Hanford High-Level Waste Vitrification Program at the Pacific Northwest National Laboratory: Technology Development—Annotated Bibliography

D. E. Larson

September 1996

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

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Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831;
prices available from (615) 576-8401.

Available to the public from the National Technical Information Service,
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Pacific Northwest National Laboratory
Richland, Washington 99352
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Summary

This report provides a collection of annotated bibliographies for documents prepared under the Hanford High-Level Waste Vitrification (Plant) Program. The bibliographies are for documents from Fiscal Year 1983 through Fiscal Year 1995, and include work conducted at or under the direction of the Pacific Northwest National Laboratory. The bibliographies included focus on the technology developed over the specified time period for vitrifying Hanford pretreated high-level waste. The following subject areas are included:

- General Documentation
- Program Documentation
- High-Level Waste Characterization
- Glass Formulation and Characterization
- Feed Preparation
- Radioactive Feed Preparation and Glass Properties Testing
- Full-Scale Feed Preparation Testing
- Equipment Materials Testing
- Melter Performance Assessment and Evaluations
- Liquid-Fed Ceramic Melter
- Cold Crucible Melter
- Stirred Melter
- High-Temperature Melter
- Melter Off-Gas Treatment
- Vitrification Waste Treatment
- Process and Product Control and Modeling
- Analytical
- Canister Closure, Decontamination, and Handling
### Acronyms and Abbreviations

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<th>Acronym</th>
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<tr>
<td>ADS</td>
<td>air displacement slurry</td>
</tr>
<tr>
<td>ADSP</td>
<td>air displacement slurry pump</td>
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<td>BWG</td>
<td>Birmingham wire gauge</td>
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<td>CAW</td>
<td>current acid waste</td>
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<td>CC</td>
<td>complexant concentrate</td>
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<tr>
<td>CCC</td>
<td>canister centerline cooled</td>
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<tr>
<td>CCM</td>
<td>cold crucible melter</td>
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<tr>
<td>CCW</td>
<td>complexant concentrate waste</td>
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<tr>
<td>CEQ</td>
<td>Council on Environmental Quality</td>
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<td>CVS</td>
<td>composition variation study</td>
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<td>D_d</td>
<td>distribution ratio</td>
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<td>DOE</td>
<td>U.S. Department of Energy</td>
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<tr>
<td>DSC</td>
<td>differential scanning calorimetry</td>
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<td>DSSF</td>
<td>double-shell slurry feed</td>
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<tr>
<td>DST</td>
<td>double-shell tank</td>
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<tr>
<td>DWPF</td>
<td>Defense Waste Processing Facility</td>
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<td>DWTT</td>
<td>decontamination waste treatment tank</td>
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<td>E1150</td>
<td>Electrical conductivity of glass melt at 1150°C</td>
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<td>EVS</td>
<td>ejector venturi scrubber</td>
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<td>EDXRF</td>
<td>energy dispersive x-ray fluorescence</td>
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<td>EPA</td>
<td>U.S. Environmental Protection Agency</td>
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<td>frit addition algorithm</td>
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<td>FTA</td>
<td>feed test algorithm</td>
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<td>FY</td>
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<td>GCED</td>
<td>glass composition envelope definition</td>
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<td>gradient furnace testing</td>
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<td>HBCM</td>
<td>high-bay ceramic melter</td>
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<td>HDW EIS</td>
<td>Hanford Defense Waste Environmental Impact Statement</td>
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<td>HEMF</td>
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<td>HEPA</td>
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<td>HLW</td>
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<td>HMBCP</td>
<td>HWVP Heat and Material Balance Computer Program</td>
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<td>HSS</td>
<td>hydrosonic scrubber</td>
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<td>HTM</td>
<td>high-temperature melter</td>
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<tr>
<td>HWVP</td>
<td>Hanford Waste Vitrification Plant</td>
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<td>HWVP</td>
<td>Hanford Waste Vitrification Program</td>
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<td>IC</td>
<td>ion chromatograph or ion chromatography</td>
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<td>IC/MS</td>
<td>inductively-coupled mass spectrometry</td>
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<td>ICCS</td>
<td>inner canister closure station</td>
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<td>inductively coupled plasma</td>
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<td>INE</td>
<td>Institut fur Nukleare Entsorgungstechnik</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>KfK</td>
<td>Kernforschungszentrum Karlsruhe</td>
</tr>
<tr>
<td>LA</td>
<td>laser ablation</td>
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<td>LFCM</td>
<td>liquid-fed ceramic melter</td>
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<td>liquid-fed mini-melter</td>
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<td>mass spectrograph</td>
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<td>NCAW</td>
<td>neutralized current acid waste</td>
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<td>NCRW</td>
<td>neutralized cladding removal waste</td>
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<tr>
<td>NEPA</td>
<td>National Environmental Policy Act</td>
</tr>
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<td>OWL</td>
<td>optimal waste loading</td>
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<tr>
<td>PCC</td>
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<td>PCCS</td>
<td>product composition control system</td>
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<tr>
<td>PCD</td>
<td>preliminary canister decontamination</td>
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<td>PCT</td>
<td>product consistency test</td>
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<td>PFP</td>
<td>Plutonium Finishing Plant</td>
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<td>PHTD</td>
<td>PNL HWVP Technology Development</td>
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<td>PHP</td>
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<td>Pacific Northwest National Laboratory</td>
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<td>process off-gas</td>
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<td>PSCM</td>
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<td>Pacific Northwest Laboratory Vitrification Technology Development</td>
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<td>RCRA</td>
<td>Resource Conservation and Recovery Act</td>
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<td>RLST</td>
<td>receipt and lag storage tank</td>
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<td>ROD</td>
<td>Record of Decision</td>
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<td>SAS</td>
<td>steam atomized scrubber</td>
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<td>SA/V</td>
<td>surface area to leachate volume ratio</td>
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<td>SBS</td>
<td>submerged bed scrubber</td>
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<td>SCR</td>
<td>selective catalytic reduction</td>
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<td>SIPT</td>
<td>systems integrated performance testing</td>
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<td>SME</td>
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<td>SN</td>
<td>solution</td>
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<td>Description</td>
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<td>SRAT</td>
<td>slurry receipt and adjustment tank</td>
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<td>SRL</td>
<td>Savannah River Laboratory</td>
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<tr>
<td>SS</td>
<td>stainless steel</td>
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<td>SSHTM</td>
<td>small-scale high-temperature melter</td>
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<td>SST</td>
<td>single-shell tank</td>
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<td>t</td>
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<td>T100P</td>
<td>temperature at which glass melt has a viscosity of 100 poise</td>
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<td>thermocouple</td>
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<td>TO</td>
<td>total oxides</td>
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<td>TRU</td>
<td>transuranic</td>
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<td>TWEAT</td>
<td>Ternary Waste Envelope Assessment Tool</td>
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<td>TWRS</td>
<td>Tank Waste Remediation System</td>
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<td>UV</td>
<td>ultraviolet</td>
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<td>UVLA</td>
<td>ultraviolet laser ablation</td>
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<td>VFT</td>
<td>Vogel-Fulcher-Tammann</td>
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<td>WAPS</td>
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<td>WFQ</td>
<td>waste form qualification</td>
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<td>waste holding tank</td>
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<tr>
<td>WO</td>
<td>waste oxides</td>
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<td>WSM</td>
<td>Waste Form Qualification Simulation Model</td>
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<td>West Valley</td>
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<td>West Valley Demonstration Project</td>
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<td>West Valley Nuclear Services</td>
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<td>x-ray fluorescence</td>
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### 6.0 Feed Preparation

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### 7.0 Radioactive Feed Preparation and Glass Properties Testing

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19.0 Canister Closure, Decontamination, and Handling

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1.0 Introduction

This annotated bibliography was written to facilitate the transfer of government-developed technology for vitrification of Hanford pretreated high-level waste to prospective users. It includes the documentation of work sponsored by the U.S. Department of Energy (DOE) and conducted at or under the direction of the Pacific Northwest National Laboratory (PNNL) as part of the Hanford High-Level Waste Vitrification (Plant) Program. Each annotation constitutes a document abstract. Planning documents such as test plans and investigation plans are included in the bibliography, but were not annotated.

The bibliography is considered comprehensive for documents issued from Fiscal Year 1983 through Fiscal Year 1995. Available documents from Fiscal Year 1996 are included. A few documents from this time period may be missing from the bibliography since records through the period are not complete. Also, some documents issued prior to Fiscal Year 1983 may not be included. The bibliography does not include papers, presentations, and articles prepared for professional meetings; publications; and cleared PNNL documents that were not included as part of the Program deliverables. However, the information included in the Program documentation generally contains the presented and published information. The documents were not affected by issues associated with national security; therefore, none of the documents were classified. Most of these documents were not cleared for public release. Those that were are designated with a PNNL document number with the prefix "PNL-" (example: PNL-xxxx). Draft documents that were subsequently completed and issued are not included. The bibliography focuses on documentation associated with technology development; most of the programmatic documentation was deleted.

The bibliography is organized by subject area as shown below:

Chapter 2 - General Documentation
Chapter 3 - Program Documentation
Chapter 4 - High-Level Waste Characterization
Chapter 5 - Glass Formulation and Characterization
Chapter 6 - Feed Preparation
Chapter 7 - Radioactive Feed Preparation and Glass Properties Testing
Chapter 8 - Full-Scale Feed Preparation Testing
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Chapter 11 - Liquid-Fed Ceramic Melter
Chapter 12 - Cold Crucible Melter
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Chapter 14 - High-Temperature Melter

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Chapter 15 - Melter Off-Gas Treatment
Chapter 16 - Vitrification Waste Treatment
Chapter 17 - Process and Product Control and Modeling
Chapter 18 - Analytical
Chapter 19 - Canister Closure, Decontamination, and Handling

Within each subject area, the material is next ordered by descending Fiscal Year. In many cases, documents were actually issued in the Fiscal Year subsequent to the one listed, but each bibliography entry lists the Fiscal Year for which the document was scheduled to be issued as a deliverable, as indicated by the document number (milestone number).

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2.0 General Documentation

Fiscal Year 1996


No annotation

Fiscal Year 1989


The Hanford Waste Vitrification Plant (HWVP) Technical Manual documents the technical bases of the current HWVP process and provides a physical description of the related equipment and plant. A data summary was compiled of product, process, and equipment development performed at PNNL for HWVP from FY 1982 through 1988. Limited Defense Waste Processing Facility (DWPF) development data as it applies to HWVP is included.

Fiscal Year 1988


Fiscal Year 1987


A computer simulation of the HWVP operations was developed to determine the capability of the system, as designed, to generate 100 lb of vitrified waste per hour while the plant is operating normally and to maintain normal operation at least 70 percent of the time. The results of a four-year simulation
of the plant operation indicated that the average availability of the melter system was approximately 0.73, which is above the required availability, and that the system could process vitrified waste at a production rate of 100 lb/h. The simulation indicated that, if the production rates were increased significantly, a pinch point in the system would occur because of the limitations imposed by the Recycle Collection Tank capabilities.


A study was performed to evaluate statutory and regulatory requirements for the current HWVP design and to determine permitting guidelines by which the HWVP will obtain permits. Information on regulatory requirements and alternative options for complying with those requirements is provided to assist HWVP staff and DOE in their decision-making processes and discussions with regulatory agencies. Environmental permit requirements set forth by certain federal and state laws as they may apply to the HWVP are discussed. These requirements include federal statutes that authorize the states to take certain responsibilities for implementing environmental requirements based on federal law. Environmental permit requirements for the construction and operation of the HWVP are discussed; these concentrate on air, water, and solid waste. It was recommended that the DOE consult with regulatory agencies early, consolidate processing federal permits, and consider the HWVP a treatment facility with a Resource Conservation and Recovery Act (RCRA) permit being applied to the entire facility.


A study was performed to identify environmental statutory and regulatory design requirements in the air emissions, liquid effluents, and solid waste management areas. Guidance is provided to meet regulatory design, monitoring, reporting, and notification requirements that are applicable. The DOE's policy is that all applicable DOE Orders with requirements not found in state and federal standards must be complied with. It was concluded that the DOE consult early with regulatory agencies to allow timely design changes as required by evolving regulations. The Washington Department of Ecology regulations state that new tanks holding dangerous wastes must be constructed above ground, which is not compatible with the HWVP design and requires further clarification.


This report and two subsequent reports (HWVP-87-V14020303-003B and HWVP-87-V14020306-006) provide an overall plan for environmental regulatory compliance for the HWVP, specifically by providing a detailed analysis of applicable regulations as they relate to the HWVP. Environmental regulatory compliance for construction, operation, and decommissioning of the HWVP consists of three major activities: 1) meeting the requirements of the National Environmental Policy Act (NEPA) and the requirements of the regulations of the Council on Environmental Quality (CEQ) that implement NEPA, 2) acquiring the necessary environmental permits, and 3) meeting statutory and regulatory regulations related to the environment that do not necessarily require the acquisition of permits. In addition, all three activities require meeting the terms and conditions of applicable state environmental laws and regulations. The final Hanford Defense Waste Environmental Impact Statement (HDW EIS) and Record of Decision (ROD) should be sufficient environmental documentation for construction of the HWVP. However, because of the U.S. Environmental Protection Agency's (EPA's) comment on the draft HDW EIS regarding NEPA requirements for the HWVP, it would be wise to allow time to prepare a supplemental EIS on the HWVP should that be necessary.

Fiscal Year 1986


Technical input prepared by PNL during FY 1986 in support of the HWVP Preliminary Conceptual Design and Reference Conceptual Design is summarized and compiled. The HWVP melter/turntable conceptual design is described, including the physical components and features of the reference melter and turntable, design bases, outline specifications, calculations, and conceptual drawings (HWVP-86-V1142B). Alternative turntable design concepts for the HWVP are evaluated (HWVP-86-V1132A). The design of an evacuated canister for remote operation is the subject of a design report (HWVP-86-V1133A). Decontamination factors for the process off-gas system are evaluated as part of the assessment of the reference process flowsheet for the HWVP (HWVP-86-V1143A). Process equipment materials selection activities that were performed for the DWPF and a preliminary assessment of unique HWVP process conditions are reviewed (HWVP-86-V1135A). A review of current HWVP process information and relevant process technology has been performed to assess and organize available information (HWVP-86-V1143B). The design rates for the HWVP process, based primarily on an average glass production rate of 100 lb/h, a reference melter feed concentration of 3.3 lb/gal total oxide, and an expected performance for the melter, are defined. The effects of losing cooling water flow in the melter cooling jacket were evaluated. The effects of cooling on the reference HWVP glass by simulating a canister filled and cooled in an open room were examined. The validity of the requirement that the surface temperature of a filled canister be at or below 212°F before canister preliminary decontamination by water spray was established for the HWVP, and its potential impact on the process was evaluated. Preliminary calculations were performed to estimate the equilibrium
centerline temperatures for canisters with a range of decay heat contents. Stress corrosion cracking of waste canisters during processing in the HWVP was considered. The potential for a steam explosion occurring in the melter as a result of water leaks was reviewed and was considered to be an unlikely occurrence not expected to compromise safety. A drawing showing additional details of the canister level detection system was prepared and transmitted to Rockwell.


HWVP process technology is provided to supply the data for the reference HWVP flowsheet development and process engineering technology. Sufficient discussion, data, and references are provided to enable traceability and technology understanding, and to assess the state of technical knowledge. Available DWPF, West Valley Demonstration Project (WVDP), and commercial high-level waste process development studies have been included as appropriate. Subject areas include HWVP process description; process technology, including design bases, Receipt and Lag Storage Tank (RLST), Slurry Receipt and Adjustment Tank (SRAT), Slurry Mix Evaporator (SME), Slurry Mix Evaporator Condensate Tank (SMECT), and Melter Feed Tank (MFT); melter, including glass technology, melter off-gas system, and process material balance; equipment description; and equipment heat transfer.

Fiscal Year 1985


The overall time requirements for batch operations supporting the melter are shown. Operational steps with the associated time requirements for supporting batch operations are contained. The batch operating equipment is based on the HWVP preconceptual design and the DWPF testing and operating data. The batch operations include feed preparation, canister handling, cold chemical preparation, and process waste treatment. The HWVP melter designed glass production rate is 99 lb/h. The design melter feed rate is 30 gph with a feed containing 400 g oxide/L. The feed preparation operation produces 1665 gal of melter feed in 50 h with the SRAT and SME operating sequentially. This time can be reduced to 34 h if the tanks are operated concurrently. The canister-handling task requires about 22 h per canister with all operations performed sequentially. If the canister tasks were performed simultaneously, one canister could be processed every 6 h. An HWVP canister is filled every 37 h at the reference production rate. The 780-gal decontamination frit feed tank needs to be filled once every 74 h, and the 2110-gal process feed tank needs to be filled once every 217 h. The total time to prepare a batch of both slurries is 16 h. The dilute formic acid solution, which is needed for frit slurry preparation, can be prepared in 2 h in 1850-gal batches.

The processes for the vitrification and related plant activities currently planned for the HWVP are described. The description includes feed preparation, vitrification, canister handling, process off-gas treatment, process vessel vent system, cold chemical preparation and services, generated waste treatment, and equipment decontamination and maintenance facilities.


The processes and flowsheet for vitrifying the HWVP reference feed are described. The HWVP chemical flowsheet consists of the following processes: feed reception and lag storage, chemical adjustment and concentration, addition of glass-forming chemicals, vitrification and packaging, treatment of process off-gases and wastes, and chemical decontamination of filled packages. The HWVP flowsheet is designed to operate the vitrification process at a nominal glass production rate of 45 kg/h with a melter feed concentration of 400 g Total Oxides (TO)/L. The nominal melter feed processing rate is 112 L/h with an estimated maximum of 150 L/h. With a maximum feed concentration of 500 g TO/L, a glass production rate of 75 kg/h is the maximum for the process.


A compilation of the design information supplied by the PNL Vitrification Task to Rockwell for the HWVP Preliminary Conceptual Design in FY 1985 is provided. The primary information included the following: HWVP Preconceptual Design Description (draft report annotated elsewhere), HWVP Operational Analyses (draft report annotated elsewhere), HWVP Reference Flowsheet (draft report annotated elsewhere), and Melter/Turntable Design Information (design description of the melter and turntable).

Fiscal Year 1984


No annotation
Fiscal Year 1982


A study was performed to recommend a distributed control system to monitor and control PNL nonradioactive high-level waste (HLW) vitrification testing equipment used to perform pilot- and full-scale process tests. The desired system was described as containing inputs/outputs, microprocessor controllers, communications module, operator station, data acquisition system, data storage and retrieval system, redundancy features, and the host computer. General specifications for system components were provided. Seven systems were assessed from the following vendors: Bailey, Fischer and Porter, Foxboro, Honeywell, Leeds and Northrup, Taylor, and Powell-Process Systems, Inc. It was recommended that Powell-Process Systems, Inc. would meet the requirements at the lowest cost.
3.0 Program Documentation

Fiscal Year 1995


No annotation


No annotation

Fiscal Year 1992


No annotation

Fiscal Year 1990


No annotation

Allen, CR, et al. August 1990. "FY 1990, Process Development Task (1.2.2.03), Equipment Adaptation and Testing Task (1.2.2.04), Waste Form Qualification Task (1.2.2.05) and Regulatory Compliance Task (1.2.2.06) Technical Work Plans," HWVP-90-1.2.2.01.00B Draft, Pacific Northwest Laboratory, Richland, Washington.

No annotation
Fiscal Year 1989


No annotation


No annotation

Fiscal Year 1988


No annotation

Fiscal Year 1985


No annotation
4.0 High-Level Waste Characterization

Fiscal Year 1987


The available data base on Complexant Concentrate (CC) and Plutonium Finishing Plant (PFP) wastes was evaluated for vitrification. No experimental data exist for pretreated CC and PFP wastes. Limited flowsheet analyses have been performed for CC and PFP wastes, but they are not comprehensive nor consistent. The major waste component that impacts glass waste loading and subsequently glass production is chromium, which could substantially reduce the waste loading. If CC and PFP wastes are vitrified separately, a significantly higher number of canisters will be produced because of the high chromium content. Waste blending should be considered to reduce the number of waste glass canisters. The CC and PFP waste oxide compositions are similar to Neutralized Current Acid Waste (NCAW) in many respects, and NCAW waste form development results will be substantially applicable, but where component limits exceed those in HW-39 glass, investigation will be required. The feed preparation process could be impacted if the pretreated CC waste contains significant amounts of organic carbon and carbonate. The possibility of high concentrations of rare earths, carbonates, and organics in the CC and PFP HWVP melter feed streams could significantly impact ceramic melter processing rates, melt redox conditions, and cold-cap characteristics.
5.0 Glass Formulation and Characterization

Fiscal Year 1996


No annotation


No annotation


No annotation


Potential glass formulations were provided for prospective Phase 1 High-Level Waste vitrification at Hanford. Westinghouse Hanford Company staff provided 24 prospective waste compositions from Tanks 101AZ, 102AZ, 106C, and 102AY with either caustic or water-washed sludge. Using PNNL models, glass formulations were provided. The preliminary study conclusions indicated that glass produced from individual tanks could be contained in 734 canisters; waste blending could reduce the glass product volume by up to 6 vol%; caustic washing does not change the glass volume as compared to water washing due to the 15 wt% study limit on the Fe₂O₃ content in the glass; the 15 wt% Fe₂O₃ study limit constrained the waste loading on 15 out of 24 glasses; the waste loading is increased by about 10 wt% by allowing the melting temperature to increase from 1150°C to about 1350°C; and the addition of B₂O₃ or Li₂O reduces the waste loading by 0.5 wt% per 1 wt%.

5.1
The incorporation of minor components (P, S, Cr, F, Cl, I, Mn, Ti, U, and Bi) into glass was evaluated by performing a literature review. Incorporating these components into glass is a function of temperature and composition. Redox and basicity of the glass can also be important. Uranium, Mn, S, and Cr typically form more than one oxidation state in glass, and properties of glass can be sensitive to oxidation state. Sulfate solubility, Cr(VI)/Cr(III) ratio, and Mn(III)/Mn(II) ratio in glass were reported to increase with basicity. Sulphur, F, Cl, and I volatilize significantly from glasses at high temperatures. Phosphate was also reported to volatilize by a factor of ten or more less than the halogens and sulfur. The solubility of U was found to be a function of oxidation state. U(VI) was reported to have a higher solubility in silicate glasses than U(IV). Mn and Cr were found in spinels, and waste loading may be limited by spinel formation in glass. Chromium may also form chromate that may segregate from melts to form a water soluble layer. Sulfate segregation was also reported when the solubility of S was exceeded in oxidized glass. The formation of gall at 1150°C was observed to remove phosphate, chromate, molybdate, boron, alkali and alkaline earths, rare earths, and cesium from the melt. Titanium solubility is strongly affected by the presence of Al₂O₃. Fluorine, Bi and Ti were all reported to decrease viscosity of glass melt. Cl and iodine were found to have much lower solubility in silicate glasses than the other minor components (typically <1 wt%). Enhanced corrosion of refractories was reported possible from Bi₂O₃ glasses. Metal piping was reported to be corroded by volatile Cl and S. Setting limits for the additions of any of these potential waste loading inhibiting compounds for all waste glasses may not be practical due to the complexity of glass chemistry and the number of processing variables. More study is needed in regard to the variables before solubility limits for a particular composition can be predicted. An evaluation of wastes from A, B, C, T, SX, AX, TY, BY, S, TX, and BX tank farms; NCAW; double-shell slurry feed (DSSF); and remaining double-shell tank (DST) waste was conducted to estimate which waste glasses would be limited in waste loading by the components studied.


Laboratory studies were performed at Pacific Northwest Laboratory and Nuclear Research Institute Rez (Czech Republic) to determine the behavior of minor components (phosphate, chromium, titanium, and sulfate) in seven borosilicate-based glass systems. The glass systems represented four Hanford waste types: complexant concentrate waste (CCW), PFP waste, double-shell tank/single-shell tank (DST/SST) waste, and complexant concentrate for tank waste SY103 (CC103-SY92SW). A West Valley high-level waste glass was studied. The studies included the following areas: molten salt sulfate phase separation, which is a kinetic process that promotes phosphate-rich phase segregation; glass component effects on sulfate solubility (0.5 - 1.4 wt%); chromate formation during batch
reaction, which produced no chromate phase separation; the effects of minor and glass components concentrations together with melting temperature, which caused crystallization in glass under the appropriate conditions; and the effects of minor components on glass melt viscosity and glass durability changes. The effects of minor components on glass properties can range from negligible to major, depending on component concentration and melting temperature.


Results are presented from Fiscal Year 1995 work to develop first- and reduced second-order empirical mixture models relating 7-day Product Consistency Test (PCT) and 28-day Materials Characterization Center (MCC)-1 test normalized element releases to glass composition. The models for the PCT and MCC-1 test component releases from quenched waste glasses and PCT from canister centerline cooled (CCC) glasses are presented together with the data used in generating the models. The data used was from the Composition Variation Studies (CVS) through CVS-II Phase 4 and quenched glasses from CVS-III Phase I, high melting temperature glasses. The first- and second-order models do not fit the PCT results on CCC glasses as well as the corresponding first- and second-order models fit the PCT results on quenched glasses. This is due in large measure to several CCC CVS-I and CVS-II glasses being prone to phase separation, and many more glasses containing crystals. Models fitted after deleting data for glasses prone to phase separation and glasses with greater than 7 vol% crystallinity fit better, but still not as well as the models for PCT data on quenched glasses. This is partially due to single PCT normalized releases being modeled for the CCC data instead of averages of duplicate PCT normalized releases for the quenched data. Additional work is needed to determine how crystallinity type and volume percent affect PCT releases and goodness-of-fit of PCT release models for CCC glasses.


Laboratory and theoretical studies were performed to predict the immiscibility boundaries of multi-component borosilicate glasses, which form the bases for many nuclear waste glasses. The method is based on superposition of immiscibility boundaries of simple systems using an appropriate parameter. The immiscibility boundaries, including critical temperatures and compositions of both binary borate systems and alkali borosilicate systems, were examined. The critical temperature of both borate systems and alkali borate systems appear to scale with field strength of cations, and the critical temperature of the mixture of two systems was equal to the average of the critical temperature of the two systems involved. This fact makes prediction of the critical temperature of the multi-component systems easier. (This effort was terminated due to expected limited applicability.)
Software and thermodynamic data bases have been developed for the calculation of liquidus temperatures of HWVP glass products containing the components SiO$_2$-B$_2$O$_3$-Na$_2$O-Li$_2$O-CaO-MgO-Fe$_2$O$_3$-Al$_2$O$_3$-ZrO$_2$-"others." The software contains the entire F*A*C*T computer system with its computational capabilities and public data bases. Private data bases for the glass and crystalline phases were developed by optimization of thermodynamic and phase diagram data. All available data for 2- and 3-component subsystems of the 9-component oxide system were collected, and parameters of the model equations for the thermodynamic properties were found which best reproduce all the data. For representing the thermodynamic properties of the glass as a function of composition and temperature, the modified quasichemical model was used. The thermodynamic properties of the 9-component glass could be predicted and thereby used to calculate the glass liquidus temperatures that could be compared with PNL data, which could be used to refine the model. Cr, Ni, Mn, and Fe$^{2+}$ were subsequently added to the data base. Modifications to the earlier capability include these: clino-pyroxine phase has now been modeled as a solid solution NaFeSi$_2$O$_6$-CaMgSi$_2$O$_6$; new thermodynamic data for acmite have been included; a sodium-calcium silicate solid solution and the compound Na$_2$ZrSi$_2$O$_7$ have been included; and models for corundum solid solution (Cr$_2$O$_3$-Fe$_2$O$_3$-Al$_2$O$_3$) and (Fe, Ni, Mn)(Fe, Al, Cr, Mn)$_3$O$_4$ spinel phase were developed. The agreement between experimental data and model calculations has improved significantly due to recent modifications. A model for sulfate, phosphate, chloride, fluoride, iodide and water in dilute solutions (<10 wt%) in glass was developed that generally agreed well with the data. Solubilities in equilibrium with solid or liquid sulfates, phosphates, and halides can also be calculated. (The software provides a powerful computational predictive capability for glass states and properties. However, this capability is not sufficiently comprehensive or accurate to eliminate the need for experimental validation. The computational capability upgrading should continue to improve predictive capability.)


No annotation


No annotation
Statistical empirical modeling techniques were applied to predict primary crystalline phase at the liquidus temperature and whether the liquidus temperature is above or below 1050°C (100°C below a melting temperature of 1150°C). Modeling data was from the CVS of Hanford waste glass compositions and properties where the majority of the data are categorized into one of 13 primary crystalline phases at the liquidus temperature, and as to whether the liquidus temperature is above or below 1050°C. Multinominal logit and classification tree methods were used to model the data. The classification tree models provided a better overall fit than did the multinominal logit models. For predicting various groupings of primary crystalline phases, misclassification rates were 5.6% to 19.3% for the classification tree models. The multinominal logit model misclassified 11.5% of the "above or below 1050°C liquidus temperature data"; the classification tree model misclassified 11.0% of the data.


A CVS was performed to characterize the relationships between glass composition and glass and melt properties. Over 120 nonradioactive glasses were melted and properties measured in five statistically designed experimental phases. Glass composition is represented by 10 components: SiO₂, B₂O₃, Al₂O₃, Fe₂O₃, ZrO₂, Na₂O, Li₂O, CaO, MgO, and others (all remaining components). The properties measured included melt viscosity, melt electrical conductivity, glass transition temperature, thermal expansion of solid and molten glass, crystallinity (quenched and canister centerline cooled glasses), liquidus temperature, durability based on normalized elemental releases from the MCC-1 28-day dissolution test and the 7-day PCT, and solution pH from the durability tests. Amorphous phase separation was also evaluated. Empirical first- and second-order mixture models were fit to the data to relate glass properties to composition and quantify prediction uncertainties. Other modeling approaches were investigated. A preliminary Qualified Composition Region was developed to identify glass compositions that met processability and waste form acceptance criteria. Models expressed in mass and mole fractions of the 10 components have similar goodness-of-fit (R²) values. First- and second-order models fit the data for melt viscosity and electrical conductivity from 950 to 1250°C with R² from 0.93 to 0.98; glass transition temperature with R² from 0.88 to 0.97; thermal expansion of solid glass with R² from 0.87 to 0.93; thermal expansion of molten glass with R² from 0.43 to 0.75; PCT durability with R² from 0.73 to 0.92; MCC-1 durability test with R² from 0.60 to 0.83; liquidus temperature with R² = 0.90 for clinopyroxine, R² = 0.64 for spinel, and R² = 0.79 for Zr-containing crystals. Within the composition range studied, Li₂O and Na₂O decrease viscosity, glass transition temperature, liquidus temperature, and durability, and increase electrical conductivity. SiO₂ increases durability, viscosity, and glass transition temperature and decreases electrical conductivity. Al₂O₃ increases viscosity and durability; ZrO₂ increases viscosity, glass transition temperature, durability, and
liquidus temperature for clinopyroxene and Zr-containing phases; MgO increases liquidus temperature and decreases durability; Fe$_2$O$_3$ increases liquidus temperature for Fe-containing phases; B$_2$O$_3$ decreases durability and liquidus temperature for spinel and clinopyroxene. The crystalline phases observed in canister centerline cooled samples were spinel, clinopyroxene, and Zr-containing phases (ZrO$_2$, zircon, and Na-Zr silicate), orthopyroxene, nepheline, olivine, CaSiO$_3$, and SiO$_2$ (cristobalite and quartz). Hematite, Li$_2$SiO$_3$, and LiAlSi$_2$O$_6$ crystallized less frequently. Durability appeared to be decreased by crystallization of nepheline, LiAlSi$_2$O$_6$, and cristobalite. A method for predicting amorphous phase separation was applied to the test glasses and predicted nine glasses to be prone to phase separation.


No annotation


No annotation


No annotation


An experimental study was performed to determine Hanford HLW glass properties as a function of composition for high melting temperature and high waste loading glasses. The test matrix was designed to vary key composition components (SiO$_2$, B$_2$O$_3$, Na$_2$O, Li$_2$O, Fe$_2$O$_3$, Al$_2$O$_3$, ZrO$_2$, Bi$_2$O$_3$, P$_2$O$_5$, UO$_2$, TiO$_2$, Cr$_2$O$_3$, and "Others") starting from a glass based on a Hanford HLW all blend waste. Forty test glass compositions were characterized for viscosity, glass transition temperature, electrical conductivity, crystallinity, liquidus temperature, and PCT release. Individual component effects on glass properties were assessed using first- and second-order empirical models. High-temperature glasses use Na$_2$O from the waste as the main flux component (low in B$_2$O$_3$ and Li$_2$O) and can accommodate higher refractory oxide concentrations (Al$_2$O$_3$, Fe$_2$O$_3$, ZrO$_2$, CeO$_2$, etc.) than low melting temperature glasses without precipitation of crystalline phases in the melter. Melting temperature
most effectively decreased by Li$_2$O, Na$_2$O, and B$_2$O$_3$ in that order. Melting temperature and liquidus temperature are most effectively simultaneously decreased by Na$_2$O and SiO$_2$. Electrical conductivity depends on alkaline oxides content, and the Na$_2$O from the waste is sufficient to conduct electricity in the melter. The Vogel-Fulcher-Tammann (VFT) equation fitted to data augmented by low-temperature viscosity is adequate for viscosity/temperature correlation over a wide temperature range. First- or second-order coefficients for VFT parameters are sufficient to cover broad composition regions, but the coefficients differ for low- and high-temperature glasses. ZrO$_2$ makes glass viscosity sensitive to temperature fluctuations, whereas Li$_2$O has the opposite effect. The transition temperature is between 440 and 550°C, which is lowered by alkaline oxides and Bi$_2$O$_3$ and raised by Al$_2$O$_3$, ZrO$_2$, B$_2$O$_3$, Fe$_2$O$_3$, and SiO$_2$. Less common components may significantly affect glass properties; for example, Bi$_2$O$_3$ decreases melting, transition, and liquidus temperatures; P$_2$O$_5$ decreases liquidus and has an anomalous effect on transition temperatures and a positive effect on durability; UO$_2$ decreases melting temperature, makes glass longer, and affects durability little; TiO$_2$ decreases melting temperature and increases durability; and Cr$_2$O$_3$ increases durability. Significant differences were found between averaged and local values of component effects on glass durability, and effects on high- and low-temperature glasses may be different. Al$_2$O$_3$ and B$_2$O$_3$ exhibit remarkably nonlinear behavior in their effects on glass durability. Canister centerline cooling slightly increases glass durability except when a substantial fraction of the glass is crystallized, a condition that may decrease the durability, but none of the study glasses exhibited unacceptable durability.


A laboratory investigation was conducted to provide generic glass formulations for low-temperature melters based on double-shell and single-shell tank (DST/SST) washed HLW blend composition; a basis for comparison of melter products from candidate melter systems, including the high-temperature melter and low-temperature melter with and without mechanical stirring; and data for laboratory-scale investigation of feed processability and minor component solubility. Nine glasses were formulated with 3 to 10 wt% B$_2$O$_3$, 1100°C to 1150°C melting temperature and 45 to 65 wt% waste loading. Glass melt viscosity (melting temperature), melt electrical conductivity, liquidus temperature, primary crystalline phase, and chemical durability were determined and modeled (first-order empirical) for properties as functions of SiO$_2$, B$_2$O$_3$, Na$_2$O, Li$_2$O, and waste blend. It was found that with the glass property/composition models currently available, low-temperature glasses (melting temperature 1100°C to 1150°C) can be formulated that are durable and have high waste loading; the maximum achievable waste loading of the low-temperature DST/SST glass is about 5 to 10 wt% lower than the maximum waste loading attainable with high-temperature glass; contrary to model predictions, neither spinel nor nepheline were the primary crystalline phases of DST/SST glasses; experimentally observed primary phases from DST/SST glasses were rare earth zirconates (waste loading ≤55 wt%) and sodium zirconium silicate (waste loading ≥55 wt%); neodymium (U substitute) may increase liquids
temperature and artificially limit the waste loading acceptable for continuous melters; cerium (minor
component) reacts with zirconium-forming crystalline phases in low-temperature glasses, which limits
waste loading; and the effect of glass components on liquidus temperature is strongly nonlinear even
within the composition range of Hanford glasses.

Investigation Plan," PVTDC95-02.01C, Pacific Northwest Laboratory, Richland, Washington.

No annotation

Waste Glasses," PVTDC95-02.01V, Nuclear Research Institute Rez, Rez, Czech Republic.

A laboratory study was conducted to study the effect of chromium on the properties of selected glasses.
Two borosilicate glasses (Glass 1 with 4.14 wt% Cr2O3 melted at 1150°C and Glass 2 containing
6.215 wt% Cr2O3 and melted at 1450°C) were prepared according to PNL "quench anneal" procedure.
Property measurements included temperature dependence of viscosity, temperature dependence of
electrical conductivity, crystallinity, dilatometry, liquidus temperature, and chemical analysis of glasses
and properties of the respective batches during the heat treatment. Samples from each glass were
subjected to uncontrolled and canister-centerline cooling heat treatment for crystallinity study. The
dependencies of the Cr(VI) content in the batches on the temperature and residence time of the heat
treatment were mathematically described. The effect of changes in the glass compositions on the
chromium behavior was studied by changes in glass acidobasicity and changes in concentrations of
alkali oxide and alumina. Five special glasses were prepared to determine the effect of Fe, Zr, Ni, and
Mn on baseline glass crystallinity. Glass 1 contained agglomerates and individual crystals of eskolaite
and is relatively stable, exhibited regular behavior for viscosity and electrical conductivity, exhibited
higher chemical durability than Glass 2, and exhibited less tendency to crystallize after heat treatment.
Glass 2 contained eskolaite and beta-eucryptite as major phases and nepheline and spinel as minor
phases and is very sensitive to thermal history and concentration changes, provided difficulty in
measuring viscosity and electrical conductivity due to high crystallinity, and exhibited lower chemical
durability than Glass 1. There were temperature ranges where Cr(VI) formed. Changes in Li, Na, Si,
and B affecting acidobasicity decreased the glass basicity, which led to lower Cr(VI)/Cr ratio and
chromium leached from the glass. Only glass with increased Mn and that was heat treated did not
contain crystals after melting, but contained small spinel crystals after decreasing the temperature
100°C.
Fiscal Year 1994


No annotation


Studies and laboratory investigations were performed to develop the glass formulation approach for the high-temperature melter (HTM), and to determine the composition and melting temperature of a glass with 50 wt% (oxide basis) NCAW for the first HTM runs and the maximum waste loading in glasses with DST/SST blend waste for future HTM runs. Glass compositions were formulated using property/composition models and were tested experimentally. For NCAW, glass development focused on finding the optimum additive at a target waste loading of 50 wt%, and for blend waste, the additive was fixed as SiO₂ only, and the waste loading was varied from 57 to 71 wt% to find the maximum waste loading. An acceptable NCAW glass was developed by adding SiO₂ and Na₂O. The maximum waste loading that can be achieved with <0.1 vol% crystallinity after 24 h at TM - 100°C in the blend waste glass was determined to be between 60 and 65 wt%, with only Si as the additive.


A laboratory study was performed to investigate the effect of water in simulated nuclear waste glasses on various glass properties, including chemical durability, glass transition temperature, liquidus temperature, viscosity, and electrical conductivity. Three simulated nuclear waste glasses were provided by PNL for the work, CVS2-18, CVS2-52, and CVS2-74. The water concentration in the glasses was altered by remelting the glasses under different water vapor pressure. The dissolution rates of Si, B, Li, and Na increased with glass water content using the PCT. There was no detectable influence of glass water on glass leachability using the MCC-1 test. Increasing the glass water content reduced the glass transition temperature. The liquidus temperature increased slightly with water content, approximately 20°C with glass treated in 355-mm Hg water vapor wet atmosphere. No detectable effect of glass water content on melt viscosity was observed. The majority of data indicates that the electrical conductivity decreases and then increases with water content.

A progress report is provided on Centre for Research in Computational Thermochemistry, Ecole Polytechnique staff activities between May 19, 1993 to May 6, 1994. Activity goals are to develop a thermodynamic database for multicomponent glasses and for crystalline and liquid phases that might precipitate from these glasses, which when used with the free energy minimization software and other data bases of the F*A*C*T thermodynamic computing system, will permit the calculation of conditions for phase equilibria including liquidus temperature. Work included PNL procuring the F*A*C*T software; refining previous optimizations; and modeling and including species in the data base such as Fe**, Cr**, Cr**, spinel model, NiO, MnO, Bi2O3, fluoride, sulfate, sulfoide, phosphorous, and water. Some liquidus calculations were performed.

Fiscal Year 1993


A study was performed to recommend frit specification requirements and the associated testing needs. Frit specifications were provided for the following areas: glass processability and acceptability, frit storage and handling, frit slurry rheology, melter feed rheology, and frit abrasiveness. Specifications were being developed or were under consideration for the glass melting rate and frit cooling rate. Additional effort was required to develop a complete set of recommended specifications.


No annotation


A study was conducted to assess the viability of laboratory screening tests that will enable identification of the cold cap processing properties, establishment of cold cap property ranges for feed processability, and ultimately, estimation of melting rate in a HWVP large-scale melter, and to recommend the development approach for these laboratory screening tests. A literature review was conducted to assess the factors that could affect melt rate, including slurry flow over the cold cap, feed demixing in the cold cap, spreadability of the cold cap over the molten glass, heat transfer from the molten glass to the cold cap, heat transfer from the melter plenum to the cold cap, and reactions between the feed components within the cold cap. It was not felt that an existing test(s) was available to provide the needed information. An approach was defined to develop the test(s).
The study results at the Centre for Research in Computational Thermochemistry, Ecole Polytechnique to develop thermodynamic models to predict the liquidus temperatures of glasses containing HWVP study glass 10 components (SiO₂, B₂O₃, Na₂O, Li₂O, CaO, MgO, Fe₂O₃, Al₂O₃, ZrO₂, and "others") were reported. A literature search was performed on available phase diagram and thermodynamic data for binary, ternary, and quaternary subsystems for use to obtain parameters of model equations for the Gibbs energies of all phases as functions of temperature and composition. A quasichemical model was then used to predict the Gibbs energy of the multicomponent liquid from the optimized parameters. With this database and a general Gibbs-energy minimization program, liquidus temperatures were calculated for 123 glass compositions supplied by PNL and compared with measured liquidus temperatures. Some systematic differences between measured and calculated values were noted which require further small adjustments of model parameters. The model appeared to give generally satisfactory results. Problems arise due to the neglect of divalent iron and the precipitation of spinels at higher temperatures. Although no solid solutions were considered, it is not evident how the inclusion of these would improve the results.


A first-order composition variation study (CVS-I) was conducted for the HWVP program to preliminarily characterize the effects on key glass properties of variations in selected glass (waste and frit) components. The components selected were SiO₂, B₂O₃, Al₂O₃, Fe₂O₃, ZrO₂, Na₂O, Li₂O, CaO, MgO, and "others" (all remaining waste components). A glass composition region was selected for the study based on the expected range of glass compositions and the results of a previous series of scoping and solubility studies. A 23-glass statistically designed mixture experiment was conducted and data obtained for viscosity, electrical conductivity, glass transition temperature, thermal expansion, crystallinity, and durability MCC-1 28-day leach test and the 7-day PCT. These data were modeled using first-order functions of composition and the models were used to investigate the effects of components on glass and melt properties. The fitted linear mixture models explain much of the variation in the properties of interest; R² values range from approximately 0.75 to 0.98. Viscosity at
1150°C of the HW-39-4 glass is increased in the order (based on mass fraction) SiO$_2$ > Al$_2$O$_3$ > ZrO$_2$ and decreased in the order Li$_2$O < Na$_2$O < B$_2$O$_3$. Electrical conductivity at 1150°C of the HW-39-4 reference glass is increased in the order Li$_2$O > Na$_2$O and decreased by SiO$_2$. Glass transition temperature is strongly decreased by Li$_2$O and to a lesser extent by Na$_2$O, and increased by SiO$_2$ and ZrO$_2$. Alkali oxides (Li$_2$O more than Na$_2$O) increase and SiO$_2$ decreases thermal expansion of both solid and molten CVS-1 glasses. Al$_2$O$_3$, ZrO$_2$, and MgO decrease the thermal expansion of molten glasses even more than SiO$_2$. All but one of the glasses that failed the liquidus criterion had the sum of mass fractions of FeO, Al$_2$O$_3$, ZrO$_2$, and "others" equal to 0.24 (the maximum allowed level). The major crystalline phases observed after 24 h at 1050°C were various silicates [MgSiO$_3$, ZrSiO$_4$, Ca$_2$Zr(SiO$_4$)$_2$], spinels, ZrO$_2$ (incompletely dissolved), and RuO$_2$ (undissolved). Normalized MCC-1 and PCT release values of B and Li were relatively high for glasses with high B$_2$O$_3$ content unless the glass was rich in Al$_2$O$_3$; these glasses are likely to be phase separated. Based on models fitted to all of the MCC-1 data, normalized B release of the HW-39-4 reference glass is increased most by Li$_2$O, followed closely by Na$_2$O and B$_2$O$_3$, and decreased most by Al$_2$O$_3$ and ZrO$_2$. Fitting to a reduced set of data, SiO$_2$ decreases the boron release most, and the component effects are somewhat different. PCT results were similar to the MCC-1 results except that MgO appeared to strongly increase PCT-normalized B release. The CVS-I model predicts a slight change in the temperature at which viscosity is 10 Pa.s by the addition of the nominal amount of treated submerged bed scrubber (SBS) recycle waste and/or the nominal amount of decontamination waste treatment tank (DWTT) evaporation/bottom recycle waste (approximately 9°C increase).


No annotation

Fiscal Year 1992


Laboratory and data analyses studies (Composition Variation Study - CVS) were being conducted for the Hanford Waste Vitrification Plant (HWVP) program to characterize the relationships between Hanford high-level waste glass composition and glass and melt properties. The glass and melt measurements included viscosity, electrical conductivity, glass transition temperature, thermal expansion, crystallinity (after controlled cooling), and durability based on the MCC-1 28-day leach test and the 7-day PCT. Study objectives were to 1) develop models relating the glass and melt properties to composition, 2) develop uncertainty equations for model predictions, and 3) use the models and uncertainty equations to develop a qualified composition region (acceptable confidence of acceptable glass). Each test phase was planned and the resulting data analyzed using statistical experimental design and empirical modeling techniques for mixture experiments, and results of previous phases.
were used for planning subsequent phases. Glass compositions from four waste types (NCAW, 
NCRW, PFP, and CC) were included for the 10 principal components: SiO₂, B₂O₃, Al₂O₃, Fe₂O₃,
ZrO₂, Na₂O, Li₂O, CaO, MgO, and "others" (all remaining waste components). Eighty-one glasses
were included in the study. Both first- and second-order mixture models were fitted to the data for
viscosity at 1150°C, electrical conductivity at 1150°C, PCT and 28-day MCC-1 normalized element
releases (Si, B, Li, Na, and Cs), glass transition temperature, and coefficients of thermal expansion for
solid and molten glass. Fulcher and Arrhenius equations with coefficients expanded as first-order
mixture models were also fitted for viscosity and electrical conductivity (Arrhenius only). First- and
second-order mixture experiment models for properties account roughly for the following fractions of
the variability in the data: a) viscosity and electrical conductivity at 1150°C, 88-98%, b) glass
transition temperature: 80-90%, and c) PCT normalized boron, lithium, and sodium releases: 65-75%
(first-order models) and 78-88% (second-order models). MCC-1 release models did not fit quite as
well as the PCT release models. First- and second-order empirical mixture models may not be
adequate to characterize PCT and MCC-1 glass durability as a function of composition over the full
range of glass compositions being studied in CVS. Varying the composition of the "others"
component had negligible to moderate effects, depending on the property and the composition of the
glass. Ranking the CVS glasses according to MCC-1 leach test results did not yield the same order as
ranking according to PCT leach test results. Prevalent primary crystalline phases within the CVS
composition region were clinopyroxene and spinel, followed by olivine and zircon. Crystallization of
clinopyroxenes and zircon during canister centerline cooling heat treatment only slightly affected glass
durability, whereas crystallization of cristobalite and nepheline had a strong negative effect on glass
durability. Plots of log PCT and MCC-1 normalized boron release versus free-energy of hydration
show essentially no relationship for CVS data or any subset thereof.

Study (CVS) Test Plan, Revision 3," PHTD-C92-03.01B Rev. 3, Pacific Northwest Laboratory, Richland,
Washington.

No annotation

Fiscal Year 1991

Composition Variation Study Test Plan (Rev. 2)," HWVP-91-1.2.2.03.01B, Pacific Northwest Laboratory,
Richland, Washington.

No annotation

5.13
Studies were performed to confirm performance of the revised simulant HWVP feed makeup procedure, revise the glass frit composition for glass properties composition, assess the effects of increased waste loading on glass properties, and revise associated chemical procurement specifications. The revised simulant HWVP NCAW feed makeup procedure was demonstrated, incorporating an approach developed at SRL for adding precipitated MnO₂ to the feed makeup. Glass studies, using glass models, concluded that 1) a 28 wt% waste oxide loading could be easily achieved (32 wt% waste loaded laboratory glass had little crystallinity), 2) frit 202 is not acceptable due to exceeding viscosity constraints for the final glass, and 3) a simple three-component frit without sodium was appropriate for the HWVP glass. (The frit composition was later modified due to the slow melter melt rate.)

A study was performed to determine if existing aqueous chemistry simulation tools could be used to improve prediction of glass durability test results. An attempt was made to apply a geochemical computer code, PHREEQE, and a glass dissolution rate equation to observed durability test results in order to calculate the initial rate of reaction of different CVS-I glasses. A regression equation could then be developed for this initial rate as a function of composition to provide a better data fit. This expression could then be combined with solution chemistry effects to predict durability test results. Since it was determined that uncertainties in the approach limit the probability of success, it was recommended that the work be discontinued.

A laboratory study was conducted to subject HW-39-4 waste glass to leach tests and to compare the glass performance with that of an earlier waste glass, HW-39-2. Thermal conductivity measurements were also made on the HW-39-4 glass. In leach testing using the MCC-1, Minimal Replacement MCC-3 (MRMCC-3), and PCT methods, the HW-39-4 nuclear waste glass composition performed satisfactorily with respect to current requirements for waste form durability, but generally had slightly less durability than HW-39-2 and SRL-200 (Savannah River Laboratory #200) compositions. The thermal conductivity of HW-39-4 glass varied from 1.1 to 1.5 W/m-K over the temperature range of 250 to 500°C.

No annotation


No annotation


The plan provides an overview of Composition Variation Study (CVS)-I and CVS-II, the phases of CVS-II testing, the experimental work, data analysis and modeling, and the statistical technique for deriving the qualified composition region. The requirements for schedule, personnel, analytical support, and funding are addressed together with a timeline of activities and methods for updating the plan. The goal of the CVS is to identify the largest possible HWVP glass composition region that satisfies several constraints on glass properties. The goal is achieved by measuring properties of glasses of varying composition, developing empirical models for properties as functions of composition using the experimental data, and defining the qualified composition region. Because the empirical property models are subject to uncertainty, a statistical approach was used to define the qualified composition region. The cost for the three-year effort for CVS-II was estimated to be $2.1 M.

Fiscal Year 1989


No annotation


A laboratory testing program was conducted to provide a technical basis for the expansion of the acceptable redox state range (measured as Fe\(^{2+}/Fe^{3+}\) ratios in the glass) in the HWVP melter glass. The testing included the evaluation of glass and melt properties (including phase behavior) over the expanded redox state range of greater or equal to 0.005 to 1.12 Fe\(^{2+}/Fe^{3+}\). The glass properties
evaluated included phase behavior (metal formation), viscosity, electrical conductivity, and durability (28-day MCC-1 testing). Because of the formation and size of metal inclusions observed in the test glasses, Fe$_2$/Total Fe ratios in the glass of 0.3 (0.43 Fe$^+$/Fe$^-$) and above were found to be unacceptable. The acceptable upper limit for Fe$_2$/Total Fe based on phase behavior was found to be between 0.2 and 0.3 Fe$_2$/Total Fe. Based on the data, the current melt redox state corresponding to a Fe$_2$/Total Fe of 0.005 to 0.23 (0.005 - 0.3 Fe$^+$/Fe$^-$) is recommended for HWVP NCAW glasses.

Changes in the redox state of the glass corresponding to Fe$_2$/Total Fe greater or equal to 0.005 and 0.32 had no significant effects on viscosity, electrical conductivity, or durability of the glass:


Laboratory studies were performed to investigate the viability of a leach test methodology for the HWVP and provide glass dissolution data for HWVP model determination and validation. Leach tests up to one year in duration were conducted on the HWVP reference glass HW-39-1 (1.3 wt% Cr$_2$O$_3$), using the Materials Characterization Center Static Leach Test (MCC-1) and the Agitated Powder Leach Test (MCC-3). The glass surface area-to-leachate volume (SA/V) ratios of 10, 530, 2000, and 20,000 m$^{-3}$ were investigated during testing. Based on data analyses, changes were recommended in the leach testing methodology, including changes in the randomization and replication plans to provide for better statistical characterization of glass durability. Statistical evaluation of test data found that the leach testing methodology provides the necessary data for characterizing some of the sources of variability in the test results, but not others, resulting in recommendations so that defensible statistical qualification statements can be made. Because the modified MCC-3 test provides data faster, requires less sample preparation, and costs less to perform, it was recommended that the modified MCC-3 techniques be used as a major part of future leach testing of HWVP glass. The (SA/V).time (t) scaling technique appears adequate to provide a general indication of the dissolution characteristics of HW-39-1 glass in solution concentrations produced with SA/V values up to 2000 m$^{-3}$, but is inadequate when the SA/V value is increased to 20,000 m$^{-3}$. Tests at higher SA/V values produced higher pHs at comparable (SA/V).t values. The HW-39-1 glass has a B release of 0.53 g/m$^{-2}$d, which is well below the specified 1 g/m$^{-2}$d limit.


Fiscal Year 1988


Fiscal Year 1987


Laboratory tests were conducted to evaluate the updated NCAW'86 waste composition and the resulting glasses to assess the changes that may be expected in glass properties due to waste composition variations. The NCAW'86 composition with the HW-39 reference frit would be processable within the HWVP and would produce a waste form with similar properties and durability to the HW-39 reference glass, and have acceptable 100 poise temperatures (T100Ps) near the lower HWVP process limit (1070 to 1150°C). The T100Ps ranged from 1086 to 1074°C as the waste loading increased from 25 to 35 wt% due to increased alkali and reduced Cr2O3 in NCAW'86. Melt electrical conductivity increased as the waste loading increased, due to the increased alkali content of NCAW'86. At 25 wt% waste loading, the phase behavior of glass made with NCAW'86 was very similar to a low Cr2O3 version of the HW-39 reference glass, and the crystallinity in quenched glass increased slightly as the waste loading increased to 30 and 35 wt% due to the small increase in insoluble noble metals. At 25 wt% waste loading, the devitrification behavior of glass made with NCAW'86 was very similar to a low Cr2O3 version of the HW-39 reference glass, but at 30 to 35 wt% waste loadings the devitrification of the NCAW'86 glasses was significant at simulated closed-turntable canister cooling rates. Based on 28-day MCC-1 leaching data, the NCAW'86 glass waste form was as durable, or more durable than, the HWVP reference glass produced from the NCAW'84 waste composition, and the glass durability increased slightly with waste loading. The glass transition temperatures (490 plus or minus 5%) and coefficients of linear thermal expansion of the glasses were not affected significantly by the changes in waste composition. Because of increased amounts of alkali in the waste, the melting rate for the NCAW'86 glass should be comparable to, or possibly faster than, the NCAW'84 melter feed.
Laboratory tests were conducted to investigate and characterize the effects of Ca, Ba, F, Mn, Mo, Ni, and Fe with low-Cr glass. Key glass properties (melt viscosity, electrical conductivity, phase behavior, and leach rates) were evaluated to determine what ranges of variance were allowable without unacceptably altering the physical properties of the glass, establishing the extreme limits of individual glass component variations if these extremes were within the tested ranges. Initial scoping variability testing determined that variations of up to 5 wt% BaO, 5 wt% MnO₂, 2 wt% MoO₃, or 2 wt% NiO in the glass (on oxide basis) had no significant effects on viscosity, electrical conductivity, or phase behavior in HW-39 reference glass composition, and these components should not be included in further variability testing. Due to potential liquid-liquid and observed crystalline phase separation at fluorine levels of 3 wt% and above in the glass, the maximum limit for fluorine in the glass should be established at the last acceptable fluorine level tested, 1.73 wt% oxides. Combined testing was performed over a range of 0 to 25 wt% Fe₂O₃ and 0 to 10 wt% CaO. For Fe₂O₃, the range of acceptable variability was determined to be from 3 to 15 wt% oxides in the glass. The lower limit was constrained by the viscosity of the glass while the upper limit was constrained by the decrease in durability. For CaO, the maximum range for acceptable variability was from 0 to 5 wt% in the glass. The maximum limit was constrained by the viscosity of the glass. The electrical conductivity of the melt was not a factor in establishing the minimum or maximum limits for component variability.

A laboratory study was conducted to assess the viability of potential scenarios to expand the current specifications of waste and frit components to allow for greater pretreatment and processing flexibility. HW-39 reference glass, frit, and NCAW’84 (0.13 wt% Cr₂O₃) waste compositions were used as the basis for the tests. Two methods evaluated included adjustment of frit to allow additional sodium in the waste and using SiO₂ or sodium additions in place of some frit to adjust viscosity. Use of compositional ratios such as (alkali)₂O/SiO₂ in glass composition to predict acceptable viscosity of a melt based on composition was evaluated. Up to 5 wt% Na₂O can be removed from the HW-39 reference frit while maintaining a processable frit composition, meaning that there is a potential addition of 0 to 20 wt% Na₂O in the waste. The existing flexibility of the reference glass composition can handle the normal fluctuation in NCAW composition. Compositional ratios, the ratios of different glass components or the ratios of the sums of difference glass components, can be used to estimate acceptable viscosity of glass melts based on composition. The ratios using the total wt% alkali oxides over the sum of the wt%’s of SiO₂, Al₂O₃, and ZrO₂ were found to predict T100P well. The addition of SiO₂ or sodium as a partial replacement for frit provides a method of adjusting the viscosity of abnormal waste batches or possibly other wastes to within operating specifications.

Laboratory and mini-melter tests were performed to obtain preliminary information on the characteristics of noble metals in a simulated HWVP glass. Testing variables included Fe²⁺/Fe³⁺ ratios from 0 to 0.65 (glass redox conditions); melt temperatures of 940°C, 1100°C, and 1170°C; noble metal feed concentrations from HWVP reference level of 0.26 wt% to 1.1 wt%; melting times of 2.4, 24, and 240 h; and one test designed to indicate noble metals behavior under melter cold cap conditions. In the crucible tests, increasing the melting temperature increased the particle settling rate and decreased the size and number of particles observed. As melting time increased, particulate size increased and particles settled to the bottom of the crucible. Increasing the concentration of noble metals in the feed increased the amount of particulate matter. Redox conditions of the glass and the type of reducing agent affected the quantity and type of particulate. Crucible tests indicated that gas bubbles may act as nucleating agents for Ru and aid in transport to the surface. Ru and Rh acted as nucleating agents and were often present in large agglomerates of spinel. The majority of particles were under 10 μm in diameter. In the mini-melter tests, the glass produced had an Fe²⁺/Fe³⁺ range from 0.18 to 0.51, which was higher than the target range. Unanticipated corrosion reactions were encountered with the Inconel mini-melter, including oxidation of chrome from the Inconel, which caused many large high-chrome spinel particles in the outlet glass together with submicron particles high in Ru and small Pd particles, not as common as Ru particles. A core sample of the glass from the mini-melter after 4 to 5 tank turnovers indicated metallic nodules as large as 0.5 cm in diameter near the base of the melter consisting of an alloy of Ru, Rh, and Pd, with some Te, Cu, Ni, Fe, and Mo.


A study was conducted to summarize and reference the specific ranges of acceptable variability that have been identified for oxide components of the HWVP reference glass (HW-39) as it incorporates the pretreated NCAW. The summary of glass composition boundaries includes variability testing conducted through FY 1987, including the evaluations of both the NCAW'84 and NCAW'86 reference pretreated NCAW compositions. Component composition limits are based on the ability of the product glass to be acceptable to a repository and processable.
Fiscal Year 1986


No annotation


No annotation


Scoping laboratory testing was performed to determine glass candidate components to include in the composition variation study. The goal of the variability testing is to characterize the effects of expected variations of selected waste components on key glass properties such as viscosity electrical conductivity, phase behavior, and durability. The effects of the following component concentrations on the reference glass (HW39) were determined: Zr, waste loading, mixed alkali (Li, Na, K), Na, Fe, Al, Si, rare earths (La, Nd), U, and Cr. For ZrO₂ concentration range of 0 to 15 wt% and waste oxide loading concentration range of 0 to 30 wt%, the following was observed. Assuming a 25 wt% total waste loading (ZrO₂ + waste oxide) and using the developed model to evaluate the temperature at which the melt viscosity is 100 Poise (T100P), the glass could contain up to 10 wt% ZrO₂ (40 wt% in the waste) before the T100P exceeds 1150°C. The T100P is predicted to be 1100°C without ZrO₂. The glass electrical conductivity does not exceed the recommended melter operating range for the composition ranges tested. Glass durability increased with ZrO₂ over the test range. With 20 wt% and 30 wt% waste oxide loading, the release rates for B, Ca, Na, Si, and Cs are similar to the release rates for elements from the reference HW39 glass (25 wt% waste oxides). For mixed alkali concentration 19.2 mole% (Li₂O, Na₂O, and K₂O components were 0 to 19.2 mole%), the following was observed. A range of about 4 to 8 mole% K₂O can be accommodated, depending on the ratio of Li₂O to Na₂O, without unacceptably altering the viscosity or electrical conductivity of the glass melt. K₂O addition to the glass generally decreases glass durability. The relative alkali strengths for reducing melt viscosity are Li₂O > Na₂O > K₂O. The relative alkali strengths for increasing melt electrical conductivity are Li₂O > Na₂O > K₂O. For the U₂O₅ concentration range of 0 to 8 wt%, the following observations were made. The T100P and the glass melt electrical conductivity at 1150°C (E1150) of the reference glass was not affected significantly over the test concentration range. The uranium was incorporated into the glass matrix with no phase separation. As the U₂O₅ concentration increased in the glass, the Fe amount in the chromite spinel phase [Fe(Fe,Cr)₂O₄] decreased. Above 2 wt% U₂O₅, the chromite crystalline phase is thought to be Cr₂O₃. The amount of uranium variation expected in the NCAW will not significantly affect the viscosity, electrical conductivity, or durability of the glass. For the multiple component variability of Na, Fe, Al, Si, and rare earths, the following observations were made. For all
five oxides tested, the glass electrical conductivity is acceptable if the viscosity is acceptable. The determined acceptability ranges for the components in glass were as follows: Na$_2$O was from 8.8 to 13.2 wt% (reference glass was 10.4 wt%); Fe$_2$O$_3$ was from 7.3 wt% in glass to 15 wt% evaluated (reference glass was 11.1 wt%); Al$_2$O$_3$ was from 0.4 to 6.5 wt% (reference glass was 4.3 wt%); SiO$_2$ was from 54.8 wt% in glass to 50.4 wt% tested (reference glass was 51.3 wt%); and rare earths oxide was 0 to 2.0 wt% tested in glass. The effects of rare earths oxide (La and Nd) concentration range on the glass viscosity and electrical conductivity is not significant. For the Cr$_2$O$_3$ concentration range of 0 to 2.0 wt%, the following observations were made. Increasing the Cr$_2$O$_3$ content from 0 to 2.0 wt% increased the T100P from 1077°C to 1116°C. The glass E1150 increased significantly to 0.35 ohm$^{-1}$cm$^{-1}$ when the concentration was 0 wt%, but remain unchanged at approximately 0.27 ohm$^{-1}$cm$^{-1}$ from 0.5 to 2.0 wt% Cr$_2$O$_3$. No crystalline phase was observed in the 0 wt% Cr$_2$O$_3$ glass. The crystalline phase (primarily spinel) increased from 1 to 5 wt% with a Cr$_2$O$_3$ concentration increase of 0.5 to 2.0 wt% in the glass. The glass durability did not change with the Cr$_2$O$_3$ content. The models produced for Zr, Na, Al, and Cr variability accurately predict the changes in T100P to within 10%. The relative effect of Fe on viscosity changes increases with higher chrome levels. For Fe$_2$O$_3$, the lower acceptable limit can be extended to 5.5 wt% in glass if the Cr$_2$O$_3$ content is near 0.1 wt%.


Laboratory studies conducted in FY 1986 to further characterize the HWVP reference glass (with 1.33 wt% Cr$_2$O$_3$) HW39 made from NCAW are reported. The initial rate of glass dissolution was 1.2 g/(m$^2$/d), and the final dissolution rate was 0.010 g/(m$^2$/d) in deionized water at 90°C over a wide range of surface area to volume ratios. The dissolution rates were within 50% of the SRL-165 glass. The HW-39 glass was found to form pyroxene devitrification products under certain conditions found to be detrimental to the chemical durability of glass. The HW39 glass was subjected to simulated conservative closed canister cooling rates, and no pyroxene formed. The glass transition temperature was 49°C. The dilatometric softening temperature was 550°C. The low thermal coefficient of linear expansion was 8.4 x 10$^{-6}$/°C. The high thermal coefficient of linear expansion was 97.2 x 10$^{-6}$/°C. The heat capacity between 0°C and 400°C can be expressed as Cp = 0.1709 + 0.0003389$t$, where $t$ is temperature in centigrade.


The report assesses the availability of waste feed stream and process stream properties data for HWVP Project needs and recommends additional data measurement needs. This study considers further development activities and requirements of the PNL HWVP feed team research task.
Fiscal Year 1985


No annotation


A study was performed to correlate the results obtained from laboratory tests for melting rate and redox response with actual melter results. The laboratory crucible melting rate test closely predicts melting rates in engineering-scale melters for most feeds. Melting rates of feeds producing thin cold-caps are not adequately predicted by the current laboratory test. A newly developed and tested continuously-fed, laboratory-scale melting rate test should not have the cold-cap limitations of the crucible melting rate test and should be evaluated. The crucible melting rate test provides a good estimation of the characteristics of the cold-cap observed in the engineering melters. The amount of reductant (carbon in the form of sugar or formic acid) required to produce the desired redox level in the laboratory melt test also produces a similar redox level within the melter.


Laboratory studies were performed to develop a working glass composition for use in slurry feed development and melter testing. A working borosilicate glass (HW-39) with a 25 wt% waste oxide loading was developed using the nominal composition of the 1985 HWVP reference waste (Neutralized Current Acid Waste and Cladding Removal Waste, NCAW/CRW). The development of the working glass composition included measuring viscosity (T100P) of 1124°C, establishing carbon phase behavior (crystallization and/or liquid-liquid phase separation) of containing small cubic spinel crystals only, electrical conductivity of 0.30 ohm-1cm-1 at 1150°C, and chemical durability similar to SRL/165 and WV-183 glasses. The amount of stable carbon necessary to adjust the redox state of the glass to $(\text{Fe}^{2+}/\text{Fe}^{3+}) = 0.16$ was found to be 0.25 wt%. The effects of limited composition changes on glass properties were also investigated.
A laboratory study was conducted to determine the solubility of sulfate in borosilicate HW39 glass (NCAW-CRW feed) as a function of glass redox state. Ferrous/ferric ratios were varied, by adding sugar to the batch, in the HW39 glasses produced from two simulated HWVP melter feeds with 0.5 and 1.0 oxide wt% sulfate. The SO$_{3}$ solubility changed little when the ferrous/ferric was less than 0.3; however, the solubility decreased strongly when the ferrous/ferric ratio was above 0.3. The solubility limit of SO$_{3}$ in HW39 glass was approximately 0.9 oxide wt% SO$_{3}$ in the recommended melter operating range of 0.001 to 0.3. To allow for process fluctuations, a concentration limit of 0.5 oxide wt% was recommended.

A laboratory study was conducted to determine the effects of Cr$_2$O$_3$ concentration (0.0 to 2.0 wt%) in HW39 glass on the following glass properties: viscosity, electrical conductivity, crystallinity, and chemical durability. The viscosity increased slightly with Cr$_2$O$_3$ concentration, and the viscosities were stable at all concentrations except 2 wt%, where at 950°C the viscosity increased slowly. The electrical conductivity did not change significantly with Cr$_2$O$_3$ concentration except at less than 0.5 wt% where the electrical conductivity increased significantly. No crystalline material was found in the glass with 0 wt% Cr$_2$O$_3$, but the amount of crystalline material (spinel) increased from 1 to 5 wt% as the Cr$_2$O$_3$ content was increased from 0.5 to 2.0 wt%; at 0.5 wt% Cr$_2$O$_3$, sesquioxide (Fe,Cr)$_2$O$_3$ crystals were also present. Using the MCC-1 28-day leaching test, no effects of Cr$_2$O$_3$ concentration were seen on glass durability. Increased crystalline content could cause melter processing problems.

Laboratory studies were performed to develop glass formulations that incorporate Hanford waste for processing in liquid-fed ceramic melters. An evaluation of waste streams and waste stream blends with regard to glass development is provided. The neutralized current acid waste (NCAW) 12% Pu waste stream was chosen to start glass development. The presence of crystals in borosilicate glasses may cause the glass viscosities to change with time. Two types of crystals are observed in borosilicate...
glasses and in some calcium silicate glasses: opaque cubic crystals (thought to be chromite spinel) and red hexagonal platelets (thought to be a solid solution of chrome oxide and hematite). The amount of crystals in glass is related to the amount of Cr in the glass. The solubility of Cr$_2$O$_3$ in borosilicate glasses tested is between 0.25 wt% and 0.5 wt%. The waste loading in the glass can be reduced to reduce crystallinity. The formation of crystals and the stability of viscosities are affected by the thermal history of the melt. If the maximum temperature is maintained to be less than 1200°C, the viscosities of the borosilicate glasses made with NCAW 12% Pu waste will be stable. From a glass formulation standpoint, it should be possible for the NCAW wastes and the CRW waste to be combined.


Laboratory studies were conducted to characterize the solubility of sulphur in simulated nuclear waste glass and to evaluate the potential for sulfate layer formation. West Valley glass formulation WV182 was used for the study. Sulfur is soluble up to 1 wt% as SO$_3$ in the glass (4 wt% in the waste at 25 wt% waste loading, oxide basis) under oxidizing conditions. Sulfate in excess of these values under oxidizing conditions will lead to the buildup of a sulfate layer. At the glass redox level recommended to control foaming, about 0.75 wt% SO$_3$ is expected to be soluble in the glass. Reducing agents are required to achieve this oxidation state. Under these conditions, the excess sulfate is expected to react with the carbon, volatilize, and be transported to the off-gas system. A sulfate layer is not expected to form. From the laboratory data, sulfate concentrations in the waste should be limited to less than 4 wt% SO$_3$.


A study was performed to identify the cause(s) of melt foaming and to propose approaches to minimize the impact of foaming upon continuous melter operation, and a laboratory test was developed to evaluate foaming behavior. Foaming is caused by the release of water vapor and oxygen from the melt. The processes of hydration and oxidation during melting may be related. The oxygen release is attributed to redox reactions involving species other than iron in the highly oxidized PNL glasses. The laboratory foaming tendency test can distinguish between the contributing factors of the total gas content and foam stability. The results indicate a strong correlation between glass oxidation state and foaming tendency. Foaming tendency increases with greater dissolved gas contents and more stable foams, and visa versa. Oxidized glasses have stable foams due to the preponderance of oxygen released. Reduced glasses have unstable foams attributed to a greater portion of water vapor in the gas mixture released. Reduced glasses are made by significant carbon additions to the feed.
Fiscal Year 1983


Laboratory tests were performed to determine the causes of the glass melt foaming that occurs during operation of the liquid-fed ceramic melter. Results of a new laboratory technique to measure foaming tendency were successfully correlated with observations of foaming from the Pilot-Scale Ceramic Melter runs with HWVP and West Valley (WV) glasses, and from earlier runs with Savannah River (SR) compositions. SR glasses made from liquid feed and WV glasses made from calcined feed show the least tendency to foam in the laboratory testing. Little or no foaming was observed in their melter runs. The foam was less stable in the laboratory tests of the SR glasses, possibly because of lower glass viscosity. The HWVP and WV glasses from melter tests experiencing foaming showed a considerably greater tendency to foam in laboratory tests. Analytical results suggest that redox reactions involving iron, cerium, and chromium do not have a major role in generating foam. Oxygen was the dominant gas in the glass foam collected from the melter. The cause for foaming tendency was not identified, and additional effort to identify foaming mechanisms and to accommodate foaming in the melter was recommended.
6.0 Feed Preparation

Fiscal Year 1995


No annotation


The procedure provides rheological measurements that are more reliable and accurate than those described in the technical procedure PNL-(WTC-006-4). Methods are provided to measure the sweep rheogram and steady shear viscosity with concentric cylinders, to measure the yield stress directly with a shear vane, and to measure the sweep rheogram with parallel plates. The procedure provides methods for rheological characterization of slurries that have Newtonian and non-Newtonian flow behavior. The rheological properties measured include Taylor vortices effect, wall slip effect, yield stress, plastic viscosity, apparent viscosity, thixotropy/rheopexy, and steady shear viscosity. The procedure uses a Haake viscometer with MV-type, FL-type, and Q-type sensors.


The HLW simulant feed specification for the waste blend composition (based on normalized track radionuclide components, historical tank data, and assumptions on the pretreatment of the waste) provides direction for preparing laboratory-scale and large-scale HLW blend simulant to be used in melter feed preparation studies and melter testing. The simulant is intended to be a chemical and physical simulant of the HLW feed to the vitrification plant.


No annotation
A laboratory study was conducted to determine the potential for an uncontrollable exothermic reaction between nitrate and organic salts while preparing a high-level waste melter feed. The thermal behavior of simulated neutralized current acid waste (NCAW) with formic acid, glycolic acid, or oxalic acid addition was characterized by differential scanning calorimetry (DSC) measurements on the simulants and their supernatants. For comparison, samples of simulant and simulant with noble metals and no organic acid additions were tested. Simulant without organic acid addition, both with and without noble metals, showed no exothermic behavior. All of the simulants with organic acid addition showed exothermic behavior. Onset temperatures of exothermic reactions were 122°C to 209°C. Many onset temperatures, particularly those with formic acid addition, are well below 181°C, the maximum estimated steam coil temperature (considered to be a "worst case" maximum temperature for chemical process tank contents). The enthalpies of the reactions were -181 J/g for the oxalic acid-treated simulant supernatant to -1153 J/g for the formic acid-treated simulant supernatant.

Melter feed preparation testing was conducted during the SSHTM testing to evaluate the use of an alternative organic acid, glycolic acid, in place of formic acid as a melter feed reductant and to reduce melter feed viscous properties at high solids content (Alternate Flowsheet 2). Testing also evaluated use of no organic reductant addition but addition of nitric acid to reduce melter feed viscous properties (Alternate Flowsheet 1). These flowsheet alternatives were developed to mitigate safety hazards that evolve with the use of formic acid. Formic acid generated H₂ and NH₃ during the melter feed makeup step. The following off-gas and slurry chemistry observations were made during the melter feed makeup step. There is a direct correlation between laboratory- and small-scale tests in regard to scaling results. Total off-gas production and peak generation rates were within a factor of two on a per-volume basis for the laboratory- and small-scale systems. No H₂ generation was observed during Alternate Flowsheet 1 tests conducted at either laboratory- or small-scale. H₂ production did appear at
both scales during Alternate Flowsheet 2 processing of non-noble metals-bearing simulants in similar per-volume quantities (about 1% of amount using formic acid in noble metal-bearing simulant). Ammonia was not observed as a reaction product. The residual amounts of nitrate and nitrite essentially paralleled each other on both scales after reaction. Similar amounts of organic carbon were found on a per-volume basis at both scales, indicating that little glycolate had reacted in the glycolic acid-prepared feed. Condensates from both scale tests were similar, containing mainly nitrate, with the small-scale condensate being a little more acidic. Flowsheet comparison indicates more nitrate is destroyed during melter feed preparation with glycolic acid for the equivalent amount of acid added. The concentrations of the melter feeds were limited by poor mixing characteristics in their vessels and exhibited non-newtonian flow characteristics (approximately Bingham plastic). The feed with glycolic acid addition could be concentrated to a higher solids content for equivalent rheological properties, and the glycolic acid feed tended to gel on aging without agitation. For small-scale testing, the melter feeds were concentrated to about 354-g TO/L and 422-g TO/L for Alternate Flowsheets 1 and 2, respectively.


[See reference preceding this one: Smith, GL, et al. February 1995. "Small-Scale High Temperature Melter - 1 (SSHTM-1) Data Package," PVTD-C95-02.02Y, Rev. 0, Pacific Northwest Laboratory, Richland, Washington.] The following additional observations were made based on data analyses. No correlation was found between the reducing potential of the feed and the oxidation state of the bottom drain glass. There was segregation of sulfate in the melting zone. There was petrographic evidence for melting reaction pathway differences between the glycolic acid- and the nitric acid-based feeds; the "glycolic" melter feed exhibited an earlier and more uniform incorporation of silica sand into the glass melt and faster formation of intermediate phases. Melter off-gas results indicate melting reaction path differences between the different feeds and confirm laboratory results. Hydrogen and ammonia are reduced during melter processing. Off-gas peak activity occurred near the same temperature regimes corresponding to the exotherms and endotherms found from thermal analyses results; weight loss due to denitrification occurs earlier for the "glycolic" melter feed compared to the "nitric" and "nitric+boric" melter feeds, indicating different reaction paths.


A laboratory study was conducted to dry and calcine DST/SST HLW simulant for assessing the process chemistry and stream properties with and without glass formers. Drying and calcination are being considered as a unit operation to increase the vitrification processing rate by minimizing the water evaporation process in the melter. Ferrocyanide breaks down to NH₃ plus formate during low-temperature calcining and does not display redox reactivity with nitrite or nitrate. Sugar displays reactivity with nitrite and nitrate. Boiling occurs below 120°C, the slurry becomes very viscous at 6.3
about 45 wt% solids, and water generation ceases at 350°C to 400°C. There was an exothermic reaction that was activated at about 250°C. Sodium sulfate with a small amount of potassium chromate separated from the glass melt during the quartz crucible melting tests.


A literature search was performed which described some past experiences on drying and calcination of radioactive materials or corresponding simulants and the information needed from testing. Also, an assessment of informational needs, including possible impacts to a full-scale plant, was included. (This search was instigated by the desire to significantly increase the waste vitrification capacity with minimal plant cost and operational impact.) The systems assessed included the spray calciner, fluid bed calciner, plasma calciner, wiped film evaporator, and rotary calciner. It was concluded that the rotary calciner, wiped film evaporator, fluid bed calciner, and spray calciner show promise for enhancing cost-effective production of large quantities of glass, but additional testing with Hanford waste and engineering evaluations is required.


Eleven laboratory tests were performed to assess the effects on off-gas composition and generation rate and slurry chemistry from modifying the feed preparation flowsheet to use reductants other than formic acid. The flowsheets evaluated included use of citric acid, glycolic acid, lactic acid, or oxalic acid to replace formic acid as a reductant and slurry rheology modifier, and the use of nitric acid without organic addition to modify slurry rheology. Very low to nondetectable generation rates of NH₃ and H₂ were observed when processing simulated nonradioactive, pretreated, neutralized current acid waste with the alternate flowsheets. The glycolic acid-treated melter feed had acceptable rheological properties at a total oxide loading of 400, while the nitric acid feed could not be concentrated above 380 and still display acceptable rheology. Oxalic acid-treated feed could be concentrated only to 280. Oxalic acid was eliminated from further testing, and a nitric acid-processed and a glycolic acid-processed feed were recommended for small-scale, high-temperature melter tests.


Fiscal Year 1994


A laboratory study was performed to evaluate oxalic, glycolic, malonic, pyruvic, lactic, levulinic, and citric acids as well as glycine as possible substitutes for formic acid (used for melt redox and slurry rheology adjustment) in the preparation of feed for Hanford Waste Vitrification Plant vitrification. Testing was conducted using a non-radioactive feed simulant UGA-12M1 slurry containing substantial amounts of aluminum and iron oxide as well as nitrate and nitrite at 90°C in the presence of hydrated rhodium trichloride. Unlike formic acid, none of the carboxylic acids liberate hydrogen under the test conditions, and only malonic and citric acids form ammonia. Glyoxylic, glycolic, malonic, pyruvic, lactic, levulinic, and citric acids all appear to have significant reducing properties under the reaction conditions of interest, as indicated by the observation of appreciable amounts of N₂O as a reduction product of nitrite or, less likely, nitrate at 90°C. Glyoxylic, pyruvic, and malonic acids all appear to be unstable toward decarboxylation at 90°C in the presence of Al(OH)₃. Among the carboxylic acid investigated in this study, the alpha-hydroxy-carboxylic acids, glycolic and lactic acids, appear to be the most interesting substitutes for formic acids in the feed preparation for the vitrification plant because of their failure to produce hydrogen or ammonia or undergo decarboxylation under the reaction conditions, although they exhibit some reducing properties in feed simulant experiments.


Laboratory studies were performed to understand the noble metal catalyzed formic acid reduction of nitrite and/or nitrate to ammonia, which is a plant hazard and would occur during melter feed preparation using the reference HWVP flowsheet. For ammonia generation from formic acid treatment of NCAW feed simulants, the predominant process appears to be heterogeneous catalysis involving rhodium or palladium metal catalysts. Nitrate rather than nitrite appears to be the major nitrogen source for ammonia production, as shown by experiments in which either nitrate or nitrite is added to a special nitrogen-free feed simulant. The following observations indicate the close similarity between noble metal-catalyzed formic acid reduction of nitrate to ammonia and organic hydrogenation processes. Supported noble metal catalysts, namely supported rhodium and palladium catalysts, are the same as those which are most active for organic hydrogenations under the mildest conditions. Ammonia production from the noble metal-catalyzed formic acid reduction of nitrate appears to occur at the expense of hydrogen production. In some of the experiments with supported palladium catalysts, some of the initially produced H₂ in the closed system is consumed as ammonia is produced. Formic acid is known to be a transfer hydrogenation reagent for conversion of nitro compounds to amines in the presence of noble metal catalysts. Palladium on charcoal is very active. Further work was recommended to increase understanding of the reaction chemistry of formic acid with nuclear wastes.
A literature survey (nonexhaustive) reviewed studies of 1) nuclear waste glass foaming and the effects of reducing agents, particularly formic acid, on foaming, and 2) the redox chemistry of many potential oxidizing and reducing species in or added to the glass-melter feed. The objective was to collect information useful for predicting some of the chemistry that occurs in the cold cap and the glass melt as it might affect the foaming phenomenon. Little is known about the causes of foaming in the nuclear waste glass melters, or of the best remedies to prevent foaming. There is significant evidence based on run experience that, in the absence of added reductants, acidic feeds do not foam nearly as much as alkaline feeds. There are many questions about whether the varying degrees of melter foaming are caused by different extents of decomposition of higher oxidation state metal oxides releasing $O_2$, and whether the foaming can be best controlled by adding reductants. Formic acid has been the most widely recommended reductant to control nuclear waste glass foaming. However, formic acid appears to be inefficient and unpredictable as a reductant in the cold cap.

A laboratory investigation was conducted to evaluate the effect of oxidants such as nitric acid and reductants such as sugar and formic acid on the cold cap behavior in the vitrification of simulated neutralized current acid waste (NCAW). The investigation included the measurement of iron oxidation state, the reaction sequence during glass melting, and laboratory batch expansion measurements of the melter feed. Offgas measurements of the formic acid-containing melter feed...
showed that formic acid/formate decomposed at temperatures too low for participation in a glass redox reaction. Sugar pyrolyzed and produced CO and H₂ at temperatures exceeding 665°C and produced a Fe²⁺/Total Fe of 0.79. The measured iron redox ratios of the glasses made from untreated waste (no reductant additions), formic acid-, and nitric acid-containing wastes were essentially indistinguishable. It was concluded that formic acid would be less than 100% efficient as a reductant in large-scale vitrification. Volume expansion measurements showed volume expansions of 7 for sugar containing sample below 200°C, about 6.5 for formic acid feed, about 1.5 for nitric acid-containing feed, and about 2.5 for untreated feed in the 720°C to 890°C range.


Laboratory-scale tests were performed at various noble metals concentrations in the Neutralized Current Acid Waste (NCAW) simulant to determine the effects of noble metals (Pd, Rh, and Ru) on HWVP feed preparation offgas generation and NH₃ production. Offgas profiles exhibited three reaction stages: stage I, CO₂ decomposition; stage II, NO₃⁻ destruction; and stage III, H₂ and NH₃ formation. Hydrogen is formed in reaction stage III as a product of noble metals-catalyzed HCOOH decomposition. The peak H₂ generation rate and total H₂ measured increased with noble metal concentration until a maximum level was reached at 25% to 50% nominal noble metals concentration. The maximum derivative of the H₂ generation rate showed an almost linear increase as a function of noble metals concentration. A test performed with only 25% Rh showed significantly different behavior than the 25% nominal noble metals test, leading to the conclusion that the other noble metals (Pd and Ru) contributed catalytic activity to H₂ production. Ammonia was formed during stage III as a product of the reaction HCOOH and NO₃⁻, and the amount appeared to increase with noble metals concentration. As the total H₂ increased with noble metals concentration, the NH₃ increased. Noble metals appeared to have been reduced to metals during the tests, which may enhance NH₃ production.
Carbon dioxide was formed in stage I primarily by carbonate decomposition when formic acid is added, which is not affected by noble metals concentration. Carbon dioxide was formed in stage II primarily by reactions of HNO$_2$ with HCOOH. The peak CO$_2$ generation rate increased with noble metals concentration, and noble metals concentration did not appear to significantly affect the total CO$_2$ generation in stage II. Carbon dioxide was formed primarily from HCOOH decomposition and as a product of the NH$_3$ formation reaction in stage III. The peak generation did not vary significantly during stage III, but the amount of CO$_2$ increased linearly with noble metals concentration. The NO$_x$ is formed in stage II by disproportionation and destruction of HNO$_2$. The peak NO$_x$ generation rate increased slightly with noble metals concentration, but the changes in total amount as a function of noble metals concentration were not significant enough to derive a correlation. The N$_2$O was produced by NO$_2$ reduction by HCOOH in stage II. The N$_2$O peak generation rate and the amount of N$_2$O increased as a function of noble metals concentration.


The noble metals Pd, Rh, and Ru that are present in the Hanford high-level waste will be processed into a melter feed for vitrification and permanent disposal. The treatment of waste slurry with HCOOH, a step in producing a melter feed, results in the production of H$_2$ and NH$_3$ due to the catalytic activity of the noble metals. The presence of H$_2$ and NH$_3$ could lead to hazardous conditions in a treatment facility. This study determined the relationship between noble metals concentration and H$_2$ and NH$_3$ production for application in future pilot-scale studies and prediction of catalytic activity for a waste with known noble metals concentration. Hydrogen production increased as noble metals concentration increased until a saturation level was reached. Ammonia production increased with noble metal concentration. Due to the limited number of tests, these relationships require confirmation.


Laboratory tests were conducted to investigate the effects of selected HWVP feed preparation process parameters on gas generation, foaming, and NCAW simulant feed chemistry. The test parameters were acid neutralization capacity, process temperature, NO\textsubscript{2} concentration, HCOOH addition rate, and additions of a processed slurry (heel) and a second organic phase. Adding NaOH to the initial NCAW simulant delayed the onset of gas generation proportional to the amount of time required to add a stoichiometric amount of HCOOH to neutralize the added base. In the absence of NO\textsubscript{2}, nitrite destruction was not observed and a reduced amount (about 65%) of H\textsubscript{2} was generated after CO\textsubscript{2} destruction. Decreasing the HCOOH addition rate extended the duration of the offgas profile and decreased the offgas generation rate during HCOOH addition, which did not mitigate foaming. Residual formated slurry (heel) from a previous test that was mixed with untreated NCAW simulant had only a small effect on the offgas production during the feed preparation process steps. Lower processing temperature during HCOOH addition extended the duration of gas generation during processing. TRUEX solvent extraction organic phase added to the slurry before HCOOH addition was not degraded during the processing, but organic components did fractionate via steam distillation. Hydrogen generation began in significant quantities after the destruction of NO\textsubscript{2} was almost complete, and NH\textsubscript{3} was generated simultaneously in molar portions H\textsubscript{2}:NH\textsubscript{3} of about 1:1 to 3:1. Foaming was controlled in some of the tests with an antifoam agent and was observed to depend on pH, and was almost independent of offgas generation rate.

**Fiscal Year 1993**


A laboratory study was performed to determine the key feed components and process variables that enhance or inhibit the production of hydrogen during formating in melter feed preparation. The chemical reactions were characterized through the production and consumption of the key gaseous components such as H\textsubscript{2}, CO\textsubscript{2}, N\textsubscript{2}O, NO, and NH\textsubscript{3} by analyses. NCAW simulants containing the major nonradioactive components were used with individual noble metals (Ru, Rh, and/or Pt) in separate experiments in closed small-scale reactors to evaluate the effects of major simulant components such as NO\textsubscript{2}, NO\textsubscript{3}, Fe\textsuperscript{3+}, Al\textsuperscript{3+}, UO\textsubscript{2}\textsuperscript{2+}, and Cd\textsuperscript{2+} on their catalytic activities for formic acid decomposition. Rhodium introduced as soluble RhCl\textsubscript{3}.3H\textsubscript{2}O was found to be the most active catalyst for hydrogen generation from formic acid from above about 80°C in the presence of nitrite ion. The rate of this rhodium-catalyzed hydrogen production appears to be enhanced by the Fe and Al present in the feed simulants, and the rhodium appears to be a homogeneous catalyst. The nitrite-promoted rhodium-catalyzed decomposition of formic acid occurs only after the formic acid has reacted with all of the carbonate and nitrite present to form CO\textsubscript{2} and NO/N\textsubscript{2}O, respectively. The catalytic activities of
ruthenium and palladium toward hydrogen generation from formic acid are quite different than those of rhodium in that they are inhibited rather than promoted by the presence of nitrite ion. Palladium is also an active catalyst for the reduction of nitrate and NO to N₂O in feed simulant media. Within 10%, all of the nitrite nitrogen in the slurry was accounted for by reactions leading to NO and N₂O.


A literature review was performed of studies addressing rheological properties of simulated process slurries conducted at SRL for DWPF and at PNL for HWVP to summarize existing data applicable to HWVP design. It was determined that existing data provided important information on the effects of feed variability, solids loading, temperature, formating, pH, and scale-up. However, the data could not serve as a basis for fundamental slurry transport calculations because they are not reported in sufficient detail over a range of shear rates and in appropriate terms to be sufficient for transport calculations.


A laboratory study was conducted to compare the rheological properties of melter feed made from simulated NCAW, recycle, and one of three frits (202, HW-39, or FY 91). The rheology was examined over a 4-week period at 50°C and the pH was monitored. Process testing variables included boiling time, concentration, aging time, noble metals, and pH adjustment. Rheology, particle size, x-ray diffraction, wt% solids, chemical analysis, and acoustophoresis were measured. It was observed that large- and laboratory-scale rheology data did not produce similar yield stress increases with aging. FY 91 frit leaches more readily than HW 39 and 202 frits. The effect of aging on the rheology of melter feed suspensions was not significant; however, aging was correlated with pH changes and frit leaching. Boiling time did not significantly affect the rheology of the melter feed. Increased solids loading caused yield stress increases, while reducing the solids loading by dilution did not show any hysteresis in yield stress. Therefore, dilution is a method to control rheology. Noble metals content did not affect the 202 and FY 91 melter feed rheology. The rheology of pH <5 was not significantly different for the 202 and FY 91 frits; however, the FY 91 frit consumed an order of magnitude more nitric acid to maintain the specified pH.


No annotation


No annotation


An analysis was performed on the data generated from 18 different tests conducted at various process scales at the Pacific Northwest Laboratory to compare, on a normalized bases, offgas data, slurry chemistry data, and test system characteristics on Neutralized Current Acid Waste (NCAW) feed preparation. The peak total offgas generation rate correlated reasonably well with the formic acid addition rate, with an upper bound on the generation rate of approximately 0.4 (moles/min)/(liter acid added/h). Total offgas generation increased in proportion to the amount of formic acid added, initial carbonate concentration, and initial nitrite concentration, with an upper bound of approximately 0.4 moles total offgas/(moles acid + moles carbonate + moles nitrite), but with considerable data scatter. Data correlations can be used to predict peak offgas generation rates of CO₂, NO₃, and H₂ based on initial chemistry and formic acid addition rate. The peak N₂O generation rate increased with the acid addition rate; the initial nitrite, carbonate, and hydroxide concentrations; and the amount of noble metals. Total N₂O was not successfully correlated with test conditions. Total H₂ offgas generation increased above a threshold point with the amount of formic acid available toward the end of nitrite destruction, i.e., formic acid - 2 x carbonate - nitrite - hydroxide. The peak H₂ generation rate was consistently proportional to the total H₂ observed. The total NH₃ generated correlated somewhat with total H₂ and increased in proportion with H₂. Small-scale tests can be reliably used to predict peak offgas generation rates and total offgas for CO₂, NO₃, N₂O, and H₂, particularly when test conditions are similar. Data on glass redox, Fe²⁺/Fe³⁺, were correlated with the molar ratio ([HCOOH] + [NO₂])/([NO₃]), which was consistent with an earlier correlation for slurries that did not contain nitrite.
Laboratory tests were conducted using pretreated neutralized current acid waste (NCAW) base case simulant to investigate the following HWVP process steps: HCOOH addition, digestion, recycle waste stream addition, and slurry concentration. The test variables were the amount of HCOOH added, HCOOH addition rate, NO; and NO; concentration, duration of digestion period, noble metals content (with and without noble metals), and processing interrupts during H₂ release. Chemical reactions which partially account for slurry preparation chemistry related to offgas generation and reductant requirements are proposed and include HCOOH, NO; NO; and CO₂ as primary reactants, and noble metals as a reaction catalyst to produce CO₂, NO, NO₂, N₂O, H₂, H₂O, and NH₄⁺.

Significant H₂ generation was observed only in the presence of noble metals and after a threshold molar ratio for HCOOH/NO; was reached. Maximum H₂ generation rates ranged from 0.31 to 1.12 mmole/min from a slurry volume of approximately 1.5 L at 125 g WO/L (waste oxide/liter). Ammonia generation increased with increasing H₂ generation, simulant NO; concentration, and process time. The maximum amount of NH₄⁺ observed was 0.197 moles NH₄⁺/1.5 L at 125 g WO/L slurry. The volume ratio of N₂O/NO; decreased by a factor of 100 in the absence of noble metals. The glass oxidation state was obtained within acceptable limits, Fe²⁺/ Total Fe = 0.005 to 0.23 (measured 0.01 to 0.1), by balancing the major reductant (HCOOH) addition and oxidant (NO; ) loading. The minimum HCOOH addition was equivalent to a HCOOH/NO; molar ratio of 2.2 (using 27 ml of 87 wt% HCOOH/L at 125 g WO/L slurry at the FY 1991 pretreated NCAW base case composition). Thermal analyses of dried slurry simulant samples showed a lower-than-expected initiation temperature (124°C) for an exothermic reaction in formated Slurry Receipt and Adjustment Tank (SRAT) slurry to produce a maximum energy release of -354 J/g dried formated simulant. No sharp exotherm was observed.

Fiscal Year 1992

Fiscal Year 1991


No annotation

Fiscal Year 1990

Wiemers, KD. June 1990. "The Effect of HWVP Feed Nitrate and Carbonate Content on Glass Redox Adjustment," HWVP-90-1.2.2.03.03A, Pacific Northwest Laboratory, Richland, Washington.

Laboratory tests were conducted to evaluate the effect of nitrate and carbonate concentrations in a pretreated neutralized current acid waste (NCAW) feed simulant on the amount of formic acid required in HWVP to obtain an acceptable glass redox state in the melter. Results suggest that formic acid requirements are more accurately prescribed by the stoichiometry of redox reactions rather than neutralization reactions. The primary redox participants were nitrate, ferric ion, and formic acid. An acceptable glass redox (Fe$^{3+}$/Fe$^{2+}$) was observed when HCOOH/NO$_3^-$ = 3. Ammonia as a formating reaction product was qualitatively detected. The threshold requirement, HCOOH/NO$_3^-$ = 3, was independent of the simulant carbonate content. Data assessment suggests that the step in which nitrate reduction occurs (forming or vitrification) may be dependent on pH (i.e., carbonate content) of the feed. No apparent trends related to nitrate or carbonate concentration were observed for the physical properties of the feed (increased nitrate reduction with increased final acidity). Data suggested that 25-50% of the chromium, manganese, and molybdenum are reduced during formating.

Fiscal Year 1988


The methodology and results of a study to collect four formic acid vapor/liquid data points (two solution concentrations each equilibrated at two temperatures) are reported and provide a basis for evaluating an empirically derived relationship between formic acid solution and vapor phase concentrations as a function of temperature. The formic acid vapor phase concentrations at 50°C (122°F) and atmospheric pressure for 0.54 wt% and 0.99 wt% formic acid solutions were 66 and 267 ppmv, respectively. The formic acid vapor phase concentrations at 10°C (50°F) and atmospheric pressure for 0.54 wt% and 0.99 wt% formic acid solutions were 11 and 17 ppmv, respectively.
Fiscal Year 1987


A laboratory study was performed to examine the effect of feed composition and formic acid addition on the redox state (ferrous to ferric acceptable in glass was 0.005 to 0.3) of the feed. Physical and rheological properties of each feed were determined. The elimination of sugar as a feed redox modification agent was being evaluated. Formic acid was added to nine different waste compositions (variable Fe, Al, Na, and Zr) at three to five different concentrations. The formated feed samples were combined with glass frit and the resultant melter feed, at about 500 g WO/L, was subjected to physical, rheological, and redox state characterization. The redox state and rheology (acceptable yield stress below 86 dyne/cm²) of all compositions were acceptable after adding 25 to 30 mL of 90 wt% formic acid per liter of feed for each composition, and sugar would not be needed to further modify the HWVP waste. Redox state of HWVP glass is primarily controlled by its composition and the amount of reducing agent present in the feed. The near linear relationship between redox state and formic acid addition is not altered by the acid-base reaction between formic acid and some hydroxides that occurs during formic acid addition. The effect of composition on the glass redox state is believed to be related to the Gibbs free energy potential of each feed component, and the order in which components are reduced by formic acid. Higher ferrous-to-ferric ratios were achieved by increasing the zirconium or sodium concentration, or by decreasing the aluminum concentration in the feed. Feed composition is the primary variable that affects feed rheology, and increased iron composition in the feed will increase the yield stress and apparent viscosity of the feed. The effect of either pH or formic acid reaction on feed rheology is not as significant as the effect of iron.


No annotation


A laboratory study was performed to physically and rheologically characterize HWVP feed simulant, NCAW '86 (HWS9), before and after formating at various concentrations, and to compare these results with data generated for the previous simulation (HWS7). That simulation was prepared based on the previous NCAW composition known as HWVP reference feed. It was concluded that the NCAW '86 composition has lower rheological properties than, and very similar physical properties to, simulants based on the previous NCAW reference composition. The change in NCAW composition resulted in reduced apparent viscosity and yield stress values for all concentrations of both unformated and formated HWVP feed simulants (perhaps due to lower ferric hydroxide concentration in NCAW '86). The previous data base would be conservative for a design basis. Treatment with formic acid to a pH
of 4 benefited the rheology of the NCAW reference composition more than that of the NCAW '86 simulants. Heat treatment of the formated simulated NCAW '86 slurry for the reference two-hour period had no significant effect on rheological or physical properties. NCAW '86 simulants contained a higher ratio of dissolved solids to total solids than simulations of HWVP reference feed. A greater increase in the ratio of total solids to total oxides occurred upon formic acid treatment of NCAW '86 simulants than with HWVP reference feed simulants.


Laboratory tests were performed to characterize the gases released during the feed formating process and relate these data to the solution kinetics. An additional objective was to develop a simulant which would more adequately represent, chemically and physically, the neutralized current acid waste (NCAW). Carbon dioxide, nitrous oxide, nitrogen oxides, and hydrogen gases were released from the feed slurry during the formating process, producing maximum detected gas concentrations of 85 mole% CO₂, 1.4 mole% N₂O, 0.02 mole% NO, and 0.62 mole% H₂. Maximum gas releases were observed in the feed pH range of 5 to 7. Gas release continued during the post-heat treatment period. Formic acid is not detectable in the off-gas downstream from the condenser, which is operated at 15°C. The amount of CO₂ and H₂ released is dependent upon both the amount of formic acid added and the rate at which it was added. Insufficient agitation resulted in foaming and sudden gas releases. A new procedure involving neutralization and washing steps was used to prepare the simulated feed. The feed made using the new procedure had significantly higher yield stress and apparent viscosity than the feed made from hydroxides by a factor of 7 and 4, respectively.

Fiscal Year 1986


Laboratory studies were performed to evaluate the effects of concentration and boiling on HWVP process slurries properties and the effects of HWVP feed simulant preparation methods on simulant properties. Formic acid treatment of the reference HWVP feed acceptably reduces apparent viscosity and yield stress such that further concentration of concentrated and formated feed after frit slurry addition can be eliminated. Boiling or the lack thereof had little effect on the yield stresses and apparent viscosities of melter feeds prepared at concentrations of 550 g TO/L or less. However, boiling melter feeds that were concentrated to 600 g TO/L reduce apparent viscosity, increase the yield stress, and produce dilatant behavior. HWVP feed simulations were made up by two separate methods: 1) a blend of dry chemicals and a concentrated iron hydroxide slurry, and 2) a nitric acid solution of all the desired elements by sugar denitration, neutralization, digestion, settling, decanting and washing. There were significant physical and chemical differences between the two simulations. The melter feeds made up from the two different simulants were characterized. Yield stress and
apparent viscosity did not appear to be a function of the concentrating process. However, the presence of dilatant properties in a slurry appeared to depend on the concentrating process.


Single-variable laboratory scoping studies were performed to investigate the effects of formic acid treatment on waste slurry rheologies, boiling on melter feed rheologies, and procedures used by PNL to prepare the simulated HWVP feed. Multivariate tests were conducted to investigate the effects of various feed processing parameters on the rheological properties of the reference simulated HWVP feed, determine if engineering-scale (as opposed to laboratory-scale) methods of feed preparation influence the rheological properties, and compare the rheological properties of feeds produced by the current PNL method to those obtained for a simulated feed generated by a more rigorous method. Formic acid addition to the waste slurry significantly reduced the yield stress and apparent viscosity for two different feed concentrations when 1 and 1.5 times the calculated stoichiometric amount of formic acid was added. No significant differences in rheological properties were observed between boiled and unboiled melter feeds below a melter feed concentration of 500 g total oxides/liter (g TO/L). A dilute simulated waste slurry of 19 g waste oxides/liter (g WO/L) was prepared and then concentrated before treating with formic acid and mixing with glass frit; the rheological properties of this slurry after addition of the frit were in good agreement with the previous data obtained by batching the waste components to an initial concentration of 140 g WO/L, then treating the waste slurry with formic acid and adding the necessary frit. The concentration of waste slurry at the time of formic acid treatment, the amount of formic acid added as a function of pH, and the degree of agitator shear encountered during processing significantly affect the slurry rheological properties. The aging of unagitated melter feed did not significantly change the rheological properties. The scale of experimental performance did not significantly affect rheological properties. There were significant differences in waste slurry physical and rheological properties related to the makeup method (chemical combination including hydroxides versus procedure more representative of slurry history).


No annotation

Fiscal Year 1985

Laboratory testing was performed to determine whether the DWPF feed preparation process resulted in a HWVP melter feed for HW39 glass with satisfactory rheological properties at concentrations exceeding 400 g TOL and the maximum concentration of HWVP melter feed that would exhibit acceptable rheological properties, and that can be achieved by controlling the formic acid addition level and the frit size used. It was determined that melter feed cannot be prepared that concurrently satisfies the requirements of being prepared using the DWPF flowsheet, having the specified DWPF equipment rheological property requirements, and having a concentration of 400 g TOL. HWVP melter feed can be prepared using the DWPF process at concentrations of 500 to 550 g TOL and meet DWPF melter feed rheological requirements. Melter feeds prepared at 400 and 500 g TOL concentrations do not meet the minimum DWPF requirements for yield stress, apparent viscosity (consistency), and concentration in terms of wt% solids. The HWVP melter feeds cannot be prepared at concentrations of 600 g TOL or greater using the frit sizes and amounts of formic acid studied and meet the DWPF rheological requirements. However, the HWVP melter feed can be prepared at 600 g TOL which meets all rheological requirements, except the apparent viscosity would be >49 cP but >70 cP. The yield stress is affected by significant interactions between the amount of formic acid used, and by both the concentration and frit size. There is significant linear effect upon the apparent viscosity due to frit size; the coarser the frit size, the lower the viscosity. The apparent viscosity is affected by significant interaction between concentration and the amount of formic acid added; viscosity generally increases with concentration and decreases with formic acid addition. The density generally increases linearly with an increase in concentration. The pH values are higher when the finer frits are used and lower when higher amounts of formic acid are used at 550 g TOL where the concentration was obtained by boiling. There is no significant difference between pH values for different frit sizes at a lower concentration that did not require boiling. At 550 g TOL, there are significantly more dissolved solids at higher formic acid concentrations. HWVP melter feeds that were prepared at 750 g TOL with 0.276 g HCOOH/g WO and -200 mesh frit have dilatant fluid behavior which is very much a function of shear history.


Screening laboratory tests were performed to develop a representative simulation of the reference HWVP melter feed from NCAW/NCRW simulant, evaluate the effects of processing simulated HWVP reference feed with the DWPF flowsheet, recommend two melter feed formulations to be tested in the high-bay ceramic melter, and identify critical melter feed rheological properties. The rheology of the melter feed was improved to the extent that the feed could be processed at concentrations of 400 g TOL, but the desired reducing effect in the melt could not be realized without the addition of sugar to the melter feed. Testing was conducted to determine the best form in which to add glass-forming chemicals to obtain improved rheological properties and the desired reduced state in the melt. For the high-bay melter run, it was recommended that one melter feed contain the glass-forming chemicals as frit and another feed contain glass-forming chemicals as 1/3 frit and 2/3 unreacted glass-forming chemicals. The chemicals included a blend of formate and nitrate to obtain the desired melt redox state. Melter feeds prepared using the HWVP reference feed simulant and treated with formic acid were found to be yield-pseudoplastic non-Newtonian fluids.
Fiscal Year 1984


Laboratory studies were performed to use organic additives and alternative chemical and physical forms of glass formers in melter feeds to improve rheological properties such as inhibition of gel formation and forming settled sludges that are difficult to resuspend for Current Acid Wastes (CAW) and Neutralized Current Acid Wastes (NCAW). Melter feeds tested were all at 300 and 400 g TO/L. Properties measured included viscosity; vol% settled solids; settled solids firmness, flowability, and/or resuspension; and pumpability. CAW feeds made with colloidal silica had the best rheological properties with respect to settled solids and pumpability. Addition of an organic polymer (NP-10) as a suspending agent reduced solids settling and improved resuspension in feeds made from CAW. Melter feeds made from CAW were more rheologically acceptable than feeds made from NCAW. Settling resistance and pumpability of melter feeds made from NCAW and frit can be improved by adding xanthan gum as a thickening agent. Hydroxide feeds made with NCAW form firmer sediments than nitrate and carbonate feeds when left unagitated. Of all feeds made with NCAW, those made with unreacted nitrate glass formers have the most desirable rheological properties at higher concentrations. The use of colloidal silica with nitrate glass formers and NCAW increases the viscosity and improves settling resistance, but does not gel. The use of colloidal silica instead of ground silica does not improve the rheology of feeds made with hydroxide glass formers.


A laboratory study was performed to determine several physical and chemical properties of simulated potential HWVP feeds to the waste solidification unit. NCAW and NCAW plus glass formers were characterized at various concentrations. The properties determined were boiling point, viscosity, vol% settled solids, vol% centrifuged solids, wt% solids, slurry density, supernate density, settling rate, and free hydroxide in the slurry. The vol% settled solids, settling rate, and viscosity were measured at room temperature, 35°C, and 45°C; the remaining properties were measured at room temperature.
Technical and laboratory studies were performed to develop melter feed rheology alteration techniques to prevent solids that cannot be resuspended from settling. Three methods have been successfully employed in the laboratory to alter the sedimentation and flowability of melter feed slurries: polymer-induced bridging flocculation, manipulation of glass former (raw SiO₂ or frit) particle size, and alteration of nitric acid content. All three methods were proven successful in altering the rheology of the simulated Current Acid Waste (CAW) feed, which initially exhibited worst-case flow and sedimentation properties, but was transformed into a flowable, resuspendable melter feed. The applicability of polymer materials in a radioactive stream is not known.
7.0 Radioactive Feed Preparation and Glass Properties Testing

Fiscal Year 1995

Morrey, EV. July 1995. "Laboratory-Scale Testing of Series 2 Core Sample(s)," PVT-D-95-02.03B, Rev. 0, Draft Test Plan, Pacific Northwest Laboratory, Richland, Washington.

No annotation


The document describes the method used to guide the laboratory-scale testing of radioactive waste samples for high-level waste vitrification testing. A strategy is presented that seeks to minimize the number of radioactive sample tests required while still maintaining reasonable assurance that the simulant-based development testing is accurate. The maximum expected range of vitrification plant feed compositions was estimated based on an assumed farm-by-farm waste blending approach. The tanks from which the waste samples are needed were then determined by comparing the estimated tank compositions to the maximum range of plant feed compositions. It was recommended to take core samples from tanks B-109, S-107, C-104, A-103, C-106, C-107, AN-103, and BX-109 or from appropriate substitute tanks.


Laboratory-scale testing was performed on three radioactive water-washed core samples from tanks 101-AZ and 102-AZ containing neutralized current acid waste (NCAW). Properties of the radioactive waste measured during vitrification, including melter feed preparation, process, and product testing were compared to simulant properties and model predictions to confirm the validity of simulant and glass property model work. The major radionuclides in the core samples were Ce-137, Sr-90, Ce-144, and Ru-106. The majority of transuranic activity was americium and plutonium. None of the supernatant or wash solutions were transuranic, and Cs-137 was the primary radionuclide in the supernatant. The density of washed core sample solids and simulants ranged from 1.04 to 1.14 g/ml, which is similar to the formated slurries. The density of melter feeds increases significantly (1.28 to 1.47 g/ml) due to addition of frit. The melter feed had a waste loading of 25 to 28 wt% and was comprised primarily of frit, including Si, Na, B, and Li. The settling rate of the washed solids and the degree of solids compaction was much greater for the core sample solids. The settling behavior of the NCAW melter feed simulant was similar to that for the 101-AZ core sample melter feed. The majority particle size of the solids in the washed core samples was less than 5 microns in diameter with a
significant number less than 1 micron, and did not change significantly during processing. Actual formated waste and melter feeds exhibited lower yield stresses and apparent viscosities than the simulants due to differences in microstructure, and they could be characterized as yield pseudoplastic materials. Glass redox, \( \text{Fe}^{2+}/\text{Fe}^{3+} \), for actual waste glasses ranged between 0.026 to 0.085 compared to a simulant redox of 0.005, and no substantial crystallinity (likely <1%) was found in any samples as expected based on modeling and simulant experience. Radioactive glass density at room temperature ranged from 2.54 to 2.67 g/cc. Seven-day Product Consistency Test boron releases for the radioactive glasses ranged from 0.13 to 0.21 g/m² compared to simulant boron releases of 0.20 to 0.34 g/m². Model predictions were higher than measured for both the radioactive and simulant glasses.

**Fiscal Year 1993**


Laboratory HWVP feed preparation formating tests were conducted with a water-washed 102-AZ core sample and with nonradioactive simulants to validate the use of simulants for HWVP process development and compare the offgas generation characteristics. Results indicated that the slurry chemistry and offgas generation reactions were similar between the core sample and the simulants. Offgas generation rates and amounts were within 25% with the exception of \( \text{H}_2 \). Observed offgas (\( \text{H}_2 \), \( \text{NO}_x \), \( \text{N}_2 \text{O} \), \( \text{NO} \), \( \text{CO}_2 \), \( \text{CO} \), and \( \text{N}_2 \)) differences between the simulant and core sample could be explained by differences in testing conditions and slurry chemical composition with the exception of \( \text{H}_2 \) (reason for lower \( \text{H}_2 \) generation from radioactive sample not apparent). It was concluded that with the exception of \( \text{H}_2 \), simulants being used for process development are appropriate. Volatile organic analyses of the offgases were also made, in addition to many analyses made on the radioactive-formated slurry sample. Ammonia generation between the core sample and simulant was comparable based on amounts of \( \text{H}_2 \) generated (measured \( \text{NH}_3/\text{measured H}_2 \) were within 16%). Simulant tests performed with variable concentrations of noble metals showed a correlation between increasing concentrations of noble metals and increasing amounts of \( \text{H}_2 \) generation. Simulant tests performed with increasing amounts of carbonate showed a relative delay in \( \text{H}_2 \) initiation. The peak \( \text{H}_2 \) generation rate was observed to increase with a decrease of slurry pH at the time of \( \text{H}_2 \) initiation. A decrease in slurry pH at the time of \( \text{H}_2 \) initiation was observed for slurry with less carbonate. \( \text{N}_2 \text{O} \) generation was generally more and \( \text{NO}_x \) generation was generally less in simulants with more carbonate. Offgas generation profiles for the 80-ml laboratory simulant test were similar on a per-unit basis to the 1500-ml laboratory simulant test, indicating that scale-up may be possible.


No annotation
Morrey, EV. August 1994. "Laboratory-Scale Testing of Series 2 Core Sample(s)," PHTD-C93-03.08C Rev. 0 Draft (Test Plan), Pacific Northwest Laboratory, Richland, Washington.

No annotation


No annotation

**Fiscal Year 1992**


No annotation

**Fiscal Year 1991**


No annotation


No annotation

**Fiscal Year 1990**

Allen. CR to RA Smith. September 27, 1990. "NCAW Core Sample Status Deliverables: HWVP-90-1.2.2.05.04A, HWVP-90-1.2.2.05.04B, HWVP-1.2.2.05.07A, and HWVP-90-1.2.2.05.07B," Letter PNL-90-460, Pacific Northwest Laboratory, Richland, Washington. (Includes: Fiscal Year 1990 Status Vitrification and Characterization of Radioactive Core Samples, 101-AZ Core #1 and 101-AZ Core #2.)

No annotation
A process flowsheet and process flow diagram are provided for the nonradioactive bench-scale vitrification system. The flowsheet is based on the simulated feed used during the PSCM-23 experiment and assumes waste starts out at 2 wt% solids. (This flowsheet and system was to be the precursor for a similar radioactive system.)

The procurement packages include the melter, canister handling system, melter feed tank, concentrator feed makeup tank, submerged bed scrubber, high efficiency mist eliminator, high-efficiency particulate air filter assembly, slurry sampling system, and support structures. The major part of the procurement drawings are detailed vendor drawings.


No annotation

Fiscal Year 1989


No annotation


No annotation
A study was performed to identify technical and administrative issues that must be resolved and the activities that must be completed to prepare for shipment of NCAW from B-Plant to the 324 Building by rail in a bowling ball cask. The following are treated: identification of technical requirements at all facilities where work will take place, assessment of regulatory criteria concerning cask transport, and first generation schedule and budget. To be ready for shipment by the end of 1991, activities must begin in FY 1989. Total PNL staff requirements are 16.5 work months. Total WHC staff requirements are 16.5 work months. Total task cost is estimated to be $440K. It was anticipated that the NCAW could be shipped and handled without difficulty.
8.0 Full-Scale Feed Preparation Testing

Fiscal Year 1995


A full-scale testing program was conducted with water and nonradioactive waste simulants to develop information for process and equipment design of the feed preparation system. The equipment systems tested included the Slurry Receipt and Adjustment Tank, Slurry Mix Evaporator, and Melter Feed Tank. The areas of data generation and analyses included heat transfer (boiling, heating, and cooling), slurry mixing, slurry pumping and transport, slurry sampling, and process chemistry. The slurries tested exhibited non-Newtonian flow characteristics at high concentrations, and the melter feed tended to "thicken" and "gel" with time and without mixing. Slurry rheologic properties could be controlled by concentration, dilution, and nitric acid addition. High concentration melter feed decreased the tank coil heat transfer coefficient by a factor of 2 to 3. Tank coil heat transfer coefficients were generally similar to comparable equipment tested for the Defense Waste Processing Facility. Process slurries could be maintained homogeneous under all mixing conditions tested, i.e., agitator speed >45 rpm and slurry volume of 5700 to 7800 gal; the agitator speed was maintained at 130 rpm for the melter feed to prevent "gelling." Process slurry sampling was representative of tank contents. When the slurry level is below the tank coil top, the slurry may become non-homogeneous because of poor mixing. The tank condenser design was not adequate to handle high vapor flows, causing high entrainment and reduced heat transfer efficiency. For boiling conditions tested, the decontamination factors between the tank contents and the condensate were between 1000 and 1,000,000. The measured slurry pipe flow pressure drops were roughly about half of the calculated value that was not resolved. Twenty seconds of water flow was required to prime the cantilevered centrifugal transfer and sample pumps. Foaming did occur with slurry concentration, forming, and digestion, but it could be controlled by using an antifoaming agent or reducing heating. Negligible amounts of H₂ and NH₃ formed during forming, which was expected due to the absence of noble metals. The condenser cooled the condensate below 50°C during periods of high NOₓ generation, but at low condensate rate, the condensate temperature could increase significantly due to the condenser design configuration.

Fiscal Year 1994

Full-scale testing was performed to evaluate the process and equipment performance of the Recycle Waste Collection Tank (RWCT) using nonradioactive simulant slurry to provide the HWVP architect-engineer with related design information. The test objectives included determining slurry mixing performance, representative sampling of tank contents, transfer and sampling pumps priming requirements and pumping performance, simulant pipe flow characterization, and evaporation and condensing process performance. Testing was conducted with and without baffles. The testing was performed with dilute NCAW melter feed simulant (52 g TO/L) at slurry volumes between 3800 and 7800 gal without baffles and a RWCT simulant with baffles. For mixing performance, the following was determined. The presence of baffles was not found to make a significant difference in the mixing and flow patterns achieved in the tank. For process volumes below the top of the tank coils (<5000 gal), agitator speeds in excess of 85 rpm were required to obtain a steady solids concentration within the tank, and the solids concentration did not appear to be homogeneous. At process levels above the coil level (>5000 gal), agitator speeds as low as 45 rpm provided homogeneous mixtures. With homogeneous tank contents during the tests, the Hydragard sampler appeared to produce the most representative samples of the tank contents; however, it is believed that one of the baffles near the pump intake may have caused slight differences in the samples collected. The agitator power requirements were found to increase with concentration, tank volume, and agitator speed. For pump priming, successful and unsuccessful water primes of the transfer and sample vertical cantilever pumps were recorded for each variation in system and operating conditions with the RWCT simulant. The sample pump had successful water primes for each condition tested except at the lowest slurry volume (4100 gal) and highest agitator speed (130 rpm). The transfer pump showed successful priming operations, at various system and operating conditions, for a back pressure of 40 psi; back pressures lower and higher than this value resulted in water prime losses for at least one condition: Information was found which supports the ability to prime the pump based on time to reach steady discharge pressure to minimize water use. The pump performance curves were comparable to those obtained with concentrated NCAW simulant. A correlation for pressure drop of RWCT simulant as a function of flow rate for variously sized pipes was developed, and pressure drops across 90-degree-long radius elbows were measured for various pipe sizes with RWCT simulant and water. Evaporator testing was performed to determine heating, boiling, and cooling heat transfer coefficients for the tank coils, which for RWCT simulant were determined to be very close to those determined for the NCAW simulant. Fouling of heat transfer surfaces was measured as a function of time, heat flux, composition, and degree of agitation, and no significant heat transfer capability reduction was observed between the NCAW tests and the RWCT tests, and the coil-cleaning procedure for caked NCAW melter feed was successful. The reduction of steam header pressure from 130 psia to 100 psia did not significantly affect heating performance. There was no evidence of coil vapor binding during boiling tests. The condenser was able to subcool the condensate below 125°F (target value) for all evaporation rates.

Fiscal Year 1993

This testing program provides data on 39-4 frit (80 to 200 mesh) slurry flow pressure drop over a flow range of 3 to 10 ft/sec in \( \frac{1}{2}\)-, 1-, 1-1/2-, 2-, and 3-in.-diameter pipe and long radius elbows using frit slurries of 0, 8, 45, and 60 wt% (nominal). No temperature control was exercised during the tests, but the testing temperatures were recorded. The physical properties evaluated and included are density (slurry, frit particle, and bulk frit), wt% solids of slurries, pH, and settling rate. Observations on slurry pumpability and system wear were made. Formic acid was added to the slurry to maintain the pH between about 3.3 and 4.0 to keep the frit from agglomerating. A correlation was developed for frit slurry flow pressure drop as a function of slurry properties, flow rate, and pipe diameter. The long radius elbow \( \frac{Le}{D} \) values did not show a significant increase over water with increasing frit concentration. An \( \frac{Le}{D} \) value of 20 should be used for the 1-, 1-1/2-, 2-, and 3-in.-diameter long radius elbows. An \( \frac{Le}{D} \) value of 10 should be used for the \( \frac{1}{2}\)-in. elbow.


This Data Package provided the subject information collected on the pilot-scale liquid-fed ceramic melter (LFCM) off-gas system. Dynamic surges needed for these tests were provided by steam injected into the melter to simulate the surge of an initial steam rate of 198 lb/h, 20 s increase to 1384 lb/h, 40 s decrease to 478 lb/h, and a 7 min decrease to 198 lb/h. Control air flow rate injection either after the film cooler or just prior to the off-gas system control valve was used to control melter vacuum. Flow, temperature, pressure, and pressure drop data were measured for normal melter operating and surge test conditions. The results indicated that the submerged bed scrubber (SBS) pressure drop or exit gas temperature does not increase significantly for a steam surge. Thus, the impact of a steam surge on equipment downstream of the SBS is not significant. For the Fluor-specified surges in which the maximum steam rate increases over 20 s, the control action for each of the control modes was sufficient to prevent melter pressurization (may not be true for full-scale system). The response of the air injection control valve was almost immediate. Air injection after the film cooler provided more rapid return to the set point vacuum. A more instantaneous surge with a 5-s. vs 20-s increase time (simulate step change) to maximum steam flow resulted in a slight melter pressurization (<2-in. H\(_2\)O) for less than 2 s using both air flow control points. Addition of a pour spout vent into the SBS was also simulated to examine melter off-gas system control behavior. This air addition ranged between about 40 to 45 scfm using air injection after the film cooler and between 18 to 22 scfm using downstream injection air; these flows were easily controlled at either injection point.


This data package provides data and analyses to determine the degree of vapor liquid disengagement (de-entrainment) that occurs in the full-scale SRAT/SME test condenser during concentration, formating, digestion, and concentration before frit addition as would occur in the HWVP process. NCAW simulant was used during process tests for dilute and concentrated waste at two different tank levels, formated waste, formated waste with recycle, and melter feed. The condenser heat transfer coefficient and overhead condensate flow varied linearly as a function of steam flow. No vapor binding in the condenser was observed. There did not appear to be any fouling of the condenser heat transfer surfaces during testing. Solids concentrations were so low in the condensate line samples that there was essentially no solids carryover to the condenser. The condenser condensate decontamination factors mostly ranged from 1000 to 1,000,000 based on condensate analyses.


This data package provides HWVP NCAW process slurries simulant physical and rheological properties data used for full-scale HWVP feed preparation testing, including composition, slurry wt% solids, slurry wt% oxides, slurry density, slurry settled solids vol% and wt%, slurry heat capacity, slurry boiling temperature, slurry pH, supernate wt% solids, supernate density, slurry rheograms, and slurry settling rates.


This data package provides data to determine the degree of foaming that occurs in the test vessel and the decontamination factors in the condenser during concentration, formating, and digestion, and to determine the effectiveness of the antifoaming agent (Dow Corning 544 Antifoam Agent) during formating and digestion as a function of foam level and decontamination factors in the condenser. The data were collected on the full-scale HWVP SRAT/SME process testing system using chemical simulants of the HWVP process streams. During testing where the tank contents were concentrated or formated and digested, an in-tank camera was used to monitor the foam layer; tank conditions recorded included condenser pressure, system temperatures, heating coil steam flow rate, agitator speed, and tank weight. For decontamination factors, the off-gas and condensate flow rates from the condenser were measured, and samples from the condensate line were taken intermittently during testing to monitor solids carryover. Condensate line samples were analyzed for wt% solids by drying the samples at 105°C. The off-gas from the condenser was isokinetically sampled, and any samples were collected on a filter. Foaming did occur but not to the extent that concentration, formating, and digestion operations were hampered. Foaming was only encountered at higher heating rates and could be controlled by either lowering the heating rate or by adding Dow Corning 544 Antifoam. The
magnitude of tank pressure fluctuations increased with increased heating coil flow rate. The tank pressure fluctuations could be controlled by lowering the steam flow in the heating coils. Solids concentrations were so low in the condensate line that intermittent line sampling methods were inadequate for determining the solids composition in the condensate line; thus, decontamination factors were not calculated.


This data package provided data to determine the degree of solids settling/accumulation at the full-scale test vessel periphery and the degree of agitation required to achieve homogeneity in the full-scale test vessel for NCAW slurry simulants as would be encountered in SRAT, SME, and MFT processes. Tests were conducted to measure specific gravity and weight percent solids as a function of agitator speed (45 to 130 rpm), tank contents volume (5700 to 7800 gal), and slurry type/concentration, and samples were taken at different slurry heights. The tank was 12 ft in diameter, 16.5 ft tall and had a maximum working capacity of 9400 gal with vertically insulated walls. There are two steam coils and one cooling coil with a heat transfer area of 343 ft$^2$ and 144 ft$^2$, respectively, all constructed of 2-in.-diameter schedule 40 Hastalloy Alloy 276 pipe. The agitator is of variable speed and 100-Hp with a 36-in.-diameter 4-bladed radial impeller mounted 7-in. above the floor bottom, and a 36-in.-diameter 3-blade hydrofoil mounted 60-in. above the radial impeller. Slurry homogeneity was achieved at all test conditions as a function of agitator speed, sample height, and slurry type/concentration. Solids buildup was noted only when testing the melter feed simulant. The most substantial buildup was between and outside the heating coils. Other modest areas of buildup were the agitator shaft, internal support structures, steam supply lines, tank sides (including bottom), and the piping. There was no buildup around cooling coils. The buildup seems to be due to the properties of the Bingham plastic fluid. Tests with melter feed simulant indicated that when the slurry dropped below the coil top, it may have become nonhomogeneous. There appeared to be no significant buildup of settled solids on the tank bottom.

Graves, RE. July 15, 1993. "Frit Slurry Testing an Addendum to Test Plan for Slurry-Integrated Performance Testing (SIPT), Hanford Waste Vitrification Program, Test Plan No. HWVP-91-1.2.2.03.03B, Rev. 1, April 21, 1992, Rev. 0," HWVP-91-1.2.2.03.03B, Rev. 1 (Addendum 2) (PHTD-C93-04.14J), Pacific Northwest Laboratory, Richland, Washington.

No annotation


This data package provides condenser shell-side cooling water flow pressure drop over the flow range from about 200 to 465 gpm. The test condenser is a full-scale HWVP SRAT/SME condenser. The
stainless steel, vertical, baffled, shell-and-tube condenser has an overall height of 14-ft, is 24-in. in diameter, and contains 0.75-in.-diameter 14 Birmingham Wire Gauge (BWG) by 88-in.-long tubes with an inside heat transfer area of 374-ft². The tank vapors flow up through an insulated 6-in. riser and down through the tube bundle to condense. The flange-to-flange pressure drop (test line losses removed) was determined to be 1.95 psi at a water flow rate of 245 gpm and 7.06 psi at a flow rate of 466 gpm. The water flow pressure drop was also successfully calculated. Whether the SRAT/SME test tank was heating, boiling, or cooling did not significantly affect the pressure drop.


This data package evaluates the SRAT/SME test tank as an evaporator using water and NCAW simulated slurries, with the objectives being to determine extent of vapor binding of the HWVP Feed Preparation Tank coils; heating, boiling, and cooling heat transfer coefficients of the HWVP Feed Preparation Tank coils; energy input from agitation; external heat losses from the tank; and fouling as a function of time, heat flux, composition, and degree of agitation. The process variables were tank contents level, steam supply flow rate, agitator speed, and slurry type/concentration. The tank was 12-ft in diameter, 16.5-ft tall and had a maximum working capacity of 9400-gal with vertically insulated walls. There are two steam coils and one cooling coil with a heat transfer area of 343-ft² and 144-ft², respectively, all constructed of 2-in.-diameter schedule 40 Hastalloy Alloy 276 pipe. The agitator is of variable speed and 100-Hp with a 36-in.-diameter 4-bladed radial impeller mounted 7-in. above the floor bottom and a 36-in.-diameter 3-blade hydrofoil mounted 60-in. above the radial impeller. For dilute NCAW at a volume of 7500-gal with an agitator speed of 85 rpm, the overall U for heating, boiling, and cooling was 125, 202, and 260 Btu/h-ft²°F. Heat transfer was found to be affected by coil steam flow, slurry concentration, agitator speed and to a lesser extent the process level in the tank. Heat transfer coefficients for dilute concentrated and formate recycle were nearly as high as for water. After frit addition and extended storage time, the melter feed significantly caked around the steam coils and resulted in poor heat transfer. In most cases, increasing process level was found to reduce heat transfer coefficients, although the effect was not significant. Increasing the agitator speed provided a modest increase in heat transfer coefficient. Vapor binding was not evident at any concentration. Tank heat loss for a contents temperature of 212°F was 207,000 Btu/h. At an agitator speed of 85 rpm, the heat input to the tank was 23,000 Btu/h.


This data package provided data to determine the effect of the cross-flow strainer in the melter feed recycle system on solids segregation that could affect equipment operation and glass quality. The recycle system continuously pumps melter feed through a recycle loop back to the Melter Feed Tank (MFT), with a small amount of the melter feed being drawn off through the strainer as melter feed. This process could allow small waste slurry particles to leave the MFT, but would recycle large particle agglomerates and frit particles that may eventually result in a build up of large particles in the
MFT. The cross-flow strainer is a sieve, with 0.082-in.-diameter holes that flare to a diameter of 0.10-in.-diameter over a thickness of 0.154-in. in the melter feed recirculation loop (2-in.-diameter pipe). The strainer's function is to prevent the passage of lumps of material in the melter feed that could result in plugging of the 3/8-in. pipe melter feed line. During melter feeding in the melter run (LFCM-8), there did not appear to be a buildup of frit-rich particles in the MFT, nor did there appear to be a tendency of the larger frit particles to separate from the balance of the melter feed. The melter feed was determined to be a cohesive yield pseudoplastic which could account for the resistance of particles to separation. In this testing, there was a difference in the target amount of frit in the melter feed and the measured amount.


This data package provides data on NOx production (rate and amount) in the full-scale SRAT test system during formating and digestion, NO to NO2 conversion in the full-scale SRAT, NOx scrubbing behavior and efficiency, and identification of the NOx-producing reactions in the full-scale system when noble metals are not present. Formic acid was added at a rate of about 1 gpm to 7400 gal of NCAW simulant without noble metals at 95°C. Offgas measurements were made during formic acid addition and digestion (N2O, CO, CO2, NO, NOx, H2, O2, N2). The condensate and slurry were sampled and NH3, nitrate, and nitrite analyses were performed. The formic acid was actually added at a rate of 1.2 gpm from a drum, followed by a drum water wash, and transferred to the SRAT before the formic was added to the SRAT from the next drum. Surges in offgas generation caused pressure spikes that tripped the automatic safety interlocks. Ninety-two percent of the initial nitrogen present in the slurry was accounted for in the mass balance calculation. A negligible amount of NH3 and H2 were produced during testing, as no noble metals were present. 5228 moles of NOx were produced with a maximum generation rate for NO2 of 37 moles/min. (These numbers are expected to be low by 10 to 15% because of the effect on NO2 by the off-gas system condensate. Discontinuous HCOOH addition rate may affect the reported maximum and minimum offgas generation rate for a 1.2-gpm HCOOH addition rate.) Continuous addition of the formic acid may be needed to determine more characteristic offgas generation. Nitrite reduction by HCOOH and disproportionation of nitrous acid are predicted to produce the NOx in the SRAT. Estimates indicate that from 22% to 58% of the NOx came from the disproportionation reaction. The NO to NO2 conversion was estimated to be 45% to 94% complete at the point at which the offgas was measured. Condenser operation was successful in cooling the condensate temperature to 50°C and below during periods of high NOx generation (condensate collection system design affected condensate temperature). Approximately 27% of the NOx generation was present in the condensate as nitrate or nitrite.

This data package provides flow pressure drop data for water, dilute NCAW feed, concentrated NCAW feed, formated NCAW feed, and NCAW melter feed simulants for ½-, 1-, and 2-in.-diameter schedule 40 stainless steel pipes over a flow range of 3 to 10 ft/s at 125°F. The physical and rheological characteristics of the slurries are provided together with settling rate information. The test results with water indicated that within experimental accuracy the piping roughness was between smooth and what would be expected for commercial steel pipe, depending on which piping is being tested.


No annotation


This data package provides melter feed flow (0.20 to 0.35 gpm) pressure drop data in the 3/8-in.-diameter feed tube at about 48°C with the HWVP melter feed piping configuration, and any indication of solids settling (plugging) should be noted. The NCAW melter feed rheology and physical properties are also provided. The pressure drop dependency in the simulated melter feed line during melter feeding was found to be highly dependent on slurry rheology for the LFCM-8 melter feed test. Assuming Bingham plastic behavior, the pressure drop data was normalized with flow rate and plotted against time, which can be used to determine the observed pressure drops for a given flow rate any time during melter feeding. The changes in fluid rheology appear to be the result of changes in oxide concentration within the slurry. This information can be used to predict similar potential changes for other melter feeding systems. Line plugging and flushing frequency were reported, and a higher flushing frequency was required toward the end of the test.


The data package quantifies the amount of cadmium deposited in the off-gas line between the liquid-fed ceramic melter (LFCM) and the submerged bed scrubber (SBS). The data was collected as part of the LFCM-8 melter campaign. It was estimated that 1.4 lb of solids could have accumulated in the melter off-gas line, with the maximum amount at the line entrance and decreasing down the line length. There was not an enrichment of Cd in the deposited solids compared to other feed
constituents. The rate of Cd release from the melter was 0.65 g/h, which corresponds to a melter decontamination factor of 350 and is similar to those for Na and K.


A study was performed to complement WHC studies on methods to increase HWVP capacity within the current structural design of the Vitrification Building through process simplification and design modifications. The HWVP design capacity can be substantially increased by reasonable extensions of existing technology that require up to five years to develop and implement. Modifications proposed included installing advanced high-capacity melter (high-temperature stirred), maximizing HWVP feed concentration received (90 g WO/L), performing process waste recycle concentration in SRAT or SME as appropriate to minimize the feed preparation time cycle, using an alternative reductant, directly adding dry process frit to the melter, and maximizing the HWVP feed processing slurry concentrations. Other capacity-increasing options include converting tank cooling coils to heating coils and placing cooling jackets on the tanks, increasing batch sizes by reducing tank heels, and performing SRAT/SME operations in one tank using two parallel feed preparation systems.


An assessment is provided of the cause of the Holledge Level Detection System failure, including a description of the geometry and operation of the Holledge Level Detection System, a detailed explanation of conditions and events leading to the failure, an analysis of the effect(s) of the damage on the overall system reliability, and results from the tests conducted to determine the extent of the damage. The Holledge Level Detection System is a prototypic liquid level/density measurement device that uses three Holledge Type PB-30 pressure sensors at three heights mounted as an assembly in the SRAT/SME/MFT testing tank. During baseline testing with water to determine the effects of agitation on level detection performance, the Holledge Level Detection System failed when significant tank equipment vibrations were encountered while agitating a low volume (1000 gal) of water in the tank at 130 rpm. The failure was detected by level detection reading changes; no physically observable damage to the detectors or assembly was detected. The specific cause of failure could not be determined. The assembly was repaired by replacing the detectors.


This data package provided the subject information collected on the pilot-scale liquid-fed ceramic melter (LFCM) off-gas system consisting of a film cooler; an off-gas line with a reamer brush section; and the SBS distribution plate, bed (Intralox ceramic saddle packing), and demister. Injection of steam to the melter plenum was used to simulate melter feeding. Steam surge cases were studied under
steady state surge conditions. Steam flow, air flow, system temperatures, and appropriate pressure drops were measured. Data tables provided by Fluor were completed. For the film cooler pressure drop data, film cooler and off-gas line gas flow pressure drops were measured for normal melter operation, steam surge, and maximum plenum temperature cases. For the SBS packing selection, SBS pressure drop and operating characteristics were evaluated over a range of operating conditions that included normal operating, steam surge, and no steam flow conditions. The overall pressure drop of the SBS, including frictional losses in the downcomer and chevron demister, increases significantly with flow rate. With a submergence of 39.2-in. H₂O, pressure drops of nearly 100-in. H₂O were measured at maximum flow conditions, with the majority of the pressure drop occurring across the SBS demister. Oscillations with a frequency of 3 Hz and magnitude of 1.6- to 4.0-in. H₂O were noted during operation of the SBS. The void fraction in the SBS increased nearly linearly up to superficial velocities of 60 to 80 ft/min of gas at SBS exit conditions, including humidity. Above this flow rate, the bed expansion per unit of flow increase decreases, and at maximum flow conditions the bed volume was approximately 1/3 liquid. The SBS cooling coil heat transfer coefficient varied from 109 to 176 Btu/h-ft²°F depending on flow conditions.

Fiscal Year 1992


The data package recommends the amount and addition rate (nominal and maximum) of formic acid to the HWVP concentrated feed in the Slurry Receipt and Adjustment Tank (SRAT). Sugar use is not addressed since the development work was not performed.

Maximum Amount: (moles, HCOOH) = 3(moles, NO₃⁻) + 1(moles, NO₂⁻)
Nominal Amount: (moles, HCOOH) = 3(moles, NO₃⁻)
Maximum Rate: 2 gpm
Nominal Rate: 1 gpm

Fiscal Year 1991


No annotation

No annotation


No annotation


Full-scale tests were performed to determine the heat transfer characteristics, process performance, and effects of noncondensible gas flow on the SRAT/SME condenser performance. The condenser was a stainless-steel, vertical, baffled, shell-and-tube heat exchanger mounted directly on top of the SRAT/SME test tank. The condenser has an overall height of 14-ft with a 24-in. shell containing 0.75-in.-diameter, 14 BWG, tubes. The tubes are 88-in. long with a heat transfer area of 450.6-ft². The gases rise through a central riser and are condensed on the tube-side during downflow. Condenser performance was determined as a function of evaporation rate, from approximately 2.5 to 13.5 gpm, and air flow rate, from nominal air-inleakage (approximately 30 scfm) to 480 scfm. At an evaporation rate of 10 gpm with an air flow rate of 50 scfm, the condenser overall heat transfer coefficient was determined to be 116 Btu/hr-ft²-°F; the associated condensate and off-gas temperatures were 110°F and 142°F, respectively. The presence of noncondensible gas in the process vapor was found to reduce the condensate flow rate, increase the liquid entrainment in the condenser off-gas, and reduce the condenser heat transfer coefficient. The detrimental effect of noncondensible gas was found to be more pronounced at higher evaporation rates. The energy balance indicated that nearly all of the process water entering the condenser is condensed, regardless of air flow, and liquid entrainment from the condenser separator section causes most of the process water lost to the condenser off-gas. Condenser tube-side pressure drop versus evaporation rate and air flow must be acceptable in the condenser design to mitigate condensate entrainment.


No annotation
This design package provides test data on gas generation rates during formatting of NCAW and on nitrate salt reactions in dried SRAT/SME NCAW feeds. The laboratory formatting tests consisted of the following steps: heat-concentrated NCAW containing noble metals to 95°C, add formic acid, digest, add recycle, and concentrate. The last three steps were performed at near 100°C. Major enthalpy and weight changes were measured as a function of temperature for dried NCAW feed simulant, formated NCAW, and two formated NCAW simulants with an added recycle stream; Henken tests were also conducted on the samples at temperatures of 380, 450, and 550°C, and no explosions were observed. The following key testing observations were made. The hydrogen generation profile was characterized by a small first release (<0.05 mmoles H₂/min-L) and followed sometimes by a significantly larger second release (0.21 to 0.75 mmoles H₂/min-L) at a concentration of 125 gWO/L. Under conditions tested, a threshold ratio of formic acid to initial nitrite must be satisfied to initiate a second hydrogen release at relatively high rates (dependence of hydrogen generation on variables not fully explored). Under the conditions tested, the hydrogen generation rate profile and peak height for the second hydrogen release appears to be quite sensitive to the point at which the formic acid addition is interrupted; a 20-fold increase in peak hydrogen generation rates was observed over a time interval of less than 10 min. The amount of ammonia measured (generated) was related to the amount of hydrogen measured and the initial nitrate concentration. An exothermic reaction in dried formatted NCAW simulant was observed in the temperature range of 125 to 250°C, with an enthalpy of about 275 J/g.

Fiscal Year 1989


No annotation


A technical study was performed to comparatively evaluate the DWPF and HWVP melter feed systems, and to verify the system will function acceptably for the HWVP feed. Low risk design adjustments specific to the HWVP melter feed system are recommended. Flush melter recirculation line only prior to jumper removal or prior to feed outages exceeding two to three weeks. The critical factor in reducing melter feed tube plugs is to flush the tube immediately following an outage in feed flow. Lid heaters, if installed, could lead to feed tube plugging problems, and the impacts of feed organic content needs to be considered. Agitation affects feed pump operation and tank level measurement. Only essential melter feed pump interlocks should be installed. The Air Displacement...
Slurry (ADS) pump should be tested as a backup to the DWPF melter feed system. Agitation, melter feed homogeneity, and tank heel volume should be evaluated by testing. Calibrating the Holledge level gauge specific to HWVP will require a calibration program for monitoring the system software. The HWVP may use the DWPF prototypic sampling system with the remote Hydragard sampler using Everlasting valves in place of the Fujikin valves. Various methods of cleaning deposits from tank internals and equipment should be evaluated.


No annotation

Fiscal Year 1988


The package contains design drawings for the full-scale HWVP feed preparation test system, including detailed drawings of the feed preparation vessel and the condenser, process and instrument drawings, and test area equipment layout drawings.


No annotation

Fiscal Year 1987


Fifteen sheets of drawings of the proposed full-scale HWVP feed preparation testing system were provided. The drawing package included piping and instrument drawings for the test systems, drawings for two SRAT/SME designs with the heating/cooling coils, condenser drawings, and equipment layout drawings.

A study was performed to evaluate the capability of the DWPF feed preparation equipment for processing HWVP feeds at HWVP processing requirements. The feed preparation equipment was evaluated in terms of slurry homogeneity and fluid mixing, heat transfer, pumping, design life, sampling, level detection, and solids decontamination factors. If feed properties varied significantly and the range of equipment performance could not be reasonably assured, then testing was recommended.


This effort was to establish a relationship between simulated HWVP feed characteristics and heat transfer rates using a bench-scale mockup of the SRAT. The bench-scale SRAT was 1/10-scale based on linear dimensions and 1/750-scale on a volumetric basis. Studies were designed to establish convective and boiling heat transfer rates as affected heating coil steam pressure and increased slurry solids loading. The testing results demonstrated that the bench-scale testing system could not provide the needed data because of the physical limitations of the equipment. Testing results indicated that as the steam pressure increased from 20 to 30 psig, the boiling heat flux increased, but further increasing the steam pressure did not result in any further significant increase in heat flux. Air inleakage, generated by the operation of the condensate collection system, contributed to about 15% heat losses during heatup and concentration. Increasing the NCAW simulant slurry solids concentration from 2.7 wt% to 10.4 wt% did not affect heat transfer rates. Solids accumulation occurred on exposed internal tank components during concentration conducted in a batch transfer mode, but no accumulations were observed on the submerged coils.

Fiscal Year 1984


Progress is reported on testing a "C"-sampler for obtaining representative samples of slurries in tanks. The "C"-sampler uses a jet to suck a sample out of a tank and into a sample bottle. Testing methods, test progress, a model to describe/predict sampling ability, results of a literature study on sampling methods, and in-cell sampler requirements were discussed. Most of the apparatus to test the sampler had been assembled, and the test procedure had been written and approved.
9.0 Equipment Materials Testing

Fiscal Year 1995


No annotation


No annotation


No annotation


Laboratory tests were conducted to evaluate a number of refractory and electrode candidate materials for high-level waste glass melting in a high-temperature (greater than 1300°C) joule-heated ceramic melter. Also, melter materials were examined from the small-scale high-temperature melter which was being rebuilt after short-term service to correct a bottom drain failure. Electrode/instrumentation materials evaluated included metals, metal alloys, and refractory oxides. Refractory materials evaluated included Monofrax E, Monofrax K3, UNICOR 1, ZS 1500, and ZIRCHROM 30. The types of laboratory tests performed include static ac-powered electrode tests, static refractory tests, and electrochemical electrode testing.
03.03C98 (PVTDC95-03.03C7), Pacific Northwest Laboratory, Richland, Washington.

The high-temperature melter materials testing strategy defines a methodology to be used for melter
materials selection primarily for electrodes and waste glass contact refractories. The phased approach
includes literature/engineering evaluation, followed by laboratory testing, with subsequent testing in
melters of increasing scale. The tests recommended are described.

Fiscal Year 1991

Contaminated Stainless Steel Coupons Using a Ce(IV)/HNO₃ Solution," HWVP-91-1.2.2.04.06A, Pacific
Northwest Laboratory, Richland, Washington.

No annotation

Waste Vitrification Plant," PNL-7729, Pacific Northwest Laboratory, Richland, Washington. (See also
and Associated Components in the Hanford Waste Vitrification Plant," HWVP-90-1.2.2.04.16B, Pacific
Northwest Laboratory, Richland, Washington.)

This materials evaluation study provides design guidance to the architect-engineer by identifying
suitable materials of construction, and provides the best available corrosion rate information for
materials under expected conditions. The strategy, approach, criteria, and technical bases for
construction materials selection are described. Based on materials testing specific to HWVP and
related outside testing, specific process equipment and piping materials were recommended, and future
testing needs were identified. Hastelloy C-22 was recommended as the construction material for
embedded pipes carrying process fluids and for most process vessels and their associated components.
For the waste hold tank, slurry mix evaporator condensate tank, and the waste adjustment tank, 316-L
stainless steel was recommended providing that proper temperature and pH control is maintained; if
these vessels were nonreplaceable, Hastelloy C-22 should be considered. For melter construction,
Monofrax K-3 was the recommended refractory material and Inconel-690 was recommended for high-
temperature metallic components.
A laboratory testing program was conducted to evaluate the impacts on HWVP process equipment materials resulting from anticipated changes to process solution compositions and proposed modifications to the process waste flowsheet. Carpenter 20 Cb-3, Hastelloy C-276, and Hastelloy C-22 were tested over extended periods to evaluate susceptibility to potential slow-initiating localized corrosion mechanisms. Test solutions consisted of a feed preparation slurry simulant and variations in process waste solutions. Any of the materials tested would be suitable as fabrication materials for feed preparation equipment and piping under the conditions tested. In the simulated acidic concentrate-halide process waste solution (simulating DWTT conditions during boildown of combined process waste for transuranic recycle), coupon tests showed severe localized corrosion on the Carpenter 20 Cb-3 samples, and uniform corrosion for the Hastelloy alloys at about 12 and 4.5 mils/yr for C-276 and C-22, respectively. In dilute process waste simulant (simulates DWTT, not including halides from off gas condensate), the alloys performed acceptably. Tests in more concentrated waste simulant with lower halides, but concentrated by a factor of 10 compared to dilute waste, resulted in unacceptable corrosion of Hastelloy C-276 (about 77 mils/yr uniform corrosion with minor preferential weld attack) and Carpenter 20 Cb-3 (about 13 mils/yr uniform corrosion), and borderline unacceptability for Hastelloy C-22 (5.7 mils/yr). Test results indicate that the materials do not appear to be suitable (Hastelloy C-22 appears marginally suitable) for TRU waste treatment process.

Fiscal Year 1989


No annotation


This study describes the strategy, approach, criteria, and technical bases for selecting materials of construction, including 1) an evaluation of materials-related project requirements, 2) review of related materials selection efforts from other projects and selection of suitable materials where information is adequate, 3) a strategy for establishing project-specific materials selection criteria, and 4) identification of testing required to complete the materials evaluation activity.
Fiscal Year 1988


A study was performed to evaluate the relative costs of procurement and fabrication of equipment with candidate materials, and to incorporate these results into a plan for the continuation of a materials selection program for the HWVP feed preparation and melter off-gas systems. The materials cost differential for equipment fabricated from Alloy 20 or C-276 appears to be small. It is estimated that the cost of Alloy 20 may be about equal to, to perhaps as much as 20% less than, the cost of C-276 for certain equipment items. This figures depends on the complexity of the equipment and the extent of fabrication and inspection requirements, as well as the price of the materials. It was recommended that C-276 be specified as the reference HWVP material of construction for corrosive service HWVP process equipment. A program and testing plan are provided.


Laboratory corrosion tests were conducted to evaluate the impacts of a proposed transuranic-containing (TRU) process waste recycle (which concentrates halides, sulfates, and nitrates in DWTT and SME) on process equipment materials for HWVP. Various types of C-276 and Alloy-20 coupons were exposed to boiling simulated DWTT solution and SME feed slurry for periods of up to two weeks. Tests indicate that neither material has acceptable corrosion resistance to the low pH simulated DWTT waste recycle stream. Alloy 20 coupons dissolved in less than 2-h, and C-276 specimens exhibited corrosion rates of about 1000 mils/yr. With neutralized DWTT simulant (pH about 4), C-276 exhibited acceptable corrosion performance (<5mils/yr uniform corrosion and no evidence of localized corrosion). Alloy 20 coupons exhibited pitting and crevice corrosion, while uniform corrosion rates were only slightly higher than for C-276 (about 7 mils/yr for Alloy 20 vs about 2 mils/yr for C-276). Tests with SME feed slurry indicate acceptable corrosion resistance for both materials under recycle conditions.

Fiscal Year 1987


Cursory laboratory testing in solutions and slurries was performed on several candidate process equipment construction materials for the feed preparation and off-gas equipment, and materials selections for further testing was performed. 304-L and two titanium alloys were found to be unsuitable. C-276 and C-22 are alloys with similar compositions and exhibit similar corrosion...
resistance. Generally, the ALLCORR performed about as well as the C-276 and C-22. It is expensive and may not be readily available. Alloy 20 exhibited higher corrosion rates than either C-276 and C-22 and is much less expensive. Alloy 20, C-276, and Stellite 6 were evaluated in preliminary abrasive slurry erosion tests. Alloy 20 was the least wear resistant, with C-276 being marginally better. Stellite 6 was much more wear resistant than Alloy 20 or C-276. Slurries of glass frit and water were about three times more abrasive than slurries of simulated HWVP melter feed. Additional testing was recommended.

Fiscal Year 1986


This study identifies relevant materials selection criteria; evaluates the significance of differences between the DWPF and HWVP operational requirements, process stream compositions, and processing conditions in terms of materials requirements; provides a preliminary list of materials of construction for the HWVP based upon this analysis; and provides recommendations for resolving identified open issues for materials selection, including necessary verification testing. Materials selection for DWPF served as the basis for some initial selections of construction materials for the HWVP process equipment. DWPF contains Hg in its feed, and HWVP feed contains much higher fluoride content and no Hg, which could make a significant difference in materials selection. A materials monitoring program during plant operation was recommended.
10.0 Melter Performance Assessment and Evaluations

Fiscal Year 1995


Data packages were compiled to provide background information to the Melter Selection Working Group in support of the evaluation of the final six melter technologies being considered for vitrifying Hanford high-level waste. The six technologies were the low-temperature, joule-heated, ceramic-lined melter; low-temperature, joule-heated, metal-lined melter (stirred melter); low-frequency induction melter; high-temperature, joule-heated, ceramic-lined melter; high-temperature, joule-heated, cold wall melter; and high-frequency induction melter (cold crucible melter). Information topics include the following: process a range of compositions, control product quality, develop the technology on schedule, integrate with the Tank Waste Remediation System process and facility, control and maintain the HLW vitrification process and facility, minimize total cost, minimize safety and environmental risks, and consider risks and limitations.


A survey was performed to compile information on existing modeling capabilities for the High-Temperature Melter and Cold Crucible Melter. The reports include strategy recommendations for future modeling efforts to support the high-level waste melter development. For the High-Temperature Melter, computer processes of buoyancy driven, highly viscous, flow and heat transfer in the melt pool can be predicted reasonably well with transient computational capabilities. Conjugate heat transfer in the adjacent refractory materials can be well coupled by some tools. In commercial glass melter modeling, most recent advances have been in attempting to address modeling of processes that affect glass quality and production. However, no software tool that exists today will satisfy all analysis requirements. Literature suggests that modeling inductive heating for glass melting and crystal growth can be done well. There has only been limited work in attempts to model inductively heated fluid flow.
Chapter 10.0: Melter Performance Assessment and Evaluations

Fiscal Year 1994


The Melter Performance Assessment task performed multiple activities, including a literature review of all work performed with noble metals in glass, to predict effects of noble metals on the full-scale melter. This includes predicting the lifetime of the reference HWVP melter. The feed used in testing was simulated neutralized current acid waste (NCAW) feed. Gradient furnace testing (GFT) was conducted to estimate the behavior of noble metals in the cold cap region of the melter glass pool. The dried feed samples at the cold (about 590°C) end of the GFT showed some agglomeration of noble metals, indicating that agglomeration took place during either feed preparation or drying. At the hotter (up to 940°C) stages of the GFT samples, most of the noble metals in the HWVP feeds were 1-μm RuO₃ particles with only a few agglomerates. Research-scale melter (RSM) testing was conducted to evaluate the effect of process and feed parameters on noble metals agglomeration. The RSM testing lasted 48 days and contained nine segments that varied glass temperature, plenum temperature, feed oxide concentration, feed redox potential, and feed noble metal concentrations to determine the effects on noble metals agglomeration in the glass. During the latter portion of the run, the resistance between the electrodes decreased. Upon destructive RSM testing, a 2- to 4-mm layer of noble metals was found on the melter floor. The noble layer impacted melter integrity by corroding/melting off about 1/3 of one paddle electrode due to localized heating, and approximately ½-in. of refractory was removed from the melter floor. It was assumed that the RSM noble metals layer was RuO₃ needles and alloys of Pd/Rh/Ag/Te until the last run segment, which was conducted under reducing conditions (Fe²⁺/Total Fe = 0.25) and caused all of the RuO₃ to be reduced to metal. Approximately 5% of the noble metals in the RSM feed were retained in the melter during the test segments with nominal noble metals concentration, and approximately 46% of the noble metals were retained during test segments with double noble metal feed concentrations. The RSM glass samples contained noble metals particles that averaged 10 μm in diameter, with many agglomerates in the 100-μm to 200-μm range. Engineering-scale melter (ESM) testing was conducted to evaluate noble metals behavior during prolonged melter operation at nominal operating conditions. The ESM operated for 49 days with noble metals in the feed, resulting in 35 wt% of the Ru, Pd, and Rh fed to the melter settling on the floor. Glass samples from the melter floor contained 20 to 45 times the noble metals concentration as that of nominal glass. The electrical resistance between the ESM lower set of electrodes decreased by 10% to 15% toward the end of the run. The noble metals particles in the exiting ESM glass samples were similar in structure, but were slightly larger than the particle properties of the RSM exiting glass. The TEMPEST computer model for the ESM predicted characteristics very similar to those observed during the run. The TEMPEST model of the HWVP melter operation predicted that after 192-d of operation with a 70% on-line efficiency, the current limit on the lower set of electrodes would be exceeded because of short circuiting.

There was a considerable error margin in the calculation.
Fiscal Year 1993


Research-Scale Melter (RSM) (6-in. cavity diameter) tests were conducted to evaluate the effects of melter operation and process variables on noble metals agglomeration on the melter floor. The test matrix consisted of nine segments that varied glass temperature, plenum temperature, feed oxide concentration, feed redox potential, and feed noble metals concentration. The RSM operated 48 d and processed 1,300 L of feed, equating to 153 tank turnovers, to produce 531 kg of glass. During the latter portion of the run, the resistance between the electrodes decreased. A 2- to 4-mm layer of noble metals was found on the melter floor after the run. The layer consisted of metallic particles (10 to 20 μm) of Ru/Rh alloy surrounded by separate continuous phases (one phase was an alloy of Pd/Ag/Te with a small amount of metal and the other was pure RuO₃). The noble metals layer impacted melter materials by melting or corroding off about 1/3 of a paddle electrode (assumed to be caused by electrical short circuiting heating), and the metal layer removed about 1/4-in. of the melter bottom refractory. Operation at highly reducing conditions (Fe²⁺/Total Fe > 0.2) could cause RuO₃ to be reduced to metal and alloy with Rh, which could increase the rate of noble metals sedimentation and shorten melter life. About 5% of the noble metals in the feed deposited on the floor when noble metals concentration was nominal in the feed, and about 46% deposited when the noble metals concentration in the feed was doubled. Samples of glass exiting from the melter contained noble metal particles averaging 10 μm in diameter, with many agglomerates of mainly RuO₂ needles in the 100- to 200-μm-diameter range, and the agglomerate size increased when the noble metals feed concentration was doubled. At a low operating temperature of 1050°C the feed could be barely processed through the melter, and at 1200°C the feed processed much faster than the nominal temperature setting at 1150°C. There was little effect of plenum heating on processing rate. TEMPEST computer code simulations were made of the RSM operations. Comparison of predicted RSM operational parameters (power, voltage, current, and resistance) agree to within 13% to 50% of measured values, predicted and measured temperatures qualitatively agree near the melter bottom and electrodes, and short-term predicted and measured noble metals retention were in agreement for nominal noble metals feed concentrations. The computer simulation also indicated that transitioning the melter to an idling state significantly increased the noble metals settling rate.


A study was performed to provide preliminary predictions of the time to reach hypothesized operational limits of the HWVP melter resulting from the buildup of a noble metals sludge layer on the melter floor. Predictions were made with the TEMPEST computer program, Version T2.9h, for use in
the melter performance assessment activity. The preliminary estimated time to reach postulated failure modes was evaluated for a sludge layer depth growth rate of 0.053 cm/d resulting from noble metals feeding conditions corresponding to a continuous glass pour rate of 100 kg/h and a RuO₂ source rate of 0.1076 kg-RuO₂/h. Time estimates are for 100% operating efficiency and are estimated in terms of days of pouring. The occurrence of deviation from the 55/45 power ratio is estimated to occur at 162 days of pouring, when the lower pair silicon-controlled rectifier current limit is reached. The maximum temperature of an electrode portion is reached after 94 days of pouring. The variability in these preliminary time estimates to reach postulated failure limits is estimated to be within a range of a factor of 2 underestimated to a factor of 4 over estimated.


An engineering scale melter (ESM) program was performed to construct an ESM, including feeding equipment; conduct a one-week shakedown processing test; conduct a noble metals processing test; determine the noble metals behavior in the melter; and provide all the operational data. A 1/10-scale (actual 0.28 m²) representation of the reference HWVP melter (DWPF-type) with plenum heaters was constructed, with a design capacity of 20-L/h NCAW melter feed simulant to produce 10 kg/h of glass (actual throughput 12 to 15 L/h). A feed make-up tank and melter feed tank were also provided. These tanks were installed and used in conjunction with existing testing facilities. A volume of 2.61 m³ of NCAW melter feed simulant with a 28 wt% waste oxide loading at 500 g TO/L concentration without noble metals, followed by 14.23 m³ of the same simulant with nominal concentrations of Ru (0.44 g/L), Rh (0.12 g/L), and Pd (0.15 g/L), were vitrified. Glass was poured using the overflow system. Melter feed line pluggage was frequent during the shakedown run due to undissolved LaF₃ and an incorrectly sized flowmeter. The melter feed was difficult to process because its viscosity increased with time after the frit was added. The feed tended to mound on the cold cap surface, and the cold cap became rigid with very few vents. Water dilution (<5%) or nitric acid addition mitigated this feed behavior. The feed at times covered the melt surface with a foamy material. To prevent full pool coverage by the foam, the feed rate had to be reduced. The Ru and Rh concentrations in the glass reached about 75% of target; for Pd, 60%. A portion of 2.13-kg Ru, 0.54-kg Rh, and 0.80-kg Pd may have settled to the melter bottom. A high concentration of noble metals was found in the glass on the
melter bottom at the end of the run, and the electrical resistance of the glass on the melter bottom was decreasing at the end of the run. It was determined that the noble metals discharge efficiency via the glass overflow from an ESM-type melter results in a risk for long-term melter operation. Melter changes were recommended, such as changes to the melt tank geometry and to specific operating procedures in order to concentrate noble metals for periodic removal via the bottom drain, or for remobilization by air sparging. The distance between the lower electrodes and melter bottom should be increased. The bottom drain should be used in addition to the overflow system.


TEMPEST is a versatile computational fluid dynamics code that offers analysis capabilities for a wide range of fluid dynamics and heat transfer problems. The theory manual describes the mathematical models implemented in TEMPEST and reviews the numerical procedures used in their solution. The user's manual describes the construction of the input file, and gives a brief description of pre- and postprocessing options and file usage and redimensioning. The verification and validation manual compares TEMPEST predictions with analytical solutions and experimental measurements for a large number of test problems. The programmer's manual describes the general code structure, lists subroutines with their purpose, defines principal variables, and gives a detailed description of redimensioning options.

Fiscal Year 1992


Subject testing completed August 30, 1992.
Fiscal Year 1991


Laboratory experiments with a gradient furnace were performed to determine the behavior of noble metals from HWVP, DWPF, and KfK melter feeds in simulated waste glass. Two HWVP feeds were tested: HWVP-1 with the noble metals precipitated with the major constituents, and HWVP-2 with the noble metals precipitated with the minor constituents. The temperature gradient in the furnace was from 579 to 929°C for the HWVP feeds, as in the melter cold cap. For the HWVP feeds at 600 to 700°C, the noble metals became concentrated in dried feed, suggesting that agglomeration of noble metals occurs during simulant preparation and/or drying. Noble metals formed pure particles or alloys with other noble metals by approximately 700 to 800°C. At the highest temperatures, noble metal particles or clusters of particles were generally less than 10 μm. Using average particle characteristics from feed HWVP-2, preliminary calculations estimated settling times for the RSM to be on the order of 1000 to 10,000 h and 10,000 to 100,000 h for the ESM, assuming unhindered spherical particles.


No annotation


No annotation


No annotation
Fiscal Year 1990


An overview of the current state of knowledge with respect to the behavior of noble metals in waste glass melters is summarized based on a literature review and work performed at KfK, Savannah River Site, and Pacific Northwest Laboratory. It was indicated that the fate of noble metals in the HWVP melter was likely as described here. Ru is likely to precipitate as RuO$_2$, the morphology of which is uncertain. Rh is likely to precipitate as the metal in alloy with Pd unless Te is present or spinels form. In the presence of Te, Pd will alloy with Te and exclude Rh. Rh is likely to precipitate in solid solution with any spinels that form. Pd will precipitate as a metal either alone or with Rh unless spinels form or Te is present in the waste. RuO$_2$ is likely to provide nucleation sites for the formation of spinels and may eventually be taken up in solid solution with the spinel-forming agents.

Fiscal Year 1989


A study was performed to examine the possible liquid momentum forces in the LFCM and their influence on noble metals sludge that may accumulate. Velocities in a flat-bottom, two-electrode melter are 0.03 to 0.3 cm/s and are lowest on the cavity bottom where the noble metals would tend to accumulate. Velocities in the 45-degree sloped-bottom, three-electrode design are estimated to be from 0.1 to 0.4 cm/s and are highest near the bottom of the cavity. The terminal velocity of 100-micron-sized Pd in molten glass is about 0.001 cm/s, far slower than normal convection currents. Accumulation of noble metals is thus attributed to trapping inside the boundary layer where fluid is near motionless. In a flat-bottom melter, the boundary layer near the cavity floor could be large due to low bulk fluid motion. Once a sludge layer forms, it takes on distinct rheological properties, having a higher viscosity with pseudo-plastic behavior. The critical velocity for resuspension, calculated from a correlation for flow in a pipe, is 1000 times higher than convection currents in the LFCM. It is thus important to keep noble metals suspended and prevent sludge formation. Gravity could play a role in directing the sludge to a bottom drain. The calculated steady-state velocity of a falling film of sludge is sufficient to keep a 45-degree sloped-bottom free from major accumulations if the sludge film is a Newtonian fluid.


No annotation
Fiscal Year 1988


Work was performed to define the HWVP melter design and functional criteria for the precipitate-compatible features; to provide supporting rationale for each criterion, develop a conceptual melter configuration based on current US and foreign technology that meets the defined criteria and HWVP-imposed constraints, and perform vitrification activities required to confirm that the melter concept developed is viable; and to obtain data needed for detailed design. It was concluded that the West Valley Demonstration Project (WVDP) melter should provide compatibility with the anticipated precipitates when modified to include the following features: minimum 45-degree sloped sidewalls, remotely replaceable bottom drain, and airlift riser inlets at staggered heights. The modified WVDP melter also appears to meet the HWVP project-imposed constraints of compatibility with the DWPF melter frame, canister-to-melter connecting sections, and pour turntable.
11.0 Liquid-Fed Ceramic Melter

Fiscal Year 1993


An energy balance model was developed that takes into consideration primary parameters of slurry-fed glass melter processing, such as slurry oxide loading and glass temperature, in order to predict melter feed rate. In combination with melter efficiencies, the model can be used to predict total power requirements.


A pilot-scale liquid-fed ceramic melter (LFCM) run was performed to obtain data to support specific process and design data needs. Operation at HWVP conditions of temperature, pressures, and flow rates was duplicated as possible. Systems evaluations included the feed delivery system (recirculation loop, feed line, cross-flow strainer, and feed nozzle), off-gas treatment system (film cooler, control air injection position, submerged bed scrubber [SBS], high efficiency mist eliminator [HEME] part time, and high efficiency metal fiber [HEMF] filter), and glass discharge control system (prototypic glass sampler/canister throat protector and differential glass pour system). Process data on the revised NCAW flowsheet included the effects of waste recycle simulant, use of plenum heaters to boost production rate, and effectiveness of the melter and off-gas system to destroy/remove organics from the melter off-gas. Glass and feed samples were taken and analyzed to analyze process performance and product quality. The LFCM-8 A and B campaign times totaled 439 h (433-h melter feeding and 6-h down time) with a total on-line efficiency of >98%. The total volume of feed slurry was 23,113-L, producing 11,105-kg glass which was discharged to full-scale West Valley Demonstration Project canisters. The melter feed system recirculation loop and cross-flow strainer provided a steady supply of melter feed; however, it was necessary to increase the feed line length and reduce its diameter to reduce the melter feed rate to that desired. The Everlasting three-way valve performed well for most of the run. Reduced valve performance was indicated toward the end of the "A" run by increased flushing needed (solids accumulation later found in valve), and valve alignment appeared to be offset. The melter feed nozzle performed well, with the exception of solids accumulation on the outside of the nozzle which extended down to the cold cap surface because the outside nozzle surface operated hot. The melter feed had poor cold cap behavior and a slow melting rate, only 64% to 70% of per unit area HWVP rate needed. The use of plenum heaters may have had a detrimental effect on melter process rate. The differential pressure glass discharge system glass flow was stable and controllable. The combination throat protector/glass sampler successfully obtained samples with minimum glass pour stream interaction; however, the sample cup could not be fully retracted when glass completely filled.
the cup due to too much glass in the cup. Cadmium deposits in the off-gas line were found to be no more significant than other semivolatile feed constituents such as Na or K (Cd DF about 350). The average mass DF for the melter was 1520 (based on metal oxides). Concentrations of potentially explosive gases (H₂ and CO) were greater than 10 times below the lower explosive limit. Only 65% of the nitrogen in the feed could be accounted for as NOₓ emissions which leads to the speculation that NH₃ could be forming. The average mass DF for the SBS was 5 (based on metal oxides); the SBS packing was lost during part of the run (no noticeable change in DF). Essentially no scrubbing of NOₓ occurred in the SBS. Pressure/flow oscillations in the off-gas line originating from the SBS were observed. Formic acid destruction and removal efficiency for the melter and off-gas system was estimated to be 99.8%. The average DF for the HEME was 107 (cascade impactor measurement) or 324 (electrical aerosol analyzer measurement). The HEMF filter was loaded with particulate during the run, and the pressure drop increased from 2.5 to 50-in. H₂O, and the clean pressure drop was restored after the filter was backflushed. The overall mass DF of the HEMF filter was 100,000 or greater during the sampling periods.

Fiscal Year 1992


No annotation

Fiscal Year 1991


No annotation


Necessary revisions were made to the waste simulant composition and preparation methods in response to a change in Neutralized Current Acid Waste (NCAW) composition. Efforts were made to revise the vendor procedure in which the major hydroxide components were prepared, including incorporation of the manganese into the vendor procedure, identification and inclusion of minor constituents not previously included in simulated NCAW, and development of compositions to be used for each of the testing activities from laboratory scale through full-scale feed preparation and liquid-fed ceramic melter testing.

No annotation


No annotation


No annotation


No annotation


A study was performed to identify suitable vitrification systems which could be used to accomplish the testing scope in the Applied Testing Plan. Also, supporting arguments are provided for the conduct of the work in the Applied Testing Plan. It was indicated that the HWVP would conduct thirteen tests over the next nine years, requiring funding of approximately $28M. The test scope would evaluate the four waste streams that the HWVP would be required to process. Significant participation and cooperation with waste form development, slurry/rheology testing, feed preparation system testing, off-gas system testing, waste recycle/treatment testing, and waste form qualification testing and modeling activities would be required. The facilities at Hanford, consisting of engineering- and pilot-scale melter systems, and the full-scale feed preparation system, combined with the planned plant-prototypic melter, will provide the needed capabilities to close the issues identified in the HWVP Applied Technology Plan.


No annotation
Fiscal Year 1990


The revised specification (make-up procedure) for procurement of mixed hydroxide chemicals to be used for synthetic Neutralized Current Acid Waste make-up for Hanford Waste Vitrification Plant process testing is provided.


No annotation


The pilot-scale ceramic melter test, run number 23, was conducted to determine the vitrification processing characteristics of simulated Hanford Waste Vitrification Plant process slurries and the integrated performance of the melter off-gas treatment system. Approximately 15,000 L of a simulated NCAW'87 melter feed at approximately 500-g total oxides/L was prepared and processed to produce 7450 kg of glass. The vitrification system was operated for a 351-h period and achieved an on-line efficiency of greater than 98%. The average melter feed rate was 57.2 L/h.m² (1.4 gal/h.ft²), resulting in a glass production rate of 28.4 kg/h.m² (5.8 lb/h.ft²). The melter off-gas treatment system included a film cooler, submerged bed scrubber, demister, high-efficiency mist eliminator, preheater, and high-efficiency particulate air filter (HEPA). Evaluation of the off-gas system included the generation, nature, and capture efficiency of gross particulate, semivolatile, and noncondensible melter products. The overall system solids decontamination factor (melter, submerged bed scrubber, demister, high-efficiency particulate mist eliminator) was 10⁶. For semivolatile Cs, the system elemental mass decontamination factor was 5x10⁶. No crystallinity was observed in the quenched product glass samples, and the glass product durability was of acceptable quality. The feed simulant was made up by a new procedure which more closely simulates the actual history of the pretreated HLW (major metal hydroxide precipitation and washing), and the apparent viscosity and yield stress were significantly less than the feed made up from hydroxides. Materials testing was also performed during the run by placing metal coupons in the melter plenum and in the submerged bed scrubber solution and plenum, and the coupons showed little corrosion except in the melter plenum during idling. During
formating of the melter feed, a stable foam formed during makeup of several feed batches. There was no significant buildup of solids in the melter/SBS off-gas jumper, and the film cooler was successfully used throughout the run.


Approval of the 1/10-scale test melter design was granted with the following modifications: provisions will be made in the design to allow for future installation of a bottom drain; the vertical position of the glass outlet to the overflow will be lowered to better approximate the reference design; the silicon carbide overflow heaters will be reoriented to the vertical position; a baffle will be included in the vacuum discharge section to prevent airflow from disrupting the glass stream during pouring; and a review will be conducted to compare the ratio of plenum heater surface area to glass surface area for the 1/10-scale and the reference design, and based on the results of this evaluation, the dimensions of the 1/10-scale plenum heaters may be changed.


A testing program was performed with physical models of the reference HWVP melter design and an alternative melter design (based on WVDP concept) to determine the ability to maintain simulated noble metals in suspension, comparing the performance of the sloped bottom and bottom electrode melter configuration with the DWPF melter configuration, liquid convection patterns, effect of a bubbler on liquid convection and particle suspension and re-suspension, temperature profiles, and shape factors for resistance heating. The models were 1:4.65 scale based on linear dimensions of melters designed for a 100-kg/h glass production rate. The liquid used to simulate the glass was glycerin with 7.5 wt% LiCl so the fluid could be joule heated. The nominal liquid operating temperature of the model was 62°C. The noble metal particles were represented by nickel and silica. Both melter models performed about the same with regard to keeping particles in suspension. Noble metals with densities of 12 g/cm³ (Pd/Rh) and with sizes from 40 to 100 micron are predicted to accumulate in the melter at a rate of half their mass feed rate under steady-state conditions. Below 40 micron, the accumulation rate is from 1% to 10%, varying with size. The bubbler was not shown to be effective for either suspension or re-suspension of particles representing the 40- to 100-micron size. For smaller sized noble metals, the results were inconclusive as to the effectiveness of the bubbler. Under idling conditions with no bubbler, Pd/Rh particles up to 40 micron in size will settle out in 30 days. In the reference design model, natural convection without the bubbler could be characterized by numerous rotating cells in the upper half of the cavity, with particle velocities of 200 to 400 cm/h. The liquid in the lower half of the cavity was much less mobile, having velocities of less than 40 cm/h and no noticeable convection cells. In the advanced design model with no bubbler, there is substantial liquid motion throughout the cavity due to the joule heating between the bottom electrode and the upper electrodes on the side of the cavity. In both models, the velocity in the updraft of the bubbler operating at 1 scfh is 5000 to 10,000 cm/h, while the velocities in the main part are lower by a factor of 3. Temperatures in both melters are essentially uniform with the bubbler. Without the bubbler, the
reference design shows stratification and the glass at the bottom is predicted to be about 150°C cooler than the reference temperature of 1150°C. The advanced melter design would keep glass near the reference design glass temperature throughout the cavity except for the cooler region near the cold cap. The shape factor between both electrodes in the reference full-scale design is 0.024 cm⁻¹. For the advanced design, the shape factors are 0.029 cm⁻¹ between the top pair and 0.032 cm⁻¹ from the bottom to top electrodes.

**Fiscal Year 1989**


The functional bottom drain valve was being developed as a melter feature compatible with the noble metal melter design. The bottom drain valve consists of a drain tube, expansion bellows and spring assembly, support housing, induction coil, and air cooling tubes. The freeze valve drain tube will be capable of being heated to 1200°C to allow glass to flow out of a ceramic melter. The valve is designed to freeze the glass in the drain tube when the induction power is turned off. The drain valve assembly is 3-ft high, 2 ft in diameter overall and weighs approximately 500 lb.


**Fiscal Year 1988**

An evaluation of a replaceable melter glass discharge system with the potential for assuring that the glass could be reliably poured into a canister was performed. The concept consists of an air lift lance, air lift pipe, and glass delivery tube. The evaluation indicated that the concept was mechanically feasible and could be designed for canyon remote service. However, it appeared that the system design would be very complex and would require significant verification testing. While the system would increase the potential for assuring that the pouring glass stream would hit the 5-in. canister opening, it would also increase the potential for glass stringing at the end of each glass pour, which could also cause operational problems. It was recommended that no additional development of the concept be conducted.

Fiscal Year 1987


No annotation


A preliminary evaluation of potential component failure modes and impacts was performed for the current HWVP melter/turntable conceptual design (similar to WVDP). Forty-two potential failures were postulated and assessed. The degree of impacts to continued processing operations ranged from insignificant to "requiring replacement of the melter or turntable." A limited operational analysis was performed to evaluate the potential for airlifting glass from the melter at the wrong time, and recovery is discussed.


Progress was reported for FY 1987 on developing and testing a prototypical evacuated canister system to provide sufficient baseline data to support the definitive design of a workable HWVP system with predictable operating and remote handling characteristics. This system would be used to vacuum transfer glass melt to empty the melter. Three semi-prototypical evacuated canister test assemblies were provided in FY 1986. These assemblies consisted of an HWVP reference canister, a suction pipe, an aluminum suction pipe plug, and a connecting mechanism, all assembled to support testing activities. The test system included a test furnace to provide the molten NCAW glass (HW-39), a speed controlled crane to lower the suction pipe into the glass furnace, a bail assembly for lifting the canister assembly, a canister vacuum pump, and testing instrumentation. Two water transfer and one
low-temperature glass transfer tests were completed. The water transfer tests provided data to characterise system hydraulics, and functionally tested instrumentation and subsystems without major problems. A low-temperature (due to partial power loss in the furnace) glass transfer was conducted with the glass at about 850°C and 2100 Pviscosity. The melt transfer rate was 3.9 kg/min of this extremely viscous glass. All design aspects of the test evacuated canister system appeared sound except for the aluminum plug. The aluminum plug would not seal and was replaced for testing with a lead plug. The aluminum plug design was changed.


The dismantling, inspection, and rebuild of the Pilot-Scale Ceramic Melter (PSCM) was documented. The PSCM operated for 5.5 years between 1978 and 1985, producing over 57,000 kg of glass. Corrosion of the tank refractories and the Inconel 690 electrodes necessitated shutdown and repair of the melter in 1985. The PSCM was rebuilt maintaining the same basic design, but with enhancements to the lid, electrodes, and overflow area. It was determined that the type and configuration of the melter tank ceramics are suitable for melter use with the glass types tested. Corrosion of the K-3 refractory was consistent with expected corrosion rates for the five years of PSCM operation. A portion of the melter lid had fallen into the melt tank due to inadequate vertical support at the walls and failure of the Inconel anchors welded to the lid. The anchors were replaced with more corrosion-resistant ceramic anchors and Inconel 690 clips. The electrodes failed at the upper bus connection and showed severe corrosion at the glass melt interface, which led to a new electrode design. The severe electrode corrosion may have been due to a combination of oxidizing material buildup and mechanical stress at the channel welds on the rear of the electrodes. The overflow trough was modified because of corrosion to the Inconel 690 pour tip. The ceramic components were replaced with an Inconel 690 trough and dam to increase corrosion resistance and prevent glass seepage. The wall and floor insulation were increased, and the lid height was decreased.


Calculations were provided as part of a design package for the HWVP melter and turntable. Melter electrode design calculations include cooling, cooling channel pressure drop, thermal expansion, busbar sizing, and shape factor. Melter calculations include refractory thermal expansion, thermal profiles, discharge dam cooling requirements, weight and center of gravity, glass residence time, glass riser diameter, design life, structural analysis, frame analysis, discharge heater sizing, water-cooled lid, cooling water pressure drop, and maximum pressure. Turntable calculations include cooling water requirements, canister thimble, turntable weight, canister weighing system, turntable water seal, turntable air temperature, carousel torque, and turntable shell stresses.
Chapter 11.0: Liquid-Fed Ceramic Melter


Engineering calculations were provided to support the design of the HWVP turntable. The turntable analysis includes calculations to determine turntable cooling water requirements, thimble dimensions to provide structural support of a filled canister, estimated weight of the turntable, required capacity of the canister weighing system, dimensions of the water seal components, average air temperature in the turntable, torque required to rotate the carousel, beam size to support turntable, and the structural strength of major turntable components.


Calculations were provided to support the design of the HWVP melter. Calculations included melter refractory thermal expansion, melter temperature profiles, discharge dam cooling requirements; glass riser sizing, melter design life, the structural strength of the melter water jacket, electrical supply requirements for the overflow heaters, and alternate refractory designs for a water-cooled melter lid.


Calculations were performed to support the design of the HWVP melter electrodes. Electrode design calculations included cooling design, cooling channel pressure drop, thermal expansion of the melter electrodes, electrode bus bar sizing to minimize joule heating, and electrode shape factor. The electrode cooling channel rupture evaluation is described.


Testing was performed with a physical model to evaluate several alternate melter glass pouring tip designs and process conditions which may cause the pouring glass stream to waver and/or drip. The glass pouring tests were performed using a half-scale Plexiglas model and molten glass simulants. The tests evaluated five pour tip designs and two trough orientations. The following was concluded. The HWVP tip design cannot be improved significantly from the present pouring configuration except for enlarging the tip diameter. Glass will deflect back underneath the trough and miss the 4-in.-diameter opening at glass flow rates above 1000 lb/h, if the modeling fluid correctly simulates the glass. At the recommended HWVP glass pouring rate of 500-lb/hr, the deflection will be approximately 1 in. A trough with a 24-degree downward slope will flow and drip more than twice as long after the airlift is turned off than a trough sloped upward 2 degrees. A pointed pouring tip can corrode to form a rounded tip with a 0.25-in. radius, with little effect on the stream deflection. Glass at 1100°C will flow and drip for a significantly less time after the airlift is turned off than glass at 1050°C.

11.9
Fiscal Year 1986


Candidate turntable concepts are evaluated, and a suitable turntable design for the HWVP is recommended. The turntable provides the equipment for handling and filling the canister under the melter. Two turntable concepts were considered, the "closed" and "open" turntable concepts. For most considerations, neither design concept appears to have significant advantages over the other. An exception to this is the impact of venting design on melter operation, turntable requirements, etc. A modified venting design (from the current HWVP reference) is proposed for the closed turntable, which should eliminate problems. This design also minimizes the risk of canister overfilling due to sudden melter pressure surges. With the incorporation of the modified venting approach, PNL recommends the closed turntable concept for the HWVP. To verify the improved venting design, simple proof-of-principle testing should be conducted.


No annotation


No annotation


Two engineering-scale melter tests (HWVP-13 and HWVP-14) were performed in the PNL high-bay ceramic melter (HBCM). The objectives of HWVP-13 were to study slurry concentration to determine the optimal oxide loading for maximum melter processing and glass production rates, demonstrate that a frit glass former could be added in a -80/+200 size fraction without impacting processing conditions, compare rheological properties of slurries prepared in engineering-scale equipment following a rigorous process simulation to those prepared in the laboratory, continue evaluation of spinel formation and settling in the tank as a result of chrome insolubility, obtain Cs and S melter volatility data, and
use temperature control algorithm to evaluate melter electrode control. The objectives of HWVP-14 were to evaluate the effects of waste variability on melter feed processing characteristics and product glass quality. Compositions tested included high sodium (13.2 glass wt% Na$_2$O), low iron (5.5 glass wt% Fe$_3$O$_4$), and high zirconium (10.0 glass wt% ZrO$_2$). Processing characteristics evaluated for each melter feed composition were cold cap properties, formation of secondary phase on the glass surface, melter feed rheology, and processing rate. Glass samples were obtained and analyzed for crystal formation. In HWVP-13, melter feed oxide concentrations of 415, 515, and 654 g/L were evaluated. At a melter feed concentration of 515-g TO/L, the glass production rate was maximized at approximately 35 kg/hr.m$^2$. Slurry rheological properties and melting characteristics were acceptable for all three melter feed concentrations, indicating the exclusive use of -80/+200 mesh frit is appropriate. The rheological properties of the laboratory- and engineering-scale melter waste slurries showed good correlation. The ferric hydroxide appears to be the most significant factor in determining rheological response to concentration and the ultimate slurry concentration achievable. A chromite spinel phase formed and crystal agglomeration occurred in the cold cap region (waste was NCAW with high Cr = 1.5 wt% Cr$_2$O$_3$ in glass). Average Cs and S DFs were 130 and 14, but can vary significantly depending on melter processing conditions, feed conditions, and melter chemistry. The constant temperature control algorithm functioned well to maintain a steady bulk glass temperature. In HWVP-14, the processing characteristics of all three melter feed concentrations tested were similar to the reference HWVP composition used in HWVP-13. The high Na and Zr feeds processed at a higher rate and the low Fe processed at a lower rate than the reference feed. Analyses of glass samples obtained during each segment of HWVP-14 showed that no crystal phases were formed, indicating that if the Cr$_2$O$_3$ of NCAW melter feed is reduced to approximately 0.2 wt%, the chrome crystalline phase settling problem will not be an issue.


The Pilot-Scale Ceramic Melter (PSCM and glass surface = 0.73 m$^2$) test run-22 was performed to evaluate the processing characteristics of the current HWVP melter feed (Cr$_2$O$_3$ = 1.3 wt% oxide basis) during actual melter operation, and to establish the product quality of HW-39 borosilicate glass. An important test objective was to investigate the effects of redox level on the stability of glass melt and overall melter operation; melter feed was processed with and without added reductant (sugar) during different parts of the test. The melter feed, defined during FY 85, consists of reference feed and glass-forming chemicals added as frit. The run consisted of 427 hours of melter operation with an on-line efficiency of above 95%, processing approximately 17,100 L of feed to produce 6,800 kg of glass. HWVP melter feed exhibited excellent processing characteristics for the majority of the test. Formating added sufficient Total Organic Carbon (TOC) to maintain a reducing melter feed without the addition of sugar; no melt foaming was observed during the experiment; and feed/glass samples were well within the acceptable redox potential range (average ferrous to ferric ratio = 0.002 to 0.42), except for the initial batch of auxiliary feed (average ferrous to ferric ratio = 1.2). Average feed (390-g TO/L) rate for the more reduced feed segment (sugar added) was 35.9 L/h (maximum 39.1 L/h); and without added reductant, the average feed rate was 39.1 L/h (maximum 50.9 L/h). Glass temperature control was difficult due to postulated current shorting through the sample boat in the melter tank. The
ADSP (Air Displacement Slurry Pump) melter feed pump operated with minimal interruptions. Concentration of feed sample waste components varied, suggesting some segregation in the waste slurry holding tank. The PSCM pour stream was stable and filled half-scale canisters with 2.5-in. neck openings. Melter gas phase losses were significant for B, C, N, S, and halogens, which all readily form volatile acidic gases. Melter decontamination factors (14) for Cs were similar to those for the processing of SRL feeds in the PSCM. Ru (melter DF = 42) volatility was minimal due to the reducing conditions of the glass. The combined overall aerosol DF across the melter (330), ejector venturi scrubber (EVS) (3.7), and steam atomized scrubber (SAS) (4.8) was essentially even, although significant melter and EVS performance changes did occur. HEME (16) and SAS aerosol DFs were a factor of 3 and 10, respectively, below design expectations. The packed scrubbing tower removed essentially no aerosol particles. Laboratory melt rate tests failed to yield quantitative results due to the thin cold cap. The crystalline phase observed in the melter run was the same composition, (Ni,Fe)(Fe,Cr)₄O₁₁, observed in laboratory and previous melter testing and settled in the tank creating a layer 1.5-cm thick and containing approximately 20 vol% crystal.


The design of an evacuated canister system to remotely empty the melter is provided by this design report. The conceptual evacuated canister system designed will use a standard HWVP canister connected to an insulated suction pipe with an aluminum plug in the end of the suction pipe. The design report contains the performance objectives, system description, operation, and alternate design concepts.


The conceptual design for the melter/turntable and melter components are described. The rationale for the design features and alternative component designs considered are discussed. Drawings are also included.

Fiscal Year 1985


A study was performed to identify modifications to the PSCM overflow section that might be required to make the melter overflow more compatible with the 5-in.-diameter throat opening in the reference HWVP canister, prepare conceptual sketches of the modifications, determine testing requirements after the modifications, and estimate costs. Modifications to permit filling full-scale canisters and demonstrate improved remote maintenance of the bellows section were also considered. The following recommendations were made: change the overflow trough so that it slopes up rather than down to...
eliminate excessive dripping, raise the floor of the overflow section to within 6-in. of the pour tip to minimize the drop distance of the glass stream and decrease the overall height of the melter/turntable system, and reduce the width of the overflow section to about 25-in. to demonstrate modifications to permit easier maintenance of the bellows section. The modifications were estimated to cost $180K and would require 2 to 3 months to complete. Recommended testing would cost about $100K.


Testing was conducted during melter runs PSCM-21 and PSCM-22 to evaluate the ability to successfully pour glass from the PSCM into simulated canisters with the reference fill opening. The melter pour tip failed at the beginning of the PSCM-21 run and was removed for the PSCM-22 run. Preliminary testing results indicated that a long drop distance from the overflow trough to the top of the canister does not have a negative impact on the compatibility of the PSCM with the reference canisters. Additional testing was recommended.


A concept for remotely positioning waste canisters under a remotely operated inertia welder that was to be used in the HWVP process as the primary canister sealing method was designed and constructed, and testing was initiated (selection of resistance upset welding for canister closure and funding reductions terminated testing.) The prototype swing-arm system operated and appeared to function correctly, but no canister positioning measurements were made.


An engineering-scale melter test was performed in the High-Bay Ceramic Melter (0.27-m² melt surface) to evaluate the processability and product quality of the newly designated initial reference glass (HW39) and reference feed, which is envisioned to be a blend of washed NCAW and the TRU fraction of CRW. The majority of feed components were added as hydroxides or rare earth fluorides, with a waste loading in the glass of 25 wt% (oxide basis) and a melter feed concentration of 365-g TO/L. There was 1095 L of feed processed to produce 390 kg of glass. Glass formers were added using two different methods. For the first three days of the run, glass formers were added as frit, and for the second two days of the run, glass formers were added as 1/3 frit and 2/3 glass-forming chemicals. The HWVP feed formating procedure and equipment was evaluated together with the heat pipe cooled feed nozzle, the infrared television viewing system, and the Hewlett-Packard Data Acquisition System. The feed using 100% frit as the glass former was recommended because it processed faster and had better cold cap characteristics. With 100% frit, the nominal feed rate was
11.0 L/h (maximum of 13.7 L/h), while the feed rate was 8.4 L/h (maximum of 8.9 L/h) with 1/3 frit - 2/3 unreacted chemicals. With 100% frit, the cold cap coverage was from 50% to 80% and was 2.5 to 5 cm thick. Flexibility was maintained with numerous vents. With the frit and unreacted glass formers, the cold cap was rigid with little or no venting visible and the thickness was 2.5 to 7.5 cm with 70% to 100% melt surface coverage. With 100% frit, the cold cap burned off faster. Forming improved the rheology of the melter feed and reduced the amount of sugar needed as a reductant to lower the melt foaming tendency. Based on laboratory tests, 3.0-g sugar/L was used with 100% frit feed, and 4.5-g sugar/L was used with the frit/unreacted chemicals glass formers feed. No melt foaming incidents were observed during the run. The only crystalline material observed in the bulk glass was cubic spinel phase in the same amounts as observed in laboratory glasses, and some crystalline settling in the melter may have occurred.


Equipment component testing for the HWVP was performed to design and test remotely operable and maintainable equipment (new or modified concepts) to enable operation of the vitrification process in a remotely operated, canyon-type facility similar to the chemical production facilities at the Hanford Works and Savannah River Plant. Equipment concepts developed and tested include a turntable for handling waste canisters under the melter; remote, mechanical, and heat transfer aspects of the melter glass overflow section; removable discharge cone in the melter overflow section; remote electrical and instrument connectors (assess SRL design); thermocouple jumper that extends into a shielded cell; closed circuit camera to view the melter interior (assess SRL design); device to retrieve samples of the glass product; and reamer to clean out plugged nozzles in the melter top. A test was also conducted to evaluate liquid metals for use in a liquid metal sealing system. (Partial testing results were reported in Heath, WO, DE Larson, RW Goles, and MM Beary. February, 1983. "Hanford Waste Vitrification Program, Task 0302 Component Development and Verification for Utilization within B-Plant," No Document Number, Pacific Northwest Laboratory, Richland, Washington.)


A study was performed to review and document concepts for emptying a melter with respect to present technology and modifications to existing systems. The two main concepts considered were an evacuated canister and a bottom melter drain. The systems were evaluated on the need to empty the melter within 8 h after melter failure, operating reliability, glass containment reliability, waste generation, space requirements, draining completeness, and readiness. The evacuated canister system was recommended because the system is more reliable, has good glass containment, and does not require excessive cell space.
Fiscal Year 1984


A study was performed to present the HWVP melter refractory design and verify that it complies with the melter design criteria. The refractory design was completed for the HWVP melter, and the engineering calculations were verified using heat transfer models (TEMPEST) in this study. The temperature profiles calculated for the final multilayered refractory combinations comply with temperature design criteria and minimize the potential excessive refractory corrosion, electrical short circuiting to the melter vessel, and thermally induced refractory fractures. The proposed refractory design can tolerate bulk glass temperatures up to 1300°C. Also, forced air convection can be used in the melter cooling jackets.


A prototype melter discharge cone and handling equipment was designed, fabricated, and tested to determine the handling characteristics during remote installation and removal from the discharge section of the melter via the turntable system. The prototype discharge cone was installed and removed several times from the discharge section from the mock melter shell that was located in the PNL remote operations testing facility. Discharge cone installation and removal was performed using the cone-handling equipment in conjunction with a radio-controlled crane and remote closed-circuit TV viewing system, as would be done in a hot cell situation. Several problem areas were identified and corrected by modifications to achieve total canyon-remote installation and removal operations of the discharge cone.


A prototype thermocouple (T/C) jumper system was designed, fabricated, and tested to determine remote handling characteristics for operation and maintenance. The T/C jumper system, consisting of the T/C jumper, thermowell, and through-the-wall spiral guide tube assembly, was tested a total of five times using canyon remote techniques in the PNL remote operations testing facility. Remote handling was performed using a radio-controlled crane and a remote closed-circuit TV viewing system, as would be done in a hot-cell environment. No problem areas were identified. The system performed as designed.
A High-Bay Ceramic Melter test was performed to examine the melting characteristics of simulated neutralized current acid waste (NCAW) and glass formulation HW-84-9. Feed for this melter test produced a high calcium glass in an attempt to control crystal growth with NCAW. A total of 550 L of melter feed was processed in approximately 50 h, resulting in a run-averaged feed rate of 11 L/h. There were no significant variations in feed composition. There was not sufficient feed to effectively displace the previous glass composition in the melter. No sludge buildup was detected in the melter. No crystallinity or precipitated metal was observed in the glass samples. The average glass melt temperature was 1125°C. The ADS II feed pump was used for 33 h, and feed rates were unstable under 15 L/h. The cold cap appeared to be flexible and bouncy and maintained thickness at < 2-in. during the test. Glass foaming occurred 17 h into the test and was likely due to overfeeding. Foaming became a problem during the last 10 h of the test and was controlled by shutting off the melter power. Operating at a cold cap coverage of 50% to 60% to assure minimal glass foaming will reduce the nominal melter feed rate.

High-Bay Ceramic Melter testing (HBCM-WG1) was performed to identify and characterize the differences in melting behavior, especially rate, caused by three different glass-forming components: frit, ground silica with soluble nitrates and borate, and colloidal silica with soluble nitrates and borate. Other test objectives were to identify the differences in off-gas parameters, especially B content, associated with the different kinds of glass formers used; assess the differences in melter behavior between a feed that does not contain Na₂SO₄ and one that contains 0.6 wt% Na₂SO₄ in the total oxide; and characterize the volatility of Ru when it is added to the simulated waste as RuNO(NO₃)₂. The melter feed waste simulant was Current Acid Waste mixed with glass formers to a concentration of 300-g TOL, with a waste loading of 25 wt% (oxide basis). Each melter feed was fed to the melter for about 8 h. The melter feed slurry with colloidal silica had an apparent viscosity of 58 cP, where the viscosities with the frit and silica flour additives were between 5 and 10 cP. Settled melter feed slurries using silica flour and frit resulted in a solids layer that was difficult to resuspend after prolonged settling. Silica flour slurry had a slower settling rate. Complete suspension of all solids was maintained by the colloidal silica-based slurry; the slurry will gel if left standing >1 h but can be easily broken up. The frit slurry could be processed in the HBCM at about 15 L/h, with the slurries containing colloidal silica and silica flour processing at 12 to 13 L/h. A fourth slurry containing silica flour but only 30% of the Na₂SO₄ had a maximum feed rate of about 11 L/h. The cold cap development and flexibility were good for all the melter feeds tested except for the depleted sulfate slurry. Melter off-gas and plenum temperatures did not reach steady state because of the short feeding periods. The tests were characterized for all feeds by melter aerosol decontamination factors (DFs) in the range of about 2000 with an exceptionally high DF of about 300 for Cs. Low Ru DFs (3) resulted from high volatility losses; however, off-gas quenching appears to be effective in removing and eliminating gaseous compound(s) of Ru.

Testing was conducted to verify the design bases and correlations used for a two-stage air lift pump and an air displacement slurry (ADS) pump. The two pumps were being developed as melter feed pumps. Long-term continuous operations were conducted using both systems. The air lift pump was operated for 1067 h, pumping an estimated 124,726 L of simulated West Valley melter feed slurry at rates of 35 to 175 L/h. Three interruptions occurred and were cleared by backflushing. Two versions of the ADS pump were tested. ADS pump I operated for 759 h, pumping an estimated 65,000 L of West Valley simulant melter feed slurry at rates from 35 to 200 L/h, and no plugging occurred. ADS pump II operated for 1167 h, pumping over 110,000 L of Hanford defense waste with glass formers at a rate of 15 to 180 L/h. The pump operated over 711 h without a plug. Best pumping results were obtained when the air pressure was varied as a function of time. The pump flow rate was moderately affected by tank level. Changes in the pump control setpoint will eliminate these effects. No excessive erosion or corrosion of pump components occurred.


No annotation


Pilotscale Ceramic Melter Test (PSCM) test run 17 (PSCM-17) was performed to evaluate the processability of current acid waste and unreacted glass former slurry. The melter feed had a nitric acid concentration of approximately 1.1 moles/L, with an oxide concentration of 300 g/L. Glass formers were introduced individually as oxide and nitrate compounds to the aqueous slurry. In PSCM-17 testing, over 2300 L of slurry was delivered to the melter, producing 690 kg of glass. The average feed rate over the entire run period was 23.4 L/h (32.2 L/h.m²), discounting down time. The total run time was 112 h with an 86% on-line efficiency. The total downtime was 15.5 h, with 9.5 h due to feed system problems, 5.4 h due to feed composition adjustments, and 1 h due to melter recovery after overfeeding. The air displacement slurry pump successfully fed the melter for 89 h without plugging. The heat-pipe cooled feed nozzle was successful in maintaining a temperature of 34°C in the feed line. The low feed rate is partially due to low boron concentration in the feed. Stable operation of the
melter was maintained using constant power control. The cold cap was stable, and very little venting in the cold cap occurred. No foaming of the glass melt occurred. Measurements on glass samples indicated that the reboil pressure climbed to and stabilized at approximately 300 torr (1150°C), which is below the foaming pressure of the glass. Corrosion rate data on metal coupons suspended in the melter plenum indicated that Cabot Alloy-214 and Inconel 690 can resist corrosion in this environment. Substantial deposits were observed in the 4-in.-diameter long radius curve off-gas pipe. Gas phase losses for B, N, and the halogens were significant. Seventy-five percent of the NOx emission from the melter was being collected at the ejector venturi scrubber. Ninety-eight percent of the Ru leaving the melter was in the gaseous form prior to quenching by the ejector venturi scrubber. No Ru was detected downstream of the scrubber either as a gas or an aerosol. For about 10 h, the temperature was increased from a range between 1125°C to 1180°C to 1225°C, and there was no incidence of foaming. Feed rates of approximately 26 L/h were maintained.


Laboratory-scale physical modeling (1/3-scale PSCM) tests were performed to measure the effects of air bubblers as flow stabilizers and of cold cap size and location. The modeling fluid was glycerine containing LiCl to conduct electricity. PSCM testing was performed with the simulated 60% offset cold cap, which was compared with 100% simulated cold cap results using plate electrodes. Well-defined temperature stratification is observed in both the 60% offset cold cap and 100% cold cap with no bubbling. Use of bubblers enhances fluid mixing, resulting in a more uniform temperature distribution throughout the melter. There was no improvement in temperature distribution using four bubblers over three bubblers. There was temperature stratification with bubbling rates of 0.2 scfh, but temperature distribution was uniform at flowrates of 0.5 and 1.0 scfh. Bubbling rate or number of bubblers had no observable effect on the potential field. Results indicate that cold cap orientation produces no changes in the potential field.

Fiscal Year 1983


A full-scale demonstration was performed to evaluate the remote operation and maintainability features of radioactive HLW vitrification system components being considered for use in B-Plant. The components would generally be manipulated with a rotating crane hook and impact wrench while being viewed through a periscope. The evaluation of the through-wall thermocouple jumper verified remote operation with respect to installation; ability to be remotely removed while containing inoperative thermocouples; insertion of long-sheathed thermocouples through the cell wall, the jumper, and into the melter thermocouple nozzle (ten thermocouples can be sequentially inserted); and remote replacement of the melter thermowell. The evaluation of the canister closure system verified the ability to remotely lower the canister lid onto the canister neck, remotely tighten the canister lid onto
the thermally hot canister, and tighten the canister lid onto a canister whose threads have been partially covered with glass. It was also verified that the tightened lid remained tight when the canister was lifted and removed from the filling area. The evaluation of the melter power electrode connector verified the electrode connector is capable of handling the 2000-A maximum current for which it was designed, and the electrical isolation between the wall plug and isolated flange is effective. The evaluation of the melt sampler verified remote operation with respect to installation and removal, ability to consistently retrieve a glass sample, collection of an acceptable glass weight, proper remote centering within the canister neck, and ability of the sample retainer (pig) to remotely separate sample cup from retainer. The evaluation of the canister turntable verified the accuracy of canister positioning, remote operability of the melter isolation valve and the turntable, ability to remotely install and replace the melter isolation valve assembly, and the rate of air inleakage during a canister filling operation (1.0 to 1.3 scfm). The evaluation of the melter overflow heater section verified the rate of air inleakage when cold (>1.4 scfm) and remote installation is feasible, but further modification is required to avoid damaging the heating elements. The evaluation of the canister level detection system verified the ability to establish the glass product level within a canister, and the ability to diagnose nonuniform (roping) filling conditions. The evaluation of the off-gas nozzle reamer verified remote operation with respect to installation and removal, alignment of the drill bit within the nozzle, ability of the drill bit to cut through simulated blockage material, ability of the vacuum to remove powder generated during the cutting operation, and an acceptable amount of damage to the melter refractory material (correct feed rate). The melter interior viewing system evaluation verified the ability to produce an image of the melting cavity interior, and the ability of the video camera assembly to remain intact during remote installation within a melter nozzle.
A brief initial review and assessment of the cold crucible melter (CCM) technology as a candidate "next generation" melter for Hanford HLW vitrification was conducted. The evaluation consisted of a literature review and interviews with proponents of the technology during a trip to France. The French and Russians have been developing and testing this technology. The Russians may have a CCM operating and vitrifying radioactive waste. The process has been under development since the 1970's and uses a calcination head-end process. The principal potential advantages of the technology are that it can operate at high vitrification temperatures and the melt does not contact the melt tank's surface. It was concluded that the CCM technology is promising and likely applicable to Hanford HLW; however, a number of technical questions need to be addressed. It was recommended that concept testing be performed to further assess concept applicability to Hanford.
13.0 Stirred Melter


No annotation
14.0 High-Temperature Melter

Fiscal Year 1996


No annotation

Fiscal Year 1995


No annotation


Two melter performance tests, SSHTM-1 and SSHTM-2, were completed using a simulated Double-Shell Tank (DST) waste stream and blended DST/Single-Shell Tank (SST) waste stream in the SSHTM with a surface area of 0.22 m². Test SSHTM-1 consisted of two segments processing neutralized current acid waste (NCAW) feed simulant that was prepared using two different feed preparation flowsheets: 1) a 50 wt% (oxide basis) waste-loaded feed with glycolic acid added as an alternate reductant to formic acid, and 2) a 50 wt% (oxide basis) waste-loaded feed with no reductant, but with nitric acid added to adjust the feed rheological properties. The primary objectives of SSHTM-1 were to assess the processability of the two feeds, evaluate glycolic acid as a reductant, and assess the feed for the need to add any reductant. Test SSHTM-2 consisted of four segments (only two completed) processing two feed types: 1) a 47 wt% (oxide basis) waste-loaded, borate-modified, nitric acid-adjusted NCAW feed simulant and 2) a 65 wt% (oxide basis) waste-loaded DST/SST waste feed simulant. The primary objective of SSHTM-2 was to demonstrate the capability of processing a high-waste-loaded glass and the operability of the high-temperature melter technology. Segment 1 of SSHTM-1 processed approximately 1200 L of feed (glycolic acid feed) at two average bulk melt temperatures, 1350°C and 1400°C, producing about 520 kg of glass product. Segment 2 of SSHTM-1 processed approximately 450 L of feed (nitric acid adjusted feed) at an average bulk melt temperature of 1350°C, producing about 150 kg of glass. Segment 1 of SSHTM-2 processed approximately 1300 L of feed (nitric acid adjusted, shimmed with boric acid) at average bulk melt temperatures of 1350°C,
1375°C, and 1400°C, producing about 440 kg of glass. Segment 2 of SSHTM-2 processed approximately 1800 L of feed (blended DST/SST) at average bulk melt temperatures of 1350°C and 1400°C, producing 940 kg of glass. The ability to vitrify Hanford high-level waste using a high-temperature melter to produce an acceptable glass with waste loadings from 46 wt% to 65 wt% was demonstrated. The vitrification processing rate increased about 80% for a 75°C increase in temperature with NCAW feed; the rate increase was 24% for NCAW feed and 30% for blended feed with a 50°C temperature increase. Glass production rates were lower than expected, apparently because of cold cap behavior (which may be modified); however, the normalized waste processing rate met or exceeded rates attained in low-temperature processing tests. Melter decontamination factors for semi-volatile and non-volatile species were comparable to values measured for low-temperature vitrification processing. There appeared to be no need for a reductant.


Two melter performance tests, SSHTM-4 Segment 1 and SSHTM-5 Segment 1, were performed to process two different feeds, an all-blend composition prepared by shimming NCAW waste simulant and an all-blend made to specifications. The melter was rebuilt before the test and the surface area was increased to 0.26 m². The melter was restarted and then underwent an 86-h acceptance test, followed by 278 h of performance testing. The SSHTM processed about 3400 L of feed, producing approximately 1220 kg of 65 wt% waste oxide-loaded glass. The total oxide loading in the feed ranged from 205 to 409 g-total oxide/L. The melter operating temperature ranged from 1350°C to 1450°C. The melter power was provided from the refractory electrodes. The glass was removed from the bottom drain. Glass and cold cap samples were not analyzed due to funding limitations. The average melter feed rate for the SSHTM-4 run ranged from 14.0 to 16.9 L/h at feed total oxide concentrations of 272 or 409 g-total oxide/L to produce glass at an average production rate of 4.6 to 5.7 kg/h. The average melter feed rate for the SSHTM-5 run was 10.2 L/h at a total oxide concentration of 376 g-total oxide/L to produce glass at an average production rate of 3.8 kg/h.


KfK developed a conceptual design for a sloped melt chamber bottom for the pilot-scale melter at PNL. The intent of the design was to collect the settling noble metals at the central bottom drain, discharge the settlements with each glass pouring via the bottom drain, support the higher viscous sludge discharge by a specially designed bottom electrode (also used as blockage protection), and keep a clearance between the lower electrodes and the bottom area to avoid electrical shorting through a high conductive metal layer.
Some preliminary design guidance was provided by KfK for a sloped bottom design for a large capacity joule-heated radioactive waste melter with a bottom drain.


**Fiscal Year 1994**


No annotation
15.0 Melter Off-Gas Treatment

Fiscal Year 1993


An experimental study was performed to obtain liquid entrainment data for the Liquid-Fed Ceramic Melter (LFCM) Submerged Bed Scrubber (SBS) for selected gas velocities (50, 130, and 210 fpm) and disengagement heights (18-20, 22, and 24 in.). After entering the SBS through a downcomer, the gas passes through a distribution plate up through a bed of 0.71 to 0.78 void fraction that is filled with a 0.5 wt% NaCl solution that acts as a tracer. A chevron mist eliminator was included in the SBS off-gas line. The total liquid entrainment from the LFCM SBS was 3x10^{-7} L soln/std L dry air for a superficial velocity of 130 fpm and a disengagement height of 22 in. The chevron demister removed approximately 75% of the total carryover at the conditions listed above. Liquid entrainment was relatively insensitive to gas velocity over the range studied. Liquid entrainment is highly sensitive to disengagement height, especially when foaming is possible. A critical disengagement height exists below which carryover increases dramatically. The critical height appears to be approximately 15 to 18 in. at a superficial velocity of 130 fpm for the LFCM SBS.

Preliminary results from LFCM-8 indicate that, for the LFCM SBS, entrainment does not contribute significantly to the solids loading downstream of the SBS during melter feeding at an SBS superficial velocity of 50 fpm.

Fiscal Year 1991


It was recommended that a V6 Instruments SXP-50 quadrupole mass spectrometer be purchased for about $92K. The instrument would support the HWVP project by providing analysis of the off-gas generated during melter feed preparation and melter operations testing. The justification was based on confirmation of measurements from other instruments, capability to simultaneously detect CH$_4$/HCOOH as separate species, improvement in monitoring H$_2$ capability, and capability for HCN measurement.

Testing was performed to evaluate the effectiveness of the HWVP sparge ring design to suspend accumulated sludge off of the submerged bed scrubber (SBS) floor. A 90-gal tank was constructed as a mockup and fitted with a perforated 6-in.-long, 2-in. Schedule 40 pipe to represent a 15-degree sector (with one set of perforations) of the SBS floor with a sparge ring. Silica particles (two sizes) in water served as the testing medium, with water used for sparging. If the behavior of the actual HWVP SBS sediment is similar to the silica simulant used, operation of the proposed sparge ring at 50 gpm will clean 35% to 43% of the floor area; at 75 gpm, 67% to 78% of the floor area may be cleaned.

Sufficiently frequent operation of the current sparge ring at 50 or 72 gpm is expected to maintain a circulation path for liquid within the SBS. Observations indicated that the areas influenced by the fluid jets from each placement of perforations will extend beyond the 15-degree sector. The vertically downward-directed jet produced the greatest cleaning radius. The 3/32-in. perforations may be susceptible to plugging the sparge ring (sparging fluid should be filtered of particles). Larger diameter silica particles (3.1 μm - number mean) proved to be more difficult to resuspend than the smaller silica (1.5 μm - number mean), which more closely resembles solids collected from the SBS during PSCM-23. Based on the testing evaluation and on the WVDSP SBS sedimentation resuspension evaluation, it appears that operating the sparge ring for more than 10 min will not significantly increase the quantity of resuspended silica.

**Fiscal Year 1990**


Calculations were performed to project on- and off-site personnel exposures to HWVP chemical and radiological effluents released under alternative process exhaust filtration conditions. The calculations show that for the chemical effluent NO₂, the HWVP will not significantly influence the Hanford site background conditions and will not affect site compliance with ambient air quality standards. The maximum individual doses resulting from projected plant emissions of radionuclides were found to be below the regulatory limit under all plant filtration conditions modeled; plant filtration was found to be quite important in determining the nature and magnitude of projected plant doses to both on- and off-site personnel.
The following design recommendations were made for the PNL Submerged Bed Scrubber design:
provisions were incorporated to allow for modification of the water sparge ring, thermowells were
added so that the radial temperature distribution within the packing can be determined; the design of
the connecting leg for the vacuum discharge was modified to reduce the fabrication costs and increase
reliability, and a view port was added.

A description of the electrostatic aerosol analyzer calibration for melter off gas particulate analyses
during Liquid-Fed Ceramic Melter testing is included.

Fiscal Year 1989

An assessment was made of the chemical and radiological effluents that are expected to be released to
the atmosphere from the Hanford Waste Vitrification Plant based on February 1989 estimates of
effluent releases at a glass production rate of 220 lb/h and the associated impacts. The impacts of CO
and NO$_2$ as NO$_x$ were estimated for areas within the Hanford site boundary. Calculations were
performed to estimate the potential radiation doses to a maximally exposed off-site individual. Based
upon comparing the emission analysis results to regulatory standards, it appears that atmospheric
releases associated with the HWVP will not present a threat to human health or the environment. The
projected HWVP contributions to the ambient NO$_x$ emission concentrations are five to six orders of
magnitude below federal and state annual ambient air concentration standards. The maximum
projected whole body and critical radiological doses from the estimated HWVP releases are three to
four orders of magnitude below regulatory standards.

A study was performed to develop analytical techniques for determining the halogen content in LFCM
glasses and off-gas samples, establish melter decontamination factors (DFs) for halogens in glasses produced
during PSCM-22 and PSCM-23 melter tests, and recommend halogen DFs for the HWVP melter and
off-gas system components. For fluorine and chlorine, pyrohydrolysis coupled with halide (ion
chromatographic) detection has proven to be a useful analytical approach suitable for glass
matrices, sensitive enough for the range of halogens encountered, and compatible with remote process support applications. PSCM-23 glass exhibited about a 90% F and Cl retention efficiency while only 20% was incorporated into the PSCM-22 glass. Iodine retention efficiency, established by x-ray fluorescence, could only be established for PSCM-22 glass, which exhibited an 8% loading. These halogen glass compositional results are found to be in good overall agreement with off-gas derived values previously obtained. Melter DF values of 4, 2, and 1 for fluorine, chlorine, and iodine, respectively, are recommended for adoption; these values were conservatively established by a team of responsible engineers at WHC and PNL on the basis of average behavior for many comparable tests.


Off-gas sampling and monitoring activities needed to support operational safety, process control, waste form qualification, and environmental protection requirements of the HWVP were evaluated. The locations of necessary sampling sites have been identified on the basis of plant requirements, and the applicability of DWPF reference sampling equipment to these HWVP requirements was assessed for all sampling sites. Equipment deficiencies, if present, were described, and the bases for modifications and/or alternative approaches have been developed. The following findings were made. Operational safety concerns require that process off-gas combustibles be monitored. Process control of the selective catalytic NOx destructor requires process monitoring of NOx influent concentrations. To provide direct equipment performance data (decontamination factors), off-gas sampling capabilities need to be established before and after each active off-gas treatment device. Waste form qualification models cannot be supported directly by process off-gas sampling, since unquenched off-gas sampling is not practical, and quenched off-gas samples cannot meet the representativeness criterion. For environmental protection purposes, it is recommended that stack emissions of H-3, C-14, I-129, radioactive aerosols, and NOx be continuously monitored. Performance sampling requirements established in the HWVP Technical Data Package cannot be strictly met by existing remote sampling technologies. DWPF remote sampling configurations can adequately support off-gas system operations when sampling data are used in conjunction with other process parameters.


A systems analysis was performed to compare the performance of vitrification off-gas technologies with respect to emissions control abatement, secondary waste generation, and energy consumption as applied to the HWVP. The off-gas performance characteristics of DWPF, WVDP, and HWVP process off-gas (POG) systems have been evaluated under normal and off-normal HWVP processing conditions. Under normal processing conditions, all three systems behave similarly and provide nominally equivalent public exposure protection due to the dominating influence of gaseous radionuclide emissions. All systems are capable of meeting public exposure limits at the point of atmospheric injection (the stack) under normal reference processing rates. Melter off-gas surging was found to have the greatest effect on the HWVP source term, which affected each technology.
The DWPF off-gas technology is 20x more efficient in reducing plant emissions during melter idling than are the HWVP and WVDP systems. DWPF melter off-gas (MOG) system failure will not influence the plant source term since the back-up system is totally redundant. HWVP MOG system failure is projected to result in 100-fold decrease in POG aerosol emission abatement capabilities. Transient plant emissions (dose basis) will increase by only <1% during cold cap burn off. Once processing has ceased, stack emissions will remain at 1% of the normal processing release rate. WVDP MOG system failure is incompatible with unfiltered HWVP process cell design as this technology does not provide for a MOG back-up system. The liquid and solid secondary waste generation rates of the HWVP and the WVDP off-gas systems are essentially equivalent. The DWPF off-gas system appears to have the potential to generate approximately twice the weight of solid waste and roughly 7.5 times the liquid waste of the HWVP off-gas system. The difference in energy consumption and energy costs between the HWVP and the WVDP off-gas systems (melter and vessel ventilation) are insignificant. The DWPF off-gas technology is the most energy consumptive, and the energy costs associated with the operation of the DWPF off-gas technology will be eight times greater than the other two systems.


An assessment was provided on the submerged bed scrubber (SBS) performance based on available test and design data and literature. Parameters considered included: packing, gas distribution, superficial velocity, packing height, and solids accumulation. The following design and operating modifications were recommended. The SBS packing (3/8-in. ceramic spheres) occupied 60 vol% of the bed volume and restricted the volume available for off-gas scrubbing cooling. It also provided low gas holdup, which is not effective in retarding gas upward mobility. The spherical packing should be replaced with one with a high void fraction and large surface area, and that creates a tortuous path through the bed, which will increase the gas residence time (½-in. ceramic Intalox saddles). The off-gas was not being uniformly distributed across the bed with the spheres. A distribution plate was recommended for the bed bottom to improve gas distribution uniformity. Testing was recommended to evaluate the effects of the design change on the SBS performance. The bed submergence level appeared adequate.

**Fiscal Year 1988**


Liquid-fed mini-melter (LFMM) tests were performed to determine the effects of redox (Fe²⁺/Fe³⁺) on metals and iodine loss in the melter off gas (decontamination factors = into melter/out of melter in off gas). The melter feed was Neutralized Current Acid Waste (NCAW)'84 low chromium where sugar...
was added to the melter feed in two of the four tests to control the glass Fe$^{2+}$/Fe$^{3+}$ to between 0.15 to 0.30. The glass redox values with the sugar additions ranged from 0.19 to 0.47, which was thought to be due to unexpected chemical interactions between the molten glass and the Inconel-625 melter vessel crucible. The high rate of Inconel-625 corrosion is thought due to interaction with precipitated noble metals observed. Metallic component, including Cs and Ru, decontamination values did not vary significantly when the sugar reductant was varied from 0.0 to 6.0 g/L of feed. The iodine decontamination factor increased from 4 to 17 with increased sugar loading, but it was unclear if this was due to the increase in glass redox value.

**Fiscal Year 1987**


This study established performance requirements for the HWVP melter off-gas system based on all applicable regulations governing process environmental releases and compared these requirements with empirically based performance expectations that are used to evaluate the functional justification for each component in the HWVP melter off-gas system. Combustible gases flammability generated during the processing of reference HWVP feed is also assessed for the current design and with exhaust-gas (non-condensible) recycle. The overall melter off-gas system design was found to be entirely adequate for controlling most process-generated effluents except possibly NO$\textsubscript{x}$. Atmospheric dispersion modeling has projected plant compliance with personnel exposure limits. However, total annual facility releases of NO$\textsubscript{x}$ may be great enough to require renegotiation of the existing Prevention of Significant Deterioration permit for the Hanford site. A study might have to be conducted to establish the best available control technology for NO$\textsubscript{x}$, which could affect the off-gas system design. The Ru sorption trap was found to serve no useful function. It was determined that an iodine sorption trap was required to control I-129 emissions, which requires removal of other volatile halides. The hydrosonic scrubber provides marginal submicron aerosol removal performance when compared to other devices.


A technology review was conducted to identify and compare applicable off-gas processing alternatives should NO$\textsubscript{x}$ emission abatement be required for HWVP. Dry NO$\textsubscript{x}$ methods of removal are, in general, more efficient (>90%) than wet scrubbing approaches (> 60%); however, the dry approaches are only applicable to NO$\textsubscript{x}$. Of the dry removal methods, selective catalytic reduction (SCR) using NH$\textsubscript{3}$ reductant and a hydrogen zeolite catalyst appears to be the most suitable technology for reducing HWVP NO$\textsubscript{x}$ emissions should emission abatement be required. SCR is a relatively simple and well-established technology that produces no secondary waste stream and is applicable to a wide range of NO$\textsubscript{x}$ concentrations (500 to 30,000 ppm). Wet scrubbing techniques are not specific to NO$\textsubscript{x}$, are not highly efficient at low NO$\textsubscript{x}$ concentrations, produce a secondary waste stream, and may require complex chemical support to reduce equipment size.

No annotation


No annotation


No annotation

Fiscal Year 1986


This study discusses process off-gas decontamination factors for chemicals and radionuclides to be used for the reference HWVP flowsheet design. Suitable references and detail are provided to enable data traceability, enhance technology understanding, and indicate process variability. Decontamination factors for the melter, ejector/venturi scrubber, steam atomized scrubber, and high efficiency mist eliminator are based primarily on development data from PNL pilot-scale ceramic melter runs. The decontamination factors for the gas scrubbing column, Ru sorber, I sorber, condenser, and filters are developed from relevant manufacturers' and development literature.


A study was performed to evaluate the Pilot-Scale Ceramic Melter (PSCM) off-gas system by identifying the acceptable operating ranges for each piece of equipment and determining if the equipment was operating within manufacturer's recommended ranges during PSCM-22. A comparison was made between the observed and manufacturer's expected decontamination factors (DFs). The ejector venturi scrubber (EVS) was operated at the lower end of its design range. The average EVS DF observed during PSCM-22, 3.5, was still above the manufacturer's anticipated DF of 2.2 for a properly sized unit. EVS aerosol removal performance can be improved by increasing the scrubbing water pressure and using once-through scrubbing water. The NOx absorption column is sized appropriately from a gas/liquid-contacting point of view. The absorption column appeared to have little effect on the exit NOx concentration due to low NOx concentration and the large percentage of
NO (80%); as expected, the aerosol DF was essentially one. The hydrosonic scrubber (HSS) was operated at the upper limit of its designed gas-handling capacity. When operating with scrubbing solution in the recycle mode, the HSS appears to be re-entrainment limited. The observed DF for the HSS during PSCM-22 was approximately 5. The outlet concentration was in the range expected by the manufacturer, but the inlet concentration was low, leading to a DF lower than might be expected. The performance of the HSS can be increased by using steam as the driving fluid and lowering the concentration of captured material in the recycled solution. The high-efficiency mist eliminator (HEME) is significantly undersized, but the observed DFs (16) during PSCM-22 were still close to the manufacturer's expected DF (20) for a properly sized filter. Some improvements in the system aerosol removal performance can be realized by using steam in the film cooler, limiting inleakage, eliminating the melter vacuum control air, and not using recycled scrub solution.

Fiscal Year 1984


A study was performed to examine aerosol removal efficiency of off-gas system equipment proposed for use during vitrification of Hanford wastes. Melter emissions during feeding are the source of off-gas aerosols which are sized in the submicron regime (measured aerosol decontamination factors (DFs) = 160 to 2,250). Initially the ejector venturi is expected to remove material larger than 1 \( \mu \text{m} \) (measured aerosol DFs on melter effluent = 6 to 37). The NO\(_x\) absorber will probably not be efficient for removal of micron and smaller sized aerosols from the ejector scrubber. The performance of the hydrosonic scrubber on aerosols from the ejector venturi scrubber has been measured as DFs ranging from 17 to 25, with an efficiency on 0.1-\( \mu \text{m} \) aerosols reported to be greater than 90%. The performance of the high-efficiency mist eliminator (HEME) on effluent from the ejector venturi scrubber has measured an overall mass DF of 15, which produced aerosols with a mean diameter of 0.2 to 0.3 \( \mu \text{m} \) leaving the HEME. Independent studies indicate that the two HEPA filters in series would produce a DF of around \( 10^6 \) for aerosols between 0.2 and 1 \( \mu \text{m} \) in size. Thus, the overall particulate DF from the feed to the cell discharge is expected to be at least \( 10^6 \) using the following aerosol DFs: melter = 200, ejector venturi scrubber = 10, NO\(_x\) absorber = 1, hydrosonic scrubber = 10, high-efficiency mist eliminator = 5, I-sorber = Ru-sorber = roughing filter = 1, and tandem HEPA filters \( 10^6 \).


An analysis of equipment failures in the conceptual HWVP off-gas system has been conducted. The analysis covers an emergency or accidental discharge of the melter exhaust to the cell or HVAC duct and single failure (loss of DF capability) of each process scrubbing unit in the off-gas system. The most serious off-gas system failure results in discharge of melter exhaust to the stack without processing through the off-gas train, such as if the melter were to evolve a larger volume of gases (i.e., steam explosion) than the off-gas system could handle. Temporary performance loss of the ejector
16.0 Vitrification Waste Treatment

Fiscal Year 1992


Laboratory studies were performed to remove smearable radioactivity (Cs-137) from radioactive-contaminated 304-L stainless steel coupons that were fully oxidized by a simulated canister-filling heat treatment cycle to support the Ce(IV)/HNO₃ decontamination of HWVP stainless steel (SS) vitrification canisters. The results reconfirmed the predictability of this unique chemical milling and decontamination process. A thin layer (2.5 to 5 μm) of oxidized SS metal surface was effectively removed from 304 L coupons by chemical milling with 0.5 M to 1 M "0, solution containing about 1.4 to 2.7 moles of Ce(IV) per square meter of surface area to provide adequate radioactive surface decontamination. Nitric acid treatment alone was not sufficient to provide adequate decontamination. A chemical milling contact time of 6 h at 65°C was adequate to decontaminate the coupons to levels below the Waste Acceptance Preliminary Specifications. Low-pressure water from a laboratory wash bottle was used to rinse the surfaces of the test coupons.

Fiscal Year 1991


Laboratory tests were performed to determine the impact of high pH on the zeolite Cs, Sr, and TRU sorption characteristics and potential physical zeolite degradation as input toward establishing a "pH control methodology" for use in HWVP neutralized SBS waste treatment during the zeolite adsorption step. The zeolite used was IE-96 granules ground to pass a 120-mesh sieve and contained in a clay binder used to form the zeolite granules from unbound zeolite crystals. Adsorption tests were conducted at 25°C at pH of 9 and 11 to establish a comparison baseline to previous tests, and then at 43.3°C at pH of 9, 11, 12, and 13. A literature review indicated that some zeolite degradation may occur at high pH but that it is very slow and should not impact HWVP operation. There was no overall detrimental impact of pH up to 13 and contact time of up to 10 d on the zeolite as evidenced by Cs and Sr distribution ratios (>11,000 except pH) and inspection. There is a significant decrease in Cs distribution ratio at a pH of 13 due to increased Na concentration competing for the exchange sites. The Cs distribution ratios were higher for the tests using the ground zeolite than with the unbound crystals, which was very high in both cases. The measured distribution ratios for TRU (Am and Pu) were typically very low (<1000) when both the test sample and the standard were filtered following
contact, and were significantly increased (>10,000) as measured at 10 d when the standard was not filtered indicating that the TRU was mostly precipitated and very little additional was sorbed on the zeolite. The Sr distribution ratio increased with increasing pH.


Laboratory- and pilot-scale tests were conducted by Mott Metallurgical Corporation to determine the adequacy of the diatomaceous earth precoated Pneumatic Hydropulse (PHP) filter using only special ground zeolite (used for Cs and Sr sorption) without diatomaceous earth (filter aid) added as a body feed during treatment of Submerged Bed Scrubber (SBS) simulant to remove solids which simulated those precipitated and present after neutralization of the HWVP SBS plant waste. The testing results indicated that the use of specially ground zeolite only in the amount required for Cs and Sr adsorption was unacceptable. The five consecutive pilot-scale filter cycles using projected HWVP conditions had an average terminal pressure drop of 42.6 psi, with three of the five tests exceeding the required pressure drop of 40 psi. The laboratory filtration tests showed an improvement in filtration characteristics (lower terminal pressure drop) when the pH was lowered from 12 to 9 which was not reflected in the pilot-scale tests. The laboratory-filtration tests showed that without diatomaceous earth body feed, the performance (volume throughput per unit pressure drop) of the specially ground zeolite was better than the previously used unground zeolite which was not reflected in the pilot-scale testing. The filtrate quality was excellent throughout testing, indicating high solids removal efficiency. The filtrate total suspended solids levels were below 0.5 ppm for all pilot-scale tests. Based on feed process solids of 180 ppm, the solids removal efficiency ranged from 99.8% to 99.97% and was generally at about 99.9% or better.


No annotation


No annotation


These laboratory tests were performed to determine the amounts that could be expected in the HWVP Waste Holding Tank (WHT). Test results indicate that the projected solids content of the WHT could be on the order of as much as 700 to 800 ppm if the submerged bed scrubber (SBS) stream were
filtered at a pH of 7. If the SBS stream were filtered at a pH of 9, the projected solids content would be expected to be much less, being on the order of about 50 ppm. Projections are based on nominal precipitated process solids content in the SBS of 1000 ppm at a flow rate of 0.25 gpm, as described for liquid transuranic waste handling, and neutralization to a pH of 13.5 following filtration.

Fiscal Year 1990


A laboratory study was conducted to evaluate candidate sorption materials to be added to plant wastes (Submerged Bed Scrubber [SBS] solutions) in a HWVP tank as a batch contact process to remove designated amounts of radioactivity (Sr, Cs, Am, and Pu). Distribution ratios ($R_d$) and sorption rates were determined for selected sorption materials as a function of aqueous sodium concentration, pH, contact time, and temperature. The sorption materials were evaluated for stability at projected concentrations of $F^-$ and $Cl^-$ anions in the HWVP waste stream. The results show that of the three zeolite materials tested, A-50 for strontium recovery and IE-96 for Cs recovery exceeded the batch distribution ratio found for IE-95. The Pu $R_d$ values were difficult to interpret because most of the Pu had precipitated before contacting the zeolite materials. The projected contact time of 2.25 h was determined to be more than sufficient to achieve the desired level of Cs removal (about 99.7% approach to equilibrium). At 100 min of contact, the Cs $R_d$ values were about 800 for A-50 and 5,000 for IE-96 at 75°C, as compared to 3,600 for A-50 and 18,000 for IE-96 at 10°C. The Sr $R_d$ values were about 100,000 for A-50 and about 800 for IE-96 at 75°C, as compared to 80,000 for A-50 and 1,300 for IE-96 at 10°C. The actual decrease was about 35% for IE-96 when the temperature was increased from 25°C to the HWVP operating temperature of 43.3°C. Aqueous SBS solutions containing actinides should be adjusted to a pH value above 7 to permit their removal by precipitation as opposed to relying on the zeolite exchanger for removal. At a pH of 5.5, the solubility of Pu and Am was 2.3 nCi/mL and 6 nCi/mL, respectively.


Laboratory- and pilot-scale filtration tests were conducted by Mott Metallurgical, Corp. to determine the adequacy of the precoated pneumatic hydropulse filter for removing process solids containing TRU elements and zeolite containing Sr and Cs from HWVP waste streams such as neutralized submerged bed scrubber and decontamination waste treatment tank wastes. The primary design objective was to achieve a terminal solids loading of 250 g/ft² (combined process solids and zeolite) at less than or equal to a 40 psi pressure drop at a 0.2 gpm/ft² flux rate. Test results indicate that the proposed filtration system is expected to reach the design volume throughput and solids loading without exceeding the design pressure drop while achieving a very high solids removal efficiency. A simulant feed stream of Fe(OH)$_3$, at approximately the same Fe concentration as expected in the SBS, is an appropriate simulant for the filtration tests. A 0.1 lb/ft² precoat of Manville Celite was effective in protecting the porous metal filter from plugging with simulant solids. The feed becomes more difficult
to filter as the pH was increased, indicating that more solids were being precipitated from the feed solution. Diatomaceous earth as a body feed will be required in addition to zeolite added for Cs and Sr removal to adequately filter the process feed. A 3:1 ratio of diatomaceous earth to process solids appears to be more than sufficient body feed with maybe as little as 0.5:1 working. With any extremely high Fe(OH)_3 concentration of 1000 ppm, the feed can be successfully filtered. The filter provided excellent clarity with very low turbidity values and low solids content; solids removal efficiency was typically on the order of 99%. Testing with the Mott Hypulse LSM filter pilot plant using feed in the down-flow configuration demonstrated that there was settling of solids. Recovery pressure drop indicated that there was no fouling of the media after repeated cycling. The slurry backwash was effective in removing all of the solids from the element. The solids backwashed from the filter were visually observed to instantly break up with no tendency to agglomerate. The design flowrate of 0.2 gpm/ft² was easily maintained over the filter feed cycle when the appropriate amount of diatomaceous earth body feed was used. The particle size of SBS solids is expected to be in the range of 2 to 10 microns which the precoated 2 micron porous metal filter with the appropriate amount of body feed can satisfactorily remove. The recommended PFP filter should perform satisfactorily in the remote process canyon with remote maintenance requirements.
17.0 Process and Product Control and Modeling

Fiscal Year 1995


Efforts were reported which updated and enhanced the Optimal Waste Loading (OWL) models in FY 1995. The glass property models were updated to be consistent with the latest models based on experimental glass formulation modeling work including property model uncertainty. OWL model architecture was revised to be more modular, enabling all OWL models to use the same core model files, facilities integrating OWL with other Hanford models, and enabling the use of the Ternary Waste Envelope Acceptance Tool (TWEAT) to view the results of all OWL calculations. The interface to TWEAT was enhanced. Several simple high-level strategies for blending all Hanford high-level waste were evaluated for a set of tank farm composition data to demonstrate the reduced waste volume benefits of selected blending strategies.


Efforts were reported which updated and enhanced the Ternary Waste Envelope Assessment Tool (TWEAT) which graphically displays the effects of glass composition on glass properties. Glass composition/property models were updated to be nonlinear as in the Composition Variation Study -II Phase 3 work. The binary window was modified to enhance information visualization on the waste/frit axis in the ternary plot. The interface between the TWEAT and Optimal Waste Loading (OWL) programs was enhanced to facilitate the use and display of OWL calculation results by TWEAT.

Fiscal Year 1994


Results of FY 1994 development work on the Optimal Waste Loading (OWL) models are presented. The base OWL model and the Total Blend Model were validated and verified. Development of a method for handling uncertainty in the composition of vitrification process feed was initiated. A file interface to the Ternary Waste Envelope Assessment Tool (TWEAT) was developed.

This work reviews the techniques to be used in estimating and updating composition uncertainties and in combining these composition uncertainties with model uncertainty to yield estimates of (univariate) uncertainties associated with estimates of batch and glass properties. The type, extent, and possible sources of data required for estimating uncertainties are identified. The context of this effort is in providing a statistical process/product control system that will be used in a plant to control the melter feed composition for product property control and to check and document product quality.


Efforts were reported which used and enhanced the Ternary Waste Envelope Assessment Tool (TWEAT) which graphically displays the effects of glass composition on glass properties. An interface was established for electronic transfer of the results of an Optimal Waste Loading (OWL) calculation to TWEAT such that the optimized glass composition/property results and the associated constraints can be displayed on a ternary diagram. Work centered on analyzing Double Shell Tank (DST) blends, Single Shell Tank (SST) blends, and various other waste blends as they were studied in OWL. Other work included developing a more complete and easier-to-use help system and designing and testing algorithms for plotting general order models on the ternary diagram.


Methods for checking and documenting compliance with melter feed and glass requirements in vitrification plant product control must account for various types of uncertainties. This work identified, implemented, and tested methods for estimating uncertainties, on manipulating uncertainty estimates, and on the effects of sample size on precision estimation. A method for using process knowledge to estimate uncertainties was developed and implemented, and data from previous studies at Pacific Northwest Laboratory were used.

Fiscal Year 1993


The applicability of the HWVP product composition control system (PCCS) Measurement Error Model (MEM) and Frit Addition Algorithm (FAA) algorithms to estimation and composition control problems arising in the context of the feed preparation test system are discussed. The MEM has been
developed for the HWVP PCCS to estimate the contents and covariance matrices for both the source and receipt tanks after a transfer operation. The FAA recommends the mass of fresh frit of known composition to transfer to the Slurry Mix Evaporator. The existing algorithms are too specialized to be directly applicable to the feed preparation test system. However, recommendations for generalizing these algorithms are presented which would improve their suitability for application to the feed preparation test system.


The Feed Test Algorithm (FTA) is described which was part of the statistical strategy for the HWVP product composition control system. The FTA tests the acceptability (conformance with requirements) of process batches in the HWVP. Although requirements and constraints will be imposed on properties of the material in the melter and resulting glass, the FTA tests the slurry acceptability while the batch is in the Slurry Mix Evaporator (SME), before the material is transferred to the Melter Feed Tank. Hence, some product properties upon which requirements will be imposed must be estimated from available data on the feed slurry. The major type of data to be used in this estimation is feed composition. The FTA must account for feed composition and model uncertainties, and thus must be statistical in nature. A reference constraint set containing the currently recognized requirements to be imposed on HWVP is identified. Several technical issues and possible modifications to the FTA are discussed.


A study was performed to recommend a statistically based procedure to verify glass product compliance with Waste Acceptance Product Specification (WAPS) 1.3 (specification for "product consistency" as measured by Product Consistency Test [PCT]). The interpretation of WAPS 1.3 in context of the Hanford HLW vitrification process is discussed in some detail. Each batch will be checked for compliance individually during production, and, after all batches in a waste type have been processed. Each process batch will be checked for compliance using a confidence interval on the PCT result for each element. Compliance in a given waste type will be verified using tolerance intervals for the population of PCT results in this waste type.


The broad structure of the HWVP product composition control (PCC) system is laid out, and technical issues and considerations relevant to this system are discussed. One tenet of the HWVP product composition control (PCC) system is to control glass and melt properties by controlling feed
composition. The PCC system will target acceptable melter feed mixtures, will use measured quantities and property models to test whether each melter feed batch in SME tank is acceptable, and will recommend remediation strategies for batches deemed unacceptable. The HWVP PCC system will draw on information about composition of waste type, contents of process tanks, and various sources of uncertainty. This information will come from sampling and analysis of material drawn from the waste stream and the tanks' themselves. The HWVP PCC system will employ the following mathematical/statistical algorithms: glass formulation algorithm, measurement error model, SME targeting algorithm, feed test algorithm, and SME remediation algorithm.


The Optimal Waste Loading (OWL) models and their development and use are described. The OWL models were developed to perform a variety of Tank Waste Remediation System (TWRS) systems process analyses and glass formulation functions relevant to the vitrification of high-level waste. The core of each model is a rigorous optimization which maximizes the glass waste loading, produces an optimal frit composition, and satisfies all of the constraints specified. The various OWL models can perform three types of tank high-level waste blending calculations (total blend, optimal continuous blend, and discrete blends), can account for glass property model uncertainty, and can formulate either two component glasses (waste + frit) or three component glasses (waste + frit + recycle). The recycle model performs a simplified HWVP flowsheet simulation as part of the optimization. Calculations with the OWL models have identified several glass compositional constraints in TWRS processing scenarios that can greatly limit waste loading. The OWL models are being used to evaluate various high-level waste blending strategies, to evaluate the effectiveness of various pretreatment methods, and to explore the effect of variability in waste compositions on waste loading.


The strategy being followed by PNL Hanford Waste Vitrification Plant Technology Development (PHTD) to provide Process and Product Models relevant to control of the vitrification process to ensure it produces an acceptable glass product is described. These models will be incorporated into a instrumentation system for product composition control and will affect many aspects of the operation of the Hanford Waste Vitrification Plant. The process and associated models are statistical in nature. Also, simulating the feed system is needed for plant startup qualification, algorithm testing, and flowsheet evaluation. Models being evaluated include: Measurement Correction Algorithm, SME Targeting Algorithm, Glass Formulation Algorithm, Product Consistency Algorithm, Feed Test Algorithm, SME Remediation Algorithm, Plant Simulation Code, Process Monitoring Algorithm, Software Implementing Product Composition Control in the HWVP, Equations for Heat Generation in a Canister, Equations for Radiation Field Surrounding a Canister, and Confirmation of Criticality Safety Margin.
The "User's Documentation" is a "how to" reference for users of the Ternary Waste Envelope Assessment Tool (TWEAT). The purpose of TWEAT is to graphically display the effects of glass composition on glass properties. TWEAT displays on a ternary diagram, using linear models based on CVS-II Phase 3 data, a "region of acceptability" for processing user specified compositions of waste, frit, and recycle subject to user specified property limits. TWEAT can generate glass property values for any selected point on the diagram and display the boundaries of the experimental data over which the models have developed as well as the model uncertainty for each property. For this TWEAT version, there is the addition of liquidus temperature models and completion of the model uncertainty calculations.

Fiscal Year 1992


No annotation


A review was performed to assess the availability of data to serve as the basis for algorithm development and preliminary investigation of the importance of composition variances and covariances. Estimation of batch-to-batch, sampling, and analytical uncertainties is essential in order to predict glass properties with a high degree of confidence. The preferred relevant information for the analysis of variance/covariance effects will not be available from DWPF. Other data such as from West Valley Demonstration Project will be examined to give preliminary variance/covariance information. The effects of zero vs non-zero covariance of any error source can then be examined to determine the effects of covariance on predicted glass properties.


A study was performed to assess the impact on glass property model predictions of various magnitudes of composition uncertainty and determine whether ignoring composition covariances and only accounting for composition variances is conservative or non-conservative. Propagating the covariance matrices from three available sets of data through the glass property models yielded property percent standard deviations ranging from 1% to 32%. Although the results are based on limited data, it appears that composition covariances cannot be ignored and that composition uncertainty can
significantly increase the uncertainty of predicted glass property values. Thus, it is important to invest appropriate effort in collecting adequate data for properly estimating composition covariance matrices for each stage or tank in the HWVP.


Essential elements of a high-level strategy for developing process and product models are proposed. HWVP models will be developed based on utilizing DWPF technology as appropriate and existing technology will be evaluated and adapted for maximum use which will involve activities ranging from qualification of existing models to development of new models. The central product of the model development activity will be a set of process control algorithms: a Frit Addition Algorithm, a Feed Test Algorithm, and a Feed Correction Algorithm. To provide an optimal foundation for use of the algorithm, Measurement Error Modeling will be used to rectify discrepancies between multiple process measurements with mass balance constraints on the relationships between the measurements. The algorithms will be qualified. Software will be provided to support vitrification testing and to facilitate obtaining data useful to model development. Simulations will be performed using a code describing mass balances in the HWVP feed preparation system.


An assessment is performed to evaluate the maintainability and to determine the effort required to reengineer the Product Composition Control System (PCCS) software of the Defense Waste Processing Facility (DWPF) for Hanford Waste Vitrification Plant (HWVP). The PCCS is a software package developed at Savannah River Laboratory to provide accurate chemical composition control in the DWPF equipment. A number of options were considered. It was concluded that developing a new PCCS software from scratch for the HWVP is the best option.

Fiscal Year 1991


A study was conducted to examine the use of the DWPF Product Composition Control System (PCCS) software for use in the HWVP. Three computer programs, developed at Savannah River to aid in determining acceptable glass mixtures, visualizing batch operations, and operating the DWPF were reviewed (Glass Composition Model, the Batch Model, and the Product Composition Control System). The models were impressive computer programs developed using state-of-the-art object-oriented programming techniques. The Glass Composition Model has been modified for HWVP use in visualizing the acceptable region size for various combinations of HWVP feeds, frit, and recycle; a
similar program is available at PNL (TWEAT) which is more suitable for exploring the property effects of compositions. The Batch Model should be modified for the HWVP process if there is a project need for its capabilities and if the batch-stepping logic can be modified to incorporate recycle. The Batch Model can be useful for understanding and visualizing batch operations and for examining the adequacy of design vessel sizes for different operations schemes. The PCCS model should be further evaluated together with its performance at DWPF and use it or parts of it as appropriate in meeting HWVP waste form qualification needs.


An experimental study was performed to evaluate a theory based on work by Grambow describing the hydration of glass as a known, linear function of solution composition. The linear rate law was tested by the dissolution of SRL-202 glass at 80°C and pH 7 for concentrations of silicic acid that were 0%, 25%, 50%, and 100% of the saturation concentration. The glass dissolution rate was found to decrease dramatically at only 25% of the silicic acid concentration, which does not conform to the linear theory. Thus, use of Grambow's linear rate law to facilitate correlation of durability was not recommended.


The "User's Documentation" is a "how to" reference for users of the Ternary Waste Envelope Assessment Tool (TWEAT). The purpose of TWEAT is to graphically display the effects of glass composition on glass properties. TWEAT displays on a ternary diagram, using linear models based on CVS-II Phase 1 data, a "region of acceptability" for processing user specified compositions of waste, frit, and recycle subject to user specified property limits. TWEAT can generate glass property values for any selected point on the diagram. This version of TWEAT is not complete. No liquidus temperature model is available. The application does not yet check to see if glass compositions being displayed are outside of the experimental ranges studied.


No annotation

Fiscal Year 1990

A presentation is provided of the HWVP Mass Balance Model (MBM) and how it can be used as part of the HWVP product control system and the MBM use with the HWVP Waste Form Qualification Simulation Model (WSM) for process and product acceptance systems evaluation.


A study was performed to develop an empirical correlation between leach results of the first order Composition Variation Study and the glass compositions investigated and to provide the correlation in the form of a product durability model that can be coupled with the Waste Form Simulation Model (WSM). The WSM models the HWVP process operations pertinent to Waste Form Qualification. A simulation was performed which provided the HWVP product glass durability (Li release) as a function of plant operating time and variables.


A presentation was provided that described the development of graphical presentation software for the Composition Variation Study model for composition effects. The modeling approach was provided together with an evaluation of the hardware and software being considered for use. Anticipated model initialization routines, user input menus/screens, property calculation routines, and plot routines were described.

**Fiscal Year 1989**


Four options were examined for completion of the HWVP Heat and Material Balance Process Simulation model. It was recommended that using existing unit operation subroutines from the HWVP Heat and Material Balance Computer Program and completing development of the flowsheet model within the framework of a personal computer-based commercial flowsheet simulator.


No annotation
A requirements specification was written to establish and document requirements for the software program and meet the requirements of WHC Standard Engineering Practices for Impact Level 2 software. The computation of the HWVP flowsheet was to be used as an aid in process evaluation, sensitivity analyses, and plant design. (The model was not procured.)


A study was performed to address the ability of Grambow's model for the durability of glass as modified by the HWVP project to explain qualitatively the leach data acquired during FY 1997 and FY 1998. The hydration rate law portion of Grambow's work was adopted as the chemical rate law. Approximate analytical mathematical solutions are developed as a simplification of and replacement for a full product durability model. (\(SA/V\),t (\(SA = \) glass surface area, \(V = \) solution volume, and \(t = \) time) scaling is obeyed sufficiently to vindicate formulating a hydration rate law based on compositions and not based explicitly on time. The sudden rate of increase in the boron concentration for the large values of \(SA/V\) as \(SA/V\).t reaches about 1000 day/m is probably not a departure from \(SA/V\).t scaling, but instead a part of the normal \(SA/V\)-scaled sequence attributable to silica precipitation. Reimus's modification to Grambow's model, which predicts that the hydration rate includes a direct proportionality to the silicic acid activity in solution, continues to be supported by the data analysis. The observed departures from this scaling law appear to be consistent with the effect of surface layers forming on the glass. It was recommended that the Grambow hydration rate law be modified to more fully explain the HWVP data base, and tests should be conducted where the composition of the initial leachate is varied to test the hydration rate law.


A review was conducted to validate and verify the Waste Form Qualification Simulation Model (WSM). The WSM can be described as a process simulator of the HWVP processes. The WSM was validated and verified.


Activities were performed to complete the FY 1989 update of the HWVP Waste Form Qualification Simulation Model (WSM) and review of TRU recycle impacts. The WSM is a HWVP process simulation model to evaluate the effects of process perturbations and uncertainties in process
measurements on product composition and to evaluate process control methods and strategies. Five development activities were completed. The input files were expanded to include the entire HWVP vitrification flowsheet. The WSM was used to determine the effects of TRU recycle on glass composition. Verification activities and a final internal development review were completed. Statistical tools to simulate correlated data and to evaluate statistical process control methods were identified for implementation in the WMS. Minor changes were made in the WMS code in order to improve the ease of use, provide additional documentation, and correct some problems with several of the algorithms. The net effect of recycle streams was to move the mean glass composition less than a percentage point from the reference composition. The combined effect of recycle streams, volume measurement uncertainty, and sampling and analytical error was a maximum relative standard deviation of 2.4% about the mean true glass composition. Thus, the impacts of recycle streams are small.

Fiscal Year 1988


No annotation


The structure, scope, implementation, and documentation of the 4/88 version of the HWP Heat and Material Balance Computer Program (HMBCP) was examined. It was concluded that the program was usable for preliminary design activities with appropriate checking of calculations. It was recommended that the HMBCP be restructured and substantially upgraded before validation and verification are performed.


This study provides verification of and describes the statistical foundation for a HWVP sampling and analysis schedule for achieving compliance with the anticipated Waste Acceptance Preliminary Specifications. Sampling schemes were identified to meet the following statistical objectives: detection of compositions outside of specification limits, prediction of final glass product, and estimation of composition in process vessels for reporting and guiding succeeding process steps. Sampling for process control requires further evaluation. Based on limited experience, the number of
samples per tank and the analyses per sample are identified for the SRAT, SFHT, SME, MFT, and Glass sample points. The sampling and analytical strategies are based on assumed values for the required precision and accuracy of the results.


A study was conducted to assess the ability of the glass dissolution model developed by Dr. Bernard Grambow to predict the dissolution behavior of HWVP glass based on results of the HWVP glass durability tests conducted in FY 1987 using the data from the HWVP reference glass (HW-39) with Materials Characterization Center (MCC) -1 and MCC-3 leaching test procedures. The Grambow glass dissolution model did not predict the early time durability behavior. A modified version of the Grambow, in which the activities of the reactants in the rate determining step remain essentially constant as a function of reaction progress, qualitatively predicts the HWVP glass dissolution behavior at all times for constant glass surface area to solution volume ratios (SA/V). Statistical analyses indicate that neither model does a particularly good job of "fitting" the data. It is important to note that when the data corresponding to different SA/V ratios are considered together, there are no apparent trends suggesting the existence of a single model capable of predicting all of the data.


This study reports the developments and modifications of the Waste Form Qualification (WFQ) Simulation Model completed in FY 1988. The WFQ Simulation Model was developed to meet the WFQ needs for a mass balance model to predict the composition of the glass product and to assess the impacts of process perturbations and measurement uncertainties on product quality. In FY 1988, the following code modifications were completed. A frit-addition algorithm was implemented in the code. The Model can predict the glass composition based on the simulated data generated by the model and using the mass balance incorporated into the model. The process uncertainties and perturbations expected in the vitrification process have been expanded to assess the impacts on glass quality. A statistically designed set of simulation runs were performed to examine the effects of previously used assumptions and parameters on glass composition.

Fiscal Year 1987

An assessment was made of the capability of two computer models to predict the leaching performance of nuclear waste glasses based on glass composition. The two models evaluated were 1) a thermodynamic model of glass durability based on the Gibbs free energy of hydration of glass "structural units" that was developed by Dr. C.M. Jansen, and 2) a thermodynamic/kinetic model developed by Dr. B.E. Grambow for the Japan, Swedish, and Swiss project. The Jansen model established a relationship of decreasing durability with increasing Gibbs free energy of hydration, although there is substantial scatter in the data. While the Jansen model can be used to predict qualitatively the early time dissolution behavior of glasses with widely different compositions, it currently lacks the precision to do this accurately. The Grambow model was found to be capable of predicting glass dissolution behavior for many elements over a broad range of conditions, such as solution contact time, glass composition, types of solutions, and static/flow conditions. The Grambow model has the potential to be a valuable tool for HWVP glass development and waste form qualification.


HWVP product and process modeling requirements were updated. In product modeling, comparing the durability model, Grambow model, with data does not suffice to explain the apparent variation in glass dissolution rate with changing chemical activity of the silicic acid in solution. Model modifications have been proposed, and it was proposed that the Grambow model be re-derived from first principles and data analysis continue. In process modeling, a Waste Form Qualification Simulation Model (WSM) was developed for HWVP to simulate transient mass balances over tanks, and treats sampling, chemical analyses, liquid level measurements, and chemical addition steps as stochastic (fluctuating randomly). Principle application of the code in FY 1988 should be to design the feed system sampling and mixing experiments. The model needs to be applied to determine sampling requirements. A chemical addition algorithm needs to be established in collaboration with the HWVP engineers for use in the model.

Fiscal Year 1986


Compositional data for glass poured into a canister during the PSCM-22 run were analyzed and reported. For the part of the run resulting in a filled canister, the mass balance model appears to be accurate, and the model written for the melter itself predicted glass composition to within about a percent for the major glass components. The error found was probably due to analytical error, since the relative standard deviation of ICP results are estimated to be about 2%. The product was homogeneous to within about 2% relative standard deviation averaged over 5 most prominent components. The slight inhomogeneity in the canister is attributable to the variation in feed composition during the run.

A study was performed to describe the need for models in terms of addressing waste acceptance specifications, following the strategy outlined in the HWVP's Waste Form Compliance Plan. Models and modeling activities are described. The required models are a mass balance process model, a thermal process model (canister filling), a durability product model, a devitrification model, and a cracking model.

Fiscal Year 1984


A study was performed to define the relationships between process control and waste product quality that will provide a basis for adequate control of the product and which can thereby become part of the justification for waste form selection. The links between repository criteria, product requirements, controllable product attributes, and process measurements have been used to define needed relationships between process measurements and product quality. The controllable product attributes are composition, microstructure, solidity, and mass of glass in a canister, to which the product quality must be related. These relationships may be developed partially by testing the product in the laboratory and partially by testing actual canisters of glass. Needed relationships between process variables and the controllable product attributes were identified, and the needed process instrumentation identified. Process models were available or were imminent that were sufficient to predict the controllable attributes of the product, with the least certainty in the area of predicting the coalescence of pouring glass into a solid mass. Some instrumentation still needed to be perfected.
18.0 Analytical

Fiscal Year 1994


This laboratory program progress report summarizes the results to date of ion chromatography (IC) separations and analysis by inductively coupled mass spectrometry (ICP/MS) and solid-scintillation beta detection to develop a method to measure a number of radionuclides which have been historically difficult to determine by more routine radiation counting techniques. A comprehensive IC-beta-ICP/MS system has been developed to separate and detect numerous radionuclides in Hanford waste tank samples for example separation and detection of over 47 elements and 160 isotopes, including 20 radionuclides, was performed from a single sample injection and a single computer controlled elution lasting 70 min. This system could reduce radionuclide analysis cost by over a factor of ten with similar decreases in analysis times. Instrumental detection limits for most elements by the ICP/MS used in this work is at the low pico-gram level. Development of dissolution procedures which can be used with IC methods is paramount in being able to provide analytical methods for these determinations.


This laboratory program progress report summarizes the results to date concerning installation and testing of a new laser ablation (LA) apparatus used to introduce solid samples into the inductively coupled plasma mass spectrometry (ICP/MS) to be used for remote analysis of highly radioactive tank and vitrified wastes in a hot cell environment (the actual plan is to perform remote sampling instead of remote analysis). It was demonstrated that laser ablation of a vitrified waste simulant at infrared (IR) (1064 nm) and ultraviolet (UV) (266 nm) yields significantly different results. The particle distribution depends on the ablation wave length; IR irradiation produces larger particle sizes compared with UV ablation. The results show that UV ablation coupled to ICP-MS gives data from which quantitative analytical information about the sample can be extracted. The results of the IR ablation show a great deal of elemental discrimination, making quantitative analysis difficult if not impossible. Thus, UV is the wavelength of choice for Laser Ablation ICP-MS.

Fiscal Year 1993

This laboratory program progress report summarizes the results to date concerning ion chromatographic (IC) separations and analysis by inductively coupled mass spectrometry (ICP/MS). Experimental results indicate that much progress has been made to effect the separation of elements which possess radioactive isotopes. These separations allow detection of most of the radionuclides found in Hanford tank wastes. Instrumental detection limits for most elements by ICP/MS is at the low picogram levels. However, since most tank wastes will have to be dissolved, actual detection limits will be subject to sample dilution and radioisotope behavior with respect to its ion exchange properties. Separations investigated included: transition metals, rare earth elements, noble metals, technetium, and iodine. Other separations methods development in progress include alkali and alkaline earth and selenium from bromine.


The results of the interlaboratory comparison of methods for analyzing noble metals in six virtually identical HWVP glass samples are reported. Participating laboratories included Savannah River Technology Center, West Valley Nuclear Services Company, Defense Waste Processing Technology Section, Monarch Analytical Laboratories, and Pacific Northwest Laboratory. Each laboratory processed and analyzed the given glass samples for noble metals by methods normally used by that laboratory; a total of three different sample dissolution procedures and four different analytical methods were employed. The results indicate that for analyzing noble metals in borosilicate glasses produced from waste simulants 1) microwave digestion is unsatisfactory as a method of dissolution; for analytical techniques requiring dissolution, sodium peroxide fusion is recommended as a reasonably effective method for putting all constituents in solution, and 2) analytical methods that involve direct analysis of solid material, such as X-Ray Fluorescence (XRF) and laser ablation-inductively coupled mass spectrometry (ICP/MS), are generally more reliable (and probably more accurate) than digested sample analysis methods.

Fiscal Year 1992


Laboratory studies were performed to 1) complete testing on HWVP standard HW-39-4A glass (or similar) using ICP/MS techniques, including laser ablation (LA) and solution nebulization (SN) sample introduction methods, 2) provide data to evaluate the accuracy, precision, and effective sensitivity of each of these sample introduction techniques and of the ICP/MS capability, and 3) evaluate isotope interferences and potential for correcting interferences on the basis of these experiments. Also, analysis of HW-39 black glass by solutions (SN) ICP/MS using acid and alkali fusions are reported. Results from ultraviolet laser ablation (UVLA) ICP/MS analysis of simulated waste glasses are reported. Data obtained by solutions and direct solids (UVLA) sample introduction
techniques are evaluated with respect to each methods' precision and accuracy for determining the stable element constituents in HWVP glasses. ICP/MS techniques for analysis of radionuclides (unstable elements) including the employment of electrothermal vaporization and ultrasonic nebulization sample introduction techniques are introduced with discussions on potential radionuclide interferences and specific examples for possible solutions for spectral correction and/or elimination. It was concluded that ICP/MS can be used to determine nearly all of the constituents observed in waste glasses with good precision and accuracy directly or after dissolution; but more than one dissolution may be required, and Ru analysis may be a problem with acid dissolution. Direct solids analysis by UVLA ICP/MS indicate that this technique in combination with energy dispersive XRF (EDXRF) can be used to completely characterize waste glasses. The employment of the UVLA ICP/MS for direct analysis of HWVP glasses and slurries look very positive with better precisions observed relative to solution nebulization not only for the major elemental constituents but also for essentially all of the minor and trace constituents including noble metals; sulfur and phosphorous may be the exceptions. Previous results obtained by using the infrared (IR) laser showed larger precision variations (> 10%) with accuracies averaging about plus or minus 15% for refractory elements and considerably more for volatile elements such as B, Na, Cd, Cs, and Zn. A comparison between radiation detection and ICP/MS detection of radionuclides indicates that radionuclides with half-lives greater than a few hundred years are more effectively determined by the ICP/MS technique.


No annotation

Fiscal Year 1991

Smith, MR. June 27, 1991. "Analytical Methods Development Subtask 1.2.2.05.05 Status Letter Report (Milestone 1.2.2.05.05D)," HWVP-C91-05.05D, Pacific Northwest Laboratory, Richland, Washington.

Progress, including design description, to date is described on the inductively coupled mass spectrometry (ICP/MS) adaptation for radioactive containment as well as a brief summary on the capabilities to be achieved with this new facility upon completion. The adaptation was well in progress.
19.0 Canister Closure, Decontamination, and Handling

Fiscal Year 1987


A study was performed to establish system criteria for the HWVP preliminary canister decontamination (PCD) system and provide a conceptual design for a nonradioactive test chamber. The concept of a low pressure water spray was the reference for filled canister decontamination in the HWVP. Testing recommendations were also made.


A drawing package for the HWVP Preliminary Decontamination Test Chamber is provided for evaluation of the HWVP canister decontamination system. The package includes drawings of the vessel, canister grapple, and water spray system. The test chamber was designed to be compatible with the test canisters fabricated for the evacuated canister system development.

Fiscal Year 1985


A study was performed to review and evaluate various glass-filled canister decontamination techniques to remove loosely adhering surface contamination which will aid in system selection for HWVP. Several techniques appear to be effective for canister decontamination, but only a low-pressure spraying system meets all of the criteria considered. Low-pressure spraying encompasses low-pressure water sprays, air-injected water sprays, and low-pressure steam sprays. Testing to date does not provide a definitive choice. Recommendations for design and testing to make a final choice are included.


A concept for remotely positioning waste canisters under a remotely maintained inertia melter, which will be used to seal the canisters, is described together with the canister positioning system functional criteria, the current equipment design, and a recommended testing program.
Work performed during fiscal years 1983 and 1984 to identify a welding process for making the canister seal weld was reported. The gas tungsten-arc, plasma arc, laser, resistance, and inertia welding processes were considered. The inertia friction welding was the preferred process with gas tungsten-arc welding as the backup process. Gas tungsten-arc welding is capable of making the necessary weld; however, there are difficulties with remote operation including maintenance of a complex device, precise adjustments to the device while the weld is being made, and the ability to visually monitor the molten weld pool and the torch to determine when adjustments are necessary. The inertia welding process should make both the primary and secondary closure weld with only a small part of the machine in the hot cell with the remainder of the machine being available for contact maintenance, and the machine would be special design.

The applicability of the DWPF canister throat protector to the HWVP and, if appropriate, suggest alternative designs are discussed. The DWPF canister throat protector could be used if adequate room in the turntable is available. However, differences in the DWPF and HWVP melter/turntable design makes the disposable seals and the thickness of the metal on the DWPF throat protector unnecessary. Several modified DWPF canister closure throat protector designs are suggested which are intended for use in a closed turntable to protect the canister closure sealing surfaces from damage and deposits.

The adequacy and reliability of the DWPF canister throat heating unit on the Inner Canister Closure Station (ICCS) for use in the Hanford Waste Vitrification Program (HWVP) was to be evaluated. The evaluation was prompted by the need for the unit to operate for each Hanford canister and its infrequent use in the DWPF for nonroutine situations. Adequate information was not available to make the assessment because the design, construction, and testing were not completed. It was recommended the evaluation be subsequently performed.
for verifying acceptable system performance while inspecting closure welds was selected; and data was obtained that will lead to design for in-cell calibration standards. The scanner, when used with a commercially available ultrasonic test instrument, can reliably detect and record 0.100-in. deep inner and outer diameter sawcut notches lying in the weld plane of an actual inertially welded closure. The scanner is acoustically coupled to the canister top by water. The technique was demonstrated at a surface temperature of 215°F. Commercially available transducers were procured (claimed to survive melter cell radiation environment) and exhibited acceptable acoustic performance. Testing showed that the best acoustic signal to monitor for system performance is the reflection from the underside of the canister top.


A study was performed to provide design considerations for the canisters that will be used to contain, transport, and store Defense-High Level Waste, which is generated at the PUREX Plant. A general description of the HWVP facility and its requirements on the canister was provided. Functional design criteria for the HWVP facility were provided. Vitrification equipment requirements were described. Functional design criteria for the equipment were provided. Canister considerations were described which include: design, fabrication, process, transportation, repository, and safety. Other general needs were discussed including criteria, codes, standards, quality assurance, and repository data submittal.

Fiscal Year 1983


A study was performed to select a reference canister closure system for the B-Plant Immobilization Pilot Plant, and the selection process and results are described. Closure criteria were established; a process survey was performed; component design studies were performed, and a recommendation was made. Welding processes considered were inertia friction welding, gas-tungsten arc welding, plasma arc welding, and resistance upset welding. The reference system selected included a vertically mounted inertia welder to seal weld a primary and secondary cap, a canister positioning arm, an ultrasonic weld inspection scanning device, and a viewing window to inspect operations.
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