capability into the TEMPEST code was successfully completed.

Additional work completed during in FY 1986 included:

1. Formulation of an improved front tracking model. This will more accurately simulate the moving glass interface and will be compatible with the radiation model to be developed next year. It is still to be installed and debugged.
2. Successful implementation of an improved time-stepping and temperature-control logic that proved very convenient during FY 1985 TEMPEST simulations.
3. A literature search of potentially valuable matrix software for the radiation work of FY 1987. Some of the software has been requested and received.

2.7.5.1 TEMPEST Applications to Transient and Steady-State Heat Transfer Problems in Cell

TEMPEST applications toward predicting transient and steady-state temperatures during B-Cell operations have been threefold this year:

1. determination of the expected transient and steady-state canister flange temperatures of Federal Republic of Germany (FRG) canisters to facilitate weld/closure operations
2. determination of the transient and steady-state glass temperatures of FRG canisters in insulated and uninsulated storage pods
3. determination of the transient and steady-state glass and canister surface temperatures expected during canister cooling and decontamination operations and their effect on glass cracking.

These temperatures must be predicted before actual operations begin, to minimize glass cracking and to maintain a high degree of canister integrity during the postfill operations. The results from these TEMPEST applications are summarized below.

Predicted Temperature Histories of the FRG Canister Flanges. It was necessary to determine the expected transient and steady-state flange temperatures for filled FRG canisters in order to ascertain the potential for oxidation of the flange surface and the necessary preheat temperature for the canister lid during closure operations. Modeling of the transient flange temperatures during canister filling involved three simulations:

- modeling of a 5-cm ceramic-fiber-insulated, thermocouple-instrumented FRG canister filled with nonradioactive glass (control simulation)
- modeling of an actual FRG canister filled with 60 L of radioactive glass containing 28 W/L decay heat (1680 W/canister)
- modeling of an actual FRG canister filled with 60 L of radioactive glass containing 34.4 W/L (2065 W/canister).

The three developed simulations were in a two-dimensional R to Z matrix and were assumed to transfer heat symmetrically in the circumferential direction. The glass properties used in the simulations were taken from measurements of Savannah River Laboratory (SRL) glass properties (No. 411), which were deemed to be reasonably similar to those for FRG glass. A glass temperature of 1050°C was assumed in the glass immediately after pouring. All other temperature-dependent properties were taken from referenced values or vendor's information, except for the thermal conductivity of the ceramic fiber insulation. Based on the control simulation, the thermal conductivity values for ceramic fiber insulation had to be increased 50 to 75%. This increase was judged to be due to the compression of the ceramic fiber insulation by the glass in the canister.

Results of the control simulation, with the increased thermal conductivity of the ceramic fiber insulation, closely approximated the actual flange temperatures after filling was complete. Based on this result, simulations of the two radioactive canisters were performed. Results of the two simulations predicted that the maximum flange temperatures observed during filling and cooling would stay below 500°C. At this temperature, little oxidation of the weld area on the flange and sensitizing of the metal was expected. As a result, precise knowledge of the canister flange temperature history, as a prerequisite for

acceptance of the welding, should not be necessary. Only the steady-state flange temperatures prior to welding are necessary for weld/closure operations.

Steady-state flange temperature predictions for the FRG canisters were performed by TEMPEST, with the canister overpack in place and the flange protector removed. The canister was assumed to be standing in 50°C cell air. Four simulations were performed. These simulations included the two different feed concentrations (28 W/L and 34.4 W/L), with and without a lid in place. Results of the steady-state simulations are shown in Table 2.4. These temperature results are not expected to be accurate to 1.0°C. They do, however, provide a good estimation of the required preheat temperature of the FRG canister lid that can be used in closure operations.

Transient and Steady-State Temperatures for FRG Canisters in Insulated and Uninsulated Storage Pods. TEMPEST was used also to predict the transient and steady-state temperatures of filled FRG canisters upon placement in insulated and uninsulated storage pods. These predictions were needed to estimate the effect of this operation on canister glass quality.

The TEMPEST code was used first to estimate the effect of insulated versus uninsulated canister storage on glass quality. An insulated storage pod had been designed for interim storage of the FRG canisters. This storage pod was originally designed to allow a slower glass cooling rate for the canisters as they cooled through the glass solidification zone. Unfortunately, it was insulated with 1 in. of ceramic fiber insulation instead of the originally recommended 0.125 in. Results from the TEMPEST simulation showed the canister glass

TABLE 2.4. Results of Steady-State Flange Temperature Simulation Tests

Glass Decay Heat Concentration, W/L	Lid in Place?	Canister flange Temperature, °C	Canister Lid Temperature, °C	Glass Surface Temperature, °C
28	no	140	--	223 to 260
28	yes	162	160 to 167	262 to 316
34.4	no	150	--	248 to 291
34.4	yes	177	174 to 185	291 to 354

temperatures increased instead of decreasing upon emplacement in the insulated pod. Eventually, the canister glass assumed steady-state temperatures between 600 and 800°C. These high temperatures would result in extensive devitrification of the glass, as well as a higher driving force for glass cracking potential, upon removal of the canister from the pod. As a result, it was recommended that the insulated storage pod not be used. New recommendations for cooling are that 1) each FRG canister stays in the turntable until the next canister has been filled and 2) the FRG canisters be placed immediately into uninsulated storage pods after removal from the turntable.

Four simulations were run to evaluate the steady-state glass temperatures of FRG canisters in uninsulated storage pods. The simulations were performed for canister decay heats of 1680 and 2065 W/canister (28 and 34.4 W/L). To bracket the canister glass temperatures for each decay heat level, two models were used. For the low-temperature bracket, a two-dimensional R to Z model with a 50°C environment was used. For the high-temperature bracket, a three-dimensional R to Z model, also with a 50°C environment, was used. An adiabatic boundary around 180° of the pod simulated adjacent pods. Results of this work are included in Table 2.5.

TABLE 2.5. Estimated Steady-State Profiles for FRG Canisters of Various Decay Heats

Description	28 W/L		34.4 W/L	
	Low Case	High Case	Low Case	High Case
Centerline glass temperature at middle of the glass, °C	536	561	615	646
Glass wall temperature at middle of the glass, °C	394	459	442	515
% of soft glass in canister (>550°C)	0	3	25	43

2.7.6 Glass-Cracking Model

Methods have been developed for minimizing crack surface area in waste-glass castings and for predicting cracking as a function of thermal history. This work includes evaluation of both small-scale canisters and full-sized canisters of glass.

Quantitative information on cracking (or particle size data from which cracking area can be inferred) from canisters with known thermal histories was found to be quite limited. Data were obtained from 17 such canisters, ranging in diameter from 15 to 60 cm and in length from 80 to 290 cm. Cooling conditions ranged from very slow (phase cooling using an annealing oven) to very rapid (the canister was immersed in water during and after filling). The canisters were made of either carbon steel or stainless steel. Four of the canisters were lined with Fiberfrax® insulation to vary the cooling rate and degree of adhesion between the glass and the canister. Reported values of the relative surface areas (the ratio of the total surface area of the glass to the surface area of a glass monolith) ranged from 1 to 48.

A simple linear relationship between relative surface area, RA, and the radial temperature difference, DELT, within the glass when its centerline temperature is 500°C was found to correlate the available data to within experimental uncertainties. The resulting correlation is:

$$RA = 1 + 0.085 \times \text{DELT} \text{ (for carbon steel canisters)}$$

$$RA = 1 + 0.19 \times \text{DELT} \text{ (for stainless steel canisters).}$$

The basis for this correlation is that, according to "quick freeze" models, stresses are locked into the glass if the glass is not isothermal as the glass passes through the transition temperature. Any subsequent change in temperature distribution following cooling below the transition temperature (generally near 525°C) will result in stress buildups that can cause cracking. Therefore the radial temperature difference when the surface temperature

®Fiberfrax is a registered trade name of the SOHIO Engineered Materials Co., Niagara Falls, New York.

reached 500°C was chosen as a measure of the magnitude of these locked-in stresses. The above correlation predicts relative surface area to within the accuracy of the existing data. More data, however, is needed to validate this correlation.

The report A Method for Predicting Cracking in Waste Glass Canisters (Faletti and Ethridge 1986) was published this year.

Model Predictions of Glass Cracking on FRG Canisters During Decontamination. The decontamination of FRG canisters will involve electropolishing. This wet operation can induce a series of thermal transients in the glass that could affect product quality by increasing the potential for cracking. This potential was examined using the TEMPEST code for the following steps in the decontamination cycle:

1. as the oxidized canister was cooled through glass solidification zone
2. as the oxidized canister cooled to steady state
3. as the oxidized canister was quenched in the decontamination solution
4. as the decontaminated canister returned to steady state in air
5. as the decontaminated canister was requenched (to simulate extra decontamination attempts).

The maximum radial temperature differences in the glass predicted for these steps were evaluated to determine the parameters that could be expected to have minimal impact on the product quality. In addition to the FRG glass decay heat concentration of 28 W/L, decay heat concentrations of 10 W/L and 2.5 W/L were examined. The effect of decontamination on glass quality was evaluated for three different quench temperatures (25°C, 75°C, and 125°C) to determine the minimum quench temperature below which extensive cracking was expected to occur. A more complete description of this simulation is available in Farnsworth (1986).

Results of this study showed that 24-in.-dia canisters with decay heat concentrations at or below 2.5 W/L would not have any increased glass fracture caused by decontamination. This decay heat concentration is representative of

most U.S. defense HLW experience. The results, however, also show a significant cracking potential for glasses with 10 W/L and 28 W/L as a result of decontamination. Possible efforts to reduce this potential are:

- To use liners consisting of ceramic fiber insulation in the canister. These liners act as thermal shock absorbers during quench operations, reducing the maximum radial temperature difference encountered (which increases cracking potential).
- To prevent the decontaminated canister surface from acquiring a highly polished, low-emissivity surface during decontamination. A low-emissivity surface acts as a radiant insulator on the canister, increasing the glass temperatures during steady state, as well as the subsequent thermal driving force upon requenching the canister (which increases cracking potential). Control of canister surface emissivity during decontamination operations is possible.

2.8 MELTING CHEMISTRY SUPPORT - S. J. Mitchell, J. L. Swanson, M. A. Reimus, and S. C. Marschman

This subtask was responsible for development of procedures for designing acceptable waste glass oxide compositions. Much of the future testing work in the NWTP was planned to study future high-fission product wastes. Estimations of future commercial waste compositions were completed under the Waste Definition activity, and a topical report was issued. Work was initiated to develop new working glass compositions, based on these future waste compositions, under the Waste Glass Development activity. As funding, however, did not support continuation of this effort, the glass development work was closed out early in FY 1986 after a letter report summarizing progress was issued.

The main thrust of work for this subtask in FY 1986 was to develop test methods for optimizing the melting characteristics of proposed nuclear waste feed formulations. Work to develop laboratory-scale testing procedures to ensure that feed formulations will perform as expected in full-scale melters with optimal and predictable characteristics was performed under the Mini-Melter Development activity. This work was coordinated with the Melter Scale-Up Study activity to allow laboratory testing results to be correlated with

larger-scale melter testing data. A topical report was issued documenting the results of the mini-melter development work. A literature search to examine analytical techniques to determine the REDOX potential of waste glasses was completed in FY 1986, and a letter report was issued under the REDOX Analysis Studies activity.

2.8.1 Waste Definition

Although the current plan in the United States is to dispose of spent fuel elements from commercial light water reactor (LWR) nuclear power plants (without treatment) in a geologic repository, future plans may include reprocessing of such fuels to recover their contained values. Reprocessing will be needed if breeder nuclear power plants are to be employed. It will be needed to provide the plutonium (from LWR fuel) for use in the initial breeder fuel as well as to recycle the breeder fuel. The wastes resulting from such commercial reprocessing activities would then be prepared for suitable disposal. The purpose of this task was to provide baseline characterizations of such wastes so that waste immobilization technologies (e.g., vitrification) can be studied.

Composition ranges likely to occur in HLW from the future reprocessing of commercial nuclear fuels were developed based on trends in fuel reprocessing procedures and in achievable fuel burnups. This was done to provide a sound basis for studies aimed at defining appropriate glass compositions for the safe disposal of such wastes.

High-level liquid waste composition ranges were developed for the PUREX reprocessing of both LWR and liquid metal reactor (LMR) fuels, and a topical report documenting these results was issued (Swanson 1986). These compositions should be representative of HLW resulting from future reprocessing activities in other countries, as well as in the U.S. Radioactive components will be comparable because they are governed by the laws of nature. Nonradioactive components will be comparable because the PUREX process, with minimal addition of materials that will contribute to waste composition and volume, is the reprocessing technique favored in all countries. This should not be taken to mean that all HLW compositions will be identical. Variations will exist

because of different operational philosophies, both within and between countries, but such variations should fall within the ranges developed here.

2.8.2 Waste Glass Development

Limited efforts were made in FY 1986 to develop a reference borosilicate HLW glass based on a reference future LWR fuel reprocessing waste (Swanson 1986). A letter report entitled "Development of a Reference Glass for Future LWR Fuel Reprocessing Wastes" describes the work performed in detail.

Based on the limited testing performed on the reference glass developed, RHLW-1, the following conclusions and recommendations for future glass development were made:

- RHLW-1 has viscosity and electrical conductivity properties acceptable for LFCM processing.
- A small amount of phase separation, possibly a molybdate, was observed that may lower the glass quality. The noble-metal inclusions observed may affect melter processability and contribute to crystal formation by acting as nucleation sites.
- RHLW-1 performs well under deionized water (DIW), MCC-1 test conditions, but does not under DIW, MCC-3 test conditions. A glass with greater chemical durability would be desirable. RHLW-1 may perform well under natural ground-water leach testing.
- Refine the composition of RHLW-1. Decreasing the waste loading may decrease the noble-metal inclusions and molybdate phase separation. Small additions of B_2O_3 and/or reductants such as graphite or silica metal may also help to decrease molybdate phase separation. Reducing conditions can increase noble-metal precipitation; therefore a balance between this and molybdate phase separation must be established.
- Perform testing on a uranium-doped version of the glass. This will help indicate whether a radioactive version of the glass performs well.

- Use RHLW-1 or a refined version (developed with minimal alteration to obtain minimal properties desired) of RHLW-1 as a base glass for optimization studies. Mixture studies such as performed by Chick et al. (1984) may be utilized to optimize the glass composition.

2.8.3 Mini-Melter Development

A continuously fed liquid-fed mini-melter (LFMM) was developed to provide for small-scale continuous testing of nuclear waste glass feeds. The LFMM could be easily and inexpensively installed in a hot cell, compared to larger-scale melters, because of its relatively small size and simple configuration, enabling testing of radioactive feeds. The LFMM was designed as a laboratory-scale melter, to be representative of engineering- and large-scale ceramic melters with respect to melting behavior. The apparatus incorporates basic components of the large-scale melters: a feed agitation tank, slurry pumping and feeding system, melting compartment, heat source, and glass discharge outlet. The large-scale melters are joule-heated while the LFMM is externally heated. Because of the LFMM's small size, joule heating was judged unnecessary. Heat transfer is high enough that the temperature in the melter would be relatively uniform regardless of heating method. The system is designed to allow continuous feeding of liquid slurry, with constant processing of molten glass. An overall schematic of the LFMM system is shown in Figure 2.14. The design specifications of the LFMM are compared in Table 2.6 with those of the PNL developmental joule-heated melters.

A total of six LFMM experimental runs were performed. Each of the six different feed compositions tested was previously run in at least two of the larger PNL developmental joule-heated melters known as the high-bay ceramic melter (HBCM), the experimental ceramic melter (ECM), and the pilot-scale ceramic melter (PSCM). Preliminary results obtained with the limited testing are promising. Feeds processed in the LFMM exhibited behavior closely resembling that observed in the large-scale melters. Feed-rate correlations between the LFMM and the ECM, HBCM, and PSCM were developed to estimate a range of expected feed rates for the large-scale melters from LFMM data. Correlations derived with maximum feed rates had better fit than those derived with nominal feed rates. Of the maximum feed-rate correlations, the PSCM-LFMM correlation

FIGURE 2.14. Schematic of Liquid-Fed Mini-Melter Experimental Apparatus

TABLE 2.6. Comparison of LFMM and PNL Larger-Scale Melter Specifications

	Melter			
	LFMM	ECM	HBCM	PSCM
Surface Area, m ²	0.0029	0.054	0.25	0.73
Volume, L	0.31	8.2	50	290
Surface Area-to-Volume Ratio, m ⁻¹	9.4	6.6	5.0	2.5
Glass Depth, cm	10.6	15	22	42

has the best fit. Of the nominal feed-rate correlations, the ECM-PSCM correlation has the best fit. More developmental work with LFMM testing needs to be done to further refine these correlations. Further testing will also eliminate bias and establish the LFMM's true correlation to, and representation of, large-scale melters. A report summarizing the development of the LFMM was issued (Reimus, Marschman and Graff 1986).

2.8.4 Redox Analysis Studies

The redox state of nuclear waste glasses has been identified as an important parameter affecting the processing of these glass types. Processing in continuously fed joule-heated melters has demonstrated that glasses foam under oxidizing conditions. This reduces the rate at which a melter can be fed and can require melter shutdown to allow foaming to dissipate. Glasses processed under reducing conditions have formed a metallic, conductive second phase. This conductive phase may form a sedimentary layer that can accumulate at the bottom of the joule-heated melter, possibly resulting in electrical shorting of the melter electrodes. Melter tests have also shown that the melting rate of glasses is affected by the oxidation state of the glass. Therefore, an analytical technique is needed to determine the oxidation state of a glass (typically the ferrous-ferric ion ratio) prior to vitrification so that the redox state of the feed can be adjusted before it enters the melter. This technique must provide a rapid result with minimal complexity and also be applicable to radioactive samples and remote operation.

The objectives of this activity were to examine the techniques used for redox determination of glasses and to identify a suitable technique meeting the above criteria. The literature was surveyed and the following techniques were reviewed: wet chemistry determinations, colorimetric methods, Mossbauer spectroscopy, electrochemical analysis, and ion chromatography. Representative procedures utilizing these techniques were reviewed and discussed in a letter report.^(a) Ion chromatography is the most promising technique currently

(a) Marschman, S. C. May 1986. "A Letter Report Summarizing the Analytical Techniques Used to Determine the Redox State of Glass and Related Materials."

available for determining the redox potential of radioactive nuclear waste glasses. This procedure offers advantages over the other techniques, including ease of operation, versatility, rapid analysis, and low risk of operator radiation exposure.

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3.0 RADIOACTIVE LIQUID-FED CERAMIC MELTER (RLFCM) OPERATIONS

J. E. Minor - Manager

3.1 OBJECTIVE

The objectives of this task are to: 1) demonstrate the operability and maintainability of RLFCM vitrification technology in a remote radioactive environment, 2) provide the radioactive portion of the information necessary to establish both nonradioactive-to-radioactive equipment performance correlations and a vitrification process control-to-glass product quality correlation, and 3) provide vitrification technology design and operations documentation to encourage future private commercialization.

3.2 SUMMARY

The heat and radiation sources being prepared for the Federal Republic of Germany (FRG) will contain ^{137}Cs and ^{90}Sr as the active isotopes. The cesium and strontium feed stocks received during FY 1986 required concentration prior to use as melter feed. Since boildown of the as-received feed stocks could result in precipitation of barium, lead, and strontium, a procedure was developed utilizing repeated blending, denitration, and volume reduction.

Production of the first ten FRG canisters began. During production of the first canisters, plugging of the melter off-gas line caused loss of melter vacuum. The off-gas line was removed and replaced with a temporary line while a modified off-gas line was designed and installed. An off-gas line reamer was designed and tested to prevent future plugging of the off-gas nozzle.

The air-displacement slurry pump, which provides feed to the melter, continued to provide dependable performance. It was found, however, that an increase in the minimum tank volume feed tank volume was necessary to maintain pump performance.

Three modes have been devised for controlling electrical power to the RLFCM; until now resistance feedback has been utilized. Resistance feedback with a glass-weight-factor correction was configured on the distributed control system but was not used during the melter operation. Temperature feedback control has now been implemented and will be used in future runs.

Characterization studies of melter effluent emissions and off-gas system performance were conducted on the RLFCM during production of isotopic heat sources for the FRG. During spike feeding of the melter, melter feed entrainment losses were found to be much greater than anticipated based upon past nonradioactive testing. Melter decontamination factors (DF) for both ^{90}Sr and ^{137}Cs were both a factor of 10 lower than cold-test predictions for normal feed processing conditions.

3.3 INTRODUCTION

Since 1973, the liquid-fed ceramic melter (LFCM) process for converting high-level liquid wastes (HLLW) to borosilicate glass has been under development and testing in the United States. Its early success and inherent simplicity led to its adoption as the reference HLLW vitrification process in the U.S., Japan, and the FRG. Currently the LFCM is the Department of Energy's (DOE) reference process for planned defense and commercial nuclear waste solidification facilities, including the West Valley Demonstration Project, the Hanford Waste Vitrification Plant (HWVP), and the Defense Waste Processing Facility (DWPF) at Savannah River. Because of the LFCM's wide acceptance as the reference waste vitrification process in the U.S., the DOE requested that PNL design, construct, and operate a prototypical radioactive pilot-scale waste solidification facility employing the LFCM process. Pilot-scale radioactive testing is necessary to provide the design and operating data that can be applied to production-scale projects. The RLFCM equipment was installed in FY 1984 (Burkholder and Rusin 1985), and underwent shakedown testing in FY 1985 using increasing levels of activity in each test. In FY 1986 preparation of isotopic heat sources for the FRG was begun. These heat sources use ^{90}Sr and ^{137}Cs as the active isotopes in borosilicate glass.

3.4 GENERAL SYSTEM DESCRIPTION

The pilot-scale RLFCM is a radioactive testing facility consisting of a vitrification system and supporting equipment systems for preparing liquid waste and treating off-gas and condensate. Figure 3.1 depicts the vitrification system, which consists of an RLFCM, a canister-positioning turntable, and a glass-level detection system.

Radioactive waste slurries are prepared by blending radioactive waste and glass-forming chemicals in the waste preparation equipment. They are fed from a feed makeup tank to the RLFCM using a slurry feed system. In the RLFCM the liquid waste is dried and melted to form a borosilicate glass. The bulk glass

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FIGURE 3.1. Schematic Flow Diagram of the Pilot-Scale RLFCM Vitrification System

entrained particulate, is treated through successive stages of scrubbing, quenching, filtration, and absorption. The decontaminated off-gas is then discharged to the building stack.

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

3.5 TESTING RESULTS - L. K. Holton, N. M. Thomas, R. D. Dierks, R. W. Goles J. E. Surma, and F. A. Graf, Jr.

3.5.1 Feed Tank Agitators

The pulse-agitation concept was selected originally for feed tanks TK-130 and TK-131 because it can homogenize slurries with a high solids content better than mechanical agitation. Due, however, to the continued unreliability of the pulse agitator, a mechanical agitator was installed in feed tank TK-131.

Pressure to the pulse drive cylinders is regulated and can be adjusted to deliver varying lengths of pulser strokes. Longer strokes provide superior mixing, but the increased volume of displaced air associated with such strokes results in larger fluctuations of pressure in the feed tanks. As a result, the pulser strokes are adjusted so that positive pressures are not attained in the feed tanks. Because of the limited vacuum available to the feed tanks, the pulse-agitation air cylinder was restricted from making a full-length stroke. The designed volume of liquid was therefore not drawn into the pulser tube and expelled back to the tank during each cycle. This decreased displacement lessened the effectiveness of the pulse-agitator system. Specific gravity indications taken during the test indicate that at cycle times $\leq 5.25/\text{min}$, the specific gravity was constant.

To improve reliability, the pulse agitator for TK-131 was replaced with a mechanical agitator. The feed tanks (TK-130 and TK-131) had been designed for pulse agitation; the configuration, consequently, is not optimum for mechanical agitators. Because of the limited duration of RLFCM-6, too few TK-131 samples were taken to assess the adequacy of mixing. As the specific-gravity dip tube leg was plugged during the entire time, a comparison through this method is not possible. Greater than anticipated amounts of heat were generated by the agitator. The agitator was run during RLFCM-6 at ~1-hr intervals for periods of ~5 min. At this frequency it was possible to maintain desired temperatures in TK-131. The intermittent operations of the mechanical agitator ultimately led to its failure.

Multiple startups impose a shock load on the agitator due to the settling of slurry solids. If much time elapses between agitator operations, the shock load may cause the grip spring assembly (Figure 3.2) to slip. To eliminate this problem, a variable-frequency controller has been purchased that will

FIGURE 3.2. Grip Spring Assembly

permit the speed of the agitator to be controlled. This may allow for continuous operation of the agitator, and thus eliminate the multiple startups and prevent future agitator failures due to slippage of the grip spring assembly.

3.5.2 Air Displacement Slurry (ADS) Pump

The air displacement slurry (ADS) pump has been used exclusively during RLFCM operations.

Operating experience with the ADS pump was gained during shakedown testing of the RLFCM system in the RLFCM-5 and -6 Runs. During these tests, constant-pressure control was found to provide larger and more stable feed rate than constant-volume control of the ADS pump. Several control parameters were examined during testing to characterize this system under conditions of low feed-flow rates. Discharge pressure had the largest effect on the feed rates. In general, air pressure of between 5 and 7 psig, and pump discharge cycle times of between 4 and 6 sec were found effective in controlling flow rates in the desired range of 15 to 20 L/hr. Discharge cycle time had no effect on the feed rate. Feed tank volume affected the feed rates only when the liquid level in the tank dropped below the top of the pump chamber, which corresponds to a tank volume of ~400 L.

The ADS pump was operated for a total of 193 trouble-free hours during RLFCM-7, which summed with the previous time on this pump totals to 508 hr. The one incident of feed-line plugging during RLFCM-7 was attributed to operational error.

The ADS pump for the RLFCM system in B-Cell is operated with a constant-pressure air-supply system. With this system the pump performance is a function of the feed tank head, the pump chamber fill time, the chamber pressurization time, and the rheological properties of the feed slurry. Although data are limited for evaluating the pump performance as a function of these parameters, analysis showed general trends that will be verified with further operation.

Figure 3.3, showing data from pump operation with a 350-g/L slurry, illustrates the general trend correlating pump performance with feed tank head. It is seen that the tank head generally has limited effect on pump performance

FIGURE 3.3. Effect of Tank Head on ADS Pump Performance

when the volume of the feed tank exceeds 600 L. The feed rate data represented in the figure corresponding to tank volumes above 750 L are lower because other parameters affecting pump operation were changed. The lowered feed rate at volumes below 600 L was due to decreased tank head. The top of the pump chamber is approached at a tank volume of 500 L, and any further reduction in volume results in decreased flow rates. When the level of slurry in the feed tank drops below the top of the pump chamber (see Figure 3.4), the chamber is only partially filled during the chamber-filling phase of the pump operation; therefore, the feed rate is correspondingly reduced. After evaluating the pump's performance with respect to tank head, it has been concluded that the pump should be operated further with feed tank volumes above 500 L. This should avoid the need to compensate for the deteriorating pump performance as is required at volumes of <500 L.

FIGURE 3.4. ADS Pump Chamber with Tank Volumes Corresponding to Top and Bottom of the Chamber

Pump chamber discharge time has until now been the primary control parameter in operation of the B-Cell ADS pumps. Figure 3.5 presents roughly the observed effect of the discharge time on the flow rate with air supplied to the pump chamber at 8.5 psig and a chamber fill time of 6.0 sec. The discharge time was changed often, however, during the run; therefore, it is difficult to state anything conclusive regarding the effect of this parameter on the pump's operation.

FIGURE 3.5. Effect of Chamber Discharge Time on Pump Performance

3.5.3 Batch Denitration

The cesium and strontium feed stocks to be used in preparing the FRG canisters were determined to be too dilute and required concentration.

Laboratory-scale tests involving mock isotopic solutions were performed to verify the feasibility of concentrating the simulated waste. The results of the laboratory-scale boildown effort were unexpected. Significant quantities of barium, sodium, lead, and strontium salts precipitated out of solution well before the target composition could be met. The cause of precipitation was later found attributable to the high concentration of nitrate in solution. The tests showed that the conventional approach to boildown could not be used and that a different method would need to be developed. The method selected, again based upon laboratory tests with simulated waste, was to treat the semiconcentrated waste solution with formic acid and then boil it down additionally to

remove any residual formic acid. The impact on the overall time schedule was seen as minimal (4 days more during waste concentration). This method of destroying free acid in nitrate solutions offers many comparative advantages:

- does not add cations to solution
- produces gaseous reaction products (NO_x , CO_2 , H_2O)
- does not contribute to liquid volume
- reaction is vigorous, but controllable.

The reaction rate is also much faster and more efficient compared to other denitration methods (i.e., sugar or formaldehyde).

Production of the waste product is keyed on repeated blending, denitration, and volume-reduction activities. The general sequence followed is discussed below. First, cesium and strontium solutions are transferred to the in-cell utility tank (TK-112), where they are mixed. The entire contents of TK-112 are then transferred to the evaporator tank (TK-113), where an initial boildown is done to increase the acid concentration, followed by the addition of formic acid to drive off excess nitric acid and by a final boildown to the desired final volume. Each batch of preblended cesium-strontium waste (equivalent to 330 reference liters) was treated with 53 L of formic acid added at a rate of 0.25 to 0.30 L/min. The reaction proceeded evenly at this rate of addition, with no observable pressurization of the reaction vessel. The cycle is repeated again, with the second-generation waste product jetted to an in-cell storage location.

A total of nearly 4.5 MCi of waste was prepared as a result of the activity. Aside from the total amount of waste prepared, the crucial ^{137}Cs and ^{90}Sr isotopic ratio came very close to the target value of 2.30, the proportion believed to be most economical and to meet the heat and dose requirements for the FRG glass. A sample analysis received on one of the earliest waste batches was used to confirm the accuracy of the storage vessel radioinventories; the results agreed to within $\pm 5\%$ of expected ^{137}Cs and ^{90}Sr concentrations based on tank dropout.

3.5.4 Melter Instrumentation

Instrumentation to monitor and control the melting process includes thermowells for monitoring temperatures and pneumatic dip tubes for measuring glass level and specific gravity.

The thermowells and dip tubes had corrosion problems; Inconel®-690, used in these components, is susceptible to corrosion from the current glass formulations. The old thermowell and thermocouple bundle removed from Nozzle-E was ~11 in. shorter than its original length, with all indications that the bottom 11 in. had simply dissolved in the corrosive glass.

The Nozzle-H thermowell, which had monitored the glass-side surface temperature of the south electrode, was removed. This thermowell and thermocouple assembly was also shorter (9-1/2 in.) than its original length, again with all indications that the bottom 9-1/2 in. had dissolved in the glass.

The Nozzle-G weight-factor/specific-gravity dip tube assembly was replaced with a new assembly. Visual appearances suggest some corrosion of the high-pressure dip tube at the glass surface and some shortening of the low-pressure specific-gravity dip tube, which is at the 10-in. level, very close to the glass surface.

One dip tube failed about 12 days after installation. While the dip tube assembly has not yet been removed for examination, it is expected that the failure will be attributed to loss of the internal weldment shown in Figure 3.6A. For this reason, the replacement unit was redesigned with a primary external weldment and an internal seal weld as shown in Figure 3.6B.

The Nozzle-E thermowell protecting the thermocouples that monitor glass temperature in the melter tank was removed and replaced with a new unit 1 in. longer than the original one. The thermocouple array in the new thermowell had been redesigned to monitor the temperatures at levels 0, 5, 8, 10, 15, 18, and 34 in. above the metal floor. The thermowell is positioned in the 1-in.-deep free-metal trough in the center of the metal floor, and the 0-in. thermocouple is level with the floor of the melter. This temperature sensor will be used to monitor the floor for power skewing through possible free metal accumulations.

®Registered trade name of Huntington Alloys, Inc., Huntington, West Virginia.

Original Design

A

Modified Design

B

FIGURE 3.6. Dip-Tube Base Plate

The 5-, 8-, and 10-in. level sensors will be used to determine the average temperature of the melter tank glass. The 15- and 18-in. sensors will be used for information on cold cap and foaming. The 34-in. level sensor will provide plenum temperature data.

3.5.5 Electrical Power Control

Three modes have been devised for controlling electrical power to the melter. To date, resistance feedback has been used during the production runs of the RLFCM. Resistance feedback with a glass weight factor correction was configured on the distributed control system but was not used during melter operation. Temperature feedback control has been implemented and will be used on future runs.

3.5.5.1 Resistance Feedback

Resistance feedback control is attractive because, within the normal operating temperature range, the glass resistivity is approximately inversely proportional to the glass temperature. For example, as the glass temperature drops due to changes in feed rate, the resistance increases and the controller demands more power to bring the temperatures back into range. Resistance feedback control has worked well when glass is poured continuously from the melter. A drawback, however, is the fact that when the melter is operated in a batch-pour mode, changes in glass level change the resistance through the glass, causing unnecessary fluctuations in power to the melter.

Batch glass transfers from the melter generally result in rapidly increased melter tank resistance values because of the rapid decrease in the cross-sectional area of the electrical current path through the glass. The constant-resistance power control system interprets these and any other resistance value increases as a decrease in glass temperature, and executes a power increase proportional to the magnitude of the resistance increase, which results in a glass temperature increase. As glass temperature increases, the resistance drops to the controller set point and the power returns to the level dictated by the existing slurry feed rate. Because of the speed with which the glass is usually transferred, the resistance change is essentially a step function and this, combined with the 3 to 4-hr time constant of the temperature

control system, generally results in a power surge for 2 to 3 hr, with possibly some overshoot of the resistance set point. However, the temperature rarely exceeds its upper limit value unless the temperature was already near its upper limit when the glass transfer began. Generally, if left alone, the resistive feedback power control system can handle glass transfers without excessive excursions in glass temperature. From this, the importance of minimum interference with operation of the power control system becomes clear.

3.5.5.2 Resistance Plus Weight-Factor Correction

The control strategy (Figure 3.7) consists of factoring the melter resistance control output signal with the weight factor for the glass as follows:

$$\text{ohms} \times \left(\frac{\text{WF}}{30}\right)^{\text{exp}}$$

This strategy will compensate for the resistance control loop's tendency to call for more power when the glass level drops. (The drop in level is sensed as an increase in melter electrode resistance, which results in more power and an unwanted increase in glass temperature.)

The factoring of the signal will compensate for this problem. Before this approach could be implemented, however, there had to be in place sufficient conditioning of the weight-factor signal so that a bad signal would not drive the electrode power wild.

The control strategy was set up so that only legitimate weight factors of 15 in. or more are accepted. Sudden changes in weight factor due to transmitter calibration will automatically latch off the weight-factor correction factor. The only exponents accepted are between 0 and 0.4. This also excludes negative exponents that would create a reverse effect.

The weight-factor correction can also be operator-selected so that during shutdowns (melter idling conditions) the correction factor can be locked out of use.

FIGURE 3.7. Melter Power Control Strategy

3.5.5.3 Temperature Feedback

It has been decided that the B-Cell melter power control will be switched from resistance control to temperature control using the Micon® process controller. The major problem with temperature control is the reliability of the thermocouples and their location within the molten glass in the melter.

The control approach is summarized in Figure 3.8. The T_{15} refers to the thermocouple at the 15-in. glass level; likewise, T_5 , T_8 , T_{10} , and T_{18} refer to thermocouples at their respective depths. T_{avg} is the averaged temperature from up to three selected thermocouples. T_{avg} is calculated from acceptable thermocouples (those that are $>1000^{\circ}\text{C}$ and $<1250^{\circ}\text{C}$). Also, each of the three thermocouples (T_5 , T_8 , and T_{10}) can be selected by the operator.

FIGURE 3.8. Melter Temperature Control Strategy

If the thermocouple drops below or goes above the acceptable range momentarily, a latch is actuated to hold it out of the calculations to obtain T_{avg} . The Micon then calculates the average from the remaining two thermocouples. A reset must then be used to manually reset the thermocouple back into use if it has returned to within the acceptable range. Otherwise, the thermocouple will not be accepted and used to calculate T_{avg} .

T_{avg} will be set up to respond to any of the following alarm points:

- alarm only at 1200°C and flash "HIGH TEMPERATURE" warning
- alarm and switch the Micon to manual model at 0% output at 1225°C
- alarm and switch off the bias power for full shutdown of power at 1240°C.

The T_{avg} is used as the feedback signal to the power controller. With either one, two, or three "good" thermocouples, there is no problem except what is expected to be a somewhat variable temperature control with only a single active thermocouple due to local moving temperature gradients within the mass of glass.

If no thermocouples are acceptable, the Micon will switch from automatic to manual model and zero output so that only the bias power is still applied to the melter. To finish a run after losing all three thermocouples, an operator-selectable override on the zero output in manual will allow one to run in manual and to enter a selected output.

The high amps interlock was changed to actuate at 1000 amps maximum instead of the 1220 amps previously used.

The thermocouple locations that were averaged for T_{avg} were agreed to be at 5-, 8-, and 10-in. glass levels.

There are several other initiations of alarms only for warnings and special messages. They are:

- T_{15} high-temperature alarm at 1200°C. Message "POSSIBLE FOAMING" to be displayed.

- T_{18} rate of change plus high-temperature (1200°C). "FOAMING" message.
- Weight-factor change. "FOAMING" message.

Graphic displays of control strategy status at all times will be used maximally to simplify this approach. The initial tests were positive, confirming the initial assignments of the tuning constants. However, the normal fluctuation of the glass temperature indication is due to convection currents in the glass, with a constant power input average about $\pm 25^\circ\text{C}$. With automatic control, this fluctuation remains about the same, but the power input fluctuates about ± 5 kW, which is not desirable. Testing is currently in progress to utilize digital filtering to smooth the 40- to 60-min temperature cycles that are noted in the average temperature indications.

3.5.6 Off-Gas System

The RLFCM off-gas system consists of an ejector venturi scrubber (EVS), packed bed scrubber, condenser, evaporator, evaporator condenser, fractionator, fractionator condenser, off-gas heaters, in-line high-efficiency particulate air (HEPA) filters, and packed bed scrubber. Additional off-gas treatment is provided by maintainable HEPA filters. This off-gas system was designed to meet the radionuclide emissions specified in DOE Order 5480.1. The NO_x concentration from the 324 Building stack is controlled to <4% in accordance with district regulations on NO_x emissions.

3.5.6.1 Off-Gas Line Plug

At the end of a melter run with spike slurry, the primary 4-in. off-gas line between the melter cavity and the ejector venturi scrubber became plugged. The plug was sufficiently solid that all attempts to free it or to draw more vacuum through any existing off-gas orifice were unsuccessful.

A temporary off-gas line was subsequently fabricated and installed that allowed venting of the melter to Rack 1A. This precautionary measure was necessary to ensure that the RLFCM would maintain system vacuum while the existing off-gas jumper was being removed. This action was designed to help preclude venting of the melter to B-Cell which, in turn, could have led to dose buildup on the building A-frame filters.

The old off-gas line was then removed and taken to the north cell window, where it was inspected. The RLFCM side of the off-gas line showed large chunks obscuring almost all of the 4-in. opening. The flange surface on the melter itself was likewise covered with solid material, requiring manual removal before the new off-gas line could be installed. Once the restriction had been cleared from the melter flange, a new 4-in. flex off-gas line was installed and the temporary jumper from the melter to 1A rack removed.

A sample of the material that blocked the off-gas jumper between the melter and the EVS was analyzed during the current report period. The material collected appeared quite porous, much like pumice. The porosity of this deposit arises from revolatilization of condensed compounds of boron, which produces the observed sample matrix voiding. The composition of this off-gas line deposit, as summarized in Table 3.1, further supports this supposition in that boron is found to be a major elemental constituent. On the molar basis, the off-gas plug contains twice as much boron as cesium and sodium--the other two major elemental constituents. The 2:1:1 molar ratio between boron, cesium, and sodium suggests that the deposit may be essentially composed of alkali metaborates (MbO_2) rather than the oxide composition assumed in Table 3.1. However, since the sample was not dried before analysis, neither assumption--the metaborate or the oxide composition--accounts for all its mass. The deposited material will be further analyzed soon to elucidate its composition.

3.5.6.2 Off-Gas Reamer

An off-gas line reamer is being developed to remove deposits in the off-gas line between the melter and the EVS. The reamer, which has undergone various changes throughout the design phase, is shown in Figure 3.9. It will have four stainless steel (SS) chains connected to a 1-in.-dia SS shaft. The reamer will be fabricated primarily from 304L SS. The two bushings for radial stabilization and a thrust bearing for axial support are to be fabricated from high-grade graphite. The reamer will be powered by a 0.7-hp air-driven motor.

To observe operation of the reamer, a mock off-gas line was constructed with critical dimensions matching those of the actual melter off-gas line. The

TABLE 3.1. Composition of Off-Gas Line Plug

<u>Element</u>	<u>Oxide, wt%</u>	<u>Normalized, wt%</u>
Al	0.27	0.33
B	20.0	25.0
Ba	0.29	0.35
Ca	0.71	0.87
Cr	3.4	4.1
Cs	44.0	54.0
Fe	0.5	0.61
K	1.7	2.1
Li	0.08	0.1
Mg	0.29	0.35
Mn	0.06	0.07
Mo	0.1	0.12
Na	9.5	12.0
Ru	0.11	0.13
Si	0.52	0.64
Sr	0.02	0.02
Zn	0.37	0.45

Wt% Normalization Factor: 81.86

<u>Derived Values or Parameters</u>	<u>^{137}Cs</u>	<u>^{90}Sr</u>
Sample Activity, dpm/g	2.38E+13	5.84E+09
Sample Curie Loading, Ci/g	10.72	2.63E-03
Isotopic Mass Loading, g/g	0.124	1.91E-05
Isotopic Oxide Loading, g/g	0.131	2.25E-05
Total Mass Loading, g/g	0.413	5.61E-05
Total Oxide Loading, g/g	0.438	6.63E-05
Assumed Isotopic, wt%	30	34

Radiochemically derived oxide wt% of strontium: 8.10E-03

8606758-2cn

FIGURE 3.9. Off-Gas Line Reamer for RLFCM

most important operational characteristic observed during testing of the prototype was the adequacy of contact between the chains and the wall of the off-gas line. For effective removal of deposits, the chains must not only contact the wall with sufficient force, but also most of the inner surface of the line through which the reamer extends.

It was determined that the optimum rotation of the reamer shaft lies between 150 and 200 rpm. At this speed the reamer adequately removes deposits with minimal wear to the chain. Figure 3.10 shows the reamer's performance when tested with a cast annulus of Alfrax-57® material. Mechanical characteristics of the Alfrax such as hardness are expected to be much more severe than

FIGURE 3.10. Performance of Reamer with Alfrax-57

®Registered trade name of the SOHIO Engineered Materials Co., Niagara Falls, New York.

those of the entrained material in the off gas; therefore, the performance in the actual off-gas line is expected to be improved over that shown in Figure 3.10. If a conservative value for a melter decontamination factor (DF) of 300 is considered and the maximum feed rate of the melter is assumed to be 30 L/hr, then it is calculated that solids would become entrained in the melter off gas at ~0.06 g/min when processing the FRG feed. From Figure 3.10 it is seen that the reamer would have to operate continuously at low rpms or intermittently at higher rpms to prevent buildup of material in the line. To reduce wear to the chains, it is expected that the reamer will be operated continuously at a lower speed, although the exact operating schedule has not yet been determined.

All tests thus far indicate the reamer will aid greatly in removing RLFCM off-gas line deposits and should allow melter operation without off-gas line plugging.

3.5.6.3 Off-Gas System Performance

Performance data for the off-gas system were collected during the RLFCM shakedown testing and during the spiked-feed phase of RLFCM-7.

Off-gas data obtained during shakedown testing are described in the RLFCM-5 and -6 Run Summary. Data on off-gas system condensate, obtained as part of RLFCM-5, indicate that at a minimum DFs of 21 for cesium and 230 for strontium can be expected from the RLFCM. Direct sampling of the off-gas stream immediately after the melter indicated a DF of 62 for cesium and 980 for strontium. Decontamination factors for the EVS were estimated to be 33 for strontium and 4.2 for cesium. These DFs compare favorably with results from the pilot-scale ceramic melter (PSCM) system and indicate that the existing off-gas treatment system will be effective in containing cesium and strontium aerosol losses to process vessels.

An empirical evaluation of the emission characteristics of PNL's RLFCM and the performance of its exhaust system quench scrubber, an EVS, was completed. This evaluation was based on the first part of the RLFCM-7 processing campaign, which was designed to produce ten isotopic heat sources for the FRG. Specifically, these heat sources are canisters of RLFCM-produced glass, each of which

contains 210 kCi of ^{137}Cs and 160 kCi of ^{90}Sr . Two separate processing phases were evaluated during RLFCM-7. To quickly bring up melter glass activity to design levels, the melter first processed highly concentrated ^{137}Cs and ^{90}Sr loaded feed. Once the desired glass loading of these isotopes was achieved, melter feeding resumed with cesium and strontium concentrations reduced by 67%. Off-gas samples were collected during both of these processing modes as is discussed below.

Melter emission and off-gas component performance is commonly expressed in terms of a unitless DF. By definition, a feed component DF is the ratio of the rate at which that particular feed component enters a device to the rate at which it exits. Consequently, melter DFs are related to the liquid-fed melter process efficiency ($1-1/\text{DF}$) for converting feed components into a borosilicate glass. Similarly, the DFs associated with off-gas system components are measures of their scrubbing efficiencies for various airborne effluents. Table 3.2 presents RLFCM-7 melter and venturi scrubber DF performance data for the two processing modes studied. Also in this table for comparison are average results derived from a previously completed cold test (PSCM-20), which served to provide baseline data and performance expectations for subsequent RLFCM operations.

During spike feeding, gross feed entrainment was the primary mechanism for melter off-gas system effluent losses. This is clearly illustrated by the fact that nearly all feed components exhibited similar DFs, which were nominally the same as the total overall melter DF value of 30. To put it another way, during RLFCM-7, gross feed entrainment was as important as the volatilization loss mechanism in determining overall melter effluent losses. Of the off-gas effluents characterized, only ruthenium--which can be, and apparently was, strongly evolved as a gas during LFCM process--exhibited higher melter emission rates.

The high rate of effluent loss due to process exhaust feed entrainment is not a typical melter emission characteristic, as the PSCM-20 comparative data in Table 3.2 illustrate. Normally melter feed component DFs for volatile and semivolatile components differ markedly from those of nonvolatile constituents.

TABLE 3.2. Melter and Off-Gas System Decontamination Factors

Element	Spike Feeding DF				Normal Processing DF			
	Melter		Venturi		Melter		Venturi	
	RLFCM-7	PSCM-20	RLFCM-7	PSCM-20	RLFCM-7	PSCM-20	RLFCM-7	PSCM-20
Al	36	2600	1.2	20	53	1900	17	110
B	23	27	3	7	12	55	89	2
Ba	25	700	1	15	28	1800	14	35
Ca	20	270	1.2	12	14	150	10	32
Cr	5	52	1	29	8	280	2	5
Cs	28	22	1	4	10	140	3	2
Fe	61	2300	1	5	--	2800	--	100
La	55	4300	1	19	110	1500	--	720
Li	34	--	1.1	--	--	--	--	--
Mg	21	680	1.2	18	17	290	11	100
Mn	52	1500	1	24	21	1300	70	96
Mo	20	--	1	--	--	--	4	--
Na	25	130	1.2	7	30	370	9	4
Nd	61	3100	1.1	49	190	1800	--	460
Ni	66	1700	1	10	100	1800	--	33
Ru	11	330	1	6	--	--	--	2
Si	40	1700	1.7	6	590	1400	7	19
Sr	50	500	1	22	130	1200	72	44
Ti	65	--	1.2	--	--	1800	--	--
Zn	53	--	1	--	11	--	--	--
Zr	--	14000	--	--	4	33000	--	--
Total	30	100	1	2.5	50	640	5	2.4

This was the case during PSCM-20, but is clearly not true for the RLFCM-7 spike feeding campaign. Since cesium melter losses are usually dominated by a volatilization/condensation mechanism, the increase in entrainment losses did not significantly influence cesium melter DF during spike feeding, as is shown in Table 3.2; however, strontium losses were a factor of 10 higher than was anticipated based upon previous cold testing data.

Melter performance during normal RLFCM-7 feed processing was much poorer than had been achieved during the analogous PSCM-20 cold-testing experiment. RLFCM feed component DFs are, with few exceptions, a factor of ~10 less than achieved then. There appears to have been slightly less feed entrainment loss during normal RLFCM-7 processing than observed during earlier spike feeding; however, overall loss rates were still much higher than previous testing would have predicted. Specifically, isotopic losses of both ^{90}Sr and ^{137}Cs exceeded expectations by an order of magnitude during normal feed processing. This finding is further corroborated by the buildup of activity of ^{137}Cs in the EVS scrub liquor. The steady-state concentration of this isotope, achieved during normal feed processing, indicated a melter cesium DF of 10, which agrees with the off-gas sampling data in Table 3.2.

The behavior of the RLFCM's quench scrubber, an ejector venturi scrubber, during RLFCM processing of FRG waste is ambiguous. During RLFCM-7 spike feeding, the EVS performed so poorly that its usefulness was seriously questioned. Since melter entrainment losses during spike feeding were quite high, one would expect a rather high EVS scrubbing efficiency rather than a low one. The use of scrubbing liquor flow to control melter vacuum may have been responsible for the loss of EVS off-gas processing performance; however, any explanation now for this result would be speculative.

In contrast to the spike-feeding behavior, EVS performance during normal melter feed processing was higher, overall, than had been achieved under cold simulation testing. More importantly, greater cesium and strontium DFs were achieved during RLFCM-7 than during the analogous phase of the PSCM-20 experiment. From the limited off-gas data that exist, it appears that the EVS performed well within design expectations during routine melter processing conditions.

The noncondensable exhaust of the RLFCM was also analyzed during FRG feed processing. Since the manufacturer had not yet completed installation of the RLFCM gas mass spectrometer, specific gas analyzers for CO , CO_2 , and NO_x were used to accomplish this analysis. The CO and CO_2 analyzers were used to directly sample the undiluted, quenched process exhaust stream. The NO_x

analyzer, a pressurized instrument, sampled the process exhaust at the stack only after process dilution. The results obtained are: CO <0.005%, CO₂ ~0.5%, and NO_x ~0.9%.

The CO monitor was utilized also to measure the total noncondensable process off-gas flow rate through tracer-gas dilution techniques. CO was injected into the process exhaust at a fixed flow rate upstream of the F-112 in-cell filter, where the process gases were being sampled. The resultant CO concentration was then related to the off-gas flow rate at that point. At the operating melter vacuum of 5 in., the inleakage-dominated process flow was measured to be 20 scfm. This flow was very consistent throughout the processing period associated with the production of the first three FRG canisters. This flow-measuring capability was also used subsequently to adjust the idling exhaust rate during replacement repairs following melter overflow.

3.5.7 Glass-Level Detection System

During shakedown testing, the glass-level detection system (GLDS) was calibrated for the FRG canisters. The tests showed also that the level-detection system can be used as a diagnostic tool to detect nesting and pillaring of glass in the canisters. These results are discussed in more detail in the RLFCM-5 and -6 Run Summary.

The canister GLDS performed flawlessly during RLFCM-7. As in previous RLFCM testing, the system response to the in-cell transmission source was used as the primary means of determining canister glass level and the extent of canister cross-sectional fill.

In addition to these tasks, the GLDS provided the means by which the FRG canisters were reproducibly filled. To ensure that canisters were filled to at least 95% of their internal volume, the level corresponding to the 85% fill mark was monitored continuously by the level system during the final glass transfer. When a full level response was detected at this monitoring point, two additional liters of glass were transferred to the canister before pouring was terminated in order to compensate for shrinkage of glass. The actual fill level achieved was then determined through a depth gauge measurement during loadout.

Although not used during the filling of the first three FRG canisters, the system's ^{90}Sr response was recorded and has been subsequently evaluated. The results of this evaluation have shown the radioactive cesium in the glass to be an adequate indicator of glass level; however, scattered radiation from the ^{60}Co transmission source requires that net rather than gross ^{137}Cs activity be recorded. Since net results were not collected, the ability of the GLDS to use in-situ glassified radioactive cesium to determine the extent of canister cross-sectional fill could not be determined from RLFCM-7 data. This potential will be fully evaluated during the remainder of the RLFCM-7 processing campaign.

Functional testing of the RLFCM canister-level detection system continued. A +0.02-in./pass creep in source positioner zero had been observed during the RLFCM-7 test. To date, the exact source of this problem remains unsolved. Several studies have been completed to resolve this problem and are summarized below:

1. The bi-phase encoder output was studied. The results indicate no observable problem with signal integrity or phase relationship.
2. The encoder register up/down count inputs were studied (observing oscillation of the source carrier screw, while decelerating in particular). The results indicate that the average sum of the algebraic counts/pass agreed with the specified amount within 0.01-in./pass. Encoder electronics appear functional.
3. The major controller output up/down counts were studied. On an average of six passes, the total number of counts from the lowest to highest position of the source translation was equal to 0.0125-in./pass less than if it were not encoder-based.

The results of these studies would seem to indicate that the creeping from pass-to-pass is not likely to be caused by the electronics. Some possibility exists that an encoder plate is slipping slightly (in relation to the screw to which it is attached).

3.5.8 Canister Contamination

Studies are under way to assess contamination levels within the canister turntable and on the canisters themselves.

During shakedown testing, stainless steel coupons were placed inside and outside a canister to determine contamination levels in the canister throat and in the turntable. A comparison of the radioactivity poured into the canister versus the observed contamination on the coupons indicated that the radionuclides (^{137}Cs and ^{134}Cs , ^{154}Eu , $^{106}\text{Ru}/^{105}\text{Rh}$, and ^{125}Sb) are not readily volatilized during glass pouring. The magnitude of the cesium contamination was surprisingly similar for the coupons inside the canister and in the turntable plenum.

Additional tests are planned for the FRG canister production campaign. Three canisters will carry small stainless steel coupons during RLFCM-7. Each canister overpack will be equipped with coupons on the ears of the canister cover and with coupons suspended from a hook assembly hung from the auxiliary overpack lifting ear. These coupons will be used to model the canister's horizontal and vertical surfaces, respectively, during glass pouring. Information obtained from the coupons will be used to identify those contaminants to which canisters are most susceptible.

3.6 REFERENCE

Burkholder, H. C., and J. M. Rusin, compilers. 1985. Nuclear Waste Treatment Program, Annual Report for FY 1984. PNL-5414, Pacific Northwest Laboratory, Richland, Washington.

4.0 A-CELL FACILITY PREPARATION

G. H. Bryan - Manager

4.1 OBJECTIVE

The objective of the A-Cell Facility Preparation Task is to provide a decontamination, characterization, and storage facility (DCSF) for radioactive canisters of glass produced during operation of the radioactive liquid-fed ceramic melter (RLFCM).

4.2 SUMMARY

A necessary component of the RLFCM Program is the capability to decontaminate, characterize, and store canisters filled with vitrified product in preparation for shipment. Equipment to be installed in A-Cell and the air lock to provide a DCSF includes: 1) leak-testing equipment to check for complete closure of the canister; 2) a system to measure surface radiation dose rate; 3) an electropolishing unit to remove contamination not removable by the high-pressure water/steam spray; 4) gamma-scanning system for determining homogeneity; 5) a gauge for checking maximum diameter and straightness of canisters; 6) equipment to measure surface temperature; 7) a load cell to determine canister weight; 8) a system to determine surface contamination; and 9) water-cooled storage racks. Some of this equipment is being bought and modified for remote use while some requires design and fabrication.

4.3 INTRODUCTION

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

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

Decontamination, characterization, and storage of the canisters of waste glass are necessary components of the RLFCM program and have been assigned to the A-Cell Facility Preparation Task within the Nuclear Waste Treatment Program. This activity will require the use of hot-cell space because the glass will contain large quantities of radioactivity. The 324 Building's A-Cell, adjacent to B-Cell where the RLFCM is located (see Figure 4.1), is a logical choice. Cleanout and renovation of A-Cell have been necessary to make space available, as the cell contained obsolete equipment used in previous programs. Extensive radionuclide decontamination of the cell was necessary to ensure that canisters decontaminated for shipment are not recontaminated.

4.4 EQUIPMENT DEVELOPMENT, DESIGN, AND FABRICATION - B. G. Place, R. P. Allen, and D. N. Berger

The design philosophy of the A-Cell decontamination, characterization, and storage facility was to ensure that it would have general applicability to the Nuclear Waste Treatment Program in order to meet the anticipated requirements of present and future waste programs. A-Cell facility design criteria have attempted to meet the characterization needs of waste canisters based on both the U.S. acceptance criteria and the needs of the Federal Republic of Germany (FRG).

The A-Cell Facility Preparation Task is to prepare a facility that will decontaminate, characterize, and store stainless steel canisters filled with radioactive glass. The task requires that the facility be operated remotely. The method selected to decontaminate the canisters is electropolishing, and the facility has been designed to electropolish single canisters in a batch operating mode. Auxiliary facilities are provided for characterization and storage of the canisters. The electropolishing system and most of the characterization equipment have been designed to accommodate canisters of varying size. The storage facilities have been designed specifically for the FRG canisters. Figure 4.2 depicts the steps required for the decontamination, characterization, and storage of the canisters.

84027-03-1cn

FIGURE 4.1. Radiochemical Engineering Cells in 324 Building

FIGURE 4.2. Necessary Steps To Decontaminate, Characterize, Store, and Ship Canisters

The electropolishing facility consists of the following major systems: electropolishing; rinse/soak; recirculation; vessel ventilation; and electrolysis power supply, electrodes, and switching. All of these systems are integral with the electropolishing rack, which is shown in Figure 4.3. The operation of each system is discussed below.

4.4.1 Electropolishing System

The electropolishing system consists of an electropolishing tank (EPT), which is provided with heating and cooling facilities; filling and emptying facilities; and instrumentation to monitor solution temperature, level, and specific gravity. The principal function of the EPT is to carry out the electropolishing of the canister by immersion in solution and the application of electric current. A diagram of the EPT is shown in Figure 4.4.

The total volume of the tank is 1100 gal; normal operating volume, however, is 700 gal. The inner wall and piping are constructed of Hastelloy C-276 to resist corrosion from the hot, concentrated phosphoric acid used as the electropolishing solution.

4.4.2 Rinse/Soak System

The rinse/soak system (diagrammed in Figure 4.5) consists of a rinse/soak (RST). A spray ring, located near the top of the RST, will be used to rinse off residual solution. The RST can function also as an immersion rinse tank. The total volume of the RST is 315 gal, but normal operating volume is 210 gal. The RST is provided with heating and cooling facilities; filling and emptying facilities; and instrumentation to monitor solution temperature, level, and specific gravity.

4.4.3 Recirculation System

The principal functions of the recirculation system are to provide agitation of solution in the EPT and to filter particulates out of the solution. The system consists primarily of a pump and a filter. The recirculation system is attached to the electropolishing rack and is connected to the EPT by means of remote jumpers.

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FIGURE 4.3. Electropolishing Rack

FIGURE 4.4. Electropolishing Tank

FIGURE 4.5. Rinse/Soak Tank

4.4.4 Vessel Ventilation System

Both the EPT and the RST are provided with steam spray facilities, which will be used to rinse off canisters. The solutions in the EPT and RST generate fugitive aerosols, which result from agitation and electrolysis. The steam and aerosols are prevented from escaping into the cell environment by the air being drawn through the tank lids into the vessel ventilation system (VVS). The VVS functions to remove moisture and aerosols from the air before expelling the air back into the cell. The VVS consists of condensation and filtration equipment and also includes the blower, which pumps the air through the system. The VVS also is attached to the electropolishing rack and is connected to the EPT and RST by means of remote jumpers.

4.4.5 Electrolysis Power Supply, Electrode, and Switching System

The purpose of the electrolysis power supply, electrode, and switching system is to provide and control the electrical current required for electropolishing. In addition to the power supply, the system includes specialized electrolysis electrodes as well as the switching circuitry necessary to provide the correct electrode polarity during a given stage in the electropolishing process. Two specialized electrodes (diagrammed in Figure 4.6) have been fabricated for electropolishing the canisters. The cathode cage functions as a counter electrode during electropolishing of the sides and bottom of the canister, and as a working electrode contact during electropolishing of the top. The cathode cage also functions to position the canister in the electrolysis bath. The anode grapple functions as a working electrode contact as well as a lifting grapple for the canister.

4.4.6 Auxiliary Equipment for Characterization and Storage

Equipment has been designed for each of the following canister characterization procedures to determine: surface temperature; surface radiation dose rate; gamma ray profile; weight; absence of leakage; absence of significant deformation; and absence of significant surface contamination. The design of the temperature-measurement equipment has been changed from one based on infrared light measurement to one using a contact thermocouple.

FIGURE 4.6. Cathode Cage/Anode Grapple

4.5 AIR LOCK DECONTAMINATION STATION - B. G. Place

The decontaminated canisters may be stored for months prior to shipment. Although every precaution will be taken to protect the canisters from recontamination, the possibility must be anticipated. A decontamination station has therefore been designed to be located in the air lock. This station will function to wash off easily removable fugitive contamination using a hot-water spray. The spray will be used if indicated necessary by the results of smear tests just prior to a canister's insertion into a shipping cask.

4.6 A-CELL LAYOUT - B. G. Place and D. N. Berger

A-Cell is 21 ft wide, 9.25 ft deep, and 34 ft high, with the two shielding windows located one above the other. The second-floor window is provided with two master-slave manipulators for the operation of equipment within the cell, while the first-floor window has only one manipulator. The decontamination and characterization equipment will be located in front of the windows so it can be seen during operation and be accessible to the manipulators and crane. Most operations will take place in front of the second-floor window. The storage rack will be located on the floor of the cell and will be accessible only by use of the crane. A layout of the equipment within A-Cell is shown in Figure 4.7.

4.7 EQUIPMENT TESTING AND EVALUATION - B. G. Place and R. P. Allen

Equipment, services, and instrumentation were tested to assess functionality, perform calibrations, and determine capacities. Dimensions were checked on the EPT and the RST, and the volume capacity of each was determined. Level and specific gravity instrumentation for the EPT and the RST were calibrated. Thermal capacity and calibration tests were performed on the heating jacket and the cooling coils on the EPT and RST. Preliminary functionality and capacity tests were performed on the spray rings in the EPT and the RST. Data from these tests were stored and processed with the use of a MICON® process controller.

The canister surface radiation dose rate will be determined in the air lock by positioning a gamma radiation probe very close to the surface.

The canister gamma ray profile will be determined in A-Cell by a detector outside the cell that measures collimated radiation beam through the hot-cell wall.

Canister weight will be determined in A-Cell using a load cell suspended from the crane.

The leak detection facility will sense a helium tracer gas from a source sealed inside the canister using a mass spectrometer.

The absence of significant canister deformation will be confirmed by insertion of the canister into a cylindrical gauge, which has been provided by the FRG.

To determine the degree of surface contamination, the canisters will be wiped with a cloth swab, which will subsequently be analyzed for radioactive contamination. A swab holder, which can be handled with a manipulator, has been fabricated for this purpose.

The initial application of the decontamination facility in A-Cell involves the electropolishing of 30 FRG canisters. It is anticipated that these canisters will be stored in A-Cell prior to shipment. Each canister will generate about 2 kW of heat due to radioactive decay. Concerns about the effects of this heat generation on the environment of a cell of this size, and also on the longevity of equipment such as the pump and the blower, prompted modification of the canister storage facility design to one in which heat is absorbed by cooling water. The canister storage rack, which has been designed, consists of an array of steel containers enclosed in a water-filled jacket. Decay heat is absorbed by cooling water flowing through the jacket. The containers have lids to protect the decontaminated canisters from fugitive aerosol contamination. This water-cooled storage rack has been specifically designed to store a total of 30 FRG canisters.

FIGURE 4.7. Layout of Equipment Within A-Cell

4.8 FACILITY PREPARATION - G. H. Bryan, B. G. Place, and R. M. Jones

The cleanout of equipment in the A-Cell (location shown in Figure 4.1) required all of FY 1985. As all equipment to be removed from the cell was radioactively contaminated, it was necessary to reduce its size sufficiently to fit into a shielded waste box for transport to the Hanford 200 Area Burial Grounds for disposal.

Decontamination activities in A-Cell were minimal during FY 1986 due to B-Cell and D-Cell activities. The preparation of the RLFCM in B-Cell to produce heat and radiation sources for the Federal Republic of Germany required extensive use of the air lock and available radiation-trained personnel. A-Cell was also needed to remove fuel rods from PWR assemblies in support of the Spent Fuel Operations Task within the Materials Characterization Center. This work was originally scheduled to be accomplished in B-Cell; however, due to RLFCM activities in the cell, time and space could not be made available.

A crane has been purchased that will be installed in A-Cell before any decontamination, characterization, or storage equipment is installed. This crane will have the capability of lifting 10 tons when in A-Cell and the lifting block and trolley are reeved in the proper configuration. The crane will normally be used in a 5-ton configuration. A new crane is required because of a need to keep A-Cell as free of radioactive contamination as possible. The existing crane available to A-Cell is also needed and shared by programs in D-Cell and is highly contaminated. The new A-Cell crane will be used for all movement of canisters once they are decontaminated by the electropolisher. It will be kept in A-Cell until such time as the FRG canisters are ready for shipment to the FRG.

5.0 WEST VALLEY SUPPORT TASK (WVST)

J. R. Carrell - Manager

5.1 OBJECTIVES

The Western New York Nuclear Services Center (WNYNSC) successfully processed commercial nuclear fuel for 5 years and operation was terminated in 1972. Underground tanks at the site contain high-level waste (HLW) produced, in part, by a commercial fuel reprocessing campaign. The State of New York has assumed responsibility for these wastes. The Department of Energy (DOE) is assisting, through the West Valley Demonstration Project (WVDP), in retrieving and solidifying these wastes. The site contractor for the WVDP is West Valley Nuclear Services Co., Inc. (WVNS).

The overall objective of the West Valley Support Task (WVST) is to provide the technical support required by the WVDP, including the transfer of DOE-developed HLW treatment technology. Specific objectives include: 1) designing an acceptable glass-waste form for West Valley waste and providing characterization data that support its acceptability and 2) assisting WVNS with the technology and equipment required to successfully vitrify the West Valley waste. The following sections summarize the FY 1986 activities of the WVST in support of these objectives.

5.2 SUMMARY

The WVST provided significant transfer of technology to the WVDP during FY 1987. Major support was focused on the remote technology design and vitrification process support areas.

Remote technology activities provided key components to the component test stand (CTS), including the V-001 concentrator and off-gas system. A hydraulic study was performed to determine the optimum pipe size for gravity flow in the CTS waste header and transfer line. A preliminary design was prepared for the waste mobilization jumper pit.

Process support includes an investigation of the zeolite ion exchanger after it has been charged with cesium, but before it is incorporated into the melter feed. Sludge-washing effectiveness has been investigated, and the tank wastes have been simulated. The valence state of plutonium has been traced through the waste mobilization steps. The chemistry has been developed to remove the crystalline formations in the 8D4 THOREX tank.

5.3 REMOTE TECHNOLOGY SUPPORT - J. M. Seay, D. N. Berger, B. G. Place, and C. A. Fow

5.3.1 Concentrator Feed Makeup Tank

During the past year PNL provided the remote design of an evaporator/concentrator to process a mixture of HLW and glass formers for the feed slurry to the glass melter as part of the vitrification process.

The concentrator feed makeup tank (V-001) is a major component in the vitrification system, System No. 63, of the WVDP, as shown in Figure 5.1. It receives the HLW from the underground HLW storage tanks on the WVDP site, concentrates this HLW, treats it chemically, and mixes it with other process streams and borosilicate glass formers. The resulting slurry mix is transferred to the feed holding tank before it is fed to the ceramic melter, where it is transformed into molten borosilicate glass and poured into stainless steel canisters for eventual disposal in a national HLW repository.

5.3.1.1 Functions

The concentrator feed makeup tank (V-001) will receive all ingredients required to make the borosilicate glass, including HLW waste from Tanks 8D2 and 8D4, glass formers, and the required amount of nitric acid to partially neutralize or acidify the waste hydroxides. The concentrator tank will also receive recycle from the first off-gas scrubber device or zeolite from supernatant processing, radioactive treatment system (RTS) evaporator bottoms, contaminated decon solution, and other potential recycle streams from within the CTS. The tank will then concentrate its contents to achieve the desired waste

FIGURE 5.1. Component Test Stand Cell

concentration. The concentrator tank is designed to complete this function within an allocated batch cycle time of 100 hr.

The concentrator tank working volume is ~18,000 L (5,000 gal) plus a minimum heel in the bottom of the tank required to maintain a continuous homogeneous mixture and uniform suspension of particulates.

5.3.1.2 Remote Design

The concentrator tank consists of a vessel, 10 ft in diameter and 14 ft high, with remote PUREX nozzles, and three bolt flanges mounted atop it for process piping connections. The bottom of the vessel consists of a 2:1 elliptical head.

The shell, head, and all nonreplaceable internal components of the concentrator will be fabricated from an alloy material. The material will be selected based on corrosion studies now being performed by WVNS. The PUREX nozzle material is ASME SA-351 Grade CD-4Mcu. All other materials are Type 304L stainless steel.

Excess water during concentration is evaporated via heat transfer from steam applied through a half-pipe jacket. The half-pipe jacket is fitted to the exterior of the bottom head. An additional half-pipe jacket is fitted around the vessel shell from the bottom tangent line to the liquid-level line estimated after evaporation.

The half-pipe jacket is insulated to minimize heat load to the cell and to facilitate maximum heat-transfer efficiency with respect to evaporation and cooling of the process fluid. The insulation is protected by a stainless steel jacket. The jacket is completely sealed and evacuated to preclude moisture from being absorbed by the insulation material and overpressurizing the jacket space at elevated temperatures.

The slurry is agitated by a remotely replaceable agitator mounted atop the concentrator tank. Internal baffles minimize vortexing.

The concentrator was designed for the following conditions:

	<u>Shell</u>	<u>Jacket</u>
<u>Design Conditions</u>		
a) Pressure	+30 in. wg/-120 in. wg	150 psig
b) Temperature	185°C	
<u>Operating Conditions</u>		
a) Pressure	-5 in. wg	90 psig
b) Temperature	40°C to 120°C	

The concentrator tank was designed to be removed from the vitrification facility (VF) cell by lifting in the vertical position and reorienting it to the horizontal position. The design of the tank includes a carbon steel lifting yoke and platform skid, which will facilitate installation, handling, transfer, and shipping. The envelope of the tank, mounted on its platform skid and transfer cart, is within the constraints for transfer in and out of this CTS facility.

5.3.1.3 Operational Characteristics

The concentrator tank will be filled to near capacity with Tank 8D2 basic PUREX sludge waste and the nitric acid required to partially neutralize or acidify the waste sufficiently to provide up to a 2 molar nitric acid melter feed after evaporation. Glass formers, Tank 8D4 acidic THOREX waste, and waste recycle streams will then be added to the concentrator tank in proportions to provide the selected melter feed recipe.

After melter feed samples from the concentrator tank have been analyzed and verified to be within an acceptable range, the prepared melter feed will be cooled in the concentrator tank and transferred to a feed hold tank.

The feed is transferred from the concentrator tank to the hold tank by way of a steam ejector jet. Prior to transferring, the contents must be cooled to below 40°C. This is done by cooling water applied through the same half-pipe jackets that are used for heating the tank.

A dip tube on a steam jet is used to transfer the slurry. The jet extends to 1 in. below the minimum liquid level required for normal operation.

On completion of the WVNS waste vitrification, the concentrator will be decontaminated for removal from the CTS facility. To accomplish this the agitator is remotely removed from the tank.

Upon remote removal of the agitator assembly, a heel removal assembly (HRA) is to be installed in its place. Its purpose is to remove the heel required for normal operation of the agitator. The HRA includes a sparge ring with a connection for air and water service. The air service is to flush the solids in the heel up into the liquid in the tank. The water service will be used for spraying down and flushing the tank's interior surfaces. The pumpout

subassembly on the HRA includes a steam ejector jet with a dip tube extending to within 1/2-in. of the low point in the center of the bottom head for removing the liquids.

Once it is flushed and the liquids removed, the concentrator will be remotely removed from the CTS facility for disposal.

5.3.2 Waste Mobilization Jumper Pit Engineering Study

The waste to be processed at the West Valley site is contained in two underground tanks. Tank 8D2 contains about 600,000 gal of cesium-containing PUREX waste, which has separated into supernatant and sludge phases. Tank 8D4 contains about 8,000 gal of thorium-containing THOREX sludge, which is ~70% solids.

The waste in Tanks 8D2 and 8D4 will be processed in stages. The PUREX supernatant in Tank 8D2 will be processed by the supernatant treatment system (STS), an ion-exchange process housed in Tank 8D1. The spent zeolite from the ion-exchange process will be discharged to the bottom of Tank 8D1. This zeolite will contain the radioactive cesium in concentrated form. It is planned to perform a series of water washes on the PUREX sludge in Tank 8D2. The supernatant from each wash will also be treated by the STS.

After the PUREX supernatant is treated, Tank 8D1 will contain a large amount of cesium-loaded zeolite. The zeolite will be mixed with water to form a 10 to 15 wt% solids slurry. The slurry will be pumped back to Tank 8D2 to be mixed with the waste sludge that remains in Tank 8D2. The zeolite-PUREX sludge mixture will then be transferred to the V-001 concentrator in the CTS for concentration and the addition of glass formers.

The study was to design a waste diversion pit and a pump pit that allow the waste to be transferred between storage tanks by routes not provided in the system's basic design. Both pits are self-contained and amenable to remote maintenance. Both are adequately radiation-shielded to allow for manual valve manipulation. Services are provided in each pit for line flushing, pit wash-down, and drainage. The pump pit contains the discharge pump for Tank 8D1.

The valving of both pits will allow for the alternative routing configurations listed below:

- from V-001 concentrator to Tank 8D4
- from V-001 concentrator to Tank 8D2
- from Tank 8D2 to V-001 concentrator
- from Tank 8D1 to V-001 concentrator
- from Tank 8D1 to Tank 8D2
- from Tank 8D4 to V-001 concentrator
- from Tank 8D4 to Tank 8D2.

The pump pit will contain, in addition to a pump and a recirculation system, a grinding unit for reducing the size of the zeolite and instrumentation to measure flow rate, density, and pressure.

The study provided the following information to be used in final design of each pit:

- layout and elevation drawings for both pits
- line drawings of individual jumpers
- specification for individual jumpers
- specifications for instrumentation
- operations procedures describing stream routing.

Shielding calculations were performed and used to establish the wall and pit cover thicknesses.

5.3.3 CTS Waste Header Hydraulic Study

A hydraulic study was performed to determine the optimum pipe size for the CTS in-cell waste header and transfer line that would allow waste, jetted into the header, to drain by gravity to Tank 8D4. The waste tank is 300 ft from the cell, and only 5 ft of vertical drop is available to slope the waste-transfer line. The waste will be jetted into the header at a maximum flow rate of 25 gpm.

The piping must be sized to prevent solids from depositing in the line and prevent backflow to other components. To prevent deposition of solids, the

velocity of the fluid must be high enough to ensure turbulent flow. To prevent waste from backing up into other in-cell components, the slurry should only partially fill the pipe.

An iterative analysis was performed involving a steady-state energy balance approach and a numerical model for non-Newtonian fluids. The rheological properties of the assumed "worst case" fluid--the concentrator feed makeup slurry--were used in the numerical model for non-Newtonian fluids. Figure 5.2 presents the results of the analysis. Both 3- and 4-in. pipes will operate partially filled and in the turbulent range. Either pipe size will give acceptable performance, but the 3-in. line is preferable because it has the higher Reynolds number and the higher depth of fill.

FIGURE 5.2. Pipe Size Optimization Results

5.4 PROCESS SUPPORT - J. R. Carrell, L. A. Bray, W. O. Heath, G. B. Mellinger, P. W. Reimus, D. W. Faletti, R. W. Goles, R. A. Brouns, J. H. Westsik, Jr., and M. E. Peterson,

5.4.1 Analytical Methods

The West Valley Tank 8D2 contains alkaline supernatant and sludge. As a part of the process support studies, the valence state of trace plutonium was determined in both actual and PNL simulated supernatant. In addition, the distribution of phosphate in the supernatant and sludge phases was determined for simulated wastes as a function of the initial concentration.

5.4.1.1 Plutonium Analysis

West Valley alkaline supernatant has been analyzed to contain $\sim 21 \mu\text{Ci}$ Pu/L. No plutonium decontamination is expected during ^{137}Cs recovery using a zeolite exchanger. Previous attempts to remove the plutonium using tailored exchangers gave uncertain results. Because the supply of actual West Valley waste at PNL was limited, synthetic waste was "spiked" with ^{239}Pu and assumed to be similar. To verify the similarity, both solutions were tested to determine their plutonium valence. The valence state of the plutonium in both was found to be predominantly ($>90\%$) Pu(IV) and/or Pu(III), as opposed to Pu(V) and/or Pu(VI).

Two samples, West Valley actual and synthetic alkaline supernatant, were analyzed using a plutonium speciation method developed earlier (Rai and Swanson 1981) to differentiate between reduced and oxidized species. This method involves first adjusting the sample to 0.3M HNO_3 + $5 \times 10^{-5}\text{M}$ NaBrO_3 [to oxidize any Pu(III) to Pu(IV)] and then immediately contacting it for 10 min with 0.5M TTA(a) in xylene to extract the plutonium that had been present initially as Pu(III) and Pu(IV). The aqueous phase from the extraction was then made 10^{-3}M in TiCl_3 and allowed to stand for ~ 5 min [to reduce Pu(V) and Pu(VI) to Pu(III)], then made 10^{-2}M in NaBrO_3 [to oxidize the Pu(III) to Pu(IV)], and then contacted immediately with a fresh TTA phase to extract the plutonium that had been present initially as Pu(V) and Pu(VI). The total plutonium found in

(a) TTA = thenoyltrifluoroacetone.

the two TTA extracts thus represents the total plutonium present in the solution sample. The TTA-xylene extracts were counted for alpha emitters using a scintillation counter.

5.4.1.2 Phosphate Distribution

Early PNL work (Bray 1984) was completed to determine the distribution of radionuclides, other cations, and anions between synthetic West Valley alkaline supernatant and sludge. Phosphate values obtained during those studies showed that about 75% of the 0.1 molar ion was in the sludge layer for alkaline supernatant values of pH 10 (after sludge washing). When the pH value for the supernatant was increased to 13, the water-washed sludge contained only 6 to 20% of the initial phosphorus ion. Additional studies were requested to determine the distribution of phosphate between the supernatant and solid phase resulting from neutralization (pH 9-10) of simulated PUREX acid waste, starting with initial phosphate levels of 0.1, 0.075, 0.05, and 0.025M (added as phosphoric acid). The phosphate concentration in the final supernatant varied from 4.5 to 10.4% of the initial concentration, Table 5.1. In a separate study, in which the initial phosphate ion was added as ferric phosphate ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$), three additional phosphate values were obtained at 0.1M, which support the above results. These studies are also shown in Table 5.1. The results confirm

TABLE 5.1. Distribution of Phosphate Between Alkaline Supernatant and Sludge

<u>Phosphate Concentration</u>		<u>Supernatant</u>		
<u>Supernatant and Solids, Initial M</u>	<u>Supernatant, Final M</u>	<u>% of Initial Phosphate</u>	<u>Volume, L</u>	<u>Final, pH</u>
0.1	0.0123	10.5	0.856	10.5
0.075	0.0048	5.5	0.864	10.0
0.05	0.0039	6.7	0.856	9.9
0.025	0.0013	4.5	0.864	9.8
0.1	0.018	14.5	0.800	9.8
0.1	0.013	9.5	0.800	9.5
0.1	0.013	10.9	0.800	9.5

the 1984 data and show that 10 to 25% of the phosphate will be found in the alkaline supernatant (pH 10), with the remaining contained in the unwashed sludge.

5.4.2 Zeolite Storage Study

The current reference process for decontaminating the West Valley Tank 8D2 supernatant involves ion exchange using IONSIV® IE-96 zeolite as the exchange material. The cesium-loaded zeolite will be sluiced from the ion-exchange columns using water and transferred to the bottom of Tank 8D1. When the cesium recovery process is completed, ~75,000 L of zeolite will fill the bottom of the 8-m-tall tank to a depth of ~0.2 m (assuming even packing distribution). The zeolite will be covered with water and maintained at ~60°C for ~1-1/2 years prior to delivery to the slurry-fed ceramic melter (SFCM) for vitrification. There the zeolite will be blended with washed Tank 8D2 sludge and THOREX acid waste, and vitrified.

The overall objective of the zeolite storage study was to provide West Valley with a data base that will address the zeolite storage issues and ensure that the cesium-loaded zeolite can be stored and retrieved in a safe and technically sound manner. Storage concerns addressed include long-term storage in water and salt solutions as a function of temperature and radiation damage. Test results at 50°C and 90°C show no significant effects that would impact the West Valley reference process. The major findings are summarized below:

- Samples of zeolite, tested in water or in a dilute solution of alkaline supernatant (100X) or in synthetic West Valley alkaline supernatant, were analyzed after heating to 50°C or 90°C for 1, 3, 6, and 12 months. The results, when compared to the original IE-96 zeolite loaded to 0.04 moles of cesium per liter of exchanger, show no significant loss of cesium to the aqueous solution or loss of metal ions from the zeolite structure.
- No significant diminution of particle size was observed for the test samples as compared to as-received IE-96 or to the original zeolite loaded with cesium. Greater than 90 wt% of each of the test samples

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was determined to be in the <20 to >40 mesh range. Less than 1 wt% of each of the standard and test samples was <70 mesh.

- Physical changes in the zeolite were determined by expanding the test columns of zeolite twofold with upflow water. A twofold expansion occurred at ~2 L/min of water at 8 to 10 psig. No major differences were noted for new zeolite, zeolite loaded with cesium, zeolite irradiated to $\sim 2.2 \times 10^8$ rad, or for any of the zeolite samples tested in the three aqueous media.
- The expected dose rate from ^{137}Cs for the IE-96 zeolite during storage in the 8D1 tank was determined to be 1.53×10^9 rad/year. Two experiments were completed to determine the G value^(a) for the production of gas during storage. The $G(\text{H}_2)$ value for water in the presence of zeolite was determined to be the same as the literature value for water under ordinary conditions, $G(\text{H}_2) = 0.4$. In one year, ~ 0.3 mol of H_2 (7.9 L H_2 at 25°C) will be produced per kg of water-saturated cesium-loaded zeolite (50 wt% H_2O).
- During zeolite resuspension testing, zeolite was found lodged in the dip leg of the equipment, which prevented flow of water. Additional West Valley plant-scale tests may be warranted to determine the extent of the problem, methods to prevent plugging, and methods to remove zeolite blockage during actual operation.
- Air-saturated zeolite storage water can become acidic due to the high radiation field and thus increase the corrosion rate of carbon steel with time. The zeolite storage water will require monitoring and may require the addition of additives or corrosion inhibitors to protect the carbon steel tank during long-term storage. On the basis of the preliminary zeolite-water corrosion tests on carbon steel, additional long-term tests were recommended.

(a) G value = number of molecules destroyed or produced for each 100 eV of energy absorbed.

5.4.3 Waste Mobilization Process Chemistry

Following treatment of the supernatant in Tank 8D2, three tanks at West Valley will contain high-level liquid waste (HLLW). Tank 8D1 will contain cesium-loaded zeolite and water, Tank 8D2 will contain PUREX sludge and residual supernatant, and Tank 8D4 will contain concentrated THOREX waste. Current plans are to remove the contents of these waste tanks and process them via an onsite vitrification facility. Before these wastes can be vitrified, two major operations must be performed. First, the PUREX sludge will be washed with water to remove excess sodium sulfate, which adversely affects waste processing. Second, to avoid the complication of processing three separate HLLW streams, the three wastes may be combined and blended in Tank 8D2.

This study investigated these two operations on a laboratory scale to determine how they should be done and whether any major difficulties will be encountered. Synthetic solutions and sludges closely approximating the three wastes' known chemical composition were prepared and used to make all observations reported in this study.

The waste mobilization process chemistry study was divided into the following tasks: 1) chemistry required for Tank 8D4 THOREX waste removal, 2) waste-stream preparation and combination, 3) rheological analysis of mixtures of PUREX, THOREX and zeolite ion-exchange wastes, 4) behavior of plutonium during the mixing of THOREX acid waste with PUREX washed sludge, and 5) washed sludge and cesium/zeolite dissolution studies.

5.4.3.1 Chemistry Required for Tank 8D4 THOREX Waste Removal

Analytical data on the composition of WVNS Tank 8D4 THOREX waste indicate that not all the thorium can be accounted for in the 8D4 tank liquid. Apparently, $\text{Th}(\text{NO}_3)_4$ solids are either floating in the tank or are deposited on the tank walls. Tests were undertaken to achieve the following objectives:

- Predict the condition and location of the solids in Tank 8D4.
- Determine a suitable chemical means of dissolving the precipitated waste in Tank 8D4.

This study yielded the following important findings:

- Large quantities of solids, primarily thorium nitrate with iron and nickel nitrates, were found collected on the cooling coils of the mockup tank when the volume was reduced to a level equivalent to the current Tank 8D4 level (31,000 L) and tank temperatures were maintained at $\sim 65^{\circ}\text{C}$.
- At a volume of 45,000 L, the 8D4 wastes will remain in solution at 64°C . At lower temperatures, thorium nitrate and other solids will crystallize out of solution.
- To keep the entire 8D4 contents in solution at 25°C , the expected temperature of the waste during transfer between tanks, it will have to be diluted to an equivalent of $\sim 59,900$ L with water ($\sim 1\text{M Th}$, $\sim 0.6 \text{H}^{+}$).

The mockup tank used for these studies was constructed using 8 in. Sch. 40 stainless steel pipe for the tank wall and 1/4-in. stainless tubing for heating/cooling coils. The $\sim 8\text{-L}$ tank was designed to approximate the geometry of the 45,000-L 8D4 tank. Hot water from a heating bath was circulated through the single inner coil to add heat, simulating decay heat to the tank. Cool water was circulated through the outer coils to simulate the cooling coils in the actual tank. Temperatures were taken at the center and at the wall.

The mockup study of Tank 8D4 provides evidence that the major metal nitrates (Th, Al, Fe) are crystallizing on the cooling coils as the waste volume is reduced (Figure 5.3). Since the waste and the crystals have similar densities ($\sim 1.7 \text{g/cm}^3$), solutions containing floating solids or "icebergs" have also been observed. At the goal composition of 1.48M Th , 0.84M H^{+} , and 45,000 L, the solution will require heating to $\sim 64^{\circ}\text{C}$ to prevent precipitation or crystallization. Water dilution of this composition to $\sim 1.1\text{M Th}$ and $\sim 0.60 \text{H}^{+}$ will allow all metal components to remain in solution at 25°C for transfer to the 8D2 tank.

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FIGURE 5.3. Mockup Tank with Crystal Deposits

5.4.3.2 Waste Stream Preparation and Combination

The current reference process for vitrification of the PUREX sludge in the West Valley Tank 8D2 involves separation of the cesium from the alkaline supernatant using zeolite ion exchange, followed by water mobilization of the sludge from the bottom of the tank. Feed for vitrification will combine this sludge, the cesium-loaded zeolite, and the THOREX acid waste currently being stored in Tank 8D4. At the request of WVNS, PNL has studied the following four options for combining the THOREX waste with the PUREX waste in Tank 8D2 prior to vitrification:

- Add the THOREX waste to Tank 8D2 prior to supernatant treatment in the supernatant treatment system (STS).
- Add the THOREX waste to Tank 8D2 after supernatant processing, but before sludge washing.
- Add the THOREX waste to Tank 8D2 after sludge washing, but before transfer to vitrification.
- Add the cesium-loaded zeolite to the combined PUREX-THOREX waste.

The important findings of this study are as follows:

- Combining the THOREX and PUREX wastes appears feasible for each of the three scenarios attempted: pouring the THOREX waste directly through the 8D2 supernatant, pouring the THOREX waste into unwashed PUREX sludge, and combining THOREX waste with washed sludge plus caustic. Release of NO_x off gas was minimized when the THOREX was added to washed sludge and was largest when the THOREX waste was added to unwashed sludge.
- The THOREX waste should be blended with washed PUREX sludge plus caustic to minimize off gassing and to ensure a well-mixed feed to the vitrification system. The THOREX waste should not be neutralized with concentrated caustic before being combined with the PUREX sludge as unmanageable solids may result. Instead, additional caustic should be added to the PUREX sludge, and then the THOREX waste should be added.

- Pouring the THOREX waste directly through the 8D2 supernatant is feasible but is not recommended without further study.
- Mixing the THOREX waste with the washed PUREX sludge appears preferable because it would eliminate the need to develop separate glass former compositions and melter campaigns. By combining the wastes, only one glass composition and one melter campaign would be required, greatly simplifying the overall site-decontamination effort. Similarly, waste variability would be reduced if the spent zeolite in Tank 8D1 were combined with the washed PUREX sludge before vitrification rather than combined with glass formers and sent to the melter as a separate waste stream.

For this study, a base-case waste-handling scenario was developed. First, a sufficient amount of sodium hydroxide is added to the washed PUREX sludge to "neutralize" the THOREX waste to a pH of 10. The amount of sodium hydroxide required was determined during this study to be 1.15 L of 10M NaOH per L of original THOREX waste (1.48M Th). This equals 52,000 L of sodium hydroxide solution added directly to the 44,000 L of washed PUREX sludge (includes 110,000 L of residual wash water). On top of this would be added the 70,000 L of diluted acidic THOREX (~1M Th) waste, bringing the combined volume of PUREX and THOREX waste in Tank 8D2 to 556,000 L. The spent zeolite in Tank 8D1 would then be pumped as a slurry through an in-line grinder and into Tank 8D2, where it would be mixed with the combined PUREX and THOREX wastes. For the purpose of this study, it was assumed that the zeolite is added as a 50 wt% slurry. The density of a 50 wt% zeolite slurry was measured as 1.205 kg/L, so for the anticipated 57,650 kg of spent zeolite in Tank 8D1, this would amount to a zeolite slurry volume of 96,000 L added to Tank 8D2. The total final volume of combined THOREX, PUREX, and spent zeolite wastes in Tank 8D2 would be 660,000 L.

Once all three wastes are combined and blended in Tank 8D2, the final combined waste stream will be pumped in batches to the feed tank concentrator. There the combined wastes will be blended with glass formers and concentrated. The concentrated waste/glass former stream will then be fed to the melter and vitrified.

5.4.3.3 Rheological Analysis of Mixtures of PUREX, THOREX, and Zeolite Exchanger

Several studies were conducted in FY 1986 in support of the West Valley front-end process, all focusing on resuspension, mixing, and removal of HLW from their waste storage tanks prior to further processing.

One study examined the flow properties of HLW, in particular the sludge at the bottom of Tank 8D2, to determine which properties must be measured to ensure that planned tank mixing equipment will be large enough for thorough sludge resuspension and mixing. Proper mixing system design is crucial because dispersion of settled waste slurries and sludge may prove the most difficult step in removing the wastes for processing.

This study determined that the following properties collectively determine the flow and dispersion behavior of settled tank sludges:

- τ_s , shear strength
- η_{app} , apparent viscosity
- τ_y , yield strength
- n , consistency index
- k , flow behavior index.

Of these parameters, shear strength is the primary determinant of whether a tank sludge will flow under given shear conditions imposed by agitation equipment. The remaining parameters determine the flow properties of the slurry formed after the sludge is dispersed.

A second series of studies was undertaken to develop a method of performing in-tank measurements of HLW flow properties. A method involving the use of shear vanes was developed, allowing all important flow properties to be measured in-tank and compared directly to measurements made in the laboratory.

Another study was performed to develop nonradioactive, easily prepared sludges that could be used in scale-model tank mixing tests as stand-ins for actual HLW sludges.

A final series of studies was performed to investigate the chemical, physical, and rheological properties of the three West Valley wastes (Tank 8D1 zeolite, Tank 8D2 sludge, and Tank 8D4 thorium waste) during various stages of

initial processing. The results of rheological measurements were made on simulated washed sludges and mixed wastes that were prepared during these studies. All of these studies are discussed in summary form in the following pages.

Plutonium Behavior During the Mixing of THOREX Acid Waste with PUREX Sludge. The above studies were completed to analyze the chemistry and physical properties of mixtures of washed PUREX sludge, THOREX acid waste, and zeolite wastes. These nonradioactive studies (except for thorium) were undertaken to predict the condition and dissolution of the solids in Tank 8D4 and to determine the feasibility of blending the 8D4 THOREX acid waste, the 8D2 PUREX alkaline waste, and the cesium-loaded zeolite waste prior to vitrification.

Additional studies were requested to add plutonium to the PUREX and THOREX wastes, to repeat several of the above studies, and to follow plutonium (Pu) removal during washing and mixing studies under the following conditions:

- Add the THOREX waste to the Tank 8D2 alkaline supernatant (45,000 L THOREX/2.1 x 10⁶ L supernatant ratio).
- Add the THOREX waste to simulated third water wash solution in which NaOH has been added to adjust the final solution to a pH of 10.
- Add THOREX waste to simulated third water washed sludge containing NaOH added to adjust the final sludge solution to a pH of 10.
- Complete a fourth wash on the combined THOREX-PUREX sludge to determine the sodium content prior to vitrification.

The important findings of this study were as follows:

- No conditions were found in which plutonium, thorium, or daughter products will impact the West Valley reference process.
- Plutonium, other than that associated with the supernatant, did not water wash out of the sludge. No Pu was found in the fourth water wash after adding THOREX waste (containing Pu) to the washed PUREX sludge/NaOH. Essentially, 100% of the thorium was found in the final washed PUREX-THOREX sludge.
- The volume of NaOH required to adjust THOREX acid waste to a pH of 10 was determined to be 1.06 L of 10M NaOH per L of acid waste

(1.48M Th). When THOREX waste was titrated to a pH of 10, in simulated third wash solution, Pu was not detected in the filtrate.

- When 1.8 mL of THOREX acid waste (0.874M Th) containing 1.1×10^{-5} M Pu was added to 50 mL of alkaline supernatant (3.9×10^{-5} M Pu) and stirred for 7 days, the pH dropped from 9.9 to 8.6, and the Pu value in the resulting filtered supernatant remained at 3.7×10^{-5} M Pu.
- No off gas was released during the addition of NaOH and THOREX acid waste to PUREX sludge, washed three times with water.
- PUREX sludge washed three times with water and blended with NaOH, THOREX waste, and wash water (fourth wash) settled to 245% of the reference sludge volume (144 mL per L of original PUREX waste) in 20 days. This rate was similar to settling rates for first, second, and third water-washing of PUREX sludge.
- THOREX feed and derivative solutions were analyzed for thorium daughter products. When THOREX acid waste was added to alkaline supernatant, ~2% of the initial ^{228}Ra was found in the clarified supernatant. When THOREX waste was added to washed sludge containing NaOH, to neutralize the resulting mixture to a pH of 10, no daughter products were found in the water wash of the combined waste streams.
- Approximately 7.5% of the initial Na^+ and ~0% of the $\text{SO}_4^{=}$ remained in the washed sludge after the addition of THOREX acid waste/NaOH to PUREX sludge (washed three times) followed by a fourth water wash.

Synthetic PUREX and THOREX wastes were analyzed along with four water-wash solutions during the evaluation of plutonium and thorium behavior. The results are shown in Table 5.2. The PUREX sludge was separated from the alkaline supernatant and washed three times with water. The NaOH required to neutralize the THOREX waste was added to the washed sludge. The THOREX acid waste was blended with the washed sludge-NaOH, and a fourth water wash was completed.

Washed Sludge and Cesium/Zelite Dissolution Studies. West Valley Tank 8D2 contains alkaline supernatant and PUREX sludge. After sludge is removed from the tank a heel will remain. The alkaline supernatant will be processed through zeolite ion exchange to recover the cesium. The zeolite will

TABLE 5.2. West Valley Sludge and Supernatant (1 L) Combined with THOREX Waste--
Washing Studies

	Volume, mL	pH	Al	B	Cr	Fe	K	Mo	Na	Ni	Pu	Zr	Th	Cl	NO ₂ ⁻	NO ₃ ⁻	SO ₄ ⁼
FEED			Moles														
Supernatant and Sludge	1000	~10	0.017	6E-4	0.027	0.306	0.19	1.5E-3	6.6	0.011	6.70E-5	2.3E-3	--	0.04	2.09	3.45	0.25
Addition After 3rd Wash																	
THOREX, 0.874M Th	33.68	--	8.8E-3	3.6E-3	3.8E-3	0.016	9.4E-4	--	3.7E-3	2.1E-3	6.57E-7	--	0.029	4.2E-4	--	0.237	6.4E-4
NaOH, 9.69M	21.6	--	--	--	--	--	--	--	0.21	--	--	--	--	--	--	--	--
RESULTS			% of Total ^(a)														
Supernatant	808	9.94		16.0	1.2	Trace	78.6	73.0	74.7	--	46.9	5.8	--	84.6	83.7	80.4	84.0
1st Wash	256	9.99		5.5	0.14		9.2	9.0	9.2	--	0.26	--	--	10.1	9.4	9.7	10.0
2nd Wash	280	10.02	0.3	1.1	0.07		4.02	4.3	--	0.004	--	ND ^(b)	2.9	4.4	4.3	4.6	--
3rd Wash	280	10.13	0.3	0.7	0.03		1.7	1.9	1.9	--	--	--	--	1.6	1.8	1.9	1.9
4th Wash	280	10.17	0.07	15.4	0.04		1.3	0.7	2.3	--	--	--	ND	1.4	0.7	3.8	0.8
Final Sludge ^(c)	--	--	99.4	61.2	98.5	~100	5.0	11.3	7.5	~100	53.0	~96	~100	~0	~0	~0	~0

(a) Percent Recovery = $\frac{\text{Material Found}}{\text{Total Added}} \times 100$

(b) ND = Not determined.

(c) Final sludge results determined by difference.

be stored in Tank 8D1 and then vitrified. Both Tanks 8D2 and 8D1 will contain unrecoverable amounts of zeolite and sludge. A study was completed to define the conditions for redissolving the washed sludge to provide the basis for final tank cleanout. In addition, the study provided the basis for determining the amount of acid required to obtain a minimum of 99.9% recovery of the cesium activity from the unrecovered zeolite in Tank 8D1. The major findings of this study are as follows:

- Oxalic acid can be used to elute cesium remaining in unrecovered zeolite in Tank 8D1 at 25°C if <1% of the total zeolite remains in the tank.
- If >1% of the zeolite remains in Tank 8D1, the oxalic acid may require heating to increase cesium separation.
- The results of cesium elution show that 10 to 12 moles of H^+ ion are consumed per kilogram of zeolite treated to release 88 to 90% of the cesium when the volume of 0.8M oxalic acid to weight of zeolite is ~20 L/kg.
- Oxalic acid will not completely dissolve sludge. A maximum of 66 wt% of the washed sludge will dissolve using ~0.7 moles of oxalic acid per unit of washed sludge (equal to 1 L of PUREX sludge and supernatant plus THOREX precipitated waste).
- The use of oxalic acid to dissolve sludge and elute zeolite is technically feasible. No other acids were found suitable for testing. However, oxalic acid corrosion of carbon steel, subsequent disposal of the oxalic acid, the safety of mixing large volumes of organic acid with nitrates during vitrification, and the impact of the oxalate carbon content on glass chemistry were not addressed. This study has not considered the oxalic acid that may be consumed in reaction with existing corrosion deposits on the walls and internal structures of the tank.

5.4.3.4 Development of a Shear Vane Method for In-Tank Measurement of Sludge Flow Parameters

A shear vane, used together with torque instrumentation, provides a convenient and reliable means to measure the shear strength of cohesive materials. A standard shear vane (ASTM 1978) consists of a shaft to which four rectangular vanes or blades are attached as shown in Figure 5.4. Shear vanes were developed by soil scientists to allow soil shear strengths to be measured in the field. This obviates the need to remove core samples and subject them to shear strength testing in the laboratory. Removal is undesirable because the sampling operation causes physical disturbances that tend to stress and weaken the samples. Often shear strengths measured in the laboratory are lower than the actual in situ shear strength of the intact soil. Since shear vanes

FIGURE 5.4. Shear Vane Geometry. Shearing involves one vertical cylindrical surface and two horizontal end surfaces (a). Twisting of the vane also induces normal stress, τ_t , on the shearing surface (b).

are designed to be positioned without disturbing the cylindrical shearing surface, they provide in situ soil strength data that reflect the actual strength of the intact soil.

Research at PNL focused on three objectives:

- investigate the scale-up of shear strength data to allow direct comparison between laboratory-scale data and full-scale data obtained in situ
- develop a method for using shear vanes to measure the viscosity of tank sludges as well as their shear strengths
- prepare a data analysis calculator program for shear vanes.

Scale-Up of Shear Vane Shear Strength Data. Shear vanes can be used to evaluate the shear strength (τ_s) of a sludge by submerging the vane portion in the sludge, rotating it at a constant speed, and measuring the amount of torque ($T_{\max}$) required to initiate vane rotation. Equation (1) is used to relate the measured startup torque to sludge shear strength.

$$T_{\max} = \pi \left[H_v \frac{D_v^2}{2} + \frac{D_v^3}{6} \right] \tau_s \quad (1)$$

To test whether measured values of τ_s are dependent upon shear vane size or rate of revolution, three shear vanes with $D_v = H_v = 0.975, 2.220,$ and 7.62 cm were fabricated and used in testing. All three shear vanes are shown in Figure 5.5.

It was determined that measurements of sludge startup torque with the two smaller shear vanes, when they were rotated at 0.05 rpm, resulted in the same values of shear strength as calculated by Equation (1). Measured values of shear strength are therefore independent of shear vane diameter, at least within the range of $0.975 \text{ cm} < D_v < 2.220 \text{ cm}$.

To investigate the effect of vane rotational speed on shear strength measurements, the two smaller shear vanes were rotated at various speeds through an

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FIGURE 5.5. Three Shear Vanes Used During Testing at PNL

iron-based and a silica-based tank sludge simulant. A Haake® viscometer was used in conjunction with the two shear vanes to perform the shear strength measurements. The results for the 0.975-cm shear vane are shown in Figure 5.6. Each plotted point represents the average of one to three data points, exhibiting minimal scatter.

The plotted test data show shear strength to be independent of shear vane rotational speed in the range of 0.3 rpm to 0.5 rpm. Below this range, shear

®Haake Mess-Technik GmbH and Company, Karlsruhe, West Germany.

FIGURE 5.6. Effect of Shear Vane Revolutions per Minute on Sludge Shear Strength Measurement

strength appears to vary as a function of vane speed as well as test material (as evidenced by the two differently shaped curves). An assumption implicit in shear vane testing is that the material behaves as an elastic solid being sheared along the outer edges of the vane. The rate of elastic strain is related to vane tip speed, suggesting that vane tip speed should be held constant in the in-tank and in-cell tests. This rationale suggests that an in-tank shear vane of 8.9 cm (3.5 in.) dia should be rotated at 0.032 rpm (1.9 revolutions per hour) during shear strength testing to achieve the same tip speed (0.015 cm/s) as that of a 0.975-cm viscometer shear vane rotated

at 0.3 rpm. Furthermore, the data suggest that rotation at this higher speed should produce data that are less sensitive to small variations in the rate of shear vane rotation. On the basis of available test data, therefore, it is recommended that the in-tank shear vane be rotated at 0.032 rpm. This recommendation, however, should be verified through additional laboratory-scale and field-scale tests.

Measurement of Apparent Viscosity Using Shear Vanes. The main uncertainty associated with use of a shear vane to obtain viscosity data is whether the measured variable, shear vane torque, will vary as a predictable function of shear vane rate of revolution. To investigate the torque versus rpm response of a shear vane over a wide set of operating conditions encompassing both laboratory-scale and full-scale (in-tank) testing, the effects of the following variables were studied:

- shear vane diameter, D
- test fluid viscosity, η
- test vessel radius, R_c .

Table 5.3 lists the specific configurations tested.

TABLE 5.3. Shear Vane/Tank/Test Fluid Configurations Investigated

Test Radius	Shear Vanes			Test Fluids, cP	Shear Vanes		
	No. 1	No. 2	No. 3		No. 1	No. 2	No. 3
1.68	X			5.4		X	
2.95	X	X		50.5		X	
4.20	X	X		475	X	X	
14.0			X	1,037 ^(a)			X
				1,237	X	X	
				12,000	X	X	
				14,650 ^(b)	X	X	X
				29,700	X	X	

(a) Glycerol at test conditions (15°C).

(b) Corn syrup at test conditions (12°C).

In a procedure common to all test configurations, a measured volume of test fluid was carefully poured into a test container to avoid bubbles; a test shear vane was installed and rotated at several rpm; torque readings were recorded at each rpm setting; and the test fluid's temperature was monitored and in most cases remained constant, $\pm 1^\circ\text{C}$.

The overall torque data (T_o) for each test were corrected to account for shaft torque (T_s) caused by frictional losses from the rotating shear vane shaft. The calculated values of shaft torque were then subtracted from the overall torque measurements to yield values of vane torque (T_v).

Based on common industrial practices (Bates, Fondy, and Fenic 1966; Calderbank and Moo-Young 1961; Metzner and Otto 1957), the test data values of T_v and N were plotted in terms of the dimensionless groups N_{RE} and N_p :

$$N_{RE} = \frac{\rho D^2 N}{\eta} \quad (2)$$

$$N_p = \frac{P}{\rho D^5 N^3} \quad (3)$$

where

N_{RE} = Reynolds number, ratio of inertial forces to viscous forces, dimensionless

N_p = Power number, ratio of pressure differences producing flow to inertial forces, dimensionless

ρ = test fluid density, g/cm^3

D = shear vane diameter, cm

N = shear vane rate of rotation, rev/s (not radians/s or degrees/s)

η = test fluid viscosity, poise (1 poise = 100 cP)

P = shear vane power applied to test fluid, dyne-cm/s.

Figure 5.7 is a plot of all the PNL shear vane test data in terms of N_p versus N_{RE} . As can be seen, there is remarkably little scatter in the data, which indicates a linear relationship between N_p and N_{RE} independent of test

FIGURE 5.7. Plot of N_p Versus N_{Re} from the Shear Vane Test Data

fluid viscosity from 5.4 to 29,700 cP, independent of shear vane diameter from 0.975 cm to full scale, and independent of container radius from 1.68 cm to 14.0 cm. Industrial turbine agitator data show similar linear behavior in the laminar region ($N_{Re} < 10$ to 15) (Oldshue 1983; Bates, Fondy, and Fenic 1966). From the test data, the relationship between N_p and N_{Re} for a shear vane is calculated as

$$\log N_p = -(0.977)\log N_{Re} + (2.190) \quad (4)$$

which is valid from Reynolds numbers ranging from 10^{-5} (lowest tested) to about 10. The viscosity of a fluid can be measured with a shear vane by calculating a power number based on torque measurements, identifying the corresponding Reynolds number, and back-calculating for viscosity (η).

Relationship Between Vane rpm and Shear Rate. Shear vanes were found to exhibit $N_{RE}-N_p$ behavior representative of impeller mixers operated at Reynolds numbers in the laminar range. The most generally accepted empirical correlation between rate of revolution and shear rate for impellers has the form $S = KN$, where S is shear rate in s^{-1} and N is rotational speed in revolutions per second. The proportionality constant (K) is usually assigned a numerical value of 10 (Bates, Fondy, and Fenic 1966), although a value of 13 is recommended by some authors (Oldshue 1983).

To investigate the relationship between N and S , shear vanes were used to measure the apparent viscosity of two non-Newtonian (pseudoplastic) liquids at several rpms. The fluids were also tested using a Haake viscometer to produce rheograms. The rheogram viscosities were compared with those calculated by using the $N_{RE}-N_p$ correlation. Then the shear rates corresponding to those viscosities were determined from the rheogram. This procedure was based on the general method developed by Metzner and Otto (1957). The results are presented in Table 5.4; the data were all taken at a shear vane rotational speed of 100 rpm for greatest accuracy in determining a value for K .

TABLE 5.4. Shear Rate Data (at 100 rpm) as a Function of Shear Vane Diameter and Sludge Type

Sample Material	Shear Vane Diameter, cm	Shear Rate, s^{-1}
Iron-based sludge simulant #1	2.220	19.7
Iron-based sludge simulant #1	2.220	20.8
Iron-based sludge simulant #1	0.975	15.6
Silica-based sludge simulant #1	0.975	32.4
Silica-based sludge simulant #2	0.975	17.8
Silica-based sludge simulant #4	0.975	5.5

If the values of shear rate are averaged as they appear in the table, K is calculated to be 11.1. Note that this value falls within the range of values recommended in the literature (10 to 13).

On the basis of the data in Table 5.4, it is recommended that the following equation be used to estimate shear rates:

$$S = (11.1) N \quad (5)$$

where

S = shear rate, inverse seconds

N = shear vane rotational speed, revolutions per second.

However, because of the large amount of scatter in the test data, additional baseline data are required to verify the shear rate equation given by Equation (5).

5.4.3.5 Simulant Sludge Development

Previously, nonradioactive testing and development efforts have employed chemical simulations of tank wastes and melter feeds. Although these simulants are prepared to match closely the chemistry of actual wastes and feeds, they do not necessarily match their flow properties. Therefore, rheological simulants of the 8D2 tank sludge were developed. The goal was to develop simulants that match known or suspected properties of the 8D2 sludge which are easy to prepare and use a minimum number of commonly available ingredients. As described below, two types of simulant, each containing a maximum of three ingredients, were developed.

Silica-Based Sludge Simulant Properties and Preparation. The first simulant consists of colloidal silica mixed with a coagulating salt to cause gelation. Dissolved salts can alter the effect of ever-present background forces (van der Waals forces) that cause small (colloidal) particles in a suspension to be attracted to one another. Depending on the salts present and their concentration, this interparticle attraction can be countered, through an electrostatic mechanism, to the extent that net interparticle repulsion can be

induced. Dissolved salts were used in this study to reduce interparticle repulsion enough to cause the particles to coagulate, forming gels of varying shear strength. The goal was to develop a gel having a shear strength of 790 dyne/cm², equivalent to the suspected shear strength of the HLW sludge in Tank 8D2.

Solutions of several coagulating salts were investigated. Each solution contained a maximum of two salts. Salts of sodium were tested along with ammonium salts, a calcium salt, and two aluminum salts. It was observed that the monovalent salts caused slower gellation than the di- or trivalent salts, but tended to produce much stiffer sludges. As the aluminum salts, Al₂(SO₄)₃ (aluminum sulfate) and AlK(SO₄)₂·12H₂O (alum), produced the softest, least stiff sludges, they were further tested, with the results as shown in Figures 5.8 and 5.9. The aluminum sulfate solutions produced sludges that bracketed

FIGURE 5.8. Shear Strength of SiO₂ Simulant Versus Al₂(SO₄)₃ Concentration

FIGURE 5.9. Shear Strength of SiO_2 Simulant Versus $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ Concentration

the target shear strength value, with shear strength being inversely proportional to salt concentration. The alum solutions produced overly stiff sludges, exhibiting little or no interdependency between shear strength and salt concentration.

Based on the results presented in Figure 5.8, a final silica-based simulant composition was established as 350 g SiO_2 and 200 g aluminum sulfate per liter of sludge. This composition corresponds to equal volumes of Ludox^(TM) and 400 g/L aluminum sulfate stock solution. The two solutions must be mixed and allowed to gel twice before the sludge simulant is ready for testing.

This silica-based sludge simulant should have a density of 1.36 g/mL, an initial shear strength of 440 dyne/cm², and a final shear strength of 1180 dyne/cm², which is a conservative approximation of the 790 dyne/cm² target value. Upon stirring, the simulant is rapidly transformed into a shear thinning (pseudoplastic) liquid.

Ludox^(TM) is a trade name of E.I. du Pont de Nemours Company, Wilmington, Delaware.

Iron-Based Sludge Simulant Development, Properties, and Preparation.

Iron-based simulants were prepared by mixing a 9.6 wt% $\text{Fe}(\text{OH})_3$ (ferric hydroxide) slurry with $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ (ferric phosphate) powder. Figure 5.10 is a plot of shear strength versus composition in which the weight ratio of ferric hydroxide to ferric phosphate was varied from 0.5 to 2.4. The target shear strength (790 dyne/cm^2) is bracketed by sludges having hydroxide-to-phosphate weight ratios between 1.7 and 2.3. Ferric hydroxide and ferric phosphate are the predominant constituents: together they account for 73% of the solids and are present in a weight ratio of 2.0. The iron-based sludge simulant is thus chemically closer to the actual sludge than is the SiO_2 -based simulant.

Based on the results presented in Figure 5.10, a final iron-based simulant composition was established as 105.6 g ferric hydroxide and 52.8 g ferric phosphate per 1.4 L of sludge. This composition corresponds to a hydroxide-to-phosphate ratio of 2.0.

FIGURE 5.10. Shear Strength of Iron-Based Simulant Versus $\text{Fe}(\text{OH})_3/\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ Weight Ratio

This iron-based sludge simulant should have a density of 1.16 g/mL and a final shear strength of 1000 dyne/cm², providing a conservative approximation of the 790 dyne/cm² target value. When stirred, the iron-based simulant is transformed to a shear thinning (pseudo-plastic) liquid, but not as rapidly as with the SiO₂-based simulant. Note that this simulant exhibits a yield stress of 94 dyne/cm².

5.4.3.6 Rheological Analysis of Washed Sludges and Mixed Wastes

The washed sludges and mixed wastes were prepared as described under the section entitled "Waste Stream Preparation and Combination." Then they were subjected to steady-state and time-dependent flow property analyses, with the results as follows.

Steady-State Flow Properties of Washed Sludges. Measurements of shear stress (τ) versus shear rate ($\dot{\gamma}$) were obtained for each sample of simulated West Valley washed sludge using a Haake rotational viscometer capable of measuring torques up to 147,000 dyne-cm. This viscometer was operated using a Haake MV-II coaxial cylinder sensor. Plots of τ versus $\dot{\gamma}$, called rheograms, were produced for each washed sludge sample using this viscometer/sensor arrangement. Two rheograms were obtained over two different ranges of shear rate for each sample.

Each rheogram was prepared by ramping shear rates up from 0 sec⁻¹ to a maximum shear rate, holding at the maximum shear rate until a steady-state torque output reading was achieved, and then ramping shear rates back down to 0 sec⁻¹. Using this procedure, two flow curves are produced per rheogram. The up-curve represents sludge flow behavior during initial, nonsteady-state conditions. This curve is used to analyze time-dependent flow behavior. The down-curve represents flow behavior of the sludge during steady-state conditions and is used in the analysis of steady-state flow behavior. Points along the down-curve were used to determine power law parameters n and k , as well as the steady-state yield stress (τ_y).

Whether or not a sludge exhibits a finite yield stress (τ_y) can be determined by the shape of its rheogram. The presence of a steady-state yield stress is indicated by a marked deflection of the down-curve near zero shear rate.

Table 5.5 shows the power law expressions derived for the washed sludge. These expressions can be used to calculate values of shear stress as a function of shear rate.

Based on this analysis, all three washed sludges can be characterized as yield-pseudoplastic fluids that exhibit good flow characteristics. Their yield stresses all fall below the 150 dyne/cm² limit considered by Savannah River Laboratory (SRL) as the maximum yield stress a slurry can exhibit and still be easily pumped through process pipes, including melter feed lines.

Time-Dependent, Initial Flow Properties of Washed Sludges. Many non-Newtonian fluids, including most sludges, exhibit time-dependent behavior. A fluid that becomes thinner (less viscous) with time when stirred at a constant rate is termed thixotropic. On a rheogram, this behavior is evident when the down-curve (plot produced with descending shear rates) falls below the up-curve. On the other hand, a fluid that becomes thicker when stirred at a constant rate is termed rheopectic and is characterized by a down-curve that rises above the up-curve. Any hysteresis in up- and down-curves on a rheogram is, in general, an indication of time-dependent (thixotropic or rheopectic) behavior.

TABLE 5.5 Power Law Equations for Washed Sludges

<u>Sludge Sample</u>	<u>Power Law Equation</u>
First wash	$\tau = 12.1 + 0.71 \dot{\gamma}^{0.68}$
Second wash	$\tau = 7.7 + 0.49 \dot{\gamma}^{0.63}$
Third wash	$\tau = 6.3 + 0.41 \dot{\gamma}^{0.61}$

A qualitative measure of thixotropy (or rheopexy) is given by the difference in shear stress for the up- and down-curves at the same shear rate. Table 5.6 compares values of shear stress along the up- and down-curves at similar shear rates for the three washed sludges. All three are somewhat thixotropic, with the first washed sludge exhibiting the least flow curve hysteresis and the third washed sludge exhibiting the largest hysteresis, hence the most pronounced thixotropy.

Many time-dependent fluids tend to grow stiffer or to gel when undisturbed for extended periods. The amount of shear stress required to initiate motion in a gelled sample is termed the shear strength (τ_s) in dyne/cm².

The presence of a finite shear strength is indicated on a Haake rheogram by a peak in the up-curve near a shear rate of zero. The torque readings associated with such peaks were used to calculate values of shear strength. These values also are listed in Table 5.6.

All three washed sludges exhibited very low shear strengths, indicating they will be easy to resuspend. For comparison, the raw (unwashed) sludge in Tank 8D2 is estimated to have a shear strength of 790 dyne/cm²(a) based on measurements made on a sample of raw sludge removed from Tank 8D2.(b)

TABLE 5.6. Time-Dependent Flow Behavior in Washed Sludges

Shear Rate Sample	Down-Curve Shear Stress, (a) dyne/cm ²	Up-Curve Shear Stress, (a) dyne/cm ²	Type of Behavior	Shear Strength, dyne/cm ²
First Wash	41.3	41.7	Thixotropic	17.7
Second Wash	22.7	25.1	Thixotropic	10.1
Third Wash	17.4	21.0	Thixotropic	9.4

(a) Measured at a shear rate of 234 sec⁻¹.

- (a) Heath, W. O. November 1985. "Recommended Laboratory Methods for Evaluating Sludge Flow Properties and for Replicating Tank 8D2 In-Situ Shear Vane Test." WVST 86/12, Letter Report to West Valley Nuclear Services Company, Inc.
- (b) Rykken, L. E., to W. H. Hannum. July 25, 1985. "In-Cell Testing of 8D2 Sludge Sample." WD:0465, West Valley Nuclear Services Technical Correspondence.

Steady-State Flow Properties of Combined Waste Streams. Rheograms were obtained for each combined waste (see Samples A through F, Table 5.7). Table 5.8 lists the power law expressions derived for the combined wastes.

Based on this analysis, all but Sample B (washed sludge mixed with THOREX waste) can be characterized as yield-pseudoplastic. Since Sample B exhibits a consistency index greater than 1 ($n=1.16$), it must be considered a yield-dilatant fluid. All of the combined wastes have yield stresses above the SRL-proposed 150 dyne/cm² maximum for pumpable fluids. However, Sample D (containing washed sludge, THOREX waste, and polymer-treated zeolite), which has the lowest yield stress at 153 dyne/cm², may still fall within experimental

TABLE 5.7. Key for Combined Waste Samples

<u>Sample</u>	<u>Waste Stream</u>
A	Washed PUREX sludge
B	Washed PUREX sludge and THOREX waste
C	Washed PUREX sludge, THOREX waste, and untreated IE-96
D	Washed PUREX sludge, THOREX waste and treated IE-96
E	Washed PUREX sludge and untreated IE-96
F	Washed PUREX sludge and treated IE-96
G	Untreated zeolite IE-96 slurry (50 wt%)
H	Treated zeolite IE-96 slurry (50 wt%)

TABLE 5.8. Power Law Equations for Combined Waste Streams

<u>Sludge Sample</u>	<u>Power Law Equation</u>
A	$\tau = 165.9 + 4.81 S^{0.79}$
B	$\tau = 280.1 + 0.43 S^{0.79}$
C	$\tau = 217.4 + 1.43 S^{0.79}$
D	$\tau = 152.6 + 4.81 S^{0.83}$
E	$\tau = 173.9 + 3.63 S^{0.70}$
F	$\tau = 244.0 + 2.03 S^{0.89}$

error of being a pumpable fluid by the SRL criterion. By comparison, Sample C, containing no polymer, has a 42% higher yield stress and would not be pumpable through process pipelines by this criterion. However, at moderate-to-high shear rates ($\dot{\gamma}=400 \text{ sec}^{-1}$) all six combined wastes exhibit viscosities below 200 cP. Therefore, while all but Sample D may tend strongly toward clogging lines at low flow rates, they all exhibit good flow behavior at high flow rates.

Time-Dependent Flow Properties of Combined Waste Streams. The rheograms obtained for Samples A through F were analyzed for time-dependent flow behavior, and the results are summarized in Table 5.9.

All six combined wastes exhibit moderate shear strengths (between 270 and 490 dyne/cm²), but should be considered easy to resuspend using the mixing equipment planned for Tank 8D2. No combined wastes investigated exhibit resuspension properties that would preclude their preparation in Tank 8D2.

5.4.4 Product Qualification Support

5.4.4.1 MASBAL Computer Code

A mass balance simulation model (MASBAL) is being developed for the West Valley vitrification plant. The model has two overall objectives: 1) to predict the composition of nuclear waste glass produced at West Valley based on a

TABLE 5.9. Time-Dependent Flow Behavior for Combined Waste Streams

<u>Sample</u>	<u>Down-Curve Shear Stress,^(a) dyne/cm²</u>	<u>Up-Curve Shear Stress,^(a) dyne/cm²</u>	<u>Type of Behavior</u>	<u>Shear Strength, dyne/cm²</u>
A	509.9	496.8	Rheopectic	401.5
B	542.9	489.8	Rheopectic	413.4
C	471.4	483.0	Thixotropic	440.5
D	587.3	598.9	Thixotropic	487.8
E	335.6	357.3	Thixotropic	269.5
F	493.7	508.1	Thixotropic	382.7

(a) Measured at a shear rate of 234 sec^{-1} .

knowledge of process conditions (i.e., from process measurements) and 2) to establish confidence limits about the predicted composition based on a knowledge of uncertainties in process measurements.

Briefly, MASBAL is designed to operate in three modes. The first mode will provide deterministic predictions of the glass composition as a function of time (thereby satisfying the first objective stated above). The latter two modes will operate stochastically to generate simulated glass composition data that are distributed randomly about the deterministic predictions of the first mode. The absolute differences between the stochastic and deterministic data will be used to establish confidence limits about the deterministic predictions (thereby satisfying the second objective).

The MASBAL code will consist of PNL-developed subroutines that are integrated with the main subprogram library of the SIMAN simulation language. SIMAN subroutines will facilitate the scheduling of discrete events in the simulation, the solution of the mass balance differential equations, and the random sampling of statistical distributions. The random sampling will be an essential feature of the code when it is operated in the stochastic modes (Modes 2 and 3).

MASBAL will have the capability to track up to 100 components (specified by the user) through the West Valley vitrification system. The code will simultaneously solve the mass balance equations around the main feed tank, melter, and canisters of the vitrification system. Material will enter the system by way of the feed tank (slurry transfer from the feed makeup tank) and will leave the system by going out either the off-gas system or into a canister. Provision will be made to model the addition of glass-forming compounds directly to either the feed tank or the melter (this action may be taken if the feed or glass composition deviates significantly from the target composition). The off-gas system will be modeled as a sink for components that have finite melter decontamination factors. The average composition of the glass in each glass pour will be calculated and reported.

Since the mixing behavior of the West Valley melter is currently unknown, MASBAL will include provisions to model the melter as either 1) a well-mixed tank, 2) a plug flow region followed by one or two well-mixed regions in

series, or 3) two to five well-mixed regions in series. The best modeling approach will be decided by the best fit to experimental data. The relative volumes of each region will be made adjustable for use in validation activities.

The MASBAL user will be required to supply the following input data:

- Design characteristics of the melter system.
- Initial conditions for the simulation.
- Times of feed rate changes and the new rate each time there is a change.
- Starting and stopping times of glass pours and the mass of each pour.
- Starting and stopping times of transfers from the makeup tank to the feed tank. The volume in the feed tank before and after each transfer will also be included in the input.
- The composition of the slurry in the feed tank after each transfer from the makeup tank.
- The composition of the slurry in the makeup tank prior to each transfer to the feed tank.
- The times at which samples are taken from the off-gas system, and the mass of each constituent that has exited the off-gas system since the last sample was taken (based on results of analyses of the samples).
- The time, volume, and composition of each slurry addition directly to the feed tank.
- The time, volume, and composition of each slurry addition directly to the melter.

When MASBAL is run in either of the two stochastic modes, the user will also be required to supply the statistical distributions that best describe the uncertainty in each process measurement and the parameters (e.g., standard deviations) that define these distributions. In the first stochastic mode, each process measurement will be treated as the mean or mode of a statistical distribution that is assumed to contain the true value of the variable being measured. This distribution will be randomly sampled, and the value returned

from the distribution will be used in subsequent mass balance calculations as the true value of the measured variable, thereby simulating measurement error. MASBAL can be run repeatedly in this mode to generate a series of curves for glass composition versus time that are distributed randomly about the curve generated when the code is run in the deterministic mode. The absolute differences between the stochastically generated composition data and the deterministic data can be used to estimate the confidence limits about the predicted composition.

In the second stochastic mode, MASBAL will generate its own feed composition data by randomly selecting the compositions of successive batches of feed from distributions defined by the user (the mass per unit volume of each constituent in the feed will be taken from a distribution that has a mean of the target composition). All process measurements will be simulated by randomly sampling a statistical distribution that has a mean or mode set equal to the simulated value of the process variable being measured. The absolute differences between the stochastically generated composition data and the target glass composition will provide a measure of the variability that can be expected in the composition of the glass. If the composition of successive batches of feed is treated deterministically (i.e., standard deviations describing feed variability are set to zero), then the differences between the stochastically generated composition data and the target glass composition will provide the same information that is provided by running MASBAL in the first stochastic mode. The advantage of running MASBAL in the second stochastic mode will be that the user can run the code without having to supply process data; all that will be required are the parameters of distributions that describe feed composition variability and uncertainties in process measurements. This feature will give MASBAL the capability to simulate thousands of hours of operation of the West Valley melter system, thus making it possible to collect enough observations to establish representative confidence limits about the predicted and target glass compositions.

The ability to establish representative confidence limits about the predicted glass composition, based on uncertainties in process measurements, will

be necessary for validating the mass balance calculations in the code. Validation will be possible only if true fluctuations in process data can be distinguished from fluctuations that occur as a result of the inability to measure process variables exactly.

5.4.4.2 Liquid-Level Measurement System

Maintaining glass product quality control and safe, efficient melter operation requires reliable and accurate process instrumentation and equipment. Liquid-level measurement systems are installed in all process tanks and are relied upon to provide accurate measurements during waste and slurry feed preparation and processing. The system must accurately measure both the liquid level and specific gravity of the slurry. Chemical additions, the overall mass balance, and process monitoring are based on both the volume and mass measurements from this system. Feed preparation errors would affect the processing and composition of the glass product.

West Valley Nuclear Services (WVNS) has been using conventional dip-tube bubblers for level measurement in the concentrator/feed makeup tank. However, operating experience at both PNL and WVNS indicates the need for a more accurate and reliable liquid-level measurement system. The application of commercially available systems to high-level nuclear waste melter feed slurries was evaluated. Systems being used at the Hanford site and at the Defense Waste Processing Facility (DWPF) were included in the evaluations. Technical staff at these two sites provided information on operating performance. Vendors were contacted regarding these systems as well as other commercially available systems.

This evaluation resulted in the selection of a pneumatically operated metal diaphragm sensor system. The metal diaphragm isolates the HLW from the sensing air. This system has been demonstrated on simulated melter feed slurries, both at PNL and at SRL. Commercial sensors with metal diaphragms were tested and proved satisfactory. These sensors have been designed for radioactive applications and are recommended for the liquid-level measurement system.

A conceptual sketch of the liquid-level measurement system is shown in Figure 5.11. Three sensors are required to measure both the liquid level in the tank and the specific gravity. Three pressure regulators and converters are required to operate the system. The metal diaphragm sensors are actually 1:1 pressure repeaters, which balance the supply of air pressure with the pressure on the diaphragm exterior. The air pressure is measured. The slurry level and specific gravity are calculated from this pressure signal using algorithms incorporated in a process controller for the liquid-level measurement system.

The liquid-level measurement system will permit more accurate level and specific gravity determinations. Therefore, process control and monitoring will be improved and product quality enhanced.

5.4.4.3 Pour Glass Sampling Plan

A report was prepared for West Valley in which a pour glass sampling plan was proposed.^(a) The purpose of this plan was to suggest a means for West Valley to obtain the information needed for developing a mass balance model for the WVDP melter process.

In the plan, PNL proposed that West Valley process seven batches of feed in the CTS melter. Nonradioactive dopants were to be added to the melter feed to allow the mixing and flow behavior of the feed system and melter to be analyzed. The second and third batches were to be doped with $\text{Ba}(\text{NO}_3)_2$. The first, fourth, and seventh batches were not to be doped with tracer elements. Cobalt and barium were chosen as dopants because 1) cobalt was not present and barium was present in low concentration in the then-current WV-205 composition processed during component test stand (CTS) melter tests, and 2) both of these elements could be added to the feed at levels that would be easily detected in the feed and glass without significantly altering the glass composition.

The recommended scheme for sampling the molten glass was designed to provide adequate data for investigating and fitting a mass balance model of the type being developed by the Nuclear Waste Treatment Program at PNL. The pour

(a) Bowen, W. M., and B. A. Pulsipher. 1985. "Sampling Plan for the WVDP Feed Concentrator Makeup Tank." Materials Characterization Center Letter Report to the West Valley Nuclear Services.

FIGURE 5.11. Conceptual Sketch of Liquid-Level Measurement System

glass sampling plan required monitoring of the contents of the feed concentrator makeup tank per the proposed feed sampling plan.^(a) The pour glass sampling plan proposed specific times for obtaining glass samples during the ~700 hr it would take to process the seven batches of feed. Fifty-eight samples were to be obtained, about half of them replicates to allow sample-to-sample variability to be determined. The compositions of these samples were to be determined by West Valley and the composition data forwarded to PNL for statistical analysis and modeling.

5.4.4.4 West Valley Waste Form Qualification Report

PNL provided draft inputs to West Valley for potential inclusion in the West Valley Waste Form Qualification Report (WQR). The inputs related to two of the specifications in the Waste Acceptance Preliminary Specifications (WAPS). West Valley will need to demonstrate compliance with the WAPS prior to being able to send its glass to the HLW repository; West Valley's compliance with a number of the WAPS will be documented in their WQR.

One WAPS specification for which an input was provided by PNL was the gas specification. The input dealt with the section that requires the producer to document in the WQR the quantities and compositions of any gases that might accumulate inside the canister after it has been heated to the glass transition temperature of the West Valley glass (~500°C).

Based on examination of literature data on waste-glass volatility behavior, it was concluded that no significant gas will accumulate inside the canister under this condition. Waste glass manufacturing temperatures are several hundred degrees above the glass transition temperature. This will ensure that any volatiles that might pressurize the canisters have been removed from the glass. Nonvolatiles such as cesium, sodium, boron, and potassium may be released if the waste form is heated to higher temperatures. Very little will be released, however, at 500°C. In any case, the vapor pressures of these elements (and compounds that they may form) will be so low that their contribution to the gas present in the canister void space will be insignificant.

The second specification for which an input was provided was the chemical compatibility specification. This specifies that the waste-form producer must

provide evidence that the canister contents will not lead to internal corrosion of the canister such that there will be an adverse effect on normal handling during storage, transportation, and repository operation.

Since West Valley is not planning to put any filler material in their canisters, the only materials available to cause internal canister corrosion will be the glass waste form and the gas present in the void space above the glass. Based on an assessment of available literature data, it was concluded that there will be no internal corrosion of the canister by the solidified glass at temperatures up to the glass transition temperature.

Although the gas present in the canister at the time that it is sealed will cause corrosion of the canister interior, failure of West Valley canisters due to this corrosion of the interior air space was judged to be a very low-probability event. Penetration of the canister wall due to uniform corrosion should not exceed 0.41% of the canister wall thickness. Pitting, in the worst scenario considered in the analysis of this occurrence, should not penetrate over one-third of the canister wall thickness. Also, although the canisters will probably become "sensitized" during glass pouring and cooling, the likelihood that intergranular corrosion or stress corrosion cracking will cause failure of West Valley canisters is considered to be low.

5.4.5 Effluent Documentation Support

During FY 1986, significant support was given to WVNS to help establish capabilities for effluent sampling and monitoring. In this regard, PNL staff have provided analytical services for characterizing off-gas sample composition and level-of-effort support for WVNS personnel involved in off-gas system design and performance studies. In addition, a letter report designed to facilitate development of WVNS sampling capabilities was prepared and issued during FY 1986.

5.4.6 Process Monitoring and Control

5.4.6.1 Temperature Control Algorithm

The temperature control system developed for the PSCM, HBCM, and RLFCM melters at PNL was adapted for use with the West Valley CTS melter system. The control configuration on the West Valley distributed control system is similar

to the configuration used with the RLFCM. Thus, the WVNS configuration checks that the thermocouples are in an acceptable operating range, spatially averages the temperatures, smooths the averaged temperatures, and calculates the appropriate PI control action. (WVNS uses six thermocouples distributed between two thermowells to indicate the bulk glass temperature.) Adaptive gain is available to make large control actions as the deviations from the set point become larger. To alleviate foaming tendency, a set point ramping constraint limits the rate that changes in the set point are made.

The WVNS melter uses three electrodes rather than the two electrodes typically used in the PNL melters and thus requires three current controller circuits. The controller for the circuit between the two wall electrodes is the primary circuit acted upon by the temperature control system. The controller action for the two circuits between the wall electrodes and the bottom electrode is determined by taking a ratio off the primary circuit control action.

5.4.6.2 RECIPE Computer Code

The purpose of the RECIPE computer code is to determine the necessary weights of oxide-producing chemicals to be added to a waste mixture of known composition such that the resulting mixture will form a glass of desired composition when processed through the West Valley vitrification system. In addition, the RECIPE code can be used to check the compositional adequacy of cold slurry batches before they are added to a tank containing the radioactive wastes. Finally, the RECIPE code can be used to compute the amounts of additives required to bring the material in the concentrator makeup tank, the main feed tank, or the melter to within an acceptable composition range.

RECIPE will operate in two modes. The first mode will tell the user the amounts of chemical additives required to produce a glass of a specific composition. The code performs this computation by calculating the amounts of chemical additive required to bring each of the 19 oxides having the highest concentrations in the glass to their desired concentration. Inputs to the code for this first mode are:

- the desired composition of the final glass product
- the composition and mass of the wastes in the target tank
- the composition, including impurities, of each additive to be used as sources for each oxide
- the ratio of additives to be used for each oxide.

The output of the RECIPE code in this first mode will be the weight of each additive that must be added to the tank to yield the desired glass composition.

In its second mode, RECIPE will be used to check whether a slurry of cold chemicals has the correct mass and composition to form a mixture with a particular batch of radioactive waste that will result in a glass that is within acceptable tolerances. Inputs for this mode are:

- the weight and composition of the cold chemical slurry whose composition is being checked
- the weight and composition of the radioactive waste slurry to which the cold chemicals will be added
- the target glass composition with associated tolerances.

The output in this mode includes a prediction of the glass composition and flags to include oxides outside the glass composition tolerances. If the slurry is out of tolerance, RECIPE can be run in the first mode to determine the amounts of additives that would be required to bring the slurry into acceptable tolerances. The operator will then have the information needed to decide whether it would be better to add the additional chemicals or better to discard the slurry.

RECIPE will have a number of additional capabilities. These include the ability to:

- compute the total amount of carbonate, formate, and nitrate in the resulting mix

- determine the amounts of additives required when Zr is substituted on a molar basis for U and Th
- if needed, determine the target glass composition that for a given waste batch results in the minimum amount of glass produced.

5.5 REFERENCES

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6.0 LOW-LEVEL WASTE COORDINATION

J. L. Buelt - Manager

The objectives of the Low-Level Waste Coordination Task are to identify and conduct appropriate long-term research and development programs for the Department of Energy (DOE) for low-level radioactive wastes. These programs include both theoretical and experimental studies on many facets of low-level waste (LLW) management, with emphasis on barrier enhancement, as with the Engineered Sorbent Barriers Program, and waste form leaching, as with the Special Waste Form Lysimeters - Arid Program.

6.1 ENGINEERED SORBENT BARRIERS - S. J. Mitchell and H. D. Freeman

6.1.1 Objective

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

6.1.2 Summary

The Engineered Sorbent Barriers Program has been directed at the identification and evaluation of sorbent materials for three radionuclides of major concern in defense low-level wastes: ^{137}Cs , ^{60}Co , and ^{90}Sr . The work was conducted over a 2-year period in two major phases. The first phase, completed in FY 1985, consisted of laboratory-scale screening studies of sorbent materials. The second phase, completed in FY 1986, consisted of effectiveness evaluations of four sorbent barrier formulations in engineering-scale columns. The programmatic milestone to submit the final report, documenting all results of the screening studies and effectiveness evaluations, to DOE-Richland Office (DOE-RL) for review was completed on schedule in September 1986.

6.1.3 Effectiveness Evaluations of Selected Sorbent Barriers

The purpose of the sorbent barriers effectiveness evaluations was to verify the performance of the four sorbent barrier formulations identified in the laboratory screening studies. Since the selection of these barriers was

based on experimental results from batch contact interactions and laboratory-scale column studies, field conditions were not adequately represented. In addition, because of the high detection limit in small sample volumes, the laboratory-scale screening studies had not identified sorption trends under conditions of low radionuclide breakthrough. The effectiveness evaluations were designed to more accurately simulate many field conditions by using large-diameter (0.6 m) columns. The columns duplicated water infiltration, physical pressure from the weight of the solid wastes above the sorbent barrier, and hydrostatic head of the leachate expected in the field. The columns also produced large sample volumes of leachate passing through the sorbent barriers to significantly improve analytical detectability of radionuclides. In some cases, the laboratory-scale column studies had not generated enough leachate through the sorbent materials for the radionuclides to be detectable.

The four sorbent barrier formulations were tested in two phases in three 0.6-m-dia exposure columns. The first phase exposed two sorbent barrier formulations and one control material (soil) to radioactive leachates for 5 months. The second phase tested the two remaining barriers and duplicated the testing of the most effective formulation from the first-phase tests. The breakthrough of radioactive contaminants was measured under controlled conditions. These measurements were compared with the breakthrough from the control material (soil) with no sorbent material amendments. This approach was taken to conclusively verify the effectiveness of the sorbent material amendments.

The criterion used to evaluate the relative effectiveness of the sorbent materials was based on the U.S. Nuclear Regulatory Commission (NRC) 10 CFR Part 20, Appendix B, Table II water concentrations for soluble contaminants. The limits and reduction factors required to meet them are shown in Table 6.1.

6.1.3.1 Test Equipment

The test equipment was arranged as shown in Figure 6.1. A self-priming pump periodically transferred simulated leachate from a 208-L (55 gal) supply drum to the exposure columns. After the leachate had interacted with and flowed through the sorbent barriers in the columns, it was drained through a

TABLE 6.1. Soluble Water Limits and Reduction Factors for Selected Radionuclides^(a)

<u>Radionuclide</u>	<u>Table II Limit, $\mu\text{Ci/mL}$</u>	<u>Reduction Factor^(b)</u>
^{60}Co	5×10^{-5}	20
^{137}Cs	2×10^{-5}	50
^{90}Sr	3×10^{-7}	3333

(a) NRC 10 CFR Part 20, Appendix B, Table II.

(b) Simulated leachate concentration divided by NRC Table II limit.

FIGURE 6.1. Plan View of Equipment for Sorbent Barrier Effectiveness Evaluations

sublayer of glass marble and frit into a 20-L container. A geotextile separated the sorbent material from the glass marble drainage layer. The leachate in the 20-L containers was sampled weekly and transferred to the waste drum at the sampling station.

Each stainless steel exposure column (Figure 6.2) had a hydraulic piston that duplicated the forces exerted on the sorbent barriers by the weight of the overlying soil and solid wastes. Each column was capable of simulating a hydraulic head of leachate over the sorbent barrier by applying a pneumatic pressure of up to 690 kPa (100 psig) to the upper portion of the column. Water infiltration (132 cm/yr) was simulated by adding the appropriate amount of leachate to the column above the sorbent barrier. Each exposure column had a sight glass in the upper section to determine the leachate level inside the

FIGURE 6.2. Exposure Column Used in Effectiveness Evaluations of Selected Sorbent Barrier Materials

column. To prevent material from entering the sight glass, a fine mesh screen was attached to the inside wall of the exposure column where the sight glass pipe was located.

6.1.3.2 Test Conditions

The simulated leachate was prepared to represent the maximum credible concentrations of cesium, cobalt, strontium, EDTA, and competing ions expected at a low-level waste disposal site. The concentration of each of these components is given below:

- EDTA (1 ppm)
- calcium (1000 ppm, nitrate form)
- sodium (1000 ppm, nitrate form)
- magnesium (1000 ppm, nitrate form)
- iron (1 ppm, nitrate form)
- concentrated HNO_3 (to maintain pH 5)
- ^{85}Sr (1.24 $\mu\text{Ci/L}$, chloride form)
- ^{60}Co (1 $\mu\text{Ci/L}$, chloride form)
- ^{137}Cs (1 $\mu\text{Ci/L}$, chloride form)

A 175-L batch of this simulated leachate was prepared every 7 weeks for weekly introduction into the three columns. The higher concentration of 1.24 $\mu\text{Ci/L}$ ^{85}Sr was used because of its short half-life. At the end of the 7 weeks, the average concentration exposed to the sorbent barriers was 1 $\mu\text{Ci/L}$.

Each week 8.3 L of simulated radioactive leachate was introduced to each column and allowed to drain through the barrier into a 20-L leachate collection vessel. A sample of this leachate (~1 L) was saved for gamma spectroscopy analysis for any radionuclides that broke through. This sequence was repeated for about 21 weeks for both series of effectiveness evaluations. At the end of the 21 weeks, the barriers in the columns were cored for analysis of radionuclides retained by the sorbent materials.

6.1.3.3 Effectiveness Evaluations - First Series

The barrier formulations selected for the first series of effectiveness evaluations were the most cost-effective based on results of K_d values determined from the laboratory studies in FY 1985. It was expected that these

barriers would show premature breakthrough of strontium since the sorbent barriers were selected before the additional strontium sorbents had been identified. The three barriers (one control) tested were:

Column A - 5 wt% A-51 zeolite, 6 wt% activated charcoal, 1 wt% greensand, and 88 wt% local soil (A51/AC/GS/LS).

Column B - 4 wt% A-51 zeolite, 6 wt% activated charcoal, 5 wt% red pottery clay, and 85 wt% local soil (A51/AC/RPC/LS).

Column C - 100 wt% local soil (control column).

No cesium breakthrough was observed in any column, including the control column with no sorbent materials added to the soil. Figure 6.3 shows that column A performed well for strontium removal during the entire exposure period. There is only one point that was near the required decontamination factor

FIGURE 6.3. First Series - Effectiveness Evaluation Decontamination Factors for Strontium

(DF). Column B, however, showed a DF below that required after ~1.5 bed volumes of simulated leachate had passed through. Similarly, the local soil did not meet the required DF except for one point. This illustrates the fact that sorbent barriers are needed to retard migration of strontium in soils. A properly designed sorbent barrier retards the migration of strontium 2000 times better than most soils.

Figure 6.4 shows that cobalt is not quite as mobile as the strontium for the two barriers tested. Most of the fluctuations in the Kds for column A are due to variations in the detection limits. The leachate samples were below the detection limits during most of the sample analyses. The calculated minimum detection limit was used to calculate the decontamination factor in these cases. Both columns A and B were able to exceed the required decontamination factors for the duration of this test. The fluctuations in the curves make it

FIGURE 6.4. First Series - Effectiveness Evaluation Decontamination Factors for Cobalt

very difficult to calculate a total capacity for the barriers. Longer-term testing would be required to reach a point of equilibrium between the leachate and barrier. The soil column (column C) responded almost identically for cobalt as for strontium. Again this illustrates the mobility of complexed cobalt in unamended soils.

After exposure for about 21 weeks, each column was disassembled and two core samples were taken through the thickness of the barriers. These core samples were sectioned, canned, and analyzed to give radionuclide concentration profiles through the barriers. The largest amount of radioactivity was retained in upper sections of the cores. For strontium, more radioactivity migrated to lower sections; for column C, which had no sorbent amendments, migration of strontium was not retarded to any extent.

6.1.3.4 Effectiveness Evaluations - Second Series

The main emphasis of the second series of effectiveness evaluations was to test two new barriers formulated to be more effective for strontium removal than those in the first series of tests. The first series of tests showed that cesium could be effectively removed from the leachate solution with greensand, and cobalt effectively removed with activated charcoal in the presence of maximum credible concentrations of competing ions. The results of the laboratory studies, however, made it clear that high concentrations of calcium in the LLW leachate would significantly reduce the sorbent barrier's effectiveness in removing strontium. Therefore, a laboratory study was launched in FY 1986 to identify additional methods and materials for removal of strontium from the leachate.

The approach of the study was to investigate new sorbent materials not tested previously and to look at strontium precipitants that could be used as part of a precipitation/sorption barrier. Of the 28 materials tested for strontium sorption, only three materials stand out as exceptionally effective: A-51 synthetic zeolite, poly antimonite acid (PAA), and manganese oxide (MnO). Unfortunately, the two most effective materials, PAA and MnO, are prohibitively expensive now. Because of its extremely low cost and fair Kd value, clinoptilolite should also be considered as an effective barrier for strontium.

Since the most promising and cost-effective materials for removal of strontium identified in the laboratory-scale tests were A-51 zeolite and clinoptilolite, formulations containing these materials were tested in the second series of engineering-scale column tests. The most effective barrier formulation from the first series of tests (containing a lower percentage of A-51 zeolite) was repeated to give statistical confidence in the results. The concentration of A-51 zeolite was selected to account for calcium loading, to achieve the 300-year lifetime criterion under maximum credible completing ion conditions. The three formulations tested were as follows:

Column A - 20 wt% A-51 zeolite, 6 wt% activated charcoal, 1 wt% greensand, and 73 wt% local soil (A51(20)/AC/GS/LS).

Column B - 93 wt% clinoptilolite, 6 wt% activated charcoal, and 1 wt% greensand (CL/AC/GS).

Column C - (repeat from FY 1985) 5 wt% A-51 zeolite, 6 wt% activated charcoal, 1 wt% greensand, and 88 wt% local soil (A51(5)/AC/GS/LS).

Samples of the leachates collected from these columns were analyzed, and the results are presented in Figures 6.5 and 6.6. No breakthrough for cesium was observed, indicating a DF of greater than 8000 for each column. Results showed that one barrier formulation met all the performance requirements established for this study. This formulation was tested in column A, and the sorbent materials comprising this barrier were 20 wt% A-51 zeolite, 6 wt% activated charcoal, and 1 wt% greensand. This barrier showed no breakthrough for strontium or cesium and only minor breakthrough for cobalt (within performance requirements).

The clinoptilolite-containing barrier did not perform as predicted by the laboratory-scale experiments. This formulation was tested in column B, and both strontium and cobalt broke through the column after a 2-week exposure. No cesium was observed in the leachate. The clinoptilolite may not be performing as expected due to insufficient contact time. The barrier is fairly permeable, which allows the leachate to percolate through it at a rapid rate. The rate of percolation could be controlled by using finer clinoptilolite or by adding small amounts of clay to decrease permeability.

FIGURE 6.5. Second Series - Effectiveness Evaluation Decontamination Factors for Strontium

FIGURE 6.6. Second Series - Effectiveness Evaluation Decontamination Factors for Cobalt

Column C, which was a repeat of one of the first series of column tests, showed some breakthrough of strontium and cobalt similar to results of the previous series. The composition of column C was the same except for a lower amount of A-51 zeolite (5 wt%). This result shows that the higher concentration of A-51 zeolite used in column A (20 wt%) is necessary for adequate removal of strontium.

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

6.2.1 Objective

The objective of the Special Waste Form Lysimeters - Arid Program is to determine the performance of solidified commercial low-level waste forms using a field-scale lysimeter facility constructed for measuring the release and migration of radionuclides from the waste forms. The performance of these waste forms, as measured by radionuclide concentrations in lysimeter effluent, will be compared to that predicted by laboratory characterization of the waste forms. Waste forms being tested include nuclear power reactor waste streams that have been solidified in cement, Dow^(a) polymer, and bitumen.

6.2.2 Summary

Low-level radioactive liquid waste generated by nuclear power plants is solidified before its transport and burial in shallow-land burial (SLB) sites. This practice is designed to limit the release of radionuclides to the environment by providing structural stability to the waste and is required by 10 CFR 61. Typical solidifying agents used to bind the radionuclides in a solid waste form are cement, bitumen, and vinyl ester-styrene (Dow^(a) polymer). Leaching tests, in which sample waste forms are contacted with water over time, are used to evaluate the ability of these waste forms to retain radionuclides. Although these tests measure radionuclide leach rates in water and allow comparison of leaching characteristics, they cannot be used directly to predict the release and migration of radionuclides in actual burial conditions. Estimating the potential for radionuclide migration from SLB sites requires knowledge of the contaminant concentration in the soil surrounding the waste form.

(a) Product of the Dow Chemical Co., Midland, Michigan.

This concentration, referred to as the source term, may be controlled by the concentration, leach rate and/or solubility of radionuclides in the waste form, the rate of water flow in the soil surrounding the waste, and solubility and adsorption processes that are present in the soil.

Pacific Northwest Laboratory (PNL) is conducting research for DOE's Low-Level Waste Management Program to evaluate the performance of solidified low-level waste forms in an arid SLB site. Under the PNL program, Special Waste Form Lysimeters-Arid (SWFL), a field test facility was constructed to monitor the leaching of commercial solidified waste (Walter, Graham and Gee 1984). Laboratory experiments being conducted in support of the field facility are designed to investigate leaching and adsorption characteristics of the waste forms in contact with soil. The major objectives of the program are to 1) monitor radionuclide release from actual commercial waste forms under field conditions, 2) evaluate the ability of laboratory leaching tests to predict leaching under actual field conditions, 3) determine which mechanisms (i.e., diffusion, solubility, adsorption) actually control the source term, and 4) ultimately, on the basis of field and laboratory measurements, develop appropriate hydrologic and geochemical modeling capability to estimate the potential for long-term transport of radionuclides at arid burial sites. Results of the laboratory experiments and field investigations completed through FY 1986 are presented in the topical report by Walter et al. (1986) and are summarized below.

6.2.3 Field Investigations

The field leaching facility is designed to monitor the release of radionuclides from commercial waste under actual field conditions. The solidified waste forms used were obtained from commercial boiling water reactors (BWR) and pressurized water reactors (PWR), and were buried in a field-scale leaching facility on the Hanford Site, located in southeastern Washington State. The field leaching facility, constructed in FY 1984, consists of ten steel lysimeters, 3 m deep by 1.8 m in diameter, surrounding a central instrument caisson (Figure 6.7). One 210-L barrel of solidified waste (with casing removed) is centered in each lysimeter and surrounded by sifted sediment excavated from the

FIGURE 6.7. Conceptual Drawing of the Special Waste-Form Lysimeters - Arid Field Facility

lysimeter construction site. The waste types and solidifying agents represented are listed in Table 6.2. Chemical and radiological analyses are performed quarterly on leachate that drains from each lysimeter to the central caisson. Soil moisture, soil temperature, micrometeorological and drainage data are also collected.

Precipitation at the SWFL facility is typical of temperature zone climates where the bulk of the water comes during winter months, largely as snow. The

TABLE 6.2. Waste Forms Contained in Special Waste-Form Lysimeters

<u>Lysimeter Number</u>	<u>Waste Stream</u>	<u>Reactor</u>	<u>Solidification Agent</u>
1	Boric acid concentrate	PWR ^(a)	Masonry cement
2	Evaporator concentrate	BWR ^(b)	Portland III cement
3	Evaporator concentrate and ion-exchange resin	BWR	Portland III cement
4	Evaporator concentrate and ion-exchange resin	BWR	Vinyl ester-styrene
5	Boric acid concentrate	PWR	Bitumen
6	Boric acid concentrate	PWR	Bitumen
7	Boric acid concentrate	PWR	Masonry cement
8	Evaporator concentrate	BWR	Portland III cement
9	Evaporator concentrate and ion-exchange resin	BWR	Portland III cement
10	Evaporator concentrate and ion-exchange resin	BWR	Vinyl ester-styrene

(a) Pressurized water reactor.

(b) Boiling water reactor.

precipitation rate can also vary significantly from year to year. Figure 6.8 shows the cumulative precipitation received from the time of burial of the waste forms in mid-March 1984 to April 1986. This figure shows that 1984 was somewhat unusual in that significant rains came in the spring and essentially no rain came in the fall. However, the expected precipitation occurred in January and February 1985. During the rapid melt of the February snow pack, the lysimeters labeled L-8, L-9, and L-10 were temporarily flooded. The second year the facility received the usual distribution of winter precipitation, with little water coming during the summer months.

The water storage records for lysimeters L-1 and L-8, which contain BWR waste with ion-exchange resins solidified in Portland III cement, are shown in Figure 6.9. An interesting feature of this figure is the response of lysimeter

FIGURE 6.8. Cumulative Precipitation: Hanford Meteorological Station, March 1984 to April 1986

FIGURE 6.9. Comparison of Total Water Storage in L-1 and L-8

L-8 to the flooding. Prior to flooding in February 1985, the storage characteristics of L-1 and L-8 were essentially identical. During the flooding, L-8 showed a substantial jump in storage from about 22 cm to over 35 cm. The storage increase corresponds to an increase in average volumetric water content from 7% to nearly 12%. During the same period, storage in L-1 increased to 28 cm, which corresponds to only 10% volumetric water content. This difference in storage is to be expected during flooding; however, what might not be expected is how quickly the water content of L-8 returned to levels equal to those found in L-1. Within 2 weeks of flooding, the water storage in both lysimeters was the same again.

The effects of variable water balance are reflected in the drainage effluent data collected at the SWFL facility. Since placement of the waste forms in April 1984, five of the ten lysimeters have shown measurable and sustained breakthrough of ^{60}Co , while the other radionuclide constituents of the waste (^{134}Cs , ^{90}Sr , and ^{54}Mn) have not reached the bottom of the caissons. Figure 6.10 shows the accumulated ^{60}Co released from the lysimeters since the initial breakthrough. All five lysimeters where ^{60}Co is observed in the

FIGURE 6.10. Mass ^{60}Co Released in SWFL Lysimeters

leachate contain waste forms made from BWR wastes (see Table 6.2). The mobility of ^{60}Co in these lysimeters is attributed to complexation of ^{60}Co with organic chelating agents found in the BWR wastes. Two of the lysimeters that show no radionuclide content in the leachates contain PWR boric acid waste solidified in masonry cement with a total inventory of $5 \times 10^2 \mu\text{Ci}$ of ^{60}Co , and two contain boric acid waste from Palisades reactor solidified in bitumen with a total inventory of $1.2 \times 10^3 \mu\text{Ci}$ of ^{60}Co per barrel.

6.2.4 Laboratory Experiments

Laboratory soil-column leaching experiments are being conducted on waste forms that are identical, except in scale, to waste forms buried in the field leaching facility. The objective of the laboratory column research is to determine source terms and solubility controls associated with the release and transport of radionuclides from laboratory-scale waste forms in Hanford sediment. This information will be used to predict and interpret leach rates and sorption at the field facility. During FY 1986 the laboratory research was initiated with the study of Portland III cement with evaporator concentrate and ion-exchange resin waste. This waste form was chosen from those obtained for the SWFL program (Table 6.2) because it has the highest radionuclide activity and contains chelating agents that increase the mobility of some radionuclides.

The laboratory experiments are conducted in three parts:

1. batch leaching of solidified waste forms
2. column adsorption of the leachate produced in the first step
3. simultaneous leaching and adsorption of solidified waste forms in soil columns.

The first two parts of the experiments are designed to permit the leaching and sorption processes to be examined separately. The combined results of parts 1 and 2 (batch leaching and soil adsorption column) are compared with the results of part 3 (the simultaneous leaching and adsorption in soil columns). The information gained will be used to evaluate the extent to which batch leaching and adsorption data, which are easily generated, predict the performance of waste forms in full contact with soil as may be found in actual field conditions.

The batch leaching test used was developed by the American Nuclear Society. The test consisted of fully immersing a sample of BWR waste solidified in Portland III cement in Hanford ground water for 35 days. The results of the test are shown in Figure 6.11, which compares the PNL results with results of similar tests conducted by Brookhaven National Laboratory (BNL) in distilled water.

The batch leaching results show that waste forms leached in Hanford ground water released ^{137}Cs and ^{60}Co at nearly the same rate as those leached in deionized water at BNL. The difference in leaching rates of the readily leachable radionuclides, such as ^{137}Cs , in ground water and deionized water may be negligible.

In the soil column adsorption test, three columns were filled with the Hanford sediment used to backfill the field lysimeters. The leachates from the batch leach tests were then pumped through the columns at a rate of 15 pore volumes/day. The effluent curve, shown in Figure 6.12, has a saw-tooth shape and appears to represent adsorption and desorption of variably complexed ^{60}Co in the soil. Cobalt-60 was present in the column effluent after only one

FIGURE 6.11. Comparison of PNL and BNL Leaching Results for ^{60}Co and ^{137}Cs

FIGURE 6.12. Breakthrough Curve of ^{60}Co in Soil Adsorption Column

pore volume of Hanford ground water had moved through the soil/waste-form column, suggesting that some ^{60}Co was present in a complexed form with a distribution coefficient (K_d) of zero.

The combined leach-adsorption test was conducted in columns similar to those used in the soil column adsorption test. Hanford ground water was pumped through the columns at a flow rate of 0.8 pore volumes/day for 115 days. The combined leach/adsorption column effluent curve shows decreasing concentration of ^{60}Co in the effluent as a result of the decreasing concentration of ^{60}Co leaching from the waste form (Figure 6.13). At the end of the test, the waste form was removed from the column and the soil segments were analyzed to determine the distribution of radionuclides. Cesium-134 and -137 were bound in the soil immediately surrounding the waste form. Cobalt-60 was detected in small amounts in several sections dispersed through the column. Sediment in contact with the waste form was cemented to the form, most likely by precipitation of carbonate minerals.

The results of the combined leach-adsorption experiment effectively predicted the breakthrough of ^{60}Co observed in the field leaching facility. Nearly all of the ^{137}Cs and ^{134}Cs was leached from the waste form in the

FIGURE 6.13. Breakthrough Curve of ^{60}Co in Combined Leach-Adsorption Column

ANS 16.1 tests, and it was readily adsorbed on the soil, as indicated in the soil adsorption and combined leaching-adsorption column experiments. Therefore, $^{137,134}\text{Cs}$ is assumed to leach from the field lysimeters, to be adsorbed by the soil, and not to be present in the effluent. Cobalt-60 was present in the laboratory waste form at a mass about ten times that of ^{137}Cs ; however, less than 1% leached from the waste form. This small mass experienced little or no retention by the soil, and a fraction moved through the soil column at the same velocity as water. Organic complexing agents found in the raw waste stream were suspected to be responsible for the mobility of ^{60}Co through the cement matrix and the soil column.

The immediate breakthrough of a small portion of ^{60}Co in the laboratory experiments (both column adsorption using ANS 16.1 leachates and the combined waste form-sediment column contacted with Hanford ground water) will require further study. Past studies with ^{60}Co tracer suggest that cobalt is readily adsorbed. Other studies have shown that ^{60}Co complexed to organic chelating agents can be quite mobile and exhibit little tendency for adsorption. Thus speciation is extremely important in determining ^{60}Co migration potential.

6.3 REFERENCES

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7.0 ACRONYMS AND ABBREVIATIONS

AC	activated charcoal
AC	alternating current
ADTP	absolute differences between true and predicted glass compositions
ADTT	absolute differences between true and targeted glass compositions
ANS	American Nuclear Society
ARM	approved reference material
BNL	Brookhaven National Laboratory
BWR	boiling-water reactor
cm	centimeter
cP	centipoise
CTS	component test stand
DC	direct current
DCSF	decontamination, characterization and storage facility
DF	decontamination factor
DOE	Department of Energy
DWPF	Defense Waste Processing Facility
ECM	experimental ceramic melter
EMS	empirical mixture study
EPT	electropolishing tank
EVS	ejector venturi scrubber
FRG	Federal Republic of Germany
g	gram
GS	greensand
HAW	high-activity waste
HBCM	high-bay ceramic melter
HEPA	high-efficiency particulate air (filter)
HLLW	high-level liquid waste
HLW	high-level waste
HWVP	Hanford Waste Vitrification Plant
HWVP	Hanford Waste Vitrification Program
IR	infra-red
kg	kilogram

L	liter
LFCM	liquid-fed ceramic melter
LFMM	liquid-fed mini-melter
LLW	low-level waste
LS	local soil
LSFM	large slurry-fed melter (at Savannah River Laboratory)
LWR	light-water reactor
m	meter
MCC	Materials Characterization Center
MRS	Monitored Retrievable Storage
MVR	maximum volume reduction
NFBH	non-fuel-bearing hardware
NRC	Nuclear Regulatory Commission
NWTP	Nuclear Waste Treatment Program
OCRWM	Office of Civilian Radioactive Waste Management
PAA	poly antimononic acid
PCB	polychlorinated biphenyls
PNL	Pacific Northwest Laboratory
PSCM	pilot-scale ceramic melter
PUREX	<u>pl</u> utonium <u>u</u> ranium <u>e</u> xtraction
PWR	pressurized-water reactor
redox	chemical <u>r</u> eduction <u>o</u> xidation
RLFCM	radioactive liquid-fed ceramic melter
rpm	revolutions per minute
RSD	relative standard deviation
RST	rinse-soak tank
RTS	radioactive treatment system
s	second
SBS	submerged bed scrubber
SLB	shallow-land burial
SPC	statistical process control
SQC	statistical quality control
SRL	Savannah River Laboratory
SWFL	special waste form lysimeters

TC	thermocouple
THOREX	<u>thorium extraction</u>
TRU	transuranic
TRUW	transuranic waste
TTA	thenoyltrifluoracetone
VVS	vessel ventilation system
W	watts
WAPS	Waste Acceptance Preliminary Specifications
WNYNSC	Western New York Nuclear Services Center
WQR	Waste Form Qualification Report
WV	West Valley
WVDP	West Valley Demonstration Project
WVNS	West Valley Nuclear Services
WVST	West Valley Support Task

APPENDIX A

OPERATIONAL HISTORY OF THE PILOT-SCALE CERAMIC MELTER

APPENDIX A

OPERATIONAL HISTORY OF THE PILOT-SCALE CERAMIC MELTER

<u>Run ID #</u>	<u>Date</u>	<u>Years</u>	<u>Comments</u>
Startup	4/24/78	0	Mark-I lid installed.
CFCM-1(a)	5/8/78	--	
CFCM-2	5/24/78	--	
CFCM-3	6/1/78	--	
CFCM-4	6/26/78	--	
CFCM-5	9/20-30/78	--	First multiday test.
Shutdown	10/24/78	0.5	Mark-I lid removed.
Startup	4/13/79	--	Mark-II lid installed, electrode feed added, throat liner installed.
CFCM-6	4/18-27/79	--	
CFCM-7	6/4-30/79	--	
CFCM-8	11/5-9/79	--	
Shutdown	11/30/79	1.13	Mark-II lid removed, CFCM tests produced total of 61,500 kg glass in 1266 hr of operation.
Startup	11/28/80	--	Mark-III lid installed, refractories replaced, electrode bus changed.
PSCM-1	12/12-19/80	--	First liquid slurry test, TDSM-131 w/coal, 2020 kg produced.
PSCM-2	3/23-27/81	--	Propane boost, TDSM-131 with coal, 2872 kg glass produced.
PSCM-3	7/19-24/81	--	TDSF-131 with formate, 2400 kg glass produced.

(a) CFCM: calcine-fed ceramic melter.

Run ID #	Date	Years	Comments
Shutdown	7/28/81	1.80	Total glass produced = 7292 kg.
Startup	11/14/81	--	Mark-IV lid installed.
PSCM-4	12/7-11/81	--	TDSF-131 with formate, 2709 kg glass produced.
PSCM-5	1/25-31/82	--	Lid heating, TDSF-131 with formate, 3338 kg glass produced.
PSCM-6	3/21-26/82	--	Lid heating, TDSF-165 with formate, 40% solids, 4125 kg glass produced.
PSCM-7	5/17-21/82	--	DWPF-165 with formate, 50% solids, 2750 kg glass produced.
PSCM-8	6/14-24/82	--	Lid heating, high-Al-165 with formate, 7630 kg glass produced.
Shutdown	6/24/82	2.41	End of SRL program support, 27,844 kg of glass produced.
Startup	7/24/82	--	
PSCM-9	8/2-5/82	--	WV-131S, about 2238 kg glass produced.
PSCM-10	8/82	--	WV-131S, HWVP instrument test for RL Treat, about 72 hr, about 900 kg glass produced.
PSCM-11	11/15-19/82	--	NCAW/frit-82-10, 220 kg glass produced, HWVP-5.
PSCM-12	12/21/82	--	Nonfeed reboil test for 17 hr, fed for 11 hr, 43 kg glass produced. HWVP-6 NCAW/82-10 frit.
PSCM-13	1/17-19/83	--	HWVP-7, 48 hr, NCAW/82-10, 182 kg glass produced.
PSCM-14	3/24,25,28-31/83	--	WV dry-fed test, 4400 kg glass produced, WV washed sludge at 30 wt%.
PSCM-15	5/17-26/83	--	WV Hydrox, waste at 30 wt%, 3650 kg glass produced.
PSCM-16	8/22-29,31, 9/1/83	--	WV nitric acid waste at 30 wt% 3000 kg glass produced.

Run ID #	Date	Years	Comments
PSCM-17	9/26-30/83	--	HWVP CAW, 694 kg glass produced.
PSCM-XX	7/9-10/84	--	MCC test, filled 36 1/4-scale cans with SRL-TDSF-165 glass, dry fed, 3500 kg glass produced.
PSCM-18	8/1/84	--	WV short test to test off-gas equipment, 300 kg glass produced.
PSCM-19/19E	8/21-31, 9/1,19-21/84	--	WV with zeolite (30 CV), chemical glass formers, 0.5 moles nitric acid, 2870 kg glass produced.
PSCM-20	4/1-10/85	--	FRG canisters filled (8), #8 feed used, 240 hr of operation, 2000 kg of glass produced.
PSCM-21	5/31 - 6/11/85	--	WV-205 feed, 296 hr of operation, 3170 kg glass produced.
PSCM-22	7/15 - 8/2/85	--	HW-39 glass composition, 10 1/2-scale canisters filled for SRL, 427 hr of operation, 6800 kg glass produced.
Undesignated	9/11-12/85	--	FRG canisters filled (2), 400 kg SRL 131 frit/calcline (dry fed), 30 hr of operation.
Shutdown	9/13/85	--	34,367 kg glass produced since last shutdown.

SUMMARY

Total operating time = 5.55 yr = 48,700 hr.

Total liquid feeding time = 0.40 yr = 142 days = 3410 hr.

Total glass produced = 119,500 kg = 262,900 lb.

Glass produced from liquid-fed operation = 57,600 kg = 126,750 lb.

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