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Nuclear Waste Treatment Program Annual Report for FY 1984

H.C. Burkholder and J.M. Rusin, Compilers

April 1985

**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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ANNUAL REPORT FOR FY 1984

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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 nuclear fuel cycle closure 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 those goals, the Office of Terminal Waste Disposal and Remedial Action of DOE established what is now called the Nuclear Waste Treatment Program (NWTP) at the Pacific Northwest Laboratory (PNL) during the second half of FY 1982. To support DOE's attainment of its goals, the NWTP has two objectives: 1) to provide documented technology necessary for the design and operation of nuclear waste treatment facilities by commercial enterprises as part of a licensed waste management system and 2) to provide 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 1984 toward meeting the two objectives. The detailed presentation is organized according to the task structure of the program, but this Executive Summary is organized by program element.

FIRST-GENERATION HIGH-LEVEL WASTE TREATMENT

A revised draft of the production requirements for vitrified high-level waste (HLW) was completed as a starting point for discussions with the DOE storage and disposal programs to establish an integrated set of production/acceptance requirements for these wastes. Peer review comments were received concerning a document on performance of borosilicate glass written in FY 1983, and these comments were considered in a revision scheduled for publication in FY 1985. The removal of sodium sulfate from a continuously operated liquid-fed ceramic melter (LFCM) by reduction using a carbon source was investigated. A 5-year study of the effects of HLW glass storage at elevated temperatures was completed. Three techniques were examined to decrease the sedimentation rate and improve the rheology of LFCM feeds. Work was begun to develop a control

algorithm for an operating LFCM that uses only inputs from process instrumentation and to develop the control instruments themselves. A method for examining the cracking and voids in full-size canisters of vitrified waste was investigated as a basis for further use in FY 1985.

A pilot-scale, radioactive liquid-fed ceramic melter (RLFCM), canister-handling turntable, glass-level detection system, feed preparation and transfer system, and off-gas treatment system were installed in B-Cell of the 324 Building. Radioactive operations began in October 1984. This was apparently the first large-scale LFCM vitrification system to be operated radioactively anywhere in the world. A 5-year coordinated nonradioactive and radioactive testing program, using a range of feed compositions and operating conditions, is scheduled for the FY 1985 to FY 1989 period.

SPENT FUEL TREATMENT

Work to develop a spent fuel treatment approach was begun. Two major treatment options, the sequence of major decisions necessary to implement both options, and the factors that affect each decision were identified. At the end of the year, DOE directed that this work be placed on hold pending a resolution of the need for such treatment. The FY 1984 work will be documented in FY 1985.

TRANSURANIC WASTE TREATMENT

Six treatment options were identified for the transuranic wastes from a reference LWR reprocessing plant. These options were evaluated, and a preferred option was recommended for implementation. This option involves the unit operations of shredding, metal melting, incineration, and cementation. Radionuclide release rates were measured for as-generated and melted fuel hulls, and the potentials for treating these hulls by both melting and decontamination were evaluated.

WEST VALLEY

A major effort was started to develop a new West Valley Demonstration Project (WVDP) feed composition and glass formulation as a result of a West Valley Nuclear Services (WVNS) decision to include the IE-95 zeolite ion-

exchange material in the melter feed. This work included the investigation of the rheological properties of comminuted zeolite, the development of primary and backup feed pumps, the performance of both bench-scale and pilot-scale, nonradioactive melter tests, the evaluation of off-gas treatment equipment, the investigation of melter foaming, redox control, and melting rate, and the study of the potential for, and effects of, a melter vapor explosion.

The evaluation of supernate treatment processes for WVDP was undertaken. This work included the characterization of both the zeolite ion-exchange process and the phosphotungstic acid precipitation process, the laboratory-scale measurement of design parameters for a zeolite-treatment system, and the documentation of a design basis for the WVDP zeolite ion-exchange system.

Equipment designs, specifications, and engineering calculations of the WVDP Component Test Stand (CTS) were completed; the CTS melter was fabricated and sent to WVNS for bricking; and the CTS turntable was partly fabricated. The CTS equipment was designed to comply with WVNS-prepared design criteria. As part of this work, process flow diagrams, material balance flowsheets, process and instrument diagrams, hydraulic diagrams, equipment arrangements, jumper layouts, and electrical diagrams were prepared.

THREE MILE ISLAND

The operation of mobile radiochemical and radioanalytical laboratories at the Three Mile Island (TMI) site at DOE expense was completed. Dosimetric support to the location of contamination within TMI pipes and vessels and a corrosion assessment of the Submerged Demineralizer System vessels as long-term containers were also completed. All NWTP work supporting the TMI cleanup ended during FY 1984.

BREEDER REPROCESSING ENGINEERING TEST

An evaluation of the design basis for the Breeder Reprocessing Engineering Test (BRET) HLW vitrification system was completed. About 50% of the conceptual design and a small amount of bench-scale melter and feed system testing was completed before all activities in this area were discontinued at DOE request. The future of the BRET is presently undefined.

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1.0 TECHNOLOGY DEVELOPMENT TASK

1.1 OBJECTIVES AND OVERVIEW - W. A. Ross

The objectives of the Technology Development Task for FY 1984 were 1) to define the documentation necessary for potential users of nuclear waste treatment technology to design and operate full-scale facilities with both efficiency and confidence, 2) to establish specifications and requirements for high-level waste (HLW) forms, 3) to determine that the planned waste forms and processes are adequate for proposed applications, 4) to develop methods for predicting product performance characteristics from knowledge of process operating parameters, and 5) select and develop technology for the treatment of nuclear wastes including high-level, transuranic, and spent fuel. To accomplish these stated objectives and additional objectives defined throughout the year, the task was divided into five major subtasks. These included Documentation, Specifications and Analysis; Waste-Form Characterization; TRU Waste Treatment; Process Modeling and Data Acquisition; and Spent Fuel Treatment.

In the documentation, specifications and analysis subtask, new drafts of the HLW production requirements were prepared, the performance of materials in repositories was assessed, and a strategy was drafted for the treatment of TRU wastes from reprocessing. This information is summarized in Sections 1.2 through 1.4.

Within the waste-form characterization subtask, data on the behavior of as-generated spent-fuel hulls were compared with samples of melted fuel hulls to show that melting can reduce the leachability of radionuclides by several orders of magnitude. Volatility during the metal melting, however, may be a problem and needs further evaluation. Data obtained on both the solubility of thorium and neptunium proved to be many orders of magnitude lower than conservative calculations had indicated. It was also determined that sodium sulfate can be removed from the liquid-fed ceramic melter (LFCM) by reduction with a carbon source. Testing was also completed on several glass compositions that had been stored for up to 5 years at temperatures of 300 to 500°C. These studies are reported in Sections 1.5 through 1.9.

The potential for treating fuel hulls by melting or by decontamination was evaluated in two separate studies, and it appears that the melting option will be preferred. This method also appears favorable for treating hardware from spent fuel element disassembly and consolidation. Efforts began on assisting DOE in establishing subcontracts with those who are decontaminating and decommissioning (D&D) several plutonium fuel fabrication facilities. Sections 1.10 through 1.12 detail these activities.

The Process Modeling and Data Acquisition subtask included 1) limited developments of the LFCM feed system, 2) acquisition of a monitor for determining the depth of glass in a melter and for determining whether sodium sulfate is separating from the glass, 3) historical evaluations of various instruments to correlate their readings with behavior in the melter, and 4) sampling and comparison of glass from different melting equipment begun to provide a base for comparison of hot (radioactive) and cold glass. These activities are summarized in Sections 1.13 through 1.16.

Under the spent fuel treatment subtask (Section 1.17), a review was made of potential treatment methods and factors of importance in selecting a treatment method.

Continued progress has been made in the development of processes for the treatment of radioactive wastes. Equipment has been improved, and the processes are being monitored and controlled more completely. The plans to document this work for future applications are continuing and are an increasingly high priority for this work.

1.2 HIGH-LEVEL WASTE PRODUCTION REQUIREMENTS - W. A. Ross, M. O. Cloninger, G. B. Mellinger, and K. J. Schneider

The objective of this activity is to establish requirements for commercial HLW canisters that can be met by the producer and may be needed by other parts of the waste management system. It is important to waste processors that production requirements be provided that clearly permit design of processes and facilities in conformance with likely requirements. Repository and storage programs are likewise developing specifications or requirements for the waste form and its canister. Requirements developed as part of this activity provide

a basis for discussion with these groups and have aided in clarifying needs and capabilities. Further interactions are necessary to complete this activity.

These production requirements are the only ones specifically addressing commercial HLW materials. Sets of specifications being developed by the repository programs are for spent fuel and for vitrified defense wastes from Savannah River and from the wastes at West Valley in New York. It has therefore been necessary to anticipate repository requirements based on a different waste type.

These production requirements are generally based on the reference glass and 304L stainless steel canister described in PNL-3838 (Slate et al. 1981) with modifications to provide for increased flexibility in waste canister sizes. They provide preliminary numerical values for canistered HLW form properties and parameters based on expected conditions throughout the waste management system, from waste-form production through overpacking of the HLW canister at the repository.

General subject areas addressed include predisposal containment, operational safety, criticality control, canistered waste identification, quality assurance, and, to some degree, testing and data requirements for ensuring compliance. Testing and data requirements will usually be met with results from generic (rather than actual production canister test) data. It is expected that existing test procedures from the Materials Characterization Center (MCC) and other nationally recognized authorities will be used as part of these specifications.

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

The FY 1983 annual report (McElroy and Burkholder 1984) summarized the results and conclusions of a preliminary evaluation of the performance of borosilicate glass HLW forms during transportation, storage, and disposal. The objective of this evaluation was to provide a preliminary technical database for scope, schedule, and budget decisions in the high-level element of the Program. In FY 1984, this work was revised to address peer review comments and incorporate new information. In particular, two comprehensive surveys were

conducted on sorption and solubility properties of species relevant to radionuclide transport through the various geologic media of interest at present in the United States. The report is scheduled for issue in FY 1985.

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

A study was initiated and documented in a draft report for internal review, "Analysis of Treatment Strategies for Transuranic Wastes from Reprocessing Plants," in collaboration with related work for DOE's Office of Civilian Radioactive Waste Management (OCRWM). An interim summary of the study was presented at the June 1984 American Nuclear Society meeting (Ross et al. 1984), and the document is planned for completion and publication in FY 1985. The objective of the study was to analyze various transuranic (TRU) waste treatment options at a fuel reprocessing plant and the cost impacts of these options on the total waste management system (i.e., treatment, storage, transportation and disposal).

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

Six potential treatment options were selected for the five categories of waste. These options were selected to represent different overall objectives and varying methods for achieving them. The six basic treatment objectives are: 1) no treatment (containerization only), 2) minimum volume reduction treatment (compaction), 3) minimum number of simple treatment processes and products (cementation), 4) maximum volume reduction without decontamination (melting, incineration, hot pressing), 5) maximum volume reduction with decontamination (decontamination, vitrification and other treatment), and 6) volume reduction with no combustible waste forms (melting, incineration, cementing).

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

Based on conceptual design requirements, life-cycle costs (excluding decommissioning costs) were estimated for treatment-plus-onsite storage, transportation, and disposal in basalt of both high-level and transuranic wastes from 70,000 MTU. The sums of these costs were estimated to range from \$10.3 billion for no treatment down to \$8.7 billion. Costs for managing the resulting incremental amounts of low-level waste were included in these considerations.

In addition, strategies and processes in each option were evaluated relative to regulations, waste forms, safety, process complexity, status of technology, and process flexibility.

Some major conclusions from the study are as follows: 1) all the treatment options appear to offer economic and waste form incentives as compared to no treatment, 2) volume reduction of the wastes generally (but not always) reduces overall system costs, 3) significant incentives exist for applying treatment options to TRU wastes that are more extensive than minimum or simple treatments, 4) fuel cladding hulls and hardware are the most important TRU waste stream from reprocessing because of their large volume, their high radioactivity, and the costs for their treatment, handling, transportation, and disposal and, 5) HEPA^(a) filters are a major waste stream that can be significantly reduced in volume, but their composition complicates their treatment.

1.5 FUEL HULL LEACHING - Y. B. Katayama

A scoping study of spent fuel hull leachability has been completed. It was initiated to provide data for a preliminary safety assessment of spent fuel hull disposal.

In this study, Zircaloy spent fuel hulls from light-water reactor (LWR) fuel rods were leach-tested in deionized water at 90°C. These hulls remain from the waste preparation phase of the Nuclear Waste Vitrification Project (NWVP), conducted from 1976 through 1979 at PNL. Fuels with burnups of 20,100 to 29,000 MWd/MTU were processed during the NWVP. About 0.007 wt% of the uranium remained on the NWVP hulls. Tritium, cesium, antimony, and ruthenium were

(a) High-efficiency particulate air.

present at much higher levels than uranium. Both as-processed hulls and hulls arc-melted into small buttons were tested. Significant quantities of radionuclides were lost during the arc-melting of the fuel hulls.

The release of radionuclides from as-processed spent fuel hulls to deionized water at 90°C reaches a maximum solution concentration within 3 days and stays near constant for up to 28 days. These releases from hulls were greater than for spent fuel. Table 1.1 lists the fractional release from as-processed spent fuel hulls and arc-melted spent fuel hulls after 28 days of leaching. Consolidating the hulls by arc-melting decreased the fractional release of the measured radionuclides, except for cesium, which increased about tenfold.

Several parameters were identified in this scoping study for further evaluation of fuel hull performance.

TABLE 1.1. Weight Fraction Released from Spent Fuel Hull to Deionized Water at 90°C After 28 Days of Leaching

<u>Radionuclides</u>	<u>As-Processed Hull</u>	<u>Arc-Melted Hull</u>
$^{239+240}\text{Pu}$	2.8×10^{-3}	6.7×10^{-5}
^{125}Sb	9.3×10^{-4}	(a)
^{60}Co	2.1×10^{-4}	(a)
^{134}Cs	2.8×10^{-3}	4.3×10^{-2}
^{137}Cs	3.2×10^{-3}	3.1×10^{-2}
^{154}Eu	2.9×10^{-4}	(a)
^3H	5.7×10^{-4}	(b)
Uranium	1.32×10^{-2}	(a)
Surface area, cm^2	7.86	1.87
Soln. vol., mL	78.6	18.7
pH	6.6	6.1

(a) Not detected or below reportable limit.

(b) Analysis not requested.

1.6 NEPTUNIUM(IV) HYDROUS OXIDE SOLUBILITY UNDER REDUCING AND CARBONATE CONDITIONS - D. Rai, J. L. Ryan, and M. McCulloch

Under reducing conditions such as those that might be present at some proposed radioactive waste disposal sites, actinides (especially uranium and neptunium) will be present in the tetravalent state. Thus solubility data for tetravalent actinide compounds are needed to determine the potential hazards of disposing of actinide-containing wastes in geologic repositories. Predictions about the solubility of different actinide compounds have recently been based on thermodynamic data selected from unreliable and questionable experimental values and/or in most cases are estimated based on techniques of uncertain validity. Therefore this study was undertaken to provide data for performance assessment activities (Section 1.3). This work is reported in more detail in a paper submitted to Inorganic Chemistry (Rai 1984).

In this study, solubility of Np(IV) hydroxide was approached from the oversaturation direction in the presence of reducing agents ($\text{Na}_2\text{S}_2\text{O}_4$ or metallic iron, zinc, lead, or nickel), with and without 0.01 M total carbonate, and with a range of pH values (6 to 14.2). The results showed that neptunium concentrations in all of the above solutions contacting Np(IV) hydroxide were at or below the detection limit for neptunium ($\sim 10^{-8.3}$ M). No evidence was found for any amphoteric behavior of neptunium.

Although it was not possible to determine any hydrolysis constant or carbonate complexation constant values for Np(IV) from these experiments, the results do set an upper limit of $\log \beta_5 < -24.7$ for $\text{Np}^{4+} + 5\text{H}_2\text{O} \rightleftharpoons \text{Np}(\text{OH})_5^+ + 5\text{H}^+$ and of $\log \beta_n [\text{Np}^{4+} + n\text{CO}_3^{2-} \rightleftharpoons \text{Np}(\text{CO}_3)_n^{4-2n}] < 22.5, < 27.9, < 33.2, < 38.5, < 41.6$ for β_1 through β_5 , respectively. The results provide no evidence for such reactions, but if such reactions are assumed to occur, then the upper limits obtained in this study are many orders of magnitude lower than those previously reported.

1.7 THORIUM(IV) HYDROUS OXIDE SOLUBILITY - J. L. Ryan and D. Rai

This study, like the Np(IV) study (Section 1.6), was undertaken to provide data for performance assessment activities. Details of this study have been submitted to Inorganic Chemistry for publication by the authors under the same title.

Solubility of Th(IV) hydroxide was determined in the pH range of 3.5 to 14. At pH values >10.5, solubilities were in all cases $<10^{-9}$ M, indicating no evidence of amphoteric behavior of Th(IV). A value of $\log K_{sp} = -45.9 \pm 0.5$ for $\text{ThO}_2 \cdot x\text{H}_2\text{O}$ is obtained from this data. The results set upper limits for $\log \beta_5 < -33.1$ for the reaction $\text{Th}^{4+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Th}(\text{OH})_5^- + 5\text{H}^+$ and for $\log \beta_4 \leq -19.0$ for the reaction $\text{Th}^{4+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Th}(\text{OH})_4^0(\text{aq}) + 4\text{H}^+$. Previously reported values of $\log \beta_5$ and of $\log \beta_4$ were much higher than determined in this work.

1.8 SODIUM SALT DESTRUCTION - L. J. Ethridge and M. E. Peterson

Sulfur, in the form of the $\text{SO}_4^{=}$ sulfate ion, is a minor component of waste streams considered for vitrification in a liquid-fed ceramic melter. Because sulfate has very limited solubility in waste glass, a molten salt layer has been noted on the surface of the glass in the melters and continues to accumulate unless it can be destroyed. Its destruction has been the subject of several studies. This study focused on a concept of suspending reducing agents in the salt layer to reduce the salt. The reducing medium would remain above the glass surface to avoid reduction of iron and other metal cations in the glass.

Several reducing agents were tested. The most successful was glass beads coated with carbon as the reducing agent. The glass beads were dense enough to give the carbon coating good contact with the salt layer. The carbon reduced the salt layer very effectively. After the carbon was consumed, the glass beads melted and mixed thoroughly with the simulated waste glass.

Graphitized coke was the other reducing agent that was very effective. The large, 1/4-inch pieces of coke had much better contact with the salt surface than did the smaller forms of carbon. The coke reduced most of the salt layer and left very little residue.

Either technique could be used to destroy a salt layer in a melter. The cold cap must be melted, however, to allow the reducing agent to contact the molten salt. Thus these techniques probably could not be used while the melter was being fed.

1.9 EFFECTS OF LONG-TERM THERMAL STORAGE OF SIMULATED NUCLEAR WASTE GLASSES - J. H. Westsik, Jr. and J. W. Wald

Radioactive decay within a nuclear waste glass will increase the temperature of the glass to above the ambient temperature of the storage area. The objective of this work is to evaluate the long-term effects of maintaining the glasses at elevated temperatures. Four glasses, designated 72-68, 76-68, 77-107, and 77-260 were stored at 300°C, 400°C, and 500°C for times to 5 years. These glasses were developed and selected for detailed characterization during the earlier High-Level Waste Immobilization Program and its predecessors (Mendel et al. 1979; Ross et al. 1978; Ross and Mendel 1979; Chick, McVay, Mellinger, and Roberts 1980). The thermal storage tests reported here were started during that earlier period and have been completed as part of this program to provide some long-term data. In the present work, the glasses were evaluated for changes in crystalline content, density, and leachability due to the long-term storage at elevated temperatures.

None of the four glasses showed any changes in crystallinity, as determined by x-ray diffraction, due to the long anneals. Only glass 77-107 demonstrated a significant increase (~2%) in density with increasing time and temperature.

An MCC-1 leach test was conducted to determine the effects of the long-term storage on the leachability of 76-68, 77-107, and 77-260 glasses. Specimens of each glass were leached 28 days in deionized water at 90°C. The resulting leachates were analyzed for elements leached from the glasses.

Glass 76-68 showed no changes in leaching behavior after the long-term thermal storage. Normalized releases based on aluminum, boron, calcium, iron, molybdenum, sodium, phosphorus, silicon, strontium, and cesium were essentially the same for the samples stored at 300°C and 400°C for up to 6 years and 500°C for up to 1 year.

Glass 77-107 showed dramatic changes with increasing time and temperature. The normalized releases for the alkaline earths (calcium, barium, strontium) decrease by a factor of two from 300°C at 2 months to 400°C at 5 years and a factor of three from 300°C at 2 months to 500°C at a year. In all the comparisons made for the three glasses, it is assumed that the sample for 300°C at 2 months is representative of the as-fabricated glass. Molybdenum releases dropped more than a factor of 10 over the same time/temperature regime. Normalized releases based on boron, potassium, sodium, and cesium also appear to decrease with time and temperature although the differences are small (<25%) and some may be statistically insignificant. Silicon releases show no trends. Zinc increases a factor of two from 300°C at 2 months to 500°C at 2 months and 400°C at 5 years. The cause of these changes is unknown.

Glass 77-260 showed decreases in the release of calcium and strontium with increasing time and temperature, although the changes are not as large as for 77-107 glass. The decrease from 300°C at 2 months to 500°C at a year is about a factor of three, and from 300°C at 2 months to 400°C for 5 years is about 25%. Aluminum, boron, potassium, sodium, silicon, and cesium show small increases in normalized release on the order of 20% with increasing time and temperature. No trends are evident in the releases of molybdenum. As with 77-107 glass, the causes of the changes are unknown at this time.

1.10 MELTING OF METALLIC TRU WASTES - D. R. Montgomery

Melting studies have been conducted using a vacuum coreless induction furnace for the consolidation of simulated nuclear metallic waste. The studies have followed the Montgomery and Nesbitt (1983) study, which recommended that a large-scale cold mock-up facility be established to refine and test the vacuum coreless induction melting system that had been selected for the consolidation of nuclear metallic waste. Because a large-scale facility was not available, scaled-down tests were performed by retrofitting PNL's present Inductoslag furnace.

Vacuum coreless induction melting includes the use of a graphite crucible with bottom-pour controlled by a water-cooled copper freeze plug. The molten metal is poured from the crucible into the canister or mold, located directly

under the crucible. The metal melted for this study was limited to the eutectic alloy of zirconium and iron. The iron was Type 316 stainless steel and the zirconium was in the form of oxidized Zircaloy 4 hulls. The components of this particular alloy constitute about 80% of the metallic waste expected from a spent fuel reprocessing facility such as BNFP if operated. Eleven heats were made during this investigation, and the following results and conclusions were obtained:

- Stainless steel canisters or molds with walls 1/4 in. thick performed most satisfactorily.
- Stainless steel canisters or molds with walls 1/8 in. thick proved to be too thin to hold the molten metal in at least one experiment.
- There were no metal-to-mold reactions when pouring into the 1/4-in.-thick stainless steel canisters.
- Preplaced scrap in the canisters was completely encapsulated by the molten metal poured on top of and around it. The density of the resulting ingot appeared to be ~99%. (Note Figure 1.1.)
- After eight consecutive heats, the only visible erosion of the crucible occurred at the top of the melt line, where an erosion line about 1/32 in. deep by 1/8 in. wide had formed. It had previously been hypothesized that a graphite crucible would last at least four heats; the estimate is now 16.
- No failures of the water-cooled copper freeze plug were observed in any of the 11 heats.
- All ingots formed open pipes upon solidification that could be filled by subsequent pours. Four successive pours were made into a stainless steel canister. The resulting ingot after sectioning appeared to be ~99% dense except for part of the last pour, which contained the open pipe.
- The best melting rate was 41 kg/hr at 40 kW with a power consumption of 1.03 kWh/kg.

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FIGURE 1.1. Cross Section of Zirconium IV-316 Stainless Steel Casting Formed by Pouring Molten Metal Around Preplaced Scrap

- Large pieces of Zircaloy 4 scrap, placed in the crucible with the appropriate amount of large stainless steel scrap, can be melted as long as all of the submerged metal is melted before pouring.
- The design of the pouring nozzle needs additional work to prevent a solidified drop from forming at the nozzle exit after a pour. This drop prevents the subsequent seating of the copper plug and therefore has to be removed by hand before the next heat.
- Heavily oxidized Zircaloy 4 hulls mixed with 316 stainless steel hulls melted rapidly at $\sim 1260^{\circ}\text{C}$ with power set at 40 kW. The best

pouring temperature was 1300 to 1325°C. After the water-cooled plug was pulled, an average of 15 sec was required for the molten metal in the crucible to melt through the skull formed in the sprue, allowing the metal to pour from the crucible.

- The melt is quieter and gives off less vapor in a static 1/3 atmosphere of argon than in a dynamic vacuum.

Additional details of this work were recently published (Montgomery 1984).

1.11 FUEL HULLS DECONTAMINATION - M. W. McCoy

The objective of this work was to develop and demonstrate a decontamination technique capable of decontaminating large volumes of spent fuel hulls to levels that will allow disposal as low-level waste.

A laboratory-scale decontamination system using centrifugal-barrel finishing was installed and cold-tested. This testing indicated that the corrosion layer on autoclaved Zircaloy tube sections could be removed by the centrifugal-barrel finishing process. To completely remove the corrosion layer from the interior surface of the Zircaloy tube section, the tube sections were first broken into approximate quadrants using a cryogenic cracking technique.

Both autoclaved and nonautoclaved Zircaloy tube sections deform without breaking when compressive forces are applied at room temperature. When cooled with liquid nitrogen, the autoclaved tube sections break usually into four sections when compressive forces are applied. Nonautoclaved Zircaloy tube sections do not break under compressive forces even when cooled with liquid nitrogen.

Actual fuel cladding from the Point Beach reactor was successfully broken open using the same cryogenic cracking technique that was used to break open the autoclaved Zircaloy tubing. In this hot test, three pieces of spent pressurized water reactor (PWR) fuel cladding were subjected to compressive forces from a 1-kg mass dropped from a height of 0.5 m. The results were generally the same as with the autoclaved tube sections: the fuel cladding section broke into three or four pieces.

Automated cryogenic cracking of Zircaloy tube sections was demonstrated using a roll mill. The roll mill produced consistently shaped sections from the Zircaloy tube sections cooled with liquid nitrogen. Earlier attempts to crack cooled tubes with a hammer mill were unsuccessful.

The cold-testing of the centrifugal-barrel machine showed that the corrosion layer on autoclaved Zircaloy tube sections could be removed from both interior and exterior surfaces in 1 hr of process time. The centrifugal-barrel machine rubbed the tube section on one another, allowing the zirconium oxide in the corrosion layer of the tube to act as an abrasive. This resulted in removal of the corrosion layer without the added volume of an external abrasive. Additionally, when the corrosion layer was completely removed from the tube sections, action decreased to a minimal rate. This permitted removal of the corrosion layer while minimizing the removal of the substrate zirconium.

1.12 FUEL FABRICATION FACILITY D&D - R. P. Allen

The objectives of this work are to assist DOE in collecting, evaluating and disseminating cooperative R&D information and data developed during demonstration and decommissioning of commercial fuel fabrication and related facilities and to provide technical assistance for relevant technology areas developed by PNL under DOE sponsorship.

PNL has been requested by DOE to assist in monitoring possible subcontracts with firms that will be decommissioning commercial TRU facilities. These D&D activities will generate information of value to DOE and the commercial nuclear industry relating to achievable volume-reduction ratios for the various sectioning and decontamination operations; cost/benefit comparison data for use of advanced techniques versus conventional operations; manpower requirements and productivity for the various operations; effectiveness and efficiency comparisons for alternative techniques; personnel exposure and industrial safety information for large D&D projects; and demonstration of instrumentation and procedures for sorting low- and high-density waste and for maintaining the nuclear-criticality safety of the operations.

The following private sector firms have contacted DOE and proposed cooperative R&D demonstration programs involving their facilities and TRU waste:

- Nuclear Fuel Services, Inc. - D&D of a large-scale plutonium fuel manufacturing facility at Erwin, Tennessee.
- Exxon Nuclear Company - D&D of a mixed-oxide fuel fabrication facility at Richland, Washington.
- Babcock and Wilcox - D&D of a nuclear fuels development laboratory at Lynchburg, Virginia.
- General Electric Company - Provision of spent fuel samples representing a wide range of compositions, conditions and burnups.

Program activities and progress have included conducting technical reviews of the unsolicited proposals and other contract submissions as requested by the DOE Richland Operations Office, identifying D&D activities and data of value to DOE and the commercial nuclear industry, helping prepare work statements and procurement justifications, providing technical information on D&D technology developed under DOE sponsorship, assisting with the estimation of TRU waste volumes that will be generated by the decommissioning activities, and reviewing other current and past TRU-related D&D projects to obtain comparison data.

1.13 IMPROVEMENT IN LFCM FEEDS - W. O. Heath

In a temporary shutdown of the melter feed system, frit or SiO_2 particles can begin to settle in process lines and equipment due to loss of turbulence. Without proper feed chemistry, particles can settle and form a sediment that cannot be resuspended simply by resumption of fluid motion. Thus the objective of this work was to prevent sedimentation or to make sediments readily resuspendable. An equally important goal of the research was to determine whether feed gellation occurs and, if so, to make the gel restirrabable.

Three colloidal techniques were investigated for their ability to improve the sedimentation and flowability of melter feed slurries:

1. polymer-induced bridging flocculation
2. manipulating glass former (raw SiO_2 or frit) particle size
3. alteration of nitric acid content.

All three methods improved the rheology of the simulated feeds. While each had advantages and disadvantages, the following three specific alternatives proved successful:

- addition of a polyelectrolyte in 2000 ppm concentration to feed slurry
- substitution of a 49 wt% SiO_2 colloidal suspension (~10-micron particle size) for the -325 mesh (≤ 44 -micron particle size) raw-chemical SiO_2
- increase of nitric acid content from the reference 1.06 M to optimum 1.35 M.

Additional details of the work can be found in the formal report (Heath and Ternes 1984).

Based on the success of this research at PNL, a 12-month subcontract was initiated with the University of Washington, Department of Chemical Engineering, to conduct in-depth melter feed rheology research. The work has thus far involved characterization of the morphology and rheology of two glass formers and two melter feeds. Methods to characterize the sedimentation properties of feeds as well as screening studies of various stabilizing agents, e.g., polymers, are currently under way.

1.14 PROCESS DATA ANALYSIS - J. H. Westsik, Jr.

The objective of this activity is to review process data from past pilot-scale ceramic melter (PSCM) runs to determine how well the data indicate the operating behavior of the melter and to develop a control algorithm for operating the melter using only the process instrumentation. Data from PSCM runs 4, 5, 6, 7, 8, 9, 11, 15, and 16 were stored on magnetic tape and can be reviewed using computer software developed in this activity. Additional data for these runs are available in log books and run summaries. Of particular interest are the temperature data obtained from the glass thermowell. Preliminary examination of these data reveals that the temperature profiles in the glass melt can

give some indication of the presence of foaming in the melter. It is not clear, however, whether the incipience of foaming can be detected. This will be evaluated further in FY 1985.

1.15 MELTER INSTRUMENT DEVELOPMENT - S. M. Barnes

Several instrumentation concepts have been evaluated for use in an operating vitrification facility. The instrument packages must enable the operators to monitor the melter performance and detect the precursors of unusual operating conditions. Several of the unusual melter conditions include production of excessive glass foam, formation of a second fluid (salt) phase on the glass surface, creation of a rigid cap of calcined feed materials above the glass, accumulation of slurry feed in the melter, and glass or electrode operating temperature out of the desired ranges. The instruments must also be able to withstand the melter environment, e.g., temperatures up to 1200°C; gaseous combinations of steam, NO_x, and various salt vapors; acidic feed slurries; and glass formulations specifically designed for high metal oxide solubilities.

Instrumentation packages currently under development include an infrared (IR) melter imaging system, a time-domain reflectometer (TDR), an acoustic feed accumulation monitor, pneumatic bridging sensors, and thermowells. Each instrument and its uses are discussed below.

The IR imaging system is based on current video monitors for melters. This system utilizes the camera and vidicon tube proven to be very resistant to radiation damage with a mirror designed to reflect the near-IR spectrum. The camera signal is then routed through a grey scale to color convertor, thereby producing a picture of the melting cavity in which the color bands correspond directly to temperature. This system permits a more quantitative analysis of the melter's interior conditions and highlights the important features of the cold cap (the reacting slurry feed materials atop the glass pool).

The TDR is similar to wave-guided radar. The instrument is sensitive to the position and the electrical conductivity of the glass/cold cap interface. This system provides the glass level in the melter, and testing is expected to show that it will indicate the presence of glass foam and molten salt phase separation.

The acoustic emission analyzer is intended to indicate overfeeding conditions. Early observations indicate that the melting cavity becomes much quieter when the feed slurry is permitted to accumulate.

Experience with pneumatic bubblers installed in the glass pool has shown that the variations in gas pressure observed are a strong function of the cold-cap conditions. During routine operation the gas pressure is relatively constant. When the flow of feed decomposition gasses from the bottom of the cold cap is restricted, such as by bridge formation, the magnitude of the pressure variations increases. These bubblers may also prove to be useful in controlling the convection patterns in the glass and increasing the heat transferred to the cold cap.

1.16 PRODUCT EVALUATION AND QUALITY CONTROL - L. J. Ethridge and W. L. Kuhn

A full-scale, instrumented, carbon steel canister was filled with simulated waste glass during the West Valley PSCM-19 melter experiment. Nineteen thermocouples were used to record the glass temperature at the 12-, 36-, and 60-in. levels. Data were obtained on the thermal behavior of the glass during batch pouring. This pouring schedule, where 1 to 2 in. of glass at a time was poured into the canister, created a very uniform fill. This canister will provide an opportunity to examine the solidity (voids, cracking) relative to the March 1983 (PSCM-14) canister, which was filled continuously at the nominal West Valley rate of 45 kg/hr.

A method for examining the cracking and voids inside a full-size canister was investigated and tested. The bottom half of a canister filled with glass was cut in half axially using an abrasive water jet operated by UNC Nuclear Industries. The cut was done in two passes, one from each side of the can. The surface of the exposed cut was rough and wavy, particularly near the center of the can, where the jet was more dispersed. However, the crack propagation in the glass was highly visible. This technique appears very promising for the inspection and comparison of glass poured into full-scale canisters at different rates.

1.17 SPENT FUEL TREATMENT - W. A. Ross

Early in FY 1984, a study was initiated on spent fuel treatment options. Late in FY 1984, the work was placed on hold pending a determination by the Office of Civilian Radioactive Waste Management (DOE-RW) that spent fuel treatment is needed. The FY 1984 work will be documented in FY 1985.

The objective of this work was to plan the type of treatment that may be appropriate for spent fuel if it should be determined that treatment is needed. Such treatment could be necessary to increase the chemical durability of the waste and thereby prevent release of problem isotopes such as cesium, iodine, and carbon at rates that exceed those allowed in the Nuclear Regulatory Commission disposal rule, 10 CFR 60.

Two major options for treatment were identified for preliminary study. The first involved incorporating the spent fuel into a durable matrix such as copper, lead, or ceramic. The second major option was to process the spent fuel into either a powder or liquid and incorporate the material into a durable waste form such as glass or ceramic. Figure 1.2 shows some of the potential variations that were identified and evaluated in the preliminary work. As part of this work, technical factors were identified that could be important in selecting a preferred strategy. These included the following major considerations:

- cost of treatment
- cost of transportation and disposal of the treated form
- performance of the waste form in disposal
- development required (state of technology)
- total waste volume including secondary wastes generated
- byproduct availability
- future availability of uranium and plutonium from the waste form
- hazards and requirements for the treatment facility.

Each consideration was to be evaluated and quantified to indicate the preferred technology for development of a spent fuel treatment process should it be determined by RW that spent fuel treatment is needed.

FIGURE 1.2. Logic Diagram for Selection of a Spent Fuel Treatment Process

1.18 REFERENCES

- Chick, L. A., G. L. McVay, G. B. Mellinger and F. P. Roberts. 1980. Annual Report on the Development and Characterization of Solidified Forms for Nuclear Wastes, 1979. PNL-3465, Pacific Northwest Laboratory, Richland, Washington.
- Heath, W. O., and R. L. Ternes. 1984. Improving Feed Slurry Rheology by Colloidal Techniques. PNL-5007, Pacific Northwest Laboratory, Richland, Washington.
- McElroy, J. L., and H. C. Burkholder, compilers. 1984. Commercial Waste Treatment Program Annual Progress Report for FY 1983. PNL-4963, Pacific Northwest Laboratory, Richland, Washington.

Mendel, J. E., et al. 1977. Annual Report on the Characteristics of High-Level Waste Glasses. BNWL-2252, Pacific Northwest Laboratory, Richland, Washington.

Montgomery, D. R., and J. F. Nesbitt. 1983. Review and Evaluation of Metallic TRU Nuclear Waste Consolidation Methods. PNL-4754, Pacific Northwest Laboratory, Richland, Washington.

Montgomery, D. R. 1984. Consolidation of Simulated Nuclear Wastes by Vacuum Coreless Induction Melting. PNL-5254, Pacific Northwest Laboratory, Richland, Washington.

Rai, D., and J. L. Ryan. 1985. "Neptunium(IV) Hydrous Oxide Solubility Under Reducing and Carbonate Conditions." Inorganic Chem.

Ross, W. A., et al. 1978. Annual Report on the Characterization of High-Level Waste Glasses. PNL-2625, Pacific Northwest Laboratory, Richland, Washington.

Ross, W. A., and J. E. Mendel. 1979. Annual Report on the Development and Characterization of Solidified Forms for High-Level Wastes: 1978. PNL-3060, Pacific Northwest Laboratory, Richland, Washington.

Ross, W. A., K. J. Schneider, J. L. Swanson, K. M. Yasutake and R. P. Allen. 1984. "Strategy for Treatment of Commercial TRU Wastes." Transactions of the American Nuclear Society, ANS 1984 Summer Meeting, New Orleans, Louisiana.

Slate, S. C., W. A. Ross, and W. L. Partain. 1981. Reference Commercial High-Level Waste Glass and Canister Definition. PNL-3838, Pacific Northwest Laboratory, Richland, Washington.

2.0 PILOT-SCALE RADIOACTIVE LFCM

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2.1 OBJECTIVE

Remote radioactive engineering-scale testing of the liquid-fed ceramic melter system is a necessary and logical step in the progression to full-scale production capabilities at designated U.S. sites to assure that the process and equipment perform as intended. The objective of this test program is to demonstrate satisfactory radioactive waste immobilization operations that will provide an adequate data base for future full-scale production facilities.

2.2 SUMMARY

Pacific Northwest Laboratory has remotely installed a pilot-scale radioactive liquid-fed ceramic melter (RLFCM) system for converting high-level liquid wastes (HLLW) to borosilicate glass in shielded manipulator cells. The pilot-scale RLFCM system consists of an RLFCM, canister-handling turntable, glass-level detection system and supporting waste preparation, off-gas treatment, and condensate treatment racks. The pilot-scale waste vitrification facilities went into hot operation in October 1984 and will be operated with radioactive wastes for the next 5 years to test remote equipment features and evaluate process performance. Special devices were engineered to assist in remote installation, operation and maintenance of the equipment system. This report discusses the remote features of this vitrification system.

2.3 INTRODUCTION

Since 1973, the liquid-fed ceramic melter (LFCM) process for conversion of high-level liquid wastes (HLLW) to borosilicate glass has been under development and testing in the United States. Its early success, inherent simplicity, and ease of operation and maintenance led to its adoption as the reference HLLW vitrification process in the U.S., Japan, and the Federal Republic of Germany

(FRG). Currently the LFCM is the Department of Energy's (DOE) reference process for planned defense and commercial nuclear waste solidification facilities, including the West Valley Demonstration Project (WVDP), the Hanford Waste Vitrification Program (HWVP), and the Defense Waste Processing Facility (DWPF) at the Savannah River Plant. Because of the LFCM's wide acceptance as the reference waste vitrification process in the U.S., the DOE requested that PNL design, construct, and operate a prototypical pilot-scale waste solidification facility employing the LFCM process. Pilot-scale radioactive testing is necessary to provide design and operating data that can be applied to production-scale projects. This pilot-scale RLFCM will be the first large-scale system to operate in the world.

2.4 GENERAL SYSTEM DESCRIPTION

The pilot-scale RLFCM is a radioactive testing facility consisting of a vitrification system and supporting equipment systems for preparation of liquid waste, off-gas treatment, and condensate treatment. The vitrification system, which consists of an RLFCM, a canister-positioning turntable and glass-level detection system, is depicted in Figure 2.1.

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

The molten-glass product formed in the RLFCM overflows into a stainless steel canister positioned underneath the RLFCM by a turntable, which can hold three canisters. The glass level in the canister being filled is monitored by

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FIGURE 2.1. Schematic Flow Diagram of the Pilot-Scale RLFCM Vittrification System

a gamma-detection system. Once filled, the canister is rotated from the filling position while another canister is rotated into the filling position. The filled canister is allowed to cool; the canister is removed from the turntable, covered and transferred to another part of the process cell for decontamination, nondestructive and/or destructive examination and final sealing.

2.5 EQUIPMENT ARRANGEMENT IN THE REMOTE CELL

The arrangement of the RLFCM equipment and its relationship to the various cell features and other equipment systems in the remote cell are shown in Figure 2.2. The remote cell, with overall dimensions of 7.6 m x 6.7 m x 9.3 m high (25 ft x 22 ft x 30.5 ft), is equipped with five shielding windows, three of which are located on a lower maintenance level and two at a higher maintenance level. The cell is serviced by two remotely operated cranes with capacities of 3 and 10.5 tons. The lower shielded windows are each accompanied by two Type E master-slave manipulators. The upper windows can accept upset manipulators for maintenance from above.

Equipment racks within this cell have name codes indicating position (e.g., 3A, 3B). In general, feed (Rack 1A, 3B) and process off-gas treatment racks (Rack 3A, 1B, 2A) are located in the corners of the cell, where the racks have process-service access to high- or low-level storage vault tanks. The RLFCM and canister-handling turntable, an induction-heated tube furnace (Rack 5A), and a spent fuel shearing and dissolution system are located in front of the shielded viewing windows to facilitate remote maintenance with manipulators. Service racks (3C, 4C, and 7C) are located adjacent to the window positions to provide access of process services to other equipment racks.

Piping connectors for the process equipment were selected to be compatible with the specific chemical process and remote maintenance requirements in the handling zone where the connector is to be used. Two different handling zones exist in the remote cell as follows:

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FIGURE 2.2. Plan View of the RLFCM Equipment System in B-Cell

- A fully remote handling zone in which all maintenance operations are performed using an overhead crane and an impact wrench suspended from the crane hook. Operations are viewed either through shielded windows or with closed-circuit television. These areas are out of

manipulator reach and are usually inside, on top of, or on the aisle of racks inaccessible from viewing windows. PUREX connectors, Hanford standard flanges, and modified pipe flanges are the connectors used in this maintenance zone.

- A semiremote handling zone in which maintenance can be performed with at least one master-slave manipulator and usually an overhead crane. These maintenance zones are located adjacent to the viewing windows. Block connectors, compression-type tubing fittings, and quick-disconnect fittings can be used in these maintenance zones.

Electrical connectors used in the remote cell are located in such a way that maintenance can be performed with manipulators. Standard multipin and twist-plug connectors are used.

Five major equipment components were recently installed in the remote cell to test the RLFCM. These equipment components are the RLFCM, canister turntable, glass-level detection system, feed rack (Rack 3B), and off-gas treatment rack (Rack 3A).

2.6 EQUIPMENT DESIGN FEATURES

RLFCM

The RLFCM (Figure 2.3) operates on the same basic principle as do many electric melters in the commercial glass industry. Molten glass is contained within a cavity made of highly corrosion-resistant, glass-contact refractory. Behind the glass-contact refractory are additional layers of lower-density corrosion-resistant and thermally insulating refractories. The glass is joule-heated by passage of an alternating current between electrodes in contact with the molten glass. The electrodes in the RLFCM are composed of a nickel and chromium alloy known as Inconel-690® (International Nickel Corporation).

The melter refractories are contained and supported by a gas-tight stainless steel and Inconel box. The melting cavity, including the vapor space above the glass surface, measures 61 cm wide x 99 cm long x 99 cm high; 36 cm is the normal glass depth. The melter is designed to operate at slurry feed rates of up to 40 L/hr, producing glass at 15-20 kg/hr. The melting cavity has

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FIGURE 2.3. Line Drawing of the RLFCM

a holdup of 0.18 m^3 of glass (500 kg glass), which provides for a mean residence time of more than 40 hr in the melting cavity at the nominal glass production rate.

Molten glass exits the melting cavity through the throat of the discharge section. The glass rises up a tunnel in the refractory into an overflow chamber and down through an Inconel-690 discharge trough into the receiving canister. The discharge section is heated with silicon carbide electrical-resistance heaters to maintain a low glass viscosity, permitting ease of glass flow into the receiving canister.

Glass flow up the refractory tunnel will be controlled by a remotely replaceable Inconel-690 airlift lance that is inserted in the rise tube. Through periodic operation of the air lift, the glass-pouring process will operate in a batch mode to permit void-free glass castings and to allow sufficient time for changeout of canisters.

A potential operating problem with the glass-pouring is pluggage in the discharge tube of the melter. To mitigate this potential problem, the RLFCM and turntable system is equipped with a remotely removable inner discharge tube (Figures 2.4 and 2.7), which fits inside the outer discharge tube. The inner discharge tube is fabricated from mild steel and will spall any glass that collects on its surface from off-normal operations, into the receiving canister. The inner discharge tube can be remotely replaced with special tools while the melter and turntable are coupled. The inner discharge tube is held in place between the melter and turntable by three gripper cams, which are positioned on the serrated surface on the lower portion of the discharge tube. The discharge cone can be removed by a special tool that sequentially forces up the gripper cams, forces down the ejector cams and catches the falling discharge cone.

The RLFCM was designed for remote crane maintenance with direct viewing through shielded windows. Remote process connectors on the RLFCM are bolted flange connections that incorporate asbestos, graphite or ceramic sealing gaskets. There are three major failure components on the RLFCM. These are the ceramic lining of the melter, melter electrodes, and discharge-section heaters. Experience has shown that both the ceramic lining and the melter electrodes

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FIGURE 2.4. Line Drawing of Canister-Handling Turntable

can be expected to last a minimum of 3 years, and for this reason these components were not designed for remote replacement. The discharge-section heaters, being more subject to failure (1-year expected life), were designed as an integral unit for remote replacement.

Minor failure components of the RLFCM system were designed for remote replacement. These components include thermowells, thermocouples, detection instrumentation (weight-factor bubblers), a feed nozzle, an air-lift lance, and a melter-viewing camera.

Canister-Handling Turntable

The canister-handling turntable was designed to provide for moving and positioning the canisters underneath the RLFCM during canister filling and initial cooldown of the thermally hot canisters while providing containment of contaminated gases in the vitrification system. The turntable dunnage also supports the RLFCM.

Turntable Design Description

The canister turntable, shown graphically in Figure 2.4, consists of a three-position, motor-driven carousel located inside a containment vessel specially developed for remote operations. The carousel consists of three containment pods equally spaced around a center axis. The carousel rotates around the center shaft supported by two bearings located at the top and bottom of the shaft. The normal rotational direction of the turntable is clockwise, although the turntable can rotate in either direction. The top of the carousel shaft extends out of the containment vessel through a bearing-seal retainer. A square hole is located atop the shaft to which the turntable positioning motor is coupled.

The three containment vessel pods will each contain removable thimbles that are used to support canisters of differing size. The thimble system can accept canisters up to 40.7 cm (16 in.) in diameter and 2.64 m (8 ft, 8-1/2 in.) long. In addition to supporting the canister, these thimbles will also collect any glass shards that fall from the discharge trough.

The carousel is driven by a three-position, right-angle index-drive unit having a double-reduction reducer and a 1.0 horsepower dc motor. The index

unit has an overload clutch attached that releases at 11,000 in.-lb of torque. The turntable rotates at an initial torque of 900 in.-lb while containing three canisters. The carousel is remotely positioned and centered underneath the melter overflow by two methods. The primary positioning method is the use of a potentiometer attached to the carousel drive system. This system, once calibrated, limits the movement of the carousel to 120° with each activation of the drive motor. The turntable drive system is equipped also with a mechanical cam that in conjunction with the potentiometer limits the rotation of the carousel to a precise 120° with each activation of the drive motor system. The identity of the carousel position under the RLFCM is also detected by radioactive source tracing. Alongside each containment vessel pod is positioned a ⁶⁰Co source of different strength (0.1, 0.4 and 1.6 Ci). The detection of these sources through a collimator verifies the position of the carousel to within ±1/4 in. The RLFCM is shown mounted on top of the turntable in Figure 2.5.

Turntable Melter Seals

The turntable has two primary openings: one for replacement of canisters and the other for mating of the RLFCM and the canister-handling turntable. Each of these openings is provided with a remotely maintainable vacuum seal.

The canister port seal-cover (Figure 2.6) was conceived to minimize air inleakage into the RLFCM system during movement of canisters into and out of the turntable. The canister-removal seal uses a water seal 61 cm (24 in.) deep to maintain vacuum in the canister-handling turntable during normal operation when the turntable port is closed. The seal consists of four basic parts: 1) a water-seal trough, 2) a removable outer cover, 3) a floating inner seal, and 4) a lever system for positioning the inner seal. During normal operation, the outer cover lid, which is weighted by a lead-filled circular block, is in place, and a vacuum seal is maintained by the water seal. In the closed position, the inner seal is elevated from the top of the canister-containment thimble via a lever which couples the inner seal to the outer cover. This allows the carousel free rotation.

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FIGURE 2.5. Photograph of RLFCM and Canister-Handling Turntable

TURNTABLE PORT OPEN

TURNTABLE PORT CLOSED

FIGURE 2.6. Canister-Removal Port Positions for Canister Turntable

The turntable is accessible by removal of the weighted outer cover; removal of the outer cover allows the inner cover to be lowered. In the turntable port open position, the inner cover and the top of the canister thimble join to provide a temporary seal that minimizes air leakage into the canister-turntable and, subsequently, air leakage into the vitrification system.

A second turntable seal was devised to remotely join the turntable to the RLFCM. This metal seal concept is shown in Figures 2.4 and 2.7. The metal

FIGURE 2.7. Metal Seal Concept - Connection of RLFCM to Canister-Handling Turntable

seal comprises three basic parts: a metal reservoir equipped with heating/cooling coils; a lip that extends down from the RLFCM containment vessel; and the seal material, an alloy with a low melting point (Eutectic metal 255, melting point 120°C). This seal concept was chosen because it is remotely maintainable and of high quality and durability compared to a mechanical seal. To form the seal, alloy shot is placed in a steam-traced cup, which is connected to the sealing trough by a steam-traced tube. The metal shot is melted in the cup and flows into the sealing trough. A predetermined mass of shot is fed to the sealing trough to achieve the required seal depth. Next the steam service is discontinued and the seal metal allowed to solidify, forming a high-integrity seal.

During normal vitrification operations, the temperature of the area around the metal seal could exceed the melting point of the seal alloy. To maintain integrity of the seal, cooling air is applied to the seal-trough coils.

Glass-Level Detection System

A glass-level detection system will remotely monitor the accumulation of glass in the receiving canister to prevent overfilling. The system consists of 11 gamma-activity detectors positioned along the vertical axis of the receiving canister within the concrete shielding wall of the remote hot-cell facility (Figure 2.8), a movable 3000-Ci ^{60}Co source, and the glass-receiving canister. The detectors are oriented and collimated such that the line-of-sight of each detector views a 2.5-cm-dia (1 in.) circular segment of the receiving canister passing horizontally through the vertical centerline of the canister. A single movable ^{60}Co source (Figure 2.9) is positioned sequentially on the opposite side of the canister from the gamma detectors in the line-of-sight of each detector. As glass accumulates at the line-of-sight level of a detector, the ^{60}Co counting rate for that particular detector decreases. The degree of the reduction of the counting rate at any particular detector level will indicate the total accumulation of glass at that level. A redundant system utilizing the same 11 gamma detectors monitors the ^{137}Cs gamma activity at each detector level. Since the ^{137}Cs is a radioactive constituent of the glass itself, as glass accumulates at the line of sight of a detector, the ^{137}Cs counting rate for that particular detector will increase. The degree of increase of the ^{137}Cs counting rate at any detector level will also indicate the total accumulation of glass at that level.

The ^{60}Co source is contained in a collimated holder attached to a ball screw. The source is moved up or down to the level of the various gamma detectors by rotating the ball screw with a reversible dc stepper motor drive. A shaft encoder attached to the bottom of the ball screw will maintain an awareness of the location of the source holder. Figure 2.9 shows the interrelationship between the in-cell mechanical equipment and the out-of-cell electronic equipment. A microprocessor will control the movement of the gamma source, the operation of the counting instruments, the interpretation of the counting

FIGURE 2.8. Plan View of the Glass-Level Detection System

FIGURE 2.9. Schematic of the Glass-Level Detection System

rates, and the display of the results. The normal operating mode for the source-positioning system consists of a repetitive cycle in which the ^{60}Co source will be positioned at the bottom detector level where the counting instruments will measure the ^{60}Co and ^{137}Cs counting rates for a predetermined period of time. The source will move up to the next detector level and repeat counting rate measurements at each detector level until the counting rates have been measured at the topmost detector. At this time, the ^{60}Co source will be returned to the bottom detector level and the process can be repeated. The ^{60}Co and ^{137}Cs counting rates that would be measured at each detector level are compared with similar counting-rate measurements that were taken when the canister was initially brought into position under the melter. The difference between the initial and current counting rates indicates glass accumulation in the canister.

Supporting Equipment Racks

Process vessels and associated piping in the remote cell are grouped together and mounted in racks. These equipment racks were devised to simplify remote handling, to benefit field installation by allowing prefabrication, to facilitate replacement of groups of equipment, and to permit adaptation of complex piping systems to the restricted cell geometry.

A typical rack (3B), shown in Figure 2.10, consists of the rack frame, integrally welded plugs that contain service piping arranged to fit sleeves in the cell walls, process vessels and equipment, piping systems, and various connectors (generally on the rack face, accessible to the cell manipulators).

Rack frames are fabricated mainly from tubular stainless steel selected for maximum rigidity and minimum weight. These racks are designed to hang from the cell wall and to be supported by the rack plugs or to rest on the cell floor. Cross-bracing gives these racks extra rigidity needed for remote handling.

The piping in the rack plugs provides process services to equipment in the rack and to the remote cell through the rack manipulator face. Typically, piping for up to 35 nonradioactive services will extend through each of two upper plugs, and piping for up to 10 radioactive process streams will extend through each of two lower plugs. Piping in the upper plugs generally terminates in the nonradioactive service galleries. The lower plugs extend into shielded areas allowing piping connections to be made between adjacent racks without entering the cells. Shielding is generally required on all plugs. Where a shielded plug is required, the piping in the plugs is bent to provide a radiation barrier and the plug is filled with lead.

Piping also extends from the rack process vessels to the manipulator face of the rack. This permits connections between process vessels through in-cell piping jumpers. The rack face is arranged so that the piping connections and nozzles are accessible with master-slave manipulators. Connectors away from the manipulator face on the process vessels for agitators, pumps, tube bundles, and off-gas lines are designed for remote maintenance using the overhead crane and an impact wrench.

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FIGURE 2.10. Photograph of Waste Preparation Rack (Rack 3B)

Waste Preparation Rack 3B

The waste-preparation system (Rack 3B) consists of two conical-bottom, pulse-agitated feed tanks and related equipment. The pulse-agitated feed tank was chosen because it better homogenizes radioactive waste slurries containing a high solids content as compared to mechanically agitated tanks. A pulse-agitated feed tank comprises three basic parts: the tank, a pulser tube, and fluid-displacement cylinders. Shown in Figure 2.10 are the pulse-agitated tanks in Rack 3B and the fluid displacement cylinders for one of the tanks.

Initial testing of the conical tank led to favorable conclusions concerning the tank design itself. Prior to testing, an item of concern was the effect of surface wear in the discharge impingement area. Tests made to determine wall thickness, using an NDT Novascope 2000 (SN 213) with a highly damped 25-MHz focused transducer, showed no erosion in the cylindrical section and an acceptable erosion rate of 77 mil/yr in the nose section. This erosion rate correlates to a 4.3-year life expectancy based on 365 day/yr usage. This number can realistically be expected to increase to 8.6 years because the pulse agitator would actually operate about 26 weeks/yr. Other findings during initial testing included: the agitator's ability to adequately suspend solids in the waste; minimal buildup of solids on the tank internals; easy removal of these solids by water flushing; and usage of the specific-gravity and weight-factor recordings to determine the operability of the pulse-agitator system as well as to measure rate of removal of liquid.

Off-Gas Treatment Rack 3A

An off-gas treatment rack (Figure 2.11) was installed to provide primary decontamination of off gas from the RLFCM. The principal components of the 3A Rack include an ejector venturi scrubber installed in an off-gas jumper between the RLFCM and the 3A Rack, a condensate recirculation tank and a seal pot.

The condensate-recirculation tank was designed with an oval shape because of space limitations. This tank was fabricated from Inconel 625® with Hastelloy® cooling coils to withstand the corrosiveness of scrub solutions. The tank was designed to be remotely replaceable and therefore has its own

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FIGURE 2.11. Photograph of Off-Gas Scrub Rack
(Rack 3A)

manipulator face for providing services to the tank. This tank is equipped with an agitator and cantilever pump for providing scrub solution to the ejector venturi. A seal pot installed in the rack provides overpressurization relief for the scrub tank in the event of steam surges in the RLFCM.

The ejector venturi was fabricated of Inconel 625. It was tested to determine the characteristics of the spray nozzle and the vacuum produced at the inlet. The spray nozzle visually appeared to have a good spray pattern when the water flow was above 40 L/min, and a maximum flow of 65 L/min was obtained with supply water from the in-cell pump to the venturi. With no air flow through the venturi, the vacuum at the inlet is -13 in. H₂O. When the RLFCM is currently in operation, the fluid flow through the venturi is 65 L/min and the vacuum on the melter is -8 in. H₂O with a downstream vacuum of -3 in. H₂O. The supply pump for the venturi is a vertical cantilevered pump with a 10-hp motor capable of supplying 20 gpm with a 185-ft head. The pump required a minimum water level of 20 in. in the tank to operate and 27 in. to be started. The scrub-solution holding tank (TK-134) was constructed of Inconel 625 and Hastelloy C-276. The tank has an overflow volume of 1505 L. The tank's heat-removal capabilities were tested, and the results showed that it can remove about 6800 Btu/H-F (deg).

The agitator for TK-134 is a mechanical mixer with two 28-cm (11 in.) props, a 6-ft shaft, and a 1-hp motor. The agitator appeared to mix the tank contents sufficiently, and it was used in the test to determine the heat-removal capabilities of TK-134.

Facility Preparation and Equipment Installation

The cleanout of B-Cell in preparation for installing the RLFCM required that large volumes of radioactive fission product-contaminated solid waste be disposed of in shielded waste boxes. Two types of waste boxes were used: 1) lightly shielded for equipment lightly contaminated or easily decontaminated and 2) heavily shielded for highly contaminated equipment. The lightly shielded box was fabricated from 5.1-cm steel plate with a wooden overpack, while the heavily shielded box was made from 5.1 cm of steel plate and 5.1 cm of lead plate.

Removal of the solid waste began in FY 1983, when 14 waste boxes (nine heavily shielded and five lightly shielded boxes) were shipped to the 200 Area burial ground. During FY 1984, nine boxes were shipped to the burial ground in seven lightly shielded and two heavily shielded boxes and contained such items as dunnage, electrical equipment, and other miscellaneous waste.

Following removal of the solid waste from B-Cell necessary to make room for the RLFCM equipment, the equipment installation phase of the task began. The first piece of equipment to be installed in B-Cell was the 3B Rack. This rack has a large piece of equipment weighing about 5200 kg and was about 5.1 m high, 1.0 m wide, and 2.4 m long (excluding wall penetration plug). The rack was moved into B-Cell from the air lock using an in-cell crane and was remotely installed in the west wall of the cell. The 3A Rack, about the same size and weight, was then installed adjacent to it in the west wall in the same way.

Following installation of these racks, the turntable was put into place. By far the largest piece of equipment installed in B-Cell, it measures 5.3 m high, 1.9 m wide and 3.4 m long and weighs 7500 kg. As the existing B-Cell crane was designed for 6 tons, it was necessary to add a support beam to the crane and install a new block to permit moving the turntable into B-Cell.

The RLFCM sits on top of the turntable and is the heaviest piece of equipment installed in B-Cell (7955 kg without the lid).

After installation of the larger pieces of RLFCM equipment, the melter lid, many jumpers, electrical connections, service hookups, instrument sensors, and other components necessary for operating and controlling the RLFCM and associated equipment were remotely placed by using the B-Cell crane and manipulators.

Preparation for Receipt of Cesium and Strontium

A comprehensive review of the requirement for unloading cesium and strontium led to selection of the 324 Building Loadout Stall as the site for cask unloading in the 324 Building. The decision was based upon several technical considerations, most notably the ease of access and comparative ALARA benefits.

High-level vault tanks TK-104 and TK-105 were designated as storage vessels for the receipt of cesium and strontium, respectively, based on their bulk

storage capacity and ability to remove decay heat during the storage of solutions. Heat-transfer analyses performed on these tanks showed that temperatures could be adequately controlled through proper agitation and cooling-water flow rates. The analyses also pointed out that the potential existed for self-boiling if cooling water were interrupted for fairly extensive periods (>20 hr). Investigation into all credible accident scenarios revealed that only very improbable event sequences could result in such lengthy interruptions of process water supply. As a precaution, however, a backup emergency cooling-water system was devised to bring process water into the building on demand if the normal source is lost for a significant period. Monitoring equipment and facility alarms have been installed to promptly detect any such anomalous condition.

Sample analysis of the cesium and strontium solutions indicated that the gases evolved by radiolytic decomposition of the aqueous media contained sufficient quantities hydrogen and oxygen to characterize the mixture as potentially flammable. To preclude such a mixture's accidentally igniting, procedures were developed to dilute these radiolytically generated mixtures with non-hydrogen-containing gases safely below recognized flammability threshold concentrations. These guidelines have been applied to both high-level vault tank storage and solution storage in transfer casks.

Preoperational Software

Before startup of the RLFCM, a comprehensive safety analysis was completed and documented in a supplement to the safety analysis report for the 324 Building. Operational Safety Requirements defining the process conditions, safe boundaries and management control needed for operations in the pilot-scale RLFCM were defined based on the results of the safety analysis reports.

RLFCM Instrument Systems

Because of the RLFCM's hazardous radiation environment, remote sensing devices are used to monitor the status of the melter and control its operation. Most of these devices yield a continuous electric dc analog value proportional to the characteristics they are monitoring, e.g., temperature, pressure, flow, volts, amperes, resistance, power, and are utilized by either

of two major data-handling systems: a microprocessor-based distributed process-control system and a minicomputer-hosted data-acquisition and data-display system.

Conditioning devices are used on each analog sensor-signal to filter spurious fluctuations from the primary sensor signals and to electrically isolate each signal completely from the others. To standardize the signal types from the various instrument brands, all of the various signal formats are converted by the signal conditioner to a 0-10V (dc) signal for the data acquisition system and simultaneously to a 4-20 Ma signal for the microprocessor-based process-control system.

Figure 2.12 shows the flow of analog sensor data from field locations, through the signal-conditioning equipment and on to the microprocessor system for process-control purposes or to the minicomputer system for data storage, processing, and display.

A microprocessor-based control system (Figure 2.13) was installed, configured, and tested during FY 1984. It is operated from three remote consoles with color video displays. Each console is capable of displaying every aspect of up to 24 control loops or 45 analog process operating parameters. Operators are able to tune one control loop while observing the trends of three selected variables on another console and evaluate the overall melter facility status on the third. The microprocessor also provides group displays, alarm displays, overview displays, and dynamic flowsheet displays. The system also controls digital-control loops such as the pulsing frequency of the pulse agitators and air-displacement slurry pumps and controls sequencing for jet stations. The control loops also provide automatic fall-back to safe values when alarm values are exceeded. An example is the electrode power control, which automatically drops to ~15 kW if the temperature exceeds 1210°C. The system also alarms if a high glass temperature is detected. If the thermocouple (TC) is open, the system monitors a secondary TC instead of alarming prematurely. The configuration will be further refined to fully utilize all capabilities as more testing of the RLFCM suggests incorporation of new features.

FIGURE 2.12. Process Control and Data Acquisition Systems

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FIGURE 2.13. Microprocessor-Based Control System

The process control is now installed and operating, controlling the glass temperature in the melter tank, the temperature of the melter discharge section, the pulse agitation of the feed tank and feed makeup tank contents, and the pumping rate of the slurry feed into the melter. Figure 2.14 shows a 30-hr trend display of the melter tank electrical resistance value (inversely related to the average melter tank glass temperature), the glass temperature at a point 6 in. above the melter tank floor, and the current flow to the melter tank electrodes.

The data acquisition and display system is now installed and operating, monitoring about 170 analog sensors and calculating about 20 additional values based on one or more of the monitored analog sensor values. Figure 2.15 shows a 100-hr, dual-trend display of the weight-factor and specific-gravity values of the molten glass in the melter tank during and after a brief cold slurry feeding experiment with the melter facility. In addition to the dual-trend displays, both single- and triple-trend displays are available for any combination of the 170 analog sensor values monitored and the 20 calculated values that are stored on the operating disk.

Additional work is planned to improve the data displays for both systems.

PROCESS SYSTEMS INC.
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2.29

SELECT TIME BASE 1 20 MINUTES
2 3 HOURS
3 30 HOURS

FIGURE 2.14. 30-hr Trend Display of Melter-Tank Electrical Resistance Value

FIGURE 2.15. 100-hr Dual-Trend Display of Weight-Factor and Specific-Gravity Values

3.0 WEST VALLEY SUPPORT TASK (WVST)

J. R. Carrell - Manager

3.1 OBJECTIVES

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

The overall objective of the 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 1984 activities of the WVST in support of the above objectives. These sections cover work done in vitrification process development, head-end process support, equipment design support, and glass characterization.

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

Major Contributors: J. M. Perez, D. S. Goldman, R. W. Goles, H. T. Blair,
P. A. Scott, W. L. Kuhn, and B. M. Wise

The focus of the Vitrification Process Development activity is to provide technology to support selection, design, and operation of the slurry feed system, glass melter, and primary effluent treatment equipment. During FY 1983, the reference vitrification approach was defined. Tests were conducted under controlled conditions to examine the process and equipment performance through comparison of the test data with design predictions. Emphasis during testing

was also given to identification of development needs and waste-specific processing problems. Task activities in FY 1984 concentrated on refinement of equipment design and development of solutions to processing problems such as glass foaming. Testing of engineering and pilot-scale equipment continued to verify proposed solutions to processing difficulties and to generate performance data under varying conditions for supporting future detailed design efforts and operation of the WVNS component test stand (CTS).

The major effort during FY 1984 was aimed at the development and processing of feeds containing IE-95 zeolite ion exchanger. The decision was made by WVNS, with PNL concurrence, to include this material in the waste to be processed by the vitrification system.

Studies of Melter Feed Slurry

Laboratory studies were carried out throughout FY 1984 in support of the formulation of melter feed slurries containing ground IE-95 zeolite and having acceptable rheological properties. The zeolite exchanger to be included in the feed had particle sizes of 100 mesh (149 μm) and less. Over 80% of the particles were less than 200 mesh (74 μm). The work concentrated on assessing methods to prevent the settling of zeolite particles, investigating the effects of nitric acid concentration, and determining whether agents that prevent foaming (surfactants) could be used effectively.

Two methods to prevent settling of zeolite particles were studied: 1) the use of suspension additives and 2) predigestion of the zeolite in concentrated nitric acid. Suspension additives that proved successful were based on colloidal or amorphous, fully hydrated silica. The suspensions were quite viscous, with apparent viscosities in the range of 60 cp. The slurries exhibited Bingham plastic fluid properties and would gel if left unagitated. They did, however, become fluid again upon reagitiation. Predigestion of zeolite was done in 2.5 M and 5 M nitric acid before its use in feed makeup. Changes in feed behavior were minimal. Therefore, little benefit would be gained by a zeolite predigestion step in the actual process at WV. Comprehensive small melter tests and pump tests are needed to complete the evaluation of suspending agents.

Feed slurries ranging in final acid concentration from 0 to 2 M were compared for settling, resuspendability of settled solids, and performance in an air-lift pump. There was no significant difference in feeds with acid concentrations between 0 and 1.4 M. At 1.6 M the settled solids layer became less firm and easier to resuspend. This desirable property improved as the acid concentration increased. At 2 M the feed slurry separated into two phases. However, the settled phase, rather than being a definite solid layer, was a very fluid suspension. Remixing of the feed was therefore very easy.

In all cases the improved suspension was accompanied by the tendency to foam. Laboratory tests indicated that the foaming could be mitigated with the use of silicon-based polymer antifoaming agents. Because the agents act as surfactants, they would prove useful in the feed tank and air-lift head pots if added separately to each vessel. Solubility tests are needed to determine how much of the agent and how frequently it should be added to prevent accumulation of surfactant in the feed tank. During large-scale equipment testing, a stable foam was observed on the surface of the slurry. Active agitation was required to break down the foam and prevent its accumulation.

Development of Slurry Feed System

The goal of the slurry feed system development activity was to demonstrate long-term operation of melter feed systems with simulated West Valley slurry. An acidic melter feed containing ground zeolite will be processed at WVNS. A two-stage air-lift pump was selected by WVNS as the melter feed pump best satisfying their requirements. An air-displacement slurry (ADS) pump with a driven two-way valve was selected as a backup feed system for the West Valley process. The prime objective of the slurry feed system development activity was to verify the design bases and/or correlations used in the design of the two pumps. Demonstration of the reliability of the pumps under continuous operating conditions in excess of 30 days was also a goal. During these demonstrations, wear and corrosion rate data were collected so that service life could be predicted.

The slurry composition used for testing consisted of simulated WV waste from the combined THOREX and acidified PUREX washed sludge flowsheet, zeolite exchanger, and glass-forming chemicals.

The air-lift pump was operated for more than 1000 hr, during which almost 125,000 L of simulated WV slurry was pumped. The air lift shown in Figure 3.1 incorporated features identical to those in the WV CTS design. Identical features included the first-stage lift line pipe size and footpiece design, second-stage line lengths and footpiece design, lift height, and submergence. Submergence is the ratio of the required lift height to that of the liquid head as measured from a reference point. Over the tested first-stage submergence range of 32% to 41%, the first stage provided an adequate supply of slurry to the splitter pot that supplied the second stage. No plugging occurred in the first-stage lift line or footpiece during testing.

The second-stage lift achieved flow rates of 35 to 175 L/hr, encompassing the expected WV operating range of 50 to 150 L/hr. The maximum time of operation without system interruption was 782 hr. Two line plugs occurred due to settling of solids. Both occurred in the second-stage liquid supply line and were easily removed by water flushing.

Based on the testing, it was concluded that the full-scale WV air-lift pump design was adequate. Recommended design changes are that a smaller-diameter second-stage liquid supply line be used and that spray nozzles be incorporated into the head pot designs. Also operational maintenance should include daily water flushes of the air-orifice footpieces to prevent buildup of solids.

The ADS pump, shown in Figure 3.2, operated successfully for more than 750 hr, during which 65,000 L of simulated WV slurry was pumped. Feed rates of 35 to 200 L/hr were demonstrated. No plugging due to solids deposition occurred during the test. Operation of the ADS pump verified its applicability to the WV process should its use be required.

The ADS pump operates through a series of four steps that are controlled by a microprocessor. This sequence of steps is shown in Figure 3.3. During the first step of the cycle, the two-way valve is driven upward, opening the inlet orifice and closing the outlet orifice. In the second step, slurry flows into the pump chamber, and the air in the chamber is vented to the tank vent. In the third step, the two-way valve is forced downward, which closes the inlet

FIGURE 3.1. Air-Lift Pump Feed System

FIGURE 3.2. Air-Displacement Slurry Pump Installation

orifice and opens the outlet orifice. During the fourth step, air pressurizes the chamber, forcing slurry out the exit line. A somewhat pulsating flow pattern is characteristic of the pump operation.

Testing showed that pump operation was affected by changes in the liquid level of the tank. The microprocessor control system, however, can be adjusted to mitigate this problem. Flow rate was best controlled by adjusting the air

FIGURE 3.3. Operating Cycles of an Air-Displacement Pump with Actuated Two-Way Valve

pressure in the pump while maintaining a cycle time of less than 30 sec. Maintaining this short cycle time kept the slurry flowing through the feed line at a more constant value. This lowered the chance of dried slurry accumulations building up on the hot tip of a melter feed nozzle.

After testing, pump parts exposed to wear were examined for signs of corrosion or erosion. Little or no effect from the extended test was found.

Ceramic Melter Studies

Experimental Ceramic Melter (ECM) Testing

The ECM was tested to determine the impacts on processing behavior caused by changes in the WV slurry composition. The ECM (Figure 3.4) is a joule-heated, ceramic-lined melter with an exposed glass surface area of 0.054 m² and a slurry-processing capacity of up to 5 L/hr. The simulated waste slurry is metered to the melter via a variable-speed peristaltic pump. Off gasses are initially scrubbed by a packed column before passing into the laboratory auxiliary off-gas treatment system.

A total of eight ECM experiments were performed. The first two experiments, ECM-84-1 and -2, used a nonzeolite WV composition that contained 2 M nitric acid. This composition was previously run in the pilot-scale ceramic melter (PSCM) experiments in FY 1983. The two tests were performed to obtain processing and glass product data for comparison with PSCM data. These data would provide the basis for predictive scale-up correlations for use with different slurry compositions subsequently tested in the ECM. Melter behavior was much like that experienced in the FY 1983 PSCM tests. Glass-foaming occurred when melt temperatures exceeded 1140°C. When the temperature was maintained between 1075°C and 1125°C, the glass melt was more stable and did not foam. A molten salt layer formed on the melt surface because the amount of sodium sulfate in the slurry exceeded the amount soluble in the glass. Post-test analyses of the glass product showed good agreement with the PSCM glass product in the oxidation state and in sulfur and water content.

The third experiment, ECM-84-3, tested a feed composed of the WV flowsheet waste, zeolite ion exchanger, and chemical glass-formers. The experiment demonstrated that zeolite could be incorporated into a melter feed slurry and processed in a ceramic melter. Processing rates were 80% of those achieved in ECM-84-1 and -2.

In the final 12 hr of ECM-84-3 formic acid was added to the slurry as a reducing agent. Feeding rates declined by about 15%, and the cold-cap melting characteristics degraded. Glass/cold cap activity (i.e., venting, surface

FIGURE 3.4. Experimental Ceramic Melter (ECM)

currents) decreased, and the cold cap became more rigid. It is believed that the formic acid caused sodium sulfate to decompose before it could serve as a flux for the zeolite.

The remaining five ECM tests were performed in preparation for an FY 1984 PSCM experiment. In these tests sugar and sodium oxalate were evaluated as reductants. These were added to reduce or eliminate glass foaming by lowering the redox level in the glass melt.

ECM-84-4 lasted 62 hr. Slow melting rates and the formation of an insoluble phase on the glass-melt surface predominated during the test. Because the initial slurry composition had performed poorly, it was varied during the last half of ECM-84-4. Additional sulfate (SO_3 increased from 0.7 to 0.9 wt%) and the addition of nitric acid (0.5 mole/L) to the slurry did not, however, improve the processability.

The next test, ECM-84-5A, lasted 9.2 hr. A difference between it and the previous test was that the SO_3 content was raised to 1 wt%. Also, additional boron and sodium were added to the feed slurry, as the ECM-84-4 slurry had been slightly below target levels in these two constituents. No noticeable improvement in processability was seen.

Conditions for the next two tests, ECM-84-5B-I and ECM-84-5B-II, were similar to those of ECM-84-5A. The duration of the two tests was 7.4 hr. The experiments were run to verify data from test ECM-84-5A. Although glass-melt temperatures were above 1150°C , the low processing rates found in ECM-84-5A were again experienced.

The final test, ECM-84-5C, was a 6.8-hr experiment in which the quantity of sugar was reduced to the equivalent of 9 wt% carbon. (In ECM-84-5A through ECM-84-5B-II its level had been 10.5 wt% carbon.) In ECM-84-5C, improved cold-cap conditions were noted compared to earlier tests. There was active venting about the cap, and higher processing rates were maintained throughout. The formation of the insoluble glassy phase at the glass-cold cap interface experienced previously was not a problem during this short test. Due to these better

processing conditions, 9 wt% carbon (57 g/L sugar) with 0.5 mole nitric acid per liter of feed and 0.2 wt% SO_3 was recommended as the base composition for the PSCM experiment.

Pilot-Scale Ceramic Melter Testing

Two PSCM experiments were completed using West Valley feed in FY 1984. The first was a 275-hr test. The primary objective was to demonstrate vitrification of simulated WV waste containing IE-95 ion exchange zeolite. The experiment succeeded in demonstrating the prevention of glass reboil/foaming through the use of reducing agents. Melting rates, however, were as much as 50% lower than rates achieved during previous PSCM tests. This was attributed to the presence of the insoluble glassy phase at the glass surface, which had been experienced during certain ECM tests. Post-test studies have linked this layer to the formation of calcium-phosphate (apatite) crystals. This will be studied further in FY 1985.

During the experiment, over 6800 L of slurry was fed to the PSCM, producing almost 2400 kg of glass product. Glass-melt temperatures were maintained quite high for most of the experiment, at 1175 to 1200°C. Feeding rates averaged 30 L/hr·m², considerably below the nominal 60 L/hr·m² rate the PSCM is capable of.

Three levels of carbon content in the melter feed were tested in the PSCM experiments: 3 wt%, 9 wt%, and 10 wt% on an oxide basis. The carbon was furnished by sugar and oxalic acid. Glass stability, as measured by the ferrous/ferric ratio and tendency to reboil (foam) under laboratory conditions, was better than any previously tested Savannah River Laboratory (SRL), Hanford Waste Vitrification Program (HWVP) or WV glasses. The measured reboil tendency and the ferrous/ferric ratios changed very quickly with changed carbon content, indicating that glass redox and reboil tendency are quite responsive to cold-cap conditions.

Glass crystallinity was not very noticeable in glass-fiber samples taken from overflowing glass during the first period of the run, when 9 wt% carbon

was used. When a 10-wt% carbon level was tested, the presence of crystals increased noticeably. Finally, with a 3-wt% carbon level, their presence declined.

The melter instrumentation performed well. The glass thermowell provided consistent temperature readings. A melter glass-level bubbler system provided good indications of glass density, cold-cap/glass stability and glass level. The indications of tank level were used effectively in determining when periodic batch glass pouring should commence. An in-melter television viewing system showed cold-cap coverage and venting behavior. Because the glass-melt surface was covered by the boundary layer phase, the light of the plenum was weak, making it difficult to estimate the cold-cap condition from the video monitor.

The air-lift feed system designed for use with the PSCM worked dependably. No plugging occurred during operation even though the slurry flow in the second-stage lift sometimes moved in intermittent plug flow; at feed rates below 30 L/hr, the slurry feed lifted in a pulsating manner up the second lift followed by a momentary no-flow situation.

A 45-hr PSCM test was completed as an extension to the 275-hr experiment. The test was designed to evaluate 1) the benefits of glass-melt convection bubblers, 2) a time-domain reflectometer (TDR) glass-level monitor probe, 3) the ADS pump, and 4) further processing of feed slurry with 3 wt% carbon (oxide basis).

Throughout this test the convection bubblers were operated at 1 L/hr (at STP). This appears to have caused the stable feed rate to increase from the 20-25 L/hr, for the last part of the 275 hr test, to 30 L/hr for this test.

The TDR system, an electronic level-detection device, was used during the experiment. Indications from the instrument's cathode-ray tube (CRT) output were that it could differentiate between cold cap and glass. However, the indication of the cold-cap/glass interface, thickness of the cold cap and true glass level drifted with time. Generally, the response to changes in the melter by the TDR were encouraging considering its early stage of development.

The ADS pump was used to meter feed to the melter. Air supply equipment failures encountered during the previous 275-hr test were corrected. Pump operation was found to be affected by liquid level in the tank, as was noted also in long-term pump tests. The slurry output rate of the pump varied about 15% with changing tank level when pump parameter set points were left constant. Otherwise the pump operated very well.

No foaming was observed during the 45-hr test. No sugar was added and sodium oxalate was the only source of carbon. This resulted in a carbon content of 3 wt% (oxide basis). Cold cap characteristics were more acceptable during this extension test than in the previous test when sugar was added to the feed. More active venting was observed, compared to the first test, which had a higher carbon content.

Effluent Treatment System Studies

Pilot-scale equipment studies were conducted to evaluate the efficiency of the proposed WVNS off-gas treatment equipment. A schematic of the current off-gas system equipment is shown in Figure 3.5. The treatment system reflects the WV reference design, and includes the film cooler, submerged-bed scrubber (SBS), NO_x scrubber, and the high-efficiency mist eliminator (HEME). The only change in the reference treatment path is the substitution of the Hydrosonic® scrubber (HSS) for the HEME. Variations of these two paths were tested during PSCM experiments.

During FY 1984, system developments included 1) a system-pressure monitoring system; 2) an off-gas film cooler device to prevent deposition of solids within the off-gas line jumper between the melter and primary scrubber (coupled with a new scheme for controlling vacuum in the melter plenum); and 3) a packed-column scrubber for removal of NO_x .

Installation of the pressure-monitoring system for the off-gas equipment provides continuous surveillance of the pressure profile. It also monitors the flow rates of the film cooler and quenched off gas. Accurate correlations for

®Hydrosonic is a registered trade name of the Lone Star Steel Co.

FIGURE 3.5. Off-Gas Treatment System

pressure drop versus flow rate and versus time (total loading) are essential for scale-up. The installed monitor is versatile and can be adapted to various flowsheet configurations.

The film cooler device is designed to reduce the potential for melter solids depositing and accumulating in the first few feet of the off-gas line. It functions by injecting a boundary layer of air through several circumferential slots in the off-gas pipe. It thus simultaneously cools the off gas while introducing an air-film barrier to the entrained solids that could be deposited on the pipe wall. The flow of boundary air will be controlled automatically to maintain melter vacuum by feedback from the melter-pressure transmitter. If the melter vacuum deviates from the set point, the film cooler gas load will be adjusted. More air will be injected to decrease the vacuum (raise the pressure) and less to increase the vacuum (lower the pressure).

The packed column scrubber utilizes a structured packing to enhance NO_x absorption efficiency and rate. Water or dilute nitric acid solution circulates through the column, irrigating the packing counter-current to the gas flow. No internal cooling is provided in the column. The recirculating tank is, however, operated with full cooling applied to the tank jacket. Absorption of NO_x is accompanied by exothermic reactions, and if the temperature of the recirculating fluid were allowed to increase substantially, the absorption fluid's efficiency would decrease.

The recommended off-gas equipment is generally amenable for remote processing operations which demand high reliability and little maintenance. The off-gas connection from the melter to the primary scrubber will be subjected to severe corrosion conditions, and a highly durable material such as Inconel®-617, -671, or Hastelloy® C-276 is recommended. The presence of F^- and Cl^- in untreated melter condensate will present a significant corrosion potential that may require special alloys for scrubbing, condensing and evaporating equipment.

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®Hastelloy is a registered trade name of Cabot Corp.

Estimates have been made of the off-gas concentrations of effluents for which emission controls apply. It is found that the recommended off-gas processing system is adequate in controlling radioactive effluents at plant boundaries. The major radionuclide emissions are from ^3H and ^{137}Cs . Emission of these radionuclides can easily be reduced further without unduly complicating the present off-gas system.

Of the noxious gases generated by the WVNS vitrification process, only NO_x emissions may need to be controlled. Since the limits on stack emissions of NO_2 are approached only under maximum reference feeding conditions, a modest effort to remove NO_2 should provide an adequate margin of safety.

Process Chemistry

The objective of the process chemistry work is to ensure that glass compositions can be melted efficiently with minimal downtime due to foaming and minimal potential for the precipitation and sedimentation of conductive metallic phases. Process chemistry work entails selecting feed components for redox control and improved melting rate that, in turn, must not adversely affect the slurry rheological properties.

Glass-Melt Foaming

Foaming has been encountered during WV melter tests. Glass foaming is a high-temperature process that involves the freeing of gases from molten glass and a subsequent buildup of foam on the melt surface. It adversely affects melter operating efficiency in several ways. It creates a thermal insulating layer between the glass melt and the incoming feed. This in turn reduces melting rates and raises melt temperatures below the foam. Foaming increases the melt volume by decreasing its density, and can potentially affect the electrical power distribution. Product quality may also be degraded if glass foam is transferred to the canister. The melter operator typically responds to the onset of a foaming event by stopping the feed and decreasing the power to the melter until the foam melts and the desired melt temperatures are restored. Frequent foaming results in considerable melter downtime and must therefore be minimized.

A laboratory test to measure foaming tendency was developed and is shown schematically in Figure 3.6. It consists of a vertical-tube furnace with gas-tight, water-cooled fittings, a vacuum system with continuous pressure readout up to 1 atm (760 torr), and a port in the upper fitting to view the melt surface. Ten grams of glass are placed in an alumina crucible in the isothermal zone of the furnace at 1150°C. After 15 min at 1 atm pressure, the furnace pressure is reduced at a predetermined rate. The pressure at which the melt surface bubbles vigorously is noted. This is referred to as the "visual reboil pressure." It determines the point of gaseous supersaturation in the melt and is a measure of the collective amount of gases dissolved in the melt. Thus lower reboil pressures reflect less dissolved gas in the melt that can be freed to cause foam. Hence, lower reboil pressures infer a lower foaming tendency in the melter.

FIGURE 3.6. Glass-Melt Reboil Furnace

Laboratory studies revealed that foaming can be caused by the release of oxygen (from redox reactions involving multivalent species other than iron, e.g., chromium and cerium) and water vapor from the melt. The laboratory test on foaming tendency was able to distinguish between the contributing factors of total gas content and foam stability. The results indicated a strong correlation between glass oxidation state and foaming tendency as follows:

- Foaming tendency increased with greater dissolved gas contents and more stable foams and vice versa.
- Oxidized glasses had stable foams due to the preponderance of oxygen released.
- Reduced glasses had unstable foams, attributed to a greater proportion of water vapor in the gas mixture released. This may have arisen from effects of water vapor upon the surface tension or viscosity of the thin glassy membranes of the foam. These effects appear to have overridden that of the bulk viscosity of the glass.
- Reduced glasses were made by significant carbon additions to the feed. The presence of undissolved carbon in the surface layer of the glass may additionally aid in mechanically destabilizing foam due to surface tension effects.

During the 275-hr PSCM-19 test it was demonstrated that the addition of reducing agents to the feed can eliminate the foaming problem. In this melter test sodium oxalate and sugar were used as the reducing agents. They decreased the amount of oxygen dissolved in the melt such that in the gas mixture released there was a greater proportion of water vapor. This destabilized the foam and prevented its accumulation on the melt surface.

Melting Rate Testing

Melting rate testing initially involved placing a clay crucible containing about 40 g of WV glass in the top of a vertical tube furnace. When the temperatures stabilized (1030°C at the top and 1130°C at bottom of the melt), 15 mL of feed was added and allowed to react. After 3 min, 15 mL of additional feed were poured into the crucible. The crucible was removed at various times

after this last feed addition, then cooled, sectioned vertically, and photographed. An acetate sheet was placed over the photograph, and an outline of the remaining cold cap was made, cut out, and weighed. The mass of the acetate cutout, representing the cold-cap mass, was plotted against time as a measure of melting rate.

Concern for edge effects and cold-cap bridging in the crucible led to altering the procedure, whereby agitated feed is transferred at a specific rate by a peristaltic pump to the crucible drop by drop. An initial feed rate of 1 mL/min is now used, which scales to about 60 L/hr-m² in the PSCM, for 30 min before the crucible is removed from the furnace. Additional experiments are performed to double and triple this rate (e.g., 2 mL/min for 15 min). This better simulates the actual process of feed addition to the melter. Bridging is not now observed until the crucible is overfed at the higher rates. The relative differences in the cold cap's permeability are still apparent with this new procedure.

WV melter feeds prepared in the laboratory from reagent grade chemicals and actual PSCM-19 feeds were evaluated with the new procedure. With sugar contents less than 50 g/L, a partial, vesicular cold cap was formed from the lab feed at a feed rate of 1 mL/min, whereas the cold cap bridged across the crucible for the melter feed. Thus initial laboratory testing revealed a difference between the melting behavior of the lab and melter feeds, with the latter being significantly worse. Centrifuging these feeds and decanting the supernatant resulted in solids with different appearances. The lab feed was primarily a homogeneously brown powder. The melter feed was stratified, with coarse particles on the bottom, brown material in the middle, and dark brown material on top. The cause of this segregation is unknown at present, but zeolite particle size was suspected. For this reason WV lab feeds were made with both -325 and -80+120 mesh zeolite particles and were tested for melting rate. A difference was not detected at a feed rate of 1 mL/min, suggesting that the difference in melting rate between the lab and melter feeds is probably not due to zeolite particle size. Other components of the melter feed will be examined. It is essential to determine the sensitivity of melting

performance to subtle variations in the feed constituents because such variations are expected in the actual process.

Melting performance deteriorated in PSCM-19 with increased addition of sugar. This problem was not found in laboratory testing and may relate to the formation of calcium phosphate (apatite) crystals, which were found at the glass-cold cap interface during PSCM-19 and previous ECM runs. Reducing agents are required to control foaming. Therefore, a major emphasis for FY 1985 will be to identify a combination of reducing agents that will optimize melting and yet adequately prevent foam.

Safety Studies

A study was performed to evaluate the potential for, and effects of, a melter vapor explosion. A hypothetical vapor explosion would be caused by the intimate mixing of liquid slurry with either a layer of molten salt present on the melt surface or the glass melt itself. The study identified the weakest structural location in the WV melter to be the center of the edges between its east and west walls and floor. A melter structural failure could occur at these points at a minimum pressurization of about 40 psig. The maximum pressure, however, generated by a steam explosion utilizing available slurry would be an order of magnitude lower than the estimated 40 psig failure pressurization.

The potential for an energetic vapor explosion was shown to be negligible for several reasons. Although the interfacial contact temperature of a water/molten sulfate salt is high enough and the ambient pressure is high enough to support a steam explosion, no process can be identified that would mix the water and molten salt sufficiently to initiate a steam explosion. A violent interaction between the feed slurry and glass melt was also discounted because the glass was too viscous to allow adequately intimate mixing.

The results of this study discount vapor explosions as a major problem in future safety analyses of the WVDP melter.

3.3 HEAD-END PROCESS SUPPORT - Activity Leader: L. A. Bray

Major Contributors: B. M. Wise, L. K. Holton, and T. R. Myers

Summary

The Head-End Process Support activity has the responsibility to aid WVNS in selecting and designing the West Valley supernatant treatment system. During FY 1984 a reference supernatant treatment process was chosen by West Valley. The system removes cesium activity from the supernatant with an inorganic (zeolite) ion exchanger. The loaded exchanger is then mixed with the melter feed and vitrified.

Several investigations were carried out during the year that supported WV's selection of the above reference process. These included: 1) characterizing the zeolite ion-exchange process; 2) evaluating an alternative supernatant-treatment process (cesium removal using phosphotungstic acid precipitation); 3) generating laboratory data needed for the design of a zeolite-treatment system; and 4) providing WVNS with the design basis needed for the WVDP zeolite ion-exchange column system.

A formal document issued during the year summarizes FY 1983 laboratory development: Experimental Data Developed to Support the Selection of a Treatment Process for West Valley Alkaline Supernatant, by L. A. Bray, L. K. Holton, T. R. Myers, G. M. Richardson, and B. M. Wise, PNL-4969 (1984). In addition, L. A. Bray presented a paper at the August 1984 American Nuclear Society International Topical Meeting--Fuel Reprocessing and Waste Management; it is titled "Selection of a Reference Process for Treatment of the West Valley Alkaline Waste," by L. A. Bray et al., PNL-SA-12283.

Characterization of the Zeolite Ion-Exchange Process

In FY 1983 an inorganic ion-exchange process using IE-95 zeolite had been chosen by WVNS as the reference supernatant-treatment option. Characterization of this process was completed in FY 1984. Characterization comprised studies of IE-95 zeolite loading and elution (including acid eluate analysis), batch distribution tests, and testing of a small hot-cell demonstration ion-exchange column subsequently used at WV. In addition, the results of a 100-mL column test using IE-95 were compared with selected Hanford B-Plant cesium recovery

runs. This work was reported to WVNS in the letter report Review of FY 1984 Laboratory Data by L. A. Bray and B. M. Wise, WVSP 84/40 (1984). Results are summarized as follows:

- An ion-exchange system for Tank 8D-2 alkaline supernatant decontamination, using three columns in series, provides a cesium DF of 10^3 - 10^4 . If the zeolite is 100% utilized and assuming undiluted supernatant feed at 25°C, the IE-95 requirement will be ~80,000 kg.
- The cesium loading capacity at a feed Na/Cs mole ratio of 4,800 was determined to be $\sim 3.7 \times 10^{-2}$ M Cs per liter of exchanger (~26 column volumes (cv) of synthetic 8D-2 feed).
- The cesium-exchange properties of IE-95 are destroyed during HNO_3 elution, and the zeolite cannot be reused.
- Inorganic exchangers IE-95, Zeolon®-500 and -900, and AW-400® have similar cesium distribution (R_d) values, $R_d \sim 30$ -38.
- A new 30-mL ion-exchange column was tested using synthetic WV alkaline supernatant. No differences were noted as compared to a 10-mL column previously tested for use in the WV hot cells.
- Comparisons of a Hanford B-Plant column (7,000 L), using AW-500 and Hanford supernatant (sodium/cesium mole ratio: 5,670), and a 100-mL IE-95 (NH_4^+ -form) laboratory column, using synthetic WV supernatant (Na/Cs mole ratio: 4,800), show similar Cs^+ breakthrough results.

Based on the above results, the zeolite process using IE-95 continued as the reference supernatant-treatment process. Two zeolite-processing scenarios had been previously proposed. In the first, the sludge phase of the alkaline PUREX waste in Tank 8D-2 would be blended with THOREX acid waste (Tank 8D-4) and nitric acid eluate from eluting the cesium-loaded zeolite ion exchanger. The eluted zeolite, free of contamination, would be sent to onsite low-level waste (LLW) burial. In the above scenario, the nitric acid from the zeolite elution was assumed to contain only ^{137}Cs and other minor fission products. In a second scenario, the THOREX acid waste - PUREX sludge would be acidified and the cesium-loaded zeolite (IE-95) would be directly blended for feed to vitrification. This approach, however, would produce more glass to accommodate

the Al_2O_3 present in the zeolite. The first process is preferable because a smaller amount of glass is produced.

Two other important results were obtained that affect the processing of loaded zeolite:

- Nitric acid elution of IE-95 did not remove all cesium from the exchanger. Using 4 M HNO_3 , 1.4% of the loaded Cs^+ remained on the zeolite after four equal-volume batch contacts. About 0.1 to 0.7% of the loaded Cs^+ remained on the exchanger after upflow or downflow column elution using 10-13 cv of 4 M HNO_3 . The addition of the cesium-contaminated spent zeolite to the LLW would reduce the WV site cesium decontamination factor (DF) from the 10^3 - 10^4 range to 10^2 - 10^3 .
- The acid eluate was found to contain ~90 wt% of the initial Al_2O_3 and ~100 wt% of the initial Fe_2O_3 - Cr_2O_3 in the exchanger due to partial dissolution of the IE-95 zeolite during column elution.

The incomplete elution made disposal of the eluted exchanger as LLW much less advisable because of the reduced cesium DF. The loaded exchanger's incorporation in the glass had appeared inadvisable because it would necessitate additional glass. However, the >90% of the Al_2O_3 removed from the exchanger during elution would still have to be accommodated in the glass as it would be added with the eluate.

As a result of these considerations, supernatant treatment with IE-95 zeolite followed by direct incorporation of the zeolite in the melter feed became the revised reference treatment option.

Additional studies were performed to obtain physical and chemical data for the zeolite head-end process. The results were reported to WVNS in a letter report, Physical and Chemical Data for the Zeolite Head-End Process, by L. A. Bray and B. M. Wise, WVNS 84/108 (1984). These studies included chemical analysis of the zeolite, examination of pretreatment scenarios, zeolite-column hydraulic properties, and batch cesium distribution data for distilled water and cesium-loaded zeolite. A cesium batch distribution (K_d) was determined to be $>10^6$ for cesium loaded zeolite in distilled water between 25 and 120°C.

Pretreatment of IE-95 to remove a fraction of the Ca^{2+} was examined in an attempt to prevent "cementing" of the exchanger with CaCO_3 during the loading cycle. Cementing does not stop the supernatant flow through the column but could impede the removal of the cesium-loaded exchanger from the column. IONSIV® IE-96 was examined as an alternative exchanger. It was found that the IE-96 did not cement in the columns like IE-95 and that the IE-96 had a cesium-loading capacity similar to that of IE-95. IE-96 was recommended for future laboratory and plant testing even though it may not provide strontium decontamination.

The chemical compositions of IE-95 and IE-96 were determined. They were found to be similar except for a lower divalent ion content for IE-96, with calcium showing the major difference (3.7 wt% versus 1.1 wt%, respectively).

Hydraulic properties of zeolite IE-95 were examined in a column 6 in. in diameter by 10 ft tall. Bed expansion tests were performed using water. The bed expanded 50% at 6 gpm/ft². The pressure drop through the bed was investigated using water and simulated supernatant. At flow rates of process interest, the pressure drop was very low, on the order of 2 to 10 in. of H_2O per ft of bed.

Physical properties of simulated alkaline supernatant were measured, including viscosity and density as a function of temperature (6 to 85°C). The saturation temperature for alkaline supernatant (i.e., point of crystallization) also was determined to be 0 to 3°C.

Phosphotungstic Acid (PTA) Precipitation Process

At the request of WVNS, the PTA ($\text{Na}_3\text{PW}_{12}\text{O}_{40}$) process for precipitation of cesium was investigated as an alternative to IE-95 zeolite ion exchange. It would have the advantage that the Al_2O_3 in the zeolite would not have to be incorporated into the glass. So little tungsten would have to be accommodated that it would not affect the amount of glass produced.

The results of the PTA investigations are contained in the letter report Laboratory and Engineering-Scale Tests and Evaluation of the Cesium Phosphotungstate Process by L. A. Bray, B. M. Wise and T. R. Myers, WVSP 84/91 (1984). Although the process was found to be a viable alternative, it exhibited two

significant disadvantages. The PTA process will affect the LLW volume and off-gas treatment. Acidification and subsequent reneutralization of the Tank 8D-2 supernatant will increase the mass of salt sent to be solidified in concrete by ~34 wt%. Acidification of the alkaline supernatant will produce large quantities of off gas requiring treatment before release.

Figure 3.7 shows a simplified flow diagram for the PTA precipitation process. The process would be implemented as follows: A measured amount of nitric acid solution is added to Tank 8D-3. Supernatant from Tank 8D-2 is then added slowly to the acid. This produces a large quantity of off gas, ~72 volumes off gas per volume supernatant, primarily CO_2 and NO_x . Supernatant is added to the acid and not vice versa to keep the reacting solution acidic and prevent surging of the off gas. A solution, containing 1 mole PTA per mole cesium in the acidified supernatant, is then added in-line to the filter. The precipitation reaction, forming the cesium-phosphotungstate $[\text{Cs}(\text{K},\text{Rb},\text{Na})\text{HPW}_{12}\text{O}_{40}]$, is complete within several minutes. Partially decontaminated supernatant (first strike cesium DF ~30) is filtered off, leaving the cesium PTA. The partially decontaminated supernatant is adjusted with PTA in-line for a second PTA strike; PTA solution, containing 1 mole PTA per mole cesium originally in the supernatant, is added. A precipitate again forms, this time primarily potassium PTA and some cesium PTA. The chemical formula for the second strike precipitate is $[\text{K}_2(\text{Cs},\text{Rb},\text{Na},\text{H})\text{PW}_{12}\text{O}_{40}]$. The overall cesium DF after this strike will be at least 2×10^4 . The cesium-decontaminated supernatant is then filtered from the precipitate and transferred to the low-level waste treatment facility (LLWTF). The acidified supernatant is neutralized before being converted into a concrete waste form. The precipitates from the first and second strikes would be dissolved in caustic and transferred to the vitrification process.

Laboratory tests showed that PTA precipitation of cesium from simulated acidified Tank 8D-2 supernatant would provide a cesium DF of $>10^4$ after two strikes. Both strikes would use an equal quantity of PTA, equivalent to 1 mole of PTA per mole cesium in the initial acidified supernatant; thus a total of 2 moles of PTA would be used per mole cesium for the entire process.

FIGURE 3.7. Simplified Flow Diagram for the Phosphotungstic Acid Precipitation Process

The first precipitation strike would provide a cesium DF of 36 to 60 and the second ~300, giving an overall cesium DF of $>10^4$. The first strike would be at equilibrium within 1 min at 25-60°C. The second strike would be at equilibrium after 30-60 min at 25°C and within 3 min at 60°C. This suggests that the PTA precipitation step could be done "in-line" at current Tank 8D-2 temperature (~60°C).

Particle size distribution tests indicate that precipitate particle size for the cesium-phosphotungstate is from 6 to 35 μm when the precipitate is in acid solution. The precipitate has shown excellent settling and filtering properties in both laboratory filtration tests and engineering-scale tests (filter DF of 4×10^4) using sintered metal cross-flow filters. Water, however, degrades particle size; and thus water washing of the precipitate is not recommended.

The alternative of storing the PTA precipitate in the THOREX waste Tank 8D-4 was investigated by blending the PTA precipitate, cesium-phosphotungstate, with an appropriate amount of synthetic THOREX waste. The precipitate settled to the bottom of the solution, but was resuspended with mild agitation after several months. In this respect, the precipitate was judged compatible with the THOREX waste.

Preliminary tests on waste glass indicate that the WO_3 and additional P_2O_5 from the PTA precipitate will have little effect on the glass properties when added in the expected quantities. Compatibility of the PTA process with the vitrification process appears excellent; however, it has not been tested in a melter.

Design Basis for the WVDP Zeolite Ion-Exchange System

At the request of WVNS, PNL completed a preliminary examination of the zeolite ion-exchange system planned for use in the West Valley Demonstration Project (WVDP). This study describes the reference process, discusses system operating and maintenance philosophy, and describes the reference zeolite ion-exchange column and supporting instrumentation. In addition, operational performance of the system was computer-modeled to determine the optimal configuration for the ion-exchange column. The results of this study are contained

in the report Design Basis for the WVDP Zeolite Ion-Exchange System by L. K. Holton, L. R. Michels, and B. M. Wise, WVSP 84/106 (1984).

The purposes of this study were to:

- provide a description of the reference ion-exchange system to include general operations and system operating and maintenance philosophy
- provide a description of a reference zeolite ion-exchange column and the equipment and instrument systems that would support operation of the column
- provide an estimation of the ion-exchange system operating performance based upon results of laboratory test data and mathematical modeling of the ion-exchange system
- examine alternative system operating approaches and identify a reference approach.

The zeolite ion-exchange system proposed for use at West Valley is a modification of zeolite ion-exchange processes used at Hanford's B-Plant and at Three Mile Island's Unit-2 (TMI-2) nuclear reactor. Experience gained at the two sites was used in preparing the design basis report. To define the ion-exchange process and equipment system, this information was combined with the following:

- data developed during experimental testing of the zeolite ion-exchange process at PNL during FY 1983 and FY 1984
- mathematical modeling of the ion-exchange system configuration
- standard operating practices and systems engineering used in radio-chemical production plants
- WVNS's decision to implement the zeolite ion-exchange process in Tank 8D-1.

The scope of this study was limited to the zeolite ion-exchange column, supporting instrumentation and the zeolite ion-exchange column system. Supporting unit operations such as supernatant filtration and zeolite storage were not part of this study and thus were covered only briefly.

Design Criteria

The following design criteria were developed for the proposed West Valley ion-exchanger system:

- Only demonstrated technology or minor extrapolations thereof shall be employed.
- Supernatant feed to the ion-exchange system shall be essentially free of insoluble material.
- The concentrated cesium product produced by the ion-exchange process shall have a chemical composition readily compatible with the downstream waste vitrification operation.
- The concentrated cesium product shall be stored to permit ready feed to the ceramic melter.
- Equipment shall be provided by others, if required, for concentrating the cesium ion-exchange product sufficiently for feed to the ceramic melter.
- Equipment shall be sized to permit processing of 90% of the supernatant (2.0×10^6 L) stored in Tank 8D-2 in a maximum of 1.5 yr.
- The ion-exchange system shall be capable of processing solutions generated from washing of the Tank 8D-2 sludge.
- The ion-exchange process shall be capable of providing a minimum cesium DF of 10^3 .
- The ion-exchange medium to be used is a synthetic zeolite, Linde Ionsiv® IE-95 or IE-96, produced by Union Carbide.
- The performance of zeolite for decontaminating the WV alkaline supernatant is based upon laboratory data from tests conducted at PNL.
- The supernatant effluent from the ion-exchange system shall be solidified by others in a form suitable for disposal in a commercial LLW burial ground.

Equipment Criteria

- The equipment system shall be designed for remote operation.
- The equipment system shall be designed for remote and/or semiremote equipment maintenance.
- The equipment system shall be designed to permit continuous 24-hr/day operation.
- Shielding of the equipment system shall be provided to reduce radiation exposure to operating and maintenance personnel in keeping with the ALARA philosophy.
- The equipment system shall be designed to eliminate the possibility of flow from pressurized ion-exchange columns and process lines into "cold" side operating and service areas.
- Provision should be made in the design for the eventual decontamination and decommissioning of all vessels and piping.
- Facilities shall be of licensable quality, but formal licensing is not required.
- Passive system components (ion-exchange columns) shall be designed to permit remote removal and replacement. Active system components (valves, instrument sensors, etc.) will be designed for contact maintenance following decontamination.

Process Description

The efforts at West Valley to decontaminate supernatant are directed primarily at removing at least 99.9% of the radiocesium (^{137}Cs , ^{134}Cs) from the supernatant before its conversion to a concrete waste form for disposal.

The reference inorganic ion-exchange process for the WVDP uses IE-96 zeolite in four columns. Three columns are loaded in series to recover cesium from the alkaline supernatant while the fourth is being regenerated with fresh zeolite. The loaded exchanger is removed from the columns, stored and eventually blended with other waste streams (principally the alkaline sludge,

acidic THOREX waste, and glass-forming chemicals), and converted to a borosilicate glass. The partially decontaminated supernatant effluent is discharged to an LLW treatment facility for conversion to a concrete waste form suitable for disposal in a commercial LLW burial ground. A simplified flow diagram for the zeolite ion-exchange process is shown in Figure 3.8.

The zeolite ion-exchange process is divided into four basic unit operations: 1) feed pretreatment, 2) ion-exchanger loading, 3) ion-exchanger replacement, and 4) effluent treatment.

The primary processing objective for the ion-exchange system is to achieve maximum loading of the zeolite ion exchanger. This will minimize the mass of zeolite generated from treating the WV Tank 8D-2 supernatant and, therefore, its impact on the vitrification system. This can be achieved by optimizing process conditions and column configuration. The following recommendations have been made to WVNS:

- Optimal ion-exchange processing conditions call for continuous operation, low feed flow rates (~ 0.2 cv/hr), low temperatures (less than 25°C), and supernatant feed diluted with water.
- The ion-exchange system should consist of four columns, three loaded in-series while the fourth is reloaded with zeolite. The ion-exchange columns should use IE-96 zeolite, which is to be loaded with cesium activity and then discharged from the ion-exchange column.
- The ion-exchange system should be operated as follows: When Column 1 achieves the limiting cesium breakthrough, and/or Column 3 reaches the technical specification limit on system decontamination, supernatant flow is stopped. After rinsing, Column 1 is removed from the supernatant flow train by valve switching or jumper changes, and Column 4, containing a new zeolite charge, is piped into the train to become the new Column 3. The other two columns advance in the train such that the previous Column 2 now becomes Column 1 and the previous Column 3 now becomes Column 2. This column-shifting approach is continued until the entire volume of Tank 8D-2 supernatant is treated.

FIGURE 3.8. Flow Diagram for the Zeolite Ion-Exchange Process

- Instrument systems required for the ion-exchange column system are well established in radiochemical facilities. Straightforward application of these instrument systems is possible with engineering.

The following concerns were expressed to WVNS about operating or implementing the zeolite ion-exchange system as presently proposed for the WVDP:

- Zeolite storage in Tank 8D-1 may lead to difficulties in handling solids because of degradation of zeolite and its consolidation into nondispersible masses.
- The system's process piping, unless properly designed and configured, can significantly reduce achievable decontamination.
- The use of valving may not be satisfactory for providing the primary isolation of the pressurized radioactive ion-exchange system from the nonradioactive service galley.

3.4 DESIGN SUPPORT - Activity Leader: D. H. Siemens

Major Contributors: M. M. Beary, D. N. Berger, S. M. Barnes,
R. A. Brouns, and R. D. Peters

The focus of the Design Support activity is design and fabrication activities relating to the West Valley component test stand (CTS). Design of the CTS equipment was based on the feed composition and design criteria specified by WVNS. Table 3.1 lists the PNL responsibilities for equipment design, specification, engineering calculation, and acquisition. The overall requirement was that the CTS components could be used to vitrify the actual WV HLW, that is, be designed for remote operation and maintenance. Stringent QA requirements were applied to their design and fabrication. Appropriate heat transfer and structural (thermal and load stress) analyses were performed on all equipment. Nondestructive testing (NDT) and examination (NDE) requirements were specified in the design documents to satisfy the appropriate codes and standards. The equipment was designed to comply with the WVNS-prepared design criteria.

TABLE 3.1. Equipment Designs, Specifications, Engineering Calculations,
and Acquisitions Provided to West Valley by PNL

<u>Item</u>	<u>Design</u>	<u>Specifi- cation</u>	<u>Engrg. Calcs.</u>	<u>Acqui- sition</u>
Slurry-Fed Ceramic Melter (SFCM)	X		X	X
SFCM Power Supply	X	X	X	
SFCM Materials of Construction				
Inconel (690)		X		
Melter Refractories (Monofrax® K-3 and E)		X		
Submerged-Bed Scrubber (SBS)	X		X	
Melter Feed Tank	X		X	
Melter Feed Tank Agitator		X		
Melter Feed Delivery System	X	X	X	
Canister	X		X	
Canister Turntable	X		X	X
Canister Turntable Drive	X	X	X	X
Glass-Level (Gamma) Detection System	X	X	X	
Canister Storage Rack	X		X	
Concentrator-Feed Makeup Tank	X		X	
Concentrator-Feed Makeup Tank Agitator		X		
In-Cell Portion of Instrumentation	X	X		
Equipment Supports	X		X	
Equipment-Handling Yokes	X		X	
Mechanism for Moving Canister Turntable Underneath Melter	X		X	X
In-Cell Jumpers for CTS Components	X	X	X	
Remote Connectors		X		
TV - for Viewing SFCM	X	X		
Gamma Source for Glass-Level Detection System		X	X	

In addition to the basic equipment designs, the following design bases drawings were also prepared for the CTS equipment:

- process flow diagrams
- material balance flowsheets
- process and instrument diagrams
- hydraulic diagrams
- equipment arrangement
- jumper layout
- one-line electrical.

These drawings were used as supplemental guidance for equipment design.

Equipment Layout

Figure 3.9 shows the proposed process flow diagram for the CTS. Both presently planned equipment and additions proposed for use during hot operation are shown. Figure 3.10 is a schematic of the melter and turntable assemblies of the CTS. Figure 3.11 shows a plan view of the in-cell locations of major CTS components. It also shows the jumpers that connect the components to each other and to cell services and indicates the complexity of the CTS.

Individual Equipment Items

The following sections briefly describe each CTS component and list the scope of PNL activities for each item.

Slurry-Fed Ceramic Melter (SFCM)

It is in the SFCM that the waste plus glass-former mixture (slurry) will be melted to form a molten glass. The metal shell of the SFCM was delivered to WVNS in FY 1984. The refractory lining will be installed at West Valley.

PNL activities related to the fabrication of the SFCM were:

- preparation of design drawings and fabrication of the SFCM (by J. A. Jones)
- preparation of specifications for the power supply to the melter electrodes
- procurement of the in-cell portion of SFCM control instrumentation

FIGURE 3.9. Proposed Process Flow Diagram for the Component Test Stand (CTS)

FIGURE 3.10. Schematic of the CTS Melter and Turntable Assembly

FIGURE 3.11. Plan View of In-Cell Locations of Major CTS Equipment

- preparation of design drawings for the in-cell portion of the in-melter TV viewing system
- preparation of specifications for the in-melter TV system
- preparation of specifications for the Inconel-690 required for melter fabrication
- preparation of specifications for the SFCM refractory materials (Monofrax® K-3 and E). All other melter materials were procured by PNL
- design and fabrication of yokes for handling and maintaining the melter subsystems
- packaging and shipment of the PNL-acquired items to WVNS
- providing adequate color photographs of melter internals during all phases of construction to pictorially document melter fabrication.

Canister Turntable

The turntable is the component which positions empty canisters under the melter pour spouts and monitors the fill height of the canisters. Its fabrication was 90% completed in FY 1984. Fabrication and testing will be completed, and the turntable will be delivered to West Valley in the first quarter of FY 1985.

PNL activities related to fabrication of the turntable were:

- preparation of design drawings and fabrication of the canister turntable
- preparation of specifications and procurement of the turntable drive
- preparation of specifications for the gamma-level detection system used to monitor canister glass level during canister fill
- designing of a fixed multiple-gamma source holder for the canister glass level detection gamma source
- preparation of specifications for the glass-level detection gamma sources

- preparation of arrangement drawings for installation of the collimators and detectors associated with the gamma glass-level detection system
- designing and fabricating the turntable supports
- designing and procuring a mechanism for moving the turntable under the melter
- designing and fabricating yokes for handling and maintaining the turntable
- packaging and shipping the PNL acquired turntable items to WVNS
- providing adequate color photographs during all phases of construction to pictorially document turntable fabrication.

Glass Canister, Canister Storage Rack, and Canister Handling Equipment

The glass canister is the metal container which contains the glass poured out of the melter. The canister storage rack holds six canisters during final cooling, subsequent to their removal from the turntable. The canister-handling equipment is used to move the canister during vitrification operations (e.g., placement in the turntable or transfer from the turntable to the storage rack). Design of these components was completed during FY 1984.

PNL activities related to the design of this equipment were:

- preparation of design drawings for the canister
- design of appropriate equipment-handling yokes and canister grapple

Melter Feed Tank

The melter feed tank is the vessel that holds the waste plus glass-former slurry mixture which is melted in the SFCM. Design of this component was completed in FY 1984.

PNL activities related to design of the melter feed tank were:

- negotiating a vendor contract for testing melter feed mixing
- supervising and reporting on the mixing test
- preparing a design drawing of the feed tank

- designing supports for the feed tank
- preparing specifications for the feed-tank agitator
- designing yokes for handling and maintaining the feed tank.

Concentrator/Feed Makeup Tank

The concentrator/feed makeup tank is the vessel in which the melter feed is initially made up. Because this feed will be more diluted than is needed for optimal melter performance, it will also be concentrated here before transfer to the melter feed tank.

PNL activities related to this component were:

- negotiation of vendor contracts to test concentration for the two types of wastes (WVNS reviewed concentration test plans before approval of vendor contracts)
- supervising and reporting of the concentration tests
- preparation of design drawings for the concentrator
- design of supports for the concentrator
- design of yokes for handling and maintaining the concentrator.

Melter-Feed Delivery System

The melter-feed delivery system is the system used to deliver the waste plus glass former slurry from the concentrator/feed makeup tank to the melter feed tank, and from this vessel into the melter. Tests indicate that an air-lift system can be successfully used.

PNL activities related to the design of this system were:

- design of the air-lift system
- design of system support hardware
- design of the yokes necessary for handling and maintaining the feed system.

Primary Off-Gas Scrubber

A submerged-bed scrubber will be used as the primary off-gas scrubber. This component will remove the particulates as well as condensibles from the off-gas stream.

PNL activities related to the design of this component were:

- providing the design of the scrubber
- designing the supports for the scrubber
- designing of the yokes necessary for handling and maintenance of the scrubber system.

In-Cell Jumpers for CTS Components

Canyon-remote jumpers are required for interconnecting the CTS components and for providing cold services, such as electricity and water, to the components. Design of the jumpers was 90% completed in FY 1984.

PNL activities related to the fabrication of the jumpers were:

- estimation of remote connector requirements and preparation of purchase specifications for the connectors
- designing of all process and cold-service jumpers required for the PNL-designed CTS components
- preparation of specifications for procured jumper components (jets, flowmeters, etc.)
- designing appropriate yokes for handling and maintaining the in-cell jumpers.

3.5 GLASS CHARACTERIZATION - Activity Leader: L. A. Chick

Major Contributors: G. D. Maupin and C. A. Church

Summary

The Glass Characterization activity of the West Valley Support Task is responsible for developing and characterizing the oxide glass composition to be used for vitrification of West Valley high-level waste. This glass must have

process properties suitable for operation of the intended joule-heated melter (viscosity, electrical conductivity, crystallinity) and meet desired product properties, such as release (leach) rate.

During FY 1984 this activity focused primarily on adjusting the WV glass composition developed in FY 1983. Adjustments were made in response to 1) changes in the WV waste treatment flowsheet (chiefly incorporation of the IE-95 zeolite into the glass) and 2) the poor melting behavior exhibited by the zeolite glass. A summary of the FY 1984 work was reported to WVNS in September 1984 in the letter report Progress Report on Glass Characterization and Process Chemistry, by D. S. Goldman and L. A. Chick, WVSP 84/142 (1984).

The glass formulation that resulted from the FY 1984 work has been designated WV-182. This glass incorporates the WV waste at a loading of 24% plus the IE-95 ion-exchange material. It is a borosilicate composition that has acceptable viscosity and electrical conductivity for processing in the joule-heated melter. Moreover, preliminary results suggest that it has leaching characteristics similar to those of Savannah River TDS-165 glass. WV-182 glass is known to devitrify under some conditions, forming iron and chromium (spinel and hematite) and calcium-rare earth-phosphate (apatite) crystals. The ingrowth of these phases accompanied large increases in melt viscosity at lower temperatures. The apatite phase appears to concentrate in the surface layers of the glass and may significantly impair melting performance. Elimination or reduction of this apatite phase will receive major emphasis during FY 1985.

Development of WV-182

During FY 1983, an oxide glass composition was developed for vitrification of WV waste based on the results of a statistically designed mixture study. The mixture study was reported in the FY 1984 document West Valley High-Level Nuclear Waste Glass Development: A Statistically Designed Mixture Study, by L. A. Chick et al., PNL-4992.

Early in CY 1984, the WV flowsheet was altered to include the IE-95 ion-exchange material in the glass. Using the FY 1983 mixture study, several glass

compositions were developed to include IE-95 zeolite while maintaining acceptable melt (viscosity, electrical conductivity) and product (leach rate) properties. The glasses included a high calcium-low boron version (similar to the optimum glass reported in the above document), a version in which boron and calcium ratio was reversed (similar to the interim glass processed during FY 1983 PSCM tests), and a version with about equal amounts of the boron and calcium oxides.

During viscosity testing it was noted that the growth of oxide crystals accompanied increased melt viscosities. Difficulty in detecting these phases by x-ray diffraction indicated that small amounts of crystals in the melt were related to unstable viscosity behavior. The problem was found to be most severe in high-boron glasses, except for Savannah River Laboratory (SRL) glass. High-calcium glasses did not appear to be affected. A WV analog of the SRL glass was made (SRL-165 glass exhibits stable viscosity behavior) and was found to contain the same crystalline phases and unstable viscosities. This suggested that the problem was inherent in the WV waste. Emphasis was shifted back to a high-calcium glass because of concerns for sedimentation of these dense phases in the melter and the potential economic impact of reducing the waste loading to minimize crystal growth. This shift was made without proof that the observed amount of crystallization was detrimental to melter performance although glasses obtained from a previous ECM test of the high-boron glass did exhibit crystals in agreement with the laboratory findings.

The substitution of lithium for sodium was investigated as it was expected to improve the chemical durability of the glass. Although this favorable effect was observed, lithium was rejected because it increased the formation of chromium-containing crystals.

Due to the crystallinity problems with a high-boron glass, a high-calcium glass was defined and tested. It included less zeolite because a reevaluation showed that less would have to be incorporated. This composition was tested for melting rate, which was found to be poor compared to high-boron WV glasses. This disadvantage was considered to outweigh the problems with oxide-phase formation in high-boron glasses, and emphasis was shifted back to optimizing a high-boron formulation.

The compositions of the radioactive and nonradioactive versions of this final high-boron glass, identified as WV-182, are shown in Table 3.2. The non-radioactive glass, used in the melter runs, contains a weight-basis substitution of zirconia and rare-earth oxides for the thorium and uranium oxides. The nonradioactive version was processed in a melter test (PSCM-19) late in FY 1984. The formation of an apatite (calcium-rare earth-phosphate) crystalline phase at the glass-cold cap interface may have contributed to the low melting rate encountered in the test. Elimination of the apatite phase will receive high priority during FY 1985.

Characterization of WV-182

The characterization of WV-182 was focused on its process-related properties, although a short-term leaching test was also performed to verify that WV-182's chemical durability is within the range found for similar waste glasses.

Chemical Durability

Table 3.3 shows leaching results for the radioactive and nonradioactive versions of WV-182 compared to those for a Savannah River glass, SRL-TDS-165. These are results for a brief MCC-1 test lasting 6 days at 90°C in deionized (DI) water with a surface area-to-volume ratio (SA/V) of 10 inverse meters. Longer-term and higher SA/V tests are under way, as are analyses of uranium, thorium, and cesium releases.

These early results show that the WV glasses are nearly as durable as the SRL glass and produce lower pH values in the final solution. The lower pH values may cause relatively slower dissolution at longer times, bringing the releases closer to those of the SRL glass.

Electrical Conductivity

The electrical conductivity of the radioactive version of WV-182 was measured and found to be 0.21 inverse ohm-cm at the processing temperature of ~1100°C. This is within the acceptable range. The conductivity of the non-radioactive glass has not been measured, but is expected to be similar to that of the radioactive version.

TABLE 3.2. West Valley Waste and Glass Compositions

Oxide	Waste + Zeolite Radioactive	Waste + Zeolite Nonradioactive Simulation	Glass Formers	WV-182 Radioactive Glass	WV-182 Nonradioactive Simulation Glass
SiO ₂	20.73	20.73	56.63	44.67	44.67
Na ₂ O	4.24	4.24	20.44	15.05	15.05
CaO	1.26	1.26	3.85	2.99	2.99
B ₂ O ₃	0.03	0.03	19.08	12.74	12.74
Fe ₂ O ₃	36.87	36.87		12.26	12.26
Al ₂ O ₃	7.25	7.25		2.41	2.41
P ₂ O ₅	7.85	7.85		2.61	2.61
BaO	0.30	0.30		0.13	0.13
Cr ₂ O ₃	2.04	2.04		0.68	0.68
MgO	0.30	0.30		0.10	0.10
MnO ₂	1.47	1.47		0.49	0.49
NiO	1.35	1.35		0.45	0.45
RuO ₂	0.24	0.24		0.08	0.08
SrO	0.12	0.12		0.04	0.04
TiO ₂	0.09	0.09		0.03	0.03
ThO ₂	11.24	0.00		3.73	0.00
UO ₂	1.74	0.00		0.58	0.00
ZrO ₂	0.48	5.02		0.16	1.67
Rh ₃ O ₃	0.03	0.03		0.01	0.01
CeO ₂	0.51	0.51		0.17	0.17
Gd ₂ O ₃	0.03	0.38		0.01	0.12
La ₂ O ₃	0.18	4.16		0.06	1.38
Nd ₂ O ₃	0.12	2.94		0.04	0.98
SmO ₂	0.03	0.55		0.01	0.18
Pr ₆ O ₁₁	0.03	0.80		0.01	0.27
Y ₂ O ₃	0.06	0.06		0.02	0.02
SO ₃	0.60	0.60		0.20	0.20
Cs ₂ O	0.30	0.30		0.10	0.10
K ₂ O	0.51	0.51		0.17	0.17
	100.00	100.00	100.00	100.00	100.00

TABLE 3.3. Short-Term Leaching Results for WV-182(a)

Element	Normalized Elemental Releases, g/m ² (average of 3 replicates)		
	Radioactive WV-182	Nonradioactive WV-182	SRL TDS-165
Al	9.2	9.7	9.0
B	18	14	12
Ca	1.0	1.7	1.9
Na	18	22	12
Si	14	12	10
pH	9.4	9.3	9.7

(a) Conditions: DI water, 90°C, SA/V = 10 m⁻¹, 6 days.

Crystallinity

Nonradioactive WV-182 glass has been observed to devitrify and form three different crystalline phases:

1. cubic crystals having a spinel crystal structure and composed of chrome-iron-nickel oxide
2. hexagonal platelets having a hematite structure and composed of chrome-iron oxide
3. dendrites having an apatite structure and composed of calcium-rare earth-phosphate.

The radioactive glass contained the same crystalline phases with some thorium, in addition to rare earths, found in the apatite. Waste and glass composition, thermal history, and oxidation state affected the final crystallinity of the glass.

The major compositional factor affecting hematite and spinel formation was the chromium content. Removal of the chromium oxide to less than 0.25 wt% in the glass eliminated these phases altogether. When chromium oxide was present at near the nominal 0.7 wt% level for the WV combined waste at 23% waste loading, either hematite or spinel or both formed in the glass. If all the

chromium was present as the hematite phase and this phase contained roughly one iron for each four chromium ions (as is indicated by SEM EDX analyses), then the total crystalline content would be about 0.9 wt%. If all the chromium devitrified spinel with a 1:1 chrome-iron ratio, then 1.5 wt% spinel could have formed. These estimates are consistent with the fact that hematite and spinel peaks are barely detectable by x-ray diffraction. The oxidation state and thermal history of the glass will affect the relative proportions of hematite and spinel. At the 0.2 ferrous-to-ferric ratio currently planned for melter operation, the hematite phase tends to predominate for thermal histories likely to occur in the melter.

The calcium phosphate phase appears to separate from the glass melt in liquid form (liquid-liquid phase separation) at high temperature. Under some conditions, dendritic apatite crystals later form in the glass. Droplet-shaped regions of the same chemical composition as the dendritic crystals are often seen by SEM, indicating that liquid-liquid phase separation took place but that later crystal growth did not. The apatite phase has been observed to concentrate in a carbon-rich "scum" layer which sometimes forms on melt surfaces. In the apatite structure, rare earths, actinides or sodium may substitute for calcium, and silicon may substitute for phosphorus. SEM EDX analyses conducted on various WV-182 samples indicate that roughly two calcium ions are present for each phosphorus ion and that substitutions may account for 10 or 20 wt% of the composition. Since WV-182 contains 3 wt% calcium oxide, the maximum amount of apatite which could form is about 7 wt%. In FY 1985 the effects on the amount of apatite of decreasing the glass calcium content will be determined.

Viscosity

Figure 3.12 shows the viscosities of WV-182 in its radioactive and non-radioactive versions. The plot also shows the percentage increase in viscosity found when the glass was held at 950°C for 24 min. For the nonradioactive version (WV-182) this increase was 73%. For the radioactive version (WV-182 Rad) the increase was 42%. Both glasses reached 100 poise viscosity near the nominal melter operating temperature, 1100°C. The plot for the nonradioactive glass shows more curvature and about twice the increase at 950°C. Both WV-182

FIGURE 3.12. Viscosities of Radioactive and Nonradioactive WV-182 Glasses

and WV-182 Rad contained hematite and apatite after heat treatment at 950°C. The viscosity increase may have been due either to increased amounts of crystallinity or increased size of crystal. The greater increase for the nonradioactive glass was presumably due to a greater crystallinity effect resulting from the substitution of zirconia and rare earths for the uranium and thorium. The samples will be further evaluated to determine the differences.

Brief scoping studies were performed to begin assessing the effects of waste composition variability on glass properties. In these tests, glasses were prepared with the amounts of chromium, phosphorus, thorium, and uranium either decreased to zero or doubled in the glass. In each case, the overall waste loading was kept at 23 wt%, the same as in WV-182. When chromium was removed from the glass, viscosity remained almost identical to that of the standard glass, but the viscosity increase at 950°C was reduced by about half and the hematite phase was not observed. This indicates that roughly half of the viscosity increase at 950°C in the standard glass was due to hematite formation. When chromium was doubled, the viscosity increased by roughly a factor of two and the 950°C measurement showed a greater than 200% increase during the 24-min treatment, and larger amounts of hematite were observed.

When the phosphate was doubled in WV-182, viscosities below 1125°C dramatically increased and a greatly increased formation of apatite was seen. When the phosphate was eliminated, very little curvature or viscosity increases with time were observed. This is somewhat surprising since hematite was observed in heat-treated samples of this glass. When the calcium content of WV-182 was decreased to 0.5 wt% (the amount contributed by IE-95 zeolite), the viscosity at 950°C was lower and more stable due to decreased apatite formation. Adoption of such a formulation, where calcium is not added as a glass former, should be considered if apatite formation is to be reduced. Use of an alternative zeolite such as IE-96, which has most of the calcium removed, may have additional benefit in reducing apatite formation.

Thorium addition stabilized viscosities while its removal caused increased curvature and greater upward drift during the 24-min soak at 950°C. This may have been due to increased levels of phosphorus and chromium, which partially

compensated for the removal of the thorium. The increase in phosphorus and chromium occurred due to the maintenance of a constant waste loading in the glass. The actual explanation requires further investigation.

4.0 THREE MILE ISLAND (TMI) COORDINATION

D. E. Knowlton - Manager

4.1 OBJECTIVE

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

4.2 BACKGROUND

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

The safe cleanup of the reactor systems and associated buildings and the disposal of the wastes generated as a result of the accident at TMI provide opportunity to demonstrate the reliability and versatility of waste treatment and disposal technologies for handling commercial nuclear wastes. The incident also provides a unique opportunity to evaluate the mechanisms and kinetics of core damage, develop analytical capabilities for assessing that damage, and develop analytical techniques that will improve assessment of, and response time to, unusual occurrences at nuclear reactors. The various activities within this task, except for the Submerged Demineralizer System (SDS) corrosion assessment, have been ongoing from last year. However, mid-year programmatic funding cuts in this task required the funding support for the analytical trailers to be transferred to General Public Utility (GPU) as well as terminating the bidirectional dosimetry activity.

The scopes of the activities within the TMI Coordination Task are multi-phase and unrelated to each other except that they are all assisting in the safe cleanup of TMI-2; thus each activity within the TMI Coordination Task will be discussed separately.

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

Summary

Two Pacific Northwest Laboratory (PNL) trailers--a mobile radiochemistry laboratory complete with modern analytical equipment necessary to perform a variety of analytical procedures and a mobile radioactivity measurement laboratory with state-of-the-art counting equipment, including computer analysis--were assembled at TMI to perform onsite analysis activities to characterize the radiochemical and physical content of samples collected during the cleanup operation at TMI-2. Samples analyzed consisted of material from the damaged core, sludge from the basement of the containment building, water from the reactor building, and concrete cores from the reactor floors and walls, as well as structural material from the reactor and from the reactor building, and environmental samples from the grounds at TMI.

Introduction

The reactor accident at TMI is probably typical of what may happen in any serious loss-of-coolant accident. It is important that radiochemical and physical content of the material released to the containment vessel be characterized and documented so that these data can be used 1) in determining how to proceed with cleanup operations, 2) to provide an inventory of radioactive debris, and 3) to assess any future reactor accident of this kind.

Pacific Northwest Laboratory placed two mobile laboratories, designed for use in related-type work, inside the controlled area at TMI-2. A mobile radiochemistry laboratory, Figure 4.1, was placed in the model room next to the Unit 2 containment vessel. This laboratory is a fully modern chemical laboratory with adequate shielding to handle samples with dose rates up to 5000 MR/hr. Analytical equipment installed allowed various procedures to be performed, including ion-exchange chromatography, solvent extraction, gravimetric analysis, and electroplating. The laboratory contains ventilated hoods, fume hoods, gas chromatograph, ion chromatograph, negative-pressure shielded glove box, macro- and micro-balances, heat, air conditioning, radioactive waste disposal, and water facilities.

FIGURE 4.1. Mobile Radiochemistry Laboratory Trailer M0-949

A mobile measurement laboratory was placed in the Unit 2 turbine building (Figure 4.2). This laboratory is equipped with the most modern, sensitive and selective analytical equipment available for the direct counting of radioactivity. All detectors were placed in shielded lead caves for reducing background radiation. An intrinsic gamma-ray spectrometer is used to measure photons ranging in energy from 100 keV to 2 MeV. The gamma-ray spectrometer system is composed of a 25%-efficiency detector, high-voltage power supplies, preamp power supplies, preamp amplifier, analog-to-digital converter, and 4096 channel memory. A thin-window spectrometer is used to measure low-energy photons and x-rays from the radionuclides of interest. This low-energy spectrometer contains the same electronics as the intrinsic germanium coaxial gamma-ray spectrometer as well as an optical feedback-inhibiting circuit. It is used to measure x-rays and photons from 5.9 keV to 122 keV, especially those of ^{55}Fe and ^{129}I .

Many of the decontamination samples at TMI-2 require an analysis of their uranium and plutonium contents. In general, these alpha-emitting species (transuranics) are isolated in the radiochemistry trailer and prepared for alpha spectroscopy by electroplating procedures. The electronics components

FIGURE 4.2. Mobile Radioactivity Measurements Trailer MO-4-51573

described earlier for the gamma-ray spectrometer are also required for this alpha spectroscopy system. At TMI-2, eight such detector systems are in routine operation. An anticoincidence shielded gas-flow proportional counter (windowless) has been installed for measuring the extremely soft beta energy of ^{63}Ni . The anticoincidence shield for this system reduces the background counting rate as well as interference from small amounts of gamma-ray emitting contaminants. A gas-flow proportional counting system is used to analyze beta emitters following their radiochemical isolation in the radiochemistry trailer. Radioisotopes such as ^{90}Sr , ^{99}Tc , and ^{14}C from the decontamination samples are analyzed in this way. A ZnS gross alpha detector, composed of a ZnS matrix on a photomultiplier tube, is used to detect gross alphas on the decontamination samples submitted for analysis. Using this technique, the radioanalyst determines which radiological techniques must be applied to sample analysis. An x-ray fluorescence system, using either ^{109}Cd or ^{241}Am as excitation source, is used to identify trace-element compositions of water and sediments at the ppm levels. This system is allowing the various elements to be identified by their characteristic x-rays. The electronic requirements of the x-ray fluorescence analysis system are the same as those of the gamma-ray spectrometer. This system allows the trace-element compositions of liquids and solids to be determined in the decontamination effort. An ion chromatograph (Dionex Corporation), housed in the radiochemistry laboratory, is used to determine the ionic concentrations of specific anionic species. A gas chromatograph, also in the radiochemistry laboratory, is used to analyze samples for their gas content, including hydrogen. A recently installed onboard dedicated PDP 11/23+ computer system, with modem and large auxiliary disc, handles data at TMI-2. If necessary, the data can be transferred by telephone modem link to the computer at Richland, Washington.

Accomplishments

The analytical program initiated in 1982 was extended to include samples from the reactor plenum, concrete cores from the reactor building floor and walls, reactor basement sludge, smear and paint chips from the reactor building air-conditioning system, reactor primary coolant demineralizer resin, and environmental material outside and near the reactor buildings. These samples were

analyzed for ^{54}Mn , ^{55}Fe , ^{60}Co , ^{63}Ni , ^{90}Sr , ^{94}Nb , ^{99}Tc , ^{125}Sb , ^{129}I , ^{134}Cs , ^{137}Cs , ^{144}Ce , ^{234}U , ^{235}U , ^{238}U , ^{238}Pu , $^{239-240}\text{Pu}$, ^{241}Am , ^{242}Cm , and ^{244}Cm .

The elemental range of the x-ray fluorescence spectrometer used in the measurement laboratory was expanded by using a 164-mCi ^{241}Am sealed annular source for activation in addition to a ^{109}Cd source. Using ^{109}Cd as an excitation source, concentrations of elements from titanium to ruthenium (atomic numbers 22 to 44) can readily be determined, while using ^{241}Am as the excitation source increases the K-x-ray range to include elements from ruthenium to hafnium (atomic numbers 44 to 73).

Several radiochemical procedural changes were made to handle radionuclide contamination problems and chemical interferences specific to TMI-2 samples. These included changes in the procedures for ^{99}Tc and ^{241}Am . A procedure for separating and measuring ^{237}Np was developed for TMI reactor fuel samples to meet 10 CFR 61 criteria.

To eliminate radiochemical interference from ^{60}Co in measuring ^{63}Ni , an anticoincidence shield for the ^{63}Ni detector was constructed. The shield consisted of a NaI(TL) detector, 9 in. in diameter by 9 in. thick, with a well 3-1/4 in. in diameter by 4 in. deep. The ^{63}Ni detector was reconstructed so that it could be positioned at the bottom of the NaI(TL) well. The NaI(TL) shield reduced the background of the ^{63}Ni detector more than an order of magnitude and also canceled any small amounts of ^{60}Co and/or ^{125}Sb inadvertently carried through the procedure.

A system was assembled that acquires the data from the several multi-channel analyzers in the radiochemistry laboratory at TMI (Figure 4.3). It replaces an older method used to transmit data by modem over telephone line to a computer at Richland, Washington, for analyses. Consisting of a DEC PDP 11/23+ as a primary controller and data manipulator, the system utilizes CAMAC (Computer Automated Measured and Control) modules to interface between computer and analyzers. In this way the computer addresses the CAMAC controller in response to its sensing a data-transfer request from various analyzers. Although only four analyzers are connected now, up to 44 analyzers/devices could be connected. Thus the CAMAC system makes the data recording more

4.4 TMI DOSIMETRY - R. I. Scherpelz

The letdown coolers and steam generators, along with a number of other pipes and vessels in the TMI-2 containment building, contain water from the reactor's primary coolant system. During the accident this water carried particles of fuel, and they were deposited in the vessels. The contamination in these vessels is still a major source of radiation in the containment building, and this task was aimed at measuring the dose rates due to radioactive material in various tanks, vessels and pipes in the containment building. Knowledge of these dose rates is useful for characterizing both the radiation fields inside the containment building and the contents of the pipes and tanks under study.

Method of Dose Rate Measurement

At the outer surface of a tank any radiation emitted from within is entirely gamma. Any weakly penetrating radiation such as betas, alphas and x-rays is stopped by the walls and does not contribute to the radiation field at the outer surface. At the outside surface, however, there are interfering radiations that must be accounted for. This is because many surfaces in the containment building are still contaminated by material that emits betas and gammas. There are also numerous other sources of gamma radiation from other tanks and pipes and from other surfaces.

The measurement technique selected for this task used two types of passive dosimeters for each measurement location. One dosimeter is the eight-element beta dosimeter previously designed during the TMI Beta Dosimetry Program. This dosimeter measures the beta dose rate at the tank surface, and using prior knowledge of the surface contamination composition, a correction can be made for the beta and gamma radiation emitted by contamination on the tank surface. The second dosimeter is a bidirectional gamma dosimeter designed specifically for this program. It can measure gamma dose rates due to radioactive sources in two opposing directions and therefore can discriminate between gamma radiation from sources inside the tank and from the general area outside the tank. Consequently, the set of two dosimeters is sufficient to account for all contributing sources of radiation at the tank surface, and the component due to material inside the tank can be determined.

Design of the Bidirectional Gamma Dosimeter

The bidirectional gamma dosimeter has three major components: the lead separator, the dosimeter inserts, and the thermoluminescent dosimeter chips (TLDs). The separator is a block of lead, 3 by 3 by 2 in., with holes drilled in the center of the two 3-by-3-in. faces to accommodate the dosimeter inserts. The lead separator is designed to attenuate radiation incident on one face of the dosimeter to reduce its effect on the TLDs located on the other face. The lead is not thick enough to totally eliminate any "back-side" TLD response but thick enough to greatly reduce that response and allow a directional discrimination.

The dosimeter inserts are designed to hold the TLDs in place, with the inside diameter chosen to accommodate three TLD chips. The insert is also designed to prevent secondary radiation produced in the lead separator from emitting an interfering signal in the TLDs. An incident gamma interacting with a lead atom produces weakly penetrating secondary radiation that can give off a TLD signal that complicates the interpretation of dosimeter responses. The inserts are a sandwich of three materials--copper, aluminum and polyethylene chosen to eliminate this interference.

The assembled dosimeter, a compact package with flat surfaces, weighs about 7.5 lb. It can thus be handled by personnel dressed in protective clothing to work in a contaminated environment and can be placed flush against a pipe or tank wall.

Dosimeter Calibration

The dosimeters' effectiveness was determined by exposing them to calibrated sources of ^{60}Co and ^{137}Cs . During these calibration exposures the responses of the TLDs were measured for exposure to radiation emitted by a point source, with separate determinations made for the "front" face (nearest the radiation source) and the "back" face TLDs. The ratio of the back to front face responses gave an indication of the dosimeters' effectiveness in discriminating the two directional components of a radiation field. The back-to-front ratios were dependent on gamma energy, as anticipated, and they varied from about 0.04 to about 0.16. These ratios are low enough to demonstrate that good

calibration studies coupled with a simple mathematical algorithm should be quite effective in discriminating the two directional components of a radiation field.

The angular response of the dosimeter was also studied using the gamma sources. The dosimeter was rotated to allow several different incident angles for the radiation striking the front face of the dosimeter. After this angular variation was determined, a computer code was written to combine the results of the calibration exposures into a simulated isotropic field of radiation. This isotropic field is a more realistic approximation to an actual radiation field than a point source would be, and this step was necessary for the eventual field use of the dosimeters.

Dosimeter Preparation

In addition to the dosimeter separators and inserts used during the calibration studies, PNL prepared 50 dosimeter inserts for use in TMI-2. Due to unanticipated budget cuts, no bidirectional dosimeters have yet been exposed in TMI-2.

Presentation

The paper "A Bidirectional Dosimeter for Measuring Gamma Radiation," by R. I. Scherpelz and F. Y. Tsang, was presented at the Personnel Radiation Dosimetry Symposium in Knoxville, Tennessee, on October 16, 1984.

4.5 CORROSION ASSESSMENT OF SDS VESSELS FOR BURIAL AS HIGH-INTEGRITY

CONTAINERS AT THE HANFORD COMMERCIAL WASTE DISPOSAL SITE - R. L. Clark

An assessment was made of the probable corrosion that would occur over a 300-yr period to a submerged demineralizer system (SDS) vessel buried at the low-level radioactive waste disposal site located at Hanford, Washington. Since the SDS vessel is built chiefly of Type 316L stainless steel, the assessment was made by reviewing the available corrosion literature to estimate the underground corrosion behavior of this material. This work was performed as part of an effort to qualify the SDS vessels as high-integrity containers (HIC) for commercial burial at the Hanford Site (the requirements for an HIC are given in 10 CFR 61).

Introduction

The potential for several different types of corrosion was evaluated: uniform corrosion, stress-corrosion cracking, galvanic corrosion, crevice corrosion, and pitting. Of these, the literature indicated that pitting and crevice corrosion were the only ones likely to be important for electrically isolated Type 316L stainless steel buried at Hanford.

The SDS vessels are constructed from Type 316L stainless steel 3/8 in. thick and contain about 8 ft³ of dewatered zeolites under vacuum. The zeolites are loaded with less than 1,000 Ci of mixed fission products, primarily cesium and strontium. The literature suggests that essentially no internal corrosion should occur in the SDS vessels over the first 300 yr due to 1) the low moisture content, 2) the radiation stability of the zeolites, and 3) the low oxygen levels inside the vessel. The absence of a conducting electrolyte inside the SDS vessels is the primary reason that internal corrosion should be negligible.

Surface moisture from precipitation penetrates only about the top 7 ft of soil at the Hanford commercial low-level waste disposal site due to transpiration and evaporation. The soil is a low-moisture, high-resistivity loamy sand. The soil resistivity is greater than 10,000 ohm-cm. At the 45-ft burial depth the soil contains only about 3% moisture, and is unsaturated with respect to moisture content. This is because the nearest aquifer is 300 ft below the surface of the burial site. Leachate from Hanford Site soil has low total acidity and moderate alkalinity. These soil conditions are generally considered to be noncorrosive (Hamner 1974).

Shallow-buried stainless steel pipe has generally performed poorly at Hanford due to oxygen concentration cells, galvanic couples, higher soil-moisture content, and sulfide-producing bacteria. Since the SDS vessels will be electrically isolated and buried at greater depths than the stainless steel pipe, the common failure modes associated with shallow-buried stainless steel pipe should not be operable.

Two National Bureau of Standards (NBS) studies (Romanoff 1957; Gerhold 1981) provided the best available corrosion data concerning the corrosion performance of electrically isolated, buried, Type 316 stainless steel. These

studies include work with stainless steels in sands and sandy loams similar to those at Hanford, and with material buried at Toppenish, Washington (located near the Hanford Site). The extent of corrosion was estimated by making linear extrapolations of the pitting rates of buried, sensitized Type 316 stainless steel. This estimate is conservative since the low-carbon material used in the SDS vessels is less susceptible to intergranular corrosion than the sensitized higher-carbon material used in these studies. In addition, pitting penetration is generally proportional to the cube root of time, rather than linear with time.

Conclusions

The uniform metal loss from the electrically isolated SDS vessels buried at a 45-ft depth at the Hanford commercial low-level radioactive waste disposal site should be less than 1 mil after 300 yr. If all the metal loss was due solely to pitting, then the maximum pit penetration in 300 yr is estimated at 220 mil. If all these pits are throughwall, and have a width-to-depth aspect ratio of one, then the pit density on the exterior surfaces of the SDS vessel should be less than one pit per square foot. These estimates were based on linear extrapolations of the NBS data. The results of the corrosion assessment were submitted to EG&G for publication as GEND-INF-057.

References

- Gerhold, W. F., et al. 1981. The Corrosion Behavior of Selected Stainless Steels in Soil Environments. NBSIR 81-2228, National Bureau of Standards, Washington, D.C.
- Hamner, N. E. 1974. Corrosion Data Survey, 5th Ed. National Association of Corrosion Engineers, Houston, Texas.
- Romanoff, M. 1957. Underground Corrosion. National Bureau of Standards Circular 579, U.S. Government Printing Office, Washington, D.C.

5.0 BREEDER FUEL REPROCESSING PLANT WASTE TREATMENT

M. S. Hanson - Manager

5.1 OBJECTIVES

The Department of Energy (DOE) has initiated the Breeder Reprocessing Engineering Test (BRET) to support breeder reactor fuel reprocessing and to close the fuel cycle for the Fast Flux Test Facility and future advanced breeder reactors. The project is to be installed in the Fuels and Materials Examination Facility near Richland, Washington. The BRET is a joint effort between the Hanford Engineering Development Laboratory (HEDL) and the Oak Ridge National Laboratory (ORNL).

An integral part of the BRET demonstration is the solidification of high-level liquid waste (HLLW) to a form acceptable for geologic disposal. The objective of this task is to ensure the availability of high-level waste treatment technology for use in BRET as a demonstration of the closure of the liquid metal fast breeder reactor fuel cycle.

5.2 OVERVIEW - M. S. Hanson

As of April 27, 1984, this task was discontinued due to DOE difficulties concerning the future and scope of the BRET. Efforts were completed to store technical and programmatic documentation in a manner that will allow recovery later.

5.3 HIGH-LEVEL LIQUID WASTE STUDY - M. S. Hanson

A study was completed to examine the basis for selecting a vitrification system for BRET HLLW, to assess the adequacy of the current preconceptual design basis, and to provide recommendations for the next design phase.

The HLLW vitrification system selected for BRET during preconceptual design was the liquid-fed ceramic melter (LFCM). The LFCM is a joule-heated, ceramic-lined molten glass bath. During operation, a feed slurry containing concentrated HLLW and glass formers is fed onto the surface of the melt; molten

glass is transferred periodically from the melter into a stainless-steel canister. The LFCM is currently being developed for use at West Valley and in the defense waste programs at Savannah River and Hanford. The technology is well founded, and LFCM units are available for engineering-scale testing.

Several technical uncertainties were identified in the BRET Preconceptual Design Report (PCDR). These were related to the relatively short projected life of the ceramic melter (about 3 yr at temperature); the weight of the LFCM, which exceeded the main process cell crane's capacity; and the anticipated difficulties in decommissioning a failed melter. In addition, the preconceptual design provided storage for HLLW from about 2 weeks' operation. At this limited surge capacity, the vitrification system would have to run concurrently with the reprocessing operations.

These problems, though not insurmountable, indicated that the original bases for the PCDR HLLW system should be reviewed and that recommendations for follow-on design activities be made based on the findings of this review. The study had seven major objectives:

1. Provide the basis for initial selection of the LFCM system.
2. Assess options to the LFCM which could meet the BRET processing needs, including demonstration objectives.
3. Identify packaging requirements (size, heat load, closure technique, decontamination methods, etc.) to meet waste disposal criteria.
4. Assess the impact of providing additional surge storage capacity for the HLLW and recommend a storage system for follow-on design.
5. Recommend a reference system for follow-on design activities.
6. Assess impact of the reference system and HLLW storage requirements on current BRET cost and schedule baseline.
7. Recommend operating philosophy for the reference system which optimizes the duty cycle (i.e., continuous operation, interim operation with no cooling between runs, interim operation with complete shut-down between runs, etc.).

The study recommended that the preconceptual design concepts be adopted as the reference for the BRET HLLW vitrification system with the following exceptions:

- The waste canister size be changed to 12 in. dia by 10 ft long.
- The weld system be changed from the gas tungsten arc welding (GTAW) to inertial, provided out-of-cell requirements can be met.
- Ultrasonic techniques be used for weld inspection for the inertial weld system.

The system, as defined in the preconceptual design, consists of a liquid-fed ceramic melter, an air-lift feed system, a canister-receiving turntable, a primary process off-gas control system and an electropolishing system for decontamination of the waste canisters. Interim storage for the canisters is to be provided in the main process cell.

The larger canister decreases the number produced in the facility and provides greater flexibility in managing non-flowsheet wastes.

The change in the weld process provides for consistent, high-quality welds and minimizes requirements for verifying quality and qualifying welds. This change will depend on solving facility-interface problems, such as space limitations. If space limitations cannot be resolved satisfactorily, the reference should be changed back to the preconceptual design, the TIG system. The solid-state inertial welder allows use of the ultrasonic inspection system.

The LFCM decommissioning problems identified in the PCDR were not resolved by this study. They should, however, be capable of solution by future development and design efforts ongoing in other programs.

Additional HLLW storage was conditionally recommended. Preliminary shielding calculations indicate a much more detailed shielding and structural analysis will be required before the full economic impacts of this option can be assessed. If adopted, the additional storage would provide at least two campaigns worth of surge storage, allowing the HLLW vitrification system to be totally decoupled from the reprocessing operations.

5.4 CONCEPTUAL DESIGN - J. M. Perez, Jr.

The conceptual design of the vitrification system was about 50% completed. A functional design criteria document was completed, approved, and transmitted to Kaiser Engineers Hanford (KEH), the architect/engineer for the program. Concurrence for the criteria was received from ORNL and HEDL. Equipment drawings and diagrams initiated include:

- Process and instrumentation
- Process flowsheet
- Liquid-fed ceramic melter
- Turntable
- Glass-level detection system
- Canister grapple
- Slurry feed system
- Process off-gas system
- Module equipment layouts.

A design review meeting was held between PNL and KEH, and the drawings revised to incorporate comments received. The drawings were processed through KEH internal checking, approved, and transmitted to ORNL and HEDL.

5.5 PROCESS DEVELOPMENT - M. K. W. Chan

The process development work completed included a melter test experiment and a mockup of the melter feed system.

A successful 72-hr continuous ceramic melter test demonstrating vitrification of simulated BRET HLLW was completed December 15, 1983. A total of 500 L of simulated waste slurry was fed to the high-bay ceramic melter during the test at an average feed rate of 6.5 L/hr and maximum feed rate of 10 L/hr. The feed contained 80% substitution of SiO_2 with LUDOX® TM colloidal silica to enhance the suspension of solids. Foaming in the liquid waste tank was observed during feed preparation. After feed had been air-lifted to the melter for 4-1/2 hr, a backup peristaltic pump was used to reduce fluctuations of feed rate to the melter. The peristaltic pump provided a constant feed rate to the melter throughout the rest of the test, allowing zero downtime.

The melter was operated under a fairly constant main electrode power of 14 kW. The average glass temperature was at 1200°C throughout the test. A steady and stable cold cap covering about 50% of the melt surface area was observed at the feed rate of 6.5 L/hr. At higher rates 100% cold cap coverage of the melt surface was observed. The foamy and porous cold cap was frequently as much as 5 in. thick during the test. Because of slow melting, the target feed rate of 15 L/hr was not achieved. The thick layer of foam appeared to act as insulation, reducing heat transfer between the molten glass and the plenum area of the melter. During the run a total of 175 kg of glass was airlifted to five canisters.

The post-test analyses of feed slurry, glass and off-gas samples, and corrosion coupons were completed. Integration of data and establishment of relationships to test parameters were also completed.

A letter report detailing the results of the test vitrification was completed and issued.

The testing of the air-lift feed system mockup was essentially completed. The air-lift was able to meter simulated BRET HLLW within the desirable feed rate range. Some minor plugging of the lift tubing occurred. However, the plugging was easily detectable, could be flushed, and was preventable by the use of programmed flushes. The flow rates were repeatable and controllable over a range of 14 to 32 L/hr. The target feed rate for the BRET is 20 L/hr. Settling of solids was not a problem during these tests. Based on this work, the detailed design parameters for the BRET air-lift feed system were issued.

6.0 ACRONYMS AND ABBREVIATIONS

ADS	Air-displacement slurry
ALARA	As Low as Reasonably Achievable
BNFP	Barnwell Nuclear Fuel Plant
BRET	Breeder Reprocessing Engineering Test
CFR	Code of Federal Regulations
CTS	Component Test Stand
cv	column volume(s)
D&D	Decontamination and Decommissioning
DF	Decontamination Factor
DOE	Department of Energy
EPA	Environmental Protection Agency
GPT	General Process Trash
GPU	General Public Utility
HEME	High-Efficiency Mist Eliminator
HEPA	High-Efficiency Particulate Air
HLLW	High-Level Liquid Waste
HLW	High-Level Waste
HWVP	Hanford Waste Vitrification Program
IR	Infrared
LFCM	Low-Level Waste Treatment Facility
LWR	Light-Water Reactor
MCC	Materials Characterization Center
NRC	Nuclear Regulatory Commission
NWTP	NWTP Waste Treatment Program
NWVP	Nuclear Waste Vitrification Project
OCRWM	Office of Civilian Radioactive Waste Management
PNL	Pacific Northwest Laboratory
PSCM	Pilot-Scale Ceramic Melter
PTA	phosphotungstic acid
PWR	Pressurized-Water Reactor
RLFCM	Radioactive Liquid-Fed Ceramic Melter
SAC	Sample and Analytical Cell

SBS	Submerged Bed Scrubber
SDS	Submerged Demineralizer System
SFCM	Slurry-Fed Ceramic Melter
TC	Thermocouple
TDR	Time-Domain Reflectometer
TMI	Three Mile Island
TRU	Transuranic
WVDP	West Valley Demonstration Project
WVNS	West Valley Nuclear Services
WVST	West Valley Support Task
WYNSC	Western New York Nuclear Services Center
ZVD	Zeolite Vitrification Demonstration

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