
**Pacific Northwest
National Laboratory**

Operated by Battelle for the
U.S. Department of Energy

Test Summary Report Vitrification Demonstration of an Optimized Hanford C-106/AY-102 Waste-Glass Formulation

R. W. Goles
W. C. Buchmiller
C. R. Hymas
B. D. MacIsaac

November 2002



Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RL01830

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, makes **any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.** Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PACIFIC NORTHWEST NATIONAL LABORATORY

operated by

BATTELLE

for the

UNITED STATES DEPARTMENT OF ENERGY

under Contract DE-AC06-76RL01830



This document was printed on recycled paper.

**Test Summary Report
Vitrification Demonstration of an Optimized
Hanford C-106/AY-102 Waste-Glass Formulation**

R. W. Goles
W. C. Buchmiller
C. R. Hymas
B. D. MacIsaac

November 2002

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RL0-1830

Pacific Northwest National Laboratory
Richland, Washington 99352

Abstract

In order to further the goal of optimizing Hanford's HLW borosilicate flowsheet, a glass-formulation effort was launched to develop an advanced high-capacity waste form exhibiting acceptable leach and crystal-formation characteristics. A simulated C-106/AY-102 waste envelope inclusive of LAW pretreatment products was chosen as the subject of these nonradioactive optimization efforts. To evaluate this optimized borosilicate waste formulation under continuous dynamic vitrification conditions, a research-scale Joule-heated ceramic melter was used to demonstrate the advanced waste form's flowsheet. The main objectives of this melter test was to evaluate 1) the processing characteristics of the newly formulated C-106/AY-102 surrogate melter-feed stream, 2) the effectiveness of sucrose as a glass-oxidation-state modifier, and 3) the impact of this reductant upon processing rates.

Summary

In Response to a U.S. Department of Energy (DOE) Headquarters directive to conduct a technical review of alternatives for solidification of high-level waste (HLW) that could achieve major cost reductions with reasonable long-term risks,^(a) the Tanks Focus Area (TFA) chartered an independent Review Team to evaluate cost incentives associated with modifications to: waste-form product requirements, waste-stream processing constraints, product glass composition, and the reference waste-vitrification technology itself.

One of the conclusions drawn from the Review Team evaluation of alternative waste forms was that the borosilicate waste form has performed predictably and is firmly entrenched in the nuclear waste remediation program. However, it was felt that the vitrification process using this waste form had not been optimized (Perez et al. 2001). To further the goal of optimizing Hanford's HLW borosilicate flowsheet, a primary focus of the Review Team's effort, a TFA-sponsored glass-formulation effort was launched to develop an advanced high-capacity waste form exhibiting acceptable leach and crystal-formation characteristics (Peeler et al. 2002). Specifically, a simulated C-106/AY-102 waste envelope inclusive of low-activity waste (LAW) pretreatment products was chosen as the subject of these nonradioactive optimization efforts.

To evaluate the processing, off-gas emission, and product glass characteristics of this optimized borosilicate waste formulation under continuous dynamic vitrification conditions, a research-scale, Joule-heated, ceramic melter was used to demonstrate the advanced waste form's flowsheet. Specifically, the Pacific Northwest National Laboratory's (PNNL's) Research-Scale Melter (RSM) was used to conduct these initial melter-flowsheet evaluations. The RSM is a small (1/100-scale, DWPF basis) joule-heated melter that is capable of processing melter feed on a continuous basis. This capability is key for:

- developing/evaluating process flowsheets
- characterizing relationships between feed composition and the properties of the final glass produced
- establishing the fate and behavior of process effluent.

This melter system's capability to produce glass in a continuous manner is also essential for estimating the behavior of a full-scale system. Moreover, the size of the RSM allows the impacts of process variables upon melter performance or glass quality to be quickly and efficiently evaluated without undue expense or waste generation.

The experimental scope of this initial, 5-d, 120-h, C-106/AY-102 vitrification test was to:

- determine the feasibility of vitrifying surrogate C-106/AY-102, at 60 wt% waste loading, to produce a regulatory-acceptable borosilicate glass waste form
- evaluate the glass product with regard to composition, crystal growth and concentration, phase separation, chemical durability, and oxidation state

(a) TTP: Advanced High-Level Waste (HLW) Melter and Waste Products Review, 25 August 2000.

- characterize the composition and concentration of condensed-phase and selected gaseous melter-generated off-gas emissions and the composition of secondary off-gas system waste streams
- establish maximum process rates at a glass temperature of 1150°C and a 95% cold-cap coverage
- access whether the melt rate or processing conditions can be optimized by changing reductant and/or melter-operating conditions
- measure the volume-reduction factor for vitrified surrogate C-106/AY-102 waste stream
- quantify specific glass-production rates and waste-vitrification energy requirements.

During the 120 h of experimental testing, a validated C-106/AY-102, Envelope-D surrogate^(a) was prepared, combined, at 60 wt% waste loading, with an optimized suite of glass formers, composed of B, Li and Si, and successfully vitrified in a Joule-heated melter. Beyond the processing characteristics of the optimized, baseline glass formulation, the impacts of a sugar-reductant additive at varying concentrations (2.5, 5, 7.5, and 9 g/L-waste) upon processing rates, gaseous emission characteristics, and glass oxidation state [Fe(II):Fe(III)] were also evaluated. The effects of a ~10% increase in melter-feed-water concentration upon melter performance was also assessed during melter testing.

The melting kinetics of the optimized CY-106/AY-102 feed formulation was found to be influenced by sugar-additive concentration. Although initial short-term processing of the baseline feed formulation, without the use of sugar additive, was quite successful, the glass formed was highly oxidized, and because of its relatively high Mn content, was quite susceptible to foaming. Without physical methods to mitigate the impact of foam-layer development, long-term processing of feeds without a supplemental reductant does not appear to be a viable option.

Less dynamic foaming occurred when a waste sugar concentration of 2.5 g/L was employed, but unstable processing conditions nevertheless resulted from a glass that remained too highly oxidized. Stable long-term melter processing conditions were achieved at all other sugar concentrations evaluated. At a sugar waste loading of 5 g/L, the product glass' Fe(II):Fe(total) ratio was <5% while at 9 g/L, a value slightly less than the limiting condition of 30% was measured

Although stable melting conditions resulted for waste sugar loadings ≥ 5 g/L, cold-cap characteristics appeared to be deleteriously affected by the sugar additive. The addition of sugar at all levels seemed to exacerbate feed coning beneath melter's feed nozzle. The collapse of dried feed matter that accumulated within the cone produced temporary processing instabilities by creating 100% cold-cap coverage conditions at all sugar loadings used. Water dilution of the incoming feed stream was used somewhat successfully to spread the incoming feed material over the entire glass pool; however, reduced glass production rates resulted from the power losses required to dry the diluted feed.

Melter-glass production rates varied from 8.3 to 4.3 lbs/h/ft² for the various feed batches processed. These values comfortably exceed the reference (cold-lid) Liquid Fed Ceramic Melter (LFCM) design production rate of 4 lbs/h/ft² that is often quoted and used for flowsheet and equipment sizing estimates

(a) WK Kot, H Gan, and IL Pegg. 2000. *Physical and Rheological Properties of Waste Simulants and Melter Feeds for RPP-WTP HLW Vitrification*, Vitreous State Laboratory, The Catholic State University, Washington, D.C.

(Perez et al. 2001). Indeed, this reference-normalized production rate is exceeded even when projections are based upon the overall average rate data (5.5 lbs/h/ft²) that are inclusive of all idle-batching periods.

Average measured Joule heating power was used with corresponding batch feeding rates, reductant loadings, and heat of combustion information to derive specific process energy requirements for the surrogate C-106/AY-102 feeds. The average value derived for all batches processed, 3.9 kW•h/kg, agrees well with typical energy requirements for slurry-fed, Joule-heated ceramic melters: 2 to 4 kW•h/kg of glass produced (Perez et al. 2001).

Representative glass samples generated throughout the duration of RSM testing were subjected to standard durability tests. Specifically, glass samples were subjected to both product consistency test (PCT) (ASTM 1997) and toxicity characteristic leach procedure (TCLP 1992) leach-testing protocols. The PCT results suggest that all C-106/AY-102 glasses were more durable than the standard environmental assessment glass to which they were compared. Although marginal Ag results were obtained, corresponding TCLP tests indicate that all glasses produced, even the more highly reduced ones, conform to all existing Resource Conservation and Recovery Act (RCRA) land-disposal limits (40 CFR 268).

Pour-stream glass samples taken throughout the melter testing campaign were examined for the presence of secondary phases. The results obtained indicated that spinel crystals were present at an average concentration of 0.5 wt% (~0.25 vol%), which was significantly lower than a comparable, pre-test, qualifying crucible test result (1.8 wt%) obtained at 1150°C. In addition, post-test core drilling of the solidified melter glass pool allowed spinel crystal uniformity throughout the melt volume to be accessed. No significant stratification of spinel could be discerned from the somewhat noisy and scattered data obtained.

For the surrogate C-106/AY-102 melter feed used during RSM testing, CO₂ and NO_x (specifically NO) were the major non-condensable (~ 25°C) gases produced by the vitrification process. Feed nitrates were found to be efficiently reduced to N₂ under all waste sugar loadings as evidenced by significantly reduced NO emission rates. Of the process-generated combustible gases of concern, CO was undetectable (<250 ppm) at all reductant concentrations, and the maximum concentration of H₂ recorded was 0.02%. These concentrations are well below the lower flammability limits of these combustible gases, 4.65% for H₂ and 15.5% for CO and, consequently pose no reasonable off-gas system hazard under any conceivable processing conditions..

Condensed-phase effluents were also monitored during C-106/AY-102 melter testing. The melter's aerosol mass decontamination factors (DFs), as measured by isokinetic filter catches, were determined while processing feed containing a waste-sugar concentration of 7.5 g/L. These melter aerosol mass DFs ranged from 500 to 1200. Cold-cap accumulation (coning) during off-gas sampling is likely responsible for the range of the observed values. The overall mass DF as determined from secondary waste stream compositions is 240.

Melter partitioning for individual feed components was also derived from the off-gas sampling and secondary waste-stream data. With the exception of boron, sulfur, and the halogens, essentially all feed constituents (excluding C, N, H₂O, etc.) were found to be primarily in a condensed state downstream of the film cooler. Overall, the element-specific DFs recorded during the current test are reasonably close to

general expectations and are generally consistent with previous melter-testing results. Furthermore, both off-gas sampling and secondary waste-stream-derived DF values exhibited the same relative trends for related groups of elements and were of comparable magnitudes for corresponding waste constituents. Indeed, the very reasonable mass closure demonstrated for most of the feed constituents for which complete analytical data exist suggests that the current melter test has successfully characterized the vitrification flowsheet of the optimized, 60 wt% C-106/AY-102 glass formulation.

During the July 2002 melter-flowsheet evaluation studies, 100 L (26 gal) of 60 wt% C-106/AY-102 simulated melter feed (~90 L-waste), having a total mass of 142 kg, was processed by the RSM, producing 20 L (5.3 gal) of glass having a total mass of 51 kg. These results suggest that an overall waste-volume-reduction factor of 4.6 was achieved during the RSM processing of the optimized C-106/AY-102 melter-feed formulation.

References

40 CFR 268. 2000. U.S. Environmental Protection Agency, "Land Disposal Restrictions." *U.S. Code of Federal Regulations*, Washington D.C.

American Society for Testing and Materials (ASTM). 1997. *Standard Test Methods for Determining Chemical Durability of Nuclear, Hazardous, and Mixed Waste Glasses: The Product Consistency Test (PCT)*, ASTM C1285-97, West Conshohocken, PA.

Peeler DK, TB Edwards, CC Herman, RJ Workman, IA Reamer, JD Vienna, JV Crum, DE Smith, and DS Kim. 2002. *Development of High Waste Loading Glasses for Advanced Melter Technologies*, WSRC-TR-2002-00426, Westinghouse Savannah River Company, Aiken, SC.

Perez JM, DF Bickford, DE Day, DS Kim, SL Lambert, SL Marra, DK Peeler, DM Strachan, MB Triplett, JD Vienna, and RS Wittman. 2001. High-Level Waste Melter Study Report, PNNL-13582, Pacific Northwest National Laboratory, Richland, WA.

Toxicity Characteristic Leaching Procedure (TCLP). 1992. *Test Methods for Evaluating Solid Waste, Volume 1C: Laboratory Manual Physical/Chemical Methods*, SW-846, Method 1311, Rev. 2, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington D.C.

Acronyms / Symbols

APEL	Applied Process Engineering Laboratory
DF	decontamination factor
DOE	U.S. Department of Energy
EA	environmental assessment
EPA	U.S. Environmental Protection Agency
EVS	ejector venturi scrubber
HEME	high-efficiency mist eliminator
HEPA	high-efficiency particulate air (filter)
HLW	high-level waste
LAW	low-activity waste
LFCM	Liquid Fed Ceramic Melter
LOD	loss on drying
LOI	loss on ignition
MOG	melter off-gas
PCT	Product Consistency Test
PLC	Programmable Logic Controller
PNNL	Pacific Northwest National Laboratory
POG	process off-gas
RCRA	Resource Conservation and Recovery Act
RSM	Research-Scale Melter
SCR	silicon-controlled rectifier
SRS	Savannah River Site
TCLP	toxicity characteristic leach procedure
TFA	Tanks Focus Area
UDS	undissolved solids
UTS	Universal Test Standard
----	not measured / not detected / not available / not applicable

Acknowledgments

The authors would like to acknowledge the following people:

- PNNL staff who performed laboratory work and RSM shift activities
- Wayne Cosby for editorial assistance
- S. K. Sundaram for Technical Review
- E. William Holtzscheiter for management and guidance.

This study was funded by the U.S. Department of Energy's (DOE's) Office of Science and Technology, through the Tanks Focus Area, and was performed and documented by Pacific Northwest National Laboratory (operated for DOE by Battelle under Contract DE-AC06-76RL01830).

Contents

Abstract	iii
Summary	v
Acronyms	ix
Acknowledgments	xi
1.0 Introduction	1.1
2.0 Test Objectives	2.1
3.0 RSM System Description	3.1
3.1 Melter	3.1
3.2 Feed System	3.5
3.3 Off-Gas Processing System	3.6
3.4 Off-Gas Sampling System	3.6
3.5 Data Acquisition and Process Control System	3.7
4.0 CY106/AY102 Simulant, Melter Feed, and Product Glass	4.1
4.1 CY106/AY102 Surrogate	4.1
4.2 Target Glass Composition	4.6
4.3 Glass Former and Chemical Additives	4.6
4.4 Melter Feed Characteristics	4.7
4.5 Product Glass Characteristics	4.8
4.5.1 Oxidation State Results	4.9
4.5.2 Compositional Data	4.10
4.5.3 TCLP Results	4.14
4.5.4 PCT Results	4.14
4.5.5 Spinel Secondary Phase	4.15
5.0 Discussion of Results	5.1
5.1 Processing Observations and Parameters	5.1
5.2 Operating Parameters	5.5
5.2.1 Process Temperatures	5.5

5.2.2	Process Pressures	5.5
5.2.3	Melter Electrical Data	5.8
5.2.4	EVS Condensate Tank, Film Cooler Injection Air	5.10
6.0	Melter Off-Gas Emission Characterization	6.1
6.1	Gaseous Effluent	6.1
6.2	Condensed Phase Effluents	6.3
6.2.1	Aerosol Mass DFs	6.4
6.2.2	Aerosol Elemental DFs	6.5
6.2.3	Volatile Partitioning and Total Elemental DFs	6.7
6.2.4	Process-Waste-Stream Composition	6.9
7.0	Byproducts, Residuals, Mass Balance, and Volume Reduction	7.1
7.1	Off-Gas Line Deposits	7.1
7.2	Process Mass Balance	7.2
7.3	Process Statistics	7.4
7.4	Process Summary	7.4
8.0	References	8.1
Appendix A: Test Plan and Test Instructions for Vitrification Demonstration Tests of		
	C-106/AY-102 Waste Simulant	A.1
Appendix B: Test Instructions for Preparing C-106/AY-102 Waste Simulant		
		B.1
Appendix C: RSM Feed Batching and Manual Data Sheets		
		C.1
Appendix D: Colorimetric Procedure for Determining Fe(II) to Total Iron Ratio		
		D.1
Appendix E: Variable Process Data Collected During the C-106/AY-102 Flowsheet Evaluations		
		E.1

Figures

3.1. Photograph of RSM Demonstration Unit.....	3.2
3.2. Research-Scale Melter Test Apparatus	3.3
3.3. Schematic View of the Research-Scale Melter	3.4
3.4. Schematic Arrangement of Off-Gas Sampling System Components	3.7
4.1. Historical Sugar Concentration and Glass-Oxidation-State Values.....	4.11
4.2. Spinel Concentrations Within the RSM's Frozen Glass Volume	4.16
5.1. Process History of RSM Feed Batches and Average Overall Processing Rate	5.2
5.2. C-106/AY-102 Glass Accumulation Data	5.4
5.3. Melter Vacuum and Off-Gas Pressure Drop Data	5.7
5.4. RSM Electrode Operating Characteristics	5.8
5.5. EVS Condensate Tank, Film-Cooler Operating History.....	5.12
6.1. Temporal Behavior of Major Process Effluent Gases.....	6.4
7.1. Melter Off-gas Jumper Configuration and Sample Site Locations	7.2

Tables

3.1. RSM Dimensions and Operational Features	3.5
3.2. RSM's Effluent Gas Analyzers.....	3.6
4.1. Composition Summary for C-106/AY-102 Waste, LAW Pretreatment Products and C-106/AY-102 Simulant.....	4.2
4.2. Composition and Preparation Recipe for C-106/AY-102 Simulant.....	4.3
4.3. RSM C-106/AY-102 Waste Surrogate Composition.....	4.4
4.4. Comparison of Analytical and Manufacturer Assay Reports.....	4.5
4.5. Physical Characteristics of C-106/AY-102 Surrogate Waste	4.5
4.6. Target Glass Composition.....	4.6
4.7. Comparative CY-106/AY-102 Glass-Former Additives	4.7
4.8. Melter Feed Glass-Former Additives and Equivalent Frit Composition	4.7
4.9. Physical Properties of Surrogate C-106/AY-102 Melter Feeds.....	4.8
4.10. Melter Feed Batch Composition	4.9
4.11. C-106/AY-102 Sugar Loadings and Glass-Oxidation States.....	4.10
4.12. Oxide Composition of Melter C-106/AY-102 Glass Samples.....	4.12
4.13. Independent (SRS) Oxide Composition Data for Melter C-106/AY-102 Glass Samples	4.13
4.14. TCLP Leachate Concentrations from C-106/AY-102 Glasses	4.14
4.15. PCT Leachate Results from C-106/AY-102 Glasses	4.15
4.16. Spinel Content of Laboratory and Melter Glasses	4.16
5.1. C-106/AY-102 Feed Processing Rates and Derived Glass Production Rates.....	5.3
5.2. Experimental C-106/AY-102 Glass Production Rate Data.....	5.4
5.3. RSM's Operating Temperature Characteristics	5.6
5.4. Melter Kiln, Pour Spout, and Canister Oven Temperatures	5.6
5.5. RSM Electrode Circuit Operating Characteristics	5.9

5.6. Specific Process Energy Requirements For C-106/AY-102 Feeds.....	5.9
5.7. Operational Characteristics of Melter Kiln and Overflow Heaters.....	5.11
6.1. Unquenched Melter Off-Gas Composition	6.2
6.2. Gross Melter Aerosol Emission Characteristics	6.5
6.3. Oxide Composition of Melter Generated Aerosols and Melter Feed.....	6.6
6.4. Elemental Melter DFs Associated With Aerosol Emissions.....	6.7
6.5. Off-Gas Sampler Condensate Solution Composition (ppm).....	6.8
6.6. Volatile Melter DFs for Boron, Halogen, and Sulfur Feed Constituents.....	6.8
6.7. Total Individual Elemental Melter DF Values.....	6.9
6.8. EVS Condensate Soluble Effluent Composition.....	6.11
6.9. HEME Waste Stream Composition For Soluble Effluent.....	6.12
6.10. Composition of EVS Undissolved Solids and Off-Gas Pipe Deposits	6.13
6.11. Off-Gas Sampler and Waste-Stream Total Melter DF Values.....	6.13
6.12. Secondary Waste Stream Physical Properties.....	6.14
7.1. Distribution of Melter Off-Gas Line Deposits	7.1
7.2. Stream-Dependent %-Partitioning of C-106/AY-102 Melter Feed Constituents	7.3