PNNL-11016
UC-810
Project Technical Information

Hanford High-Level Waste Melter System Evaluation Data Packages

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March 1996

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

Pacific Northwest National Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute

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Summary

The Tank Waste Remediation System (TWRS) is in the process of selecting a reference melter system for the Hanford High-Level Waste (HLW) vitrification plant. As a part of this selection process, a melter evaluation was conducted in FY 1994 to downselect the long list of potential melter technologies to a few that could be carried forward to testing. A formal evaluation was performed by an 11-member Melter Selection Working Group (MSWG): five outside vitrification experts and six Westinghouse Hanford Company (WHC) staff. The MSWG met in June and August 1994. At the June meeting, the MSWG evaluated 15 technologies and selected six for more thorough evaluation at the August meeting. All six technologies were variations of joule-heated or induction-heated melters, and were considered to have the highest probability of success compared with the alternative technologies.

Between the June and August meetings, Hanford Site staff and outside consultants compiled data packages for each of the six melter technologies as well as variants of the baseline technologies. Information was solicited from melter candidate vendors to supplement existing information/data available through open literature and glass industry experience. Where information was unavailable or nonexistent, assumptions, predictions, and scoping evaluations were performed to provide information such as scaleup factors, glass production capacity, waste composition processing flexibility, expected operability/maintainability, etc. The assumptions, predictions, and evaluations were primarily qualitative but represented best available information without performing extensive testing. This document contains the data packages compiled to provide background information to the MSWG in support of the evaluation of the final six melter technologies.

A separate evaluation was performed by Fluor Daniel, Inc. to identify balance of plant impacts if a given melter system was selected. Balance of plant impacts include those related to facility layout, melter support systems (e.g., feed preparation, melter offgas, etc.), and failed melter dismantlement and packaging. Rough order-of-magnitude plant cost impacts associated with the melter systems evaluated were also estimated. This information was provided to the MSWG under a separate cover,(a) and the reader is referred to this report throughout sections of the data packages contained in this document.

(a) Fluor Daniel, Inc. August 1994. "Alternative Melter Systems Assessment 20 Metric Tons Per Day HLW Glass Production." Prepared under contract #04-436304 with Westinghouse Hanford Company.

Acknowledgments

The information in this document was gathered from numerous sources. The following people made significant contributions to the melter data packages in very short periods of time. Mr. Mike Elliott and Ms. Phyllis Shafer compiled the overall data package document. Dr. G. Roth, Mr. W. Tobie, and Mr. W. Grünewald of Kerforschungszentrum Karlsruhe provided much of the information for Appendix A of Data Package 1, Appendix B of Data Package 4, as well as significant input to the sections on development of joule-heated melters in Japan and Germany. Mr. Rick Merrill of PNL supplied information for Data Package 1, Appendix B. Mr. David Lamar of PNL supplied much of the information and text for Data Package 4. Mr. Antoine Jouan of Commissariat A L'Énergie Atomique supplied much of the information for Data Packages 3 and 6. Mr. Ken Kormonyos of Stir Melter, Inc., Mr. Ray Richards of Associated Technology Consultants, Mr. David Bennert of Clemson University, and Ms. Connie Cicero of Savannah River Technology Center provided information for Data Package 2. Mr. Larry Penberthy provided all of the information for Appendix A of Data Package 4. Mr. Tac Wang of Ferro Corp, Mr. Jim Kosanke of GAF, and Mr. Leon Bass at Cataphote, Inc. provided information for Data Package 5.

Abbreviations and Acronyms

ϕ	diameter
Ω	ohm
ALARA	As Low As Reasonably Achievable
AM	Alkaline Metal
AZS	Alumina Zirconia Silica
BNFL	British Nuclear Fuels Ltd.
CCM	Cold Crucible Melter
CEA	Commissariat A L'Énergie Atomique
CFCM	Calcine-Fed Ceramic Melter
CVS	Compositional Variability Study
DF	Decontamination Factor
DOE	U.S. Department of Energy
DOE-HQ	U.S. Department of Energy (Headquarters)
DOE-RW	U.S. Department of Energy Radioactive Waste Management
DOV	Diaphragm-Operated Valve
DRE	Destruction and Removal Efficiency
DWPF	Defense Waste Processing Facility
EA	Environmental Assessment
ECA	Environmental Corporation of America
ESCM	Engineering-Scale Ceramic Melter
FMEA	Failure Modes and Effects Analysis
HBCM	High-Bay Ceramic Melter
HEPA	High-Efficiency Particulate Air (filter)
HEWC	High Enriched Waste Content
HLW	High-Level Waste
HTCM	High-Temperature Ceramic Melter
HTM	High-Temperature Melter
HWVP	Hanford Waste Vitrification Plant
IDMS	Integrated DWPF Melter System
IR	Infrared
JNFS	Japan Nuclear Fuel Service
KfK	Kerforschungszentrum Karlsruhe GmbH
LEWC	Low Enriched Waste Content
LFCM	Liquid-Fed Ceramic Melter
LFIM	Low-Frequency Induction Melter
LLW	Low-Level Waste
LRW	Liquid Radioactive Waste
LTCM	Low-Temperature Ceramic Melter
MCC	Materials Characterization Center
MSWG	Melter Selection Working Group
MT	Metric Ton
NCAW	Neutralized Current Acid Waste
ORNL	Oak Ridge National Laboratory

Pa-s	Pascal Second
PCT	Product Consistency Test
PNC	Power Reactor and Nuclear Fuel Development Corporation
PNL	Pacific Northwest Laboratory
PSCM	Pilot-Scale Ceramic Melter
PSHTM	Pilot-Scale High-Temperature Melter
PUREX	Plutonium Uranium Extraction
PVTD	PNL Vitrification Technology Development
RLFCM	Radioactive Liquid-Fed Ceramic Melter
SCR	Silicon-Controlled Rectifier
SFCM	Slurry-Fed Calcine Melter
SGM	Scale Glass Melter
SM	Stirred Melter
SRL	Savannah River Laboratory
SRS	Savannah River Site
SRTC	Savannah River Technology Center
SSHTM	Small-Scale High-Temperature Melter
TAC	Technical Advisory Committee
TOE	Total Operating Efficiency
TPA	Tri-Party Agreement
TVF	Tokai Vitrification Facility
TWRS	Tank Waste Remediation System
USSR	Union of Soviet Socialist Republic (Former Soviet Union)
WAPS	Waste Acceptance Preliminary Specifications
WETF	West End Treatment Facility
WFE	Wiped Film Evaporator
WHC	Westinghouse Hanford Company
WSRC	Westinghouse Savannah River Company
WTF	Waste Treatment Facility
WVNS	West Valley Nuclear Services

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Introduction

The Tank Waste Remediation System (TWRS) is in the process of selecting a reference melter system for the Hanford High-Level Waste (HLW) vitrification plant. As a part of this selection process, a melter evaluation was conducted in fiscal year 1994 to downselect the long list of potential melter technologies to a few that could be carried forward to testing. A formal evaluation was performed by an 11-member Melter Selection Working Group (MSWG): five outside vitrification experts and six Westinghouse Hanford Company (WHC) staff. The evaluation process and results are described in a separate document. The MSWG met in June and August 1994. At the June meeting, the MSWG evaluated 15 technologies and selected six for more thorough evaluation at the August meeting. All six technologies were variations of joule-heated or induction-heated melters.

Between the June and August meetings, Hanford Site staff and outside consultants compiled data packages for each of the six melter technologies as well as variants of the baseline technologies. A specific format for the data packages was agreed upon at the June meeting. This format was consistent with the evaluation criteria that would be used to rank the melter technologies at the August meeting. The MSWG and other Hanford Site staff identified potential sources of information (proponents) for each technology. In many cases, there were several proponents for a single technology. Letters were sent to the proponents along with the format for their responses. Any gaps in the data packages were filled by WHC and Pacific Northwest Laboratory (PNL)[a] staff. The source for each piece of information was identified in the data packages so that the MSWG could tell if the information was from Hanford staff, a proponent, or open literature.

When alternative configurations existed for the melter technologies evaluated, a data package was provided for the baseline system and then an appendix for each alternative configuration. In some cases the appendix was a proponent's design that was significantly different from the baseline technology. The six data packages and their appendices are the following:

1. Low-temperature, joule-heated, ceramic-lined melter (LTCM)

   Appendix A. LTCM with sloped bottom

   Appendix B. LTCM with evaporator

   Appendix C. LTCM with agitation (bubbling system)

2. Low-temperature, joule-heated, metal-lined melter (Stirred Melter)

3. Low frequency induction melter (LFIM) with calciner

4. High-temperature, joule-heated, ceramic lined melter (HTCM)

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[a] Pacific Northwest Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO 1830.

Appendix A. HTCM, Penberthy design

Appendix B. HTCM, Russian design

5. High-temperature, joule-heated, cold wall melter (Pochet melter)
6. High-frequency induction melter with calciner [cold crucible melter (CCM)]

Most of the data packages were supplied to the MSWG before the August meeting. One of the data packages and a few of the appendices were not available to the MSWG until the start of the August meeting.

After the melter evaluation was completed, the MSWG realized that the data packages contained a useful compilation of current melter technologies and that this information should be cleared for public release. This document presents the data packages in nearly the same format as used in the melter evaluation. The only changes are that some of the grammar has been corrected and business sensitive information has been removed. Each package was sent back to the persons or companies that supplied the information so that they could delete business sensitive information. The reader must remember that the data packages were written to be free-standing documents, so that similar information may be repeated for each melter technology. Some of the sections of the data packages may seem confusing without a background of their original use. The section titles represent the evaluation criteria for the downselection process; that is, the capacity of each melter technology to

- process a range of compositions
- control product quality
- develop the technology on schedule
- integrate with the TWRS process and facility
- control and maintain the HLW vitrification process and facility
- minimize total cost
- minimize safety and environmental risk
- consider other risks and limitations.

The above list shows only the section titles; a consistent format was used for each data package subsection. The data packages in this document do not contain all of the information for each of the above criteria. Further information for Sections 4 and 6 were provided by Fluor Daniel, Inc. under a separate activity.

Data Package 1

Low-Temperature, Joule-Heated, Ceramic-Lined Melter

The low-temperature, joule-heated, ceramic-lined melter was selected as the reference process for High-Level Waste (HLW) vitrification for the Defense Waste Processing Facility (DWPF) in South Carolina, the West Valley Demonstration Plant in New York and in Germany, Japan, and China. Before recent Tri-Party Agreement (TPA) changes, it was also the reference for the Hanford Waste Vitrification Plant (HWVP). This data package was prepared first because significant data were readily available.

For purposes of discussion, the baseline melter has:

- submerged Inconel-690 electrodes[(a)]
- a rectangular glass surface
- a flat bottom
- an inductively heated bottom drain and an overflow system for routine discharge of glass to a 2 ft x 15 ft canister
- plenum heaters for boosting and startup
- Monofrax K-3 fused cast refractory[(b)] or equivalent (chrome AZS is used in the German melters).

The electrodes are arranged in a three-phase system with two side electrodes and one bottom electrode (see Figure 1.1). For larger melters, the number of electrodes may increase, but the electrodes on each side will be fired from the same phase. The melter surface geometry will be set by two criteria: the surface area required to meet production requirements, and the depth required to provide adequate glass residence time. The baseline melter will be slurry fed, similar to the way the previous HWVP melter was fed. Glass can be discharged by either an inductively heated bottom drain or a vacuum overflow. The bottom drain can be used for final draining of the melter as well as routine glass pouring. From the assumptions presented in this data package (25% waste loading in the glass, 16 MT/day of glass production, and 40 kg/hr•m^2 specific process rate) the total glass surface area required for this technology is 17 m^2, which can be accomplished with one or more melter lines. For example, the glass pool geometry for a single, 16 ton/day melter would be 3 m x 6 m (assuming a 2:1 aspect ratio). If two melter lines are used, the glass surface would be 2 m x 4 m (8 m^2). A plan view schematic of a representative 8 m^2 low-temperature, joule-heated, ceramic-lined melter is shown in Figure 1.2. Use of only one or two melters will require multiple feed nozzles to ensure complete slurry coverage. Basic parameters for this melter technology are presented in Table 1.1.

(a) Inconel alloy 690 from Huntington Alloys, 60% Ni, 30% Cr, 9.5% Fe, 0.25% Ti, 0.25% Al, 0.03% C.

(b) The Carborundum Company.

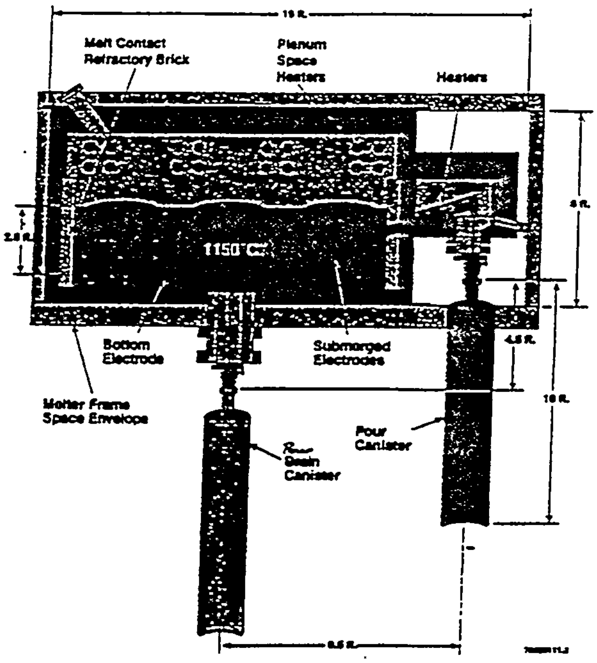
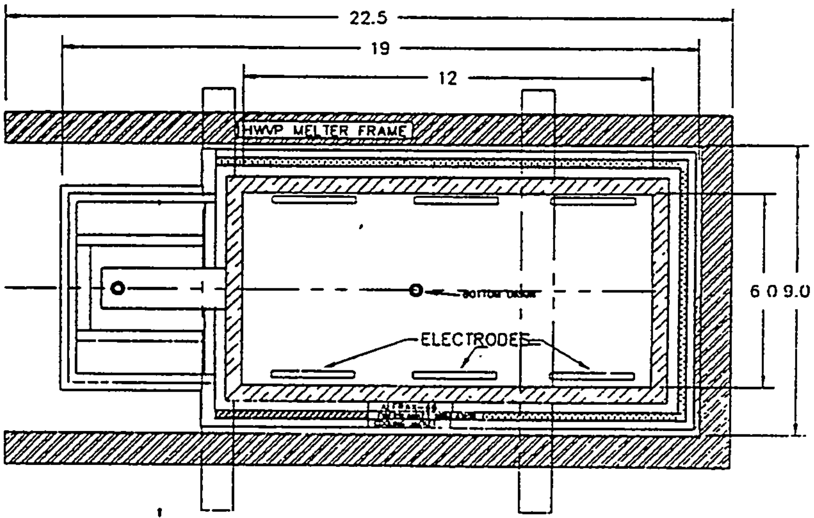


Figure 1.1. Three-Phase System



HIGH CAPACITY MODIFIED REFERENCE MELTER
CELL WIDTH 26'
WEIGHT APPROXIMATELY 94 TONS

Figure 1.2. Schematic of an 8 m^2 Low-Temperature, Joule-Heated, Ceramic-Lined Melter

Table 1.1. Operating Parameters for Low-Temperature, Joule-Heated, Ceramic-Lined Melter(s)

Specific Glass Production Rate	40 kg/hr•m^2			
Waste Loading in Glass	25 wt%			
Oxide Loading in Slurry	500 g/L			
Bulk Glass Temperature	1150°C			
Plenum Temperature	650°C			
Glass Depth[a]	0.8 m			
Glass Residence Time	50 h			
Total Operating Efficiency	60%			
Number of Melter Lines	1	2	3	4
Glass Surface Area (m^2)	17	8.5	5.7	4.3
Glass Production Rate (MT/day)	16	8	5.4	4
Glass Production Rate (kg/h)	680	340	230	170
Slurry Feed Rate (L/h)	1360	680	450	340
Glass Holdup[b] (MT)	34	17	11	9

(a) Assumed based on WHC Phase I study.
(b) Assumes a molten glass density of 2500 kg/m^3.

Variations of this melter design (e.g., sloped bottom, dry fed with an evaporator, agitated) will be discussed in appendices. A flat-bottom melter was chosen as the baseline case because information on the sloped-bottom melters had not been gathered at the time this document was written.

Most of the information was supplied by PNL and Kerforschungszentrum Karlsruhe GmbH (KfK). WHC contracted Fluor Daniel, Inc. to evaluate the effect of the six candidate melters on the balance of the plant equipment. This study has been released as a separate document.[1] The sections of this data package that are covered in the Fluor Daniel study are left blank, and the reader is referred to the other document.

1. Process Range of Composition

For the low-temperature melters, the waste form is assumed to be borosilicate glass. Several reviews (DOE/RL 1990) recommended borosilicate glass for the low-temperature melters because of its durability and process ability. In 1981, an independent peer review panel evaluated eight waste forms for the solidification and disposal of HLW (DOE/TIC 1981). These waste forms were borosilicate glass, SYNROC, porous glass matrix, tailored ceramics, pyrolytic C- and SiC-coated particles, concrete, metal matrices, and plasma spray coatings. Borosilicate glass was recommended because it can immobilize a wide range of wastes and is insensitive to radiation damage, thermally stable, chemically durable, and processable.

A. Temperature

The maximum operating temperature of these melters is limited by the melting point of Inconel-690. Their nominal operating temperature is 1150°C, and the maximum operating temperature is 1200°C.

B. Range of Waste Handling Capabilities

Several different waste streams and waste stream simulants have been vitrified with this melter technology. As an example, Table 1.2 shows the acceptable range of melter feed/glass compositions from the HWVP plant, which contained 25 to 28% waste by weight. The Japanese HLW glass (25% waste loading) is similar except that the nominal iron concentration is only 2 wt%. The information shown in Table 1.2 was developed for Hanford Neutralized Current Acid Waste (NCAW), which is only a small fraction of the waste to be treated in the current vitrification plant.

The actual compositions of the Hanford Site wastes remain uncertain. Initial scoping studies use various assumptions about the extent of blending that will be possible among the 177 Hanford Site tanks. The first study used an "All-Blend" composition that assumed perfect mixing of all 177 tanks. The "All-Blend" waste composition was calculated from tank inventory records that are only approximate. The Composition Variability Study (CVS) model developed for the NCAW predicts that this melter technology can produce a glass with 45 to 50% waste loading at 1150°C. This has not been confirmed with experimental results.

A more realistic scenario is that complete blending of all tank wastes will not be possible. The CVS model predicted maximum waste loadings for 15 different wastes only if the wastes in each tank farm were blended. This results in high waste loading for some tank farms and low-waste loading for others, ranging from 17 wt% to 65 wt%. The resulting 15 waste compositions are shown in Table 1.3, the "All-Blend" waste (referred to as Case C in the table), and the NCAW for reference. The row labeled "Low-T" is the predicted maximum waste loading achievable at 1150°C. The first row of the table shows the limiting constituent in each glass formulation

Table 1.2. HWVP Melter Feed Constraints (wt%)

Oxide Component	Lower Bound	Upper Bound
Single-Component Constraints		
SiO_2	46	56
B_2O_3	7	17
Na_2O	7	12.5
SiO_2	2	6
CaO	0	7
MgO	0	5
Fe_2O_3	4	12
Al_2O_3	1	11
ZrO_2	0	10
Others	2	8
Solubility Components		
Cr_2O_3	--	0.5
F	--	1.7
P_2O_5	--	1.0
Sulfur as SO_3	--	0.5
$Rh_2O_3 + PdO + Ru_2O_3$	--	0.25

Table 1.3. Tank Farm Waste Compositions

	Others Components			Zr-Phase		Spinel				Durability			Si	Al			
Oxide	TF-B (Wt%)	TF-T (Wt%)	TF-SX (Wt%)	TF-C (Wt%)	TF-DST (Wt%)	TF-A (Wt%)	TF-AX (Wt%)	TF-TY (Wt%)	TF-BY (Wt%)	TF-S (Wt%)	TF-DSSF (Wt%)	TF-U (Wt%)	TF-TX (Wt%)	TF-BX (Wt%)	Oxide	Case C (Wt%)	NCAW (Wt%)
SiO2	0.76	0.49	9.37	0.06	8.31	0.32	0.57	29.20	5.84	2.13	29.44	18.85	17.33	21.37	SiO2	10.00	4.03
B2O3					0.47		0.00				0.00				B2O3	0.00	0.01
Na2O	52.19	56.03	33.93	10.38	31.98	17.31	51.89	22.29	23.75	69.31	66.00	39.89	30.07	25.14	Na2O	25.30	21.42
Li2O					0.01		0.00								LiO2	0.00	0.00
CaO	0.03	0.00	1.24	9.39	0.79	0.03	2.79	0.00	5.66	0.00	0.62	0.00	0.01	0.12	CaO	2.06	0.79
MgO					0.27		0.00				0.00				MgO	0.08	0.20
Fe2O3	7.93	8.95	12.76	11.00	8.75	59.60	23.52	15.42	9.89	2.70	0.00	2.28	3.91	5.91	Fe2O3	11.00	28.21
Al2O3	1.20	0.66	22.74	7.55	2.65	1.48	1.46	10.06	12.33	13.20	2.00	16.73	15.83	22.98	Al2O3	13.00	9.04
ZrO2	0.22	0.42	0.01	25.85	35.20	0.04	0.05	2.52	0.22	2.93		0.30	0.40	0.33	ZrO2	7.08	15.11
Others	37.67	33.45	19.93	35.77	11.56	21.23	19.71	20.51	42.31	9.74	1.94	21.96	32.45	24.14	Others	31.41	21.19
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	Total	100.00	100.00
Bi2O3	6.43	8.83		0.05				0.33	0.03			0.04	0.05	0.04	Bi2O3	1.95	
CeO2	4.23	5.38	2.07	0.03	0.08	0.48	0.33	1.05	1.99	1.11		2.24	2.76	2.96	CeO2	2.73	0.60
Cr2O3	0.02	0.02	3.92	0.01	0.40	0.00	0.43	0.03	0.00	0.72	0.02	0.19	0.01	0.00	Cr2O3	0.45	0.26
F	0.72	0.50	0.04	1.56	1.43	0.00	0.01	0.04	0.52	0.12	0.07	00.07	0.12	0.17	F	0.56	0.10
La2O3	0.04	0.12			0.66										La2O3	0.43	0.65
MnO2	0.48	1.09	1.67	7.76	0.87	7.18	11.48	0.10	0.41	0.46	0.00	0.21	0.75	0.84	MnO2	1.82	2.14
NiO	0.23	0.03	0.30	5.69	0.47	0.22	0.66	0.00	11.64	0.17	0.00	0.01	0.25	1.25	NiO	2.27	2.30
P2O5	14.20	15.39	0.42	0.28	00.34	0.02	0.02	3.47	1.82	0.54	0.02	0.74	4.10	2.56	P2O5	4.71	0.87
SO3	0.18	0.03	0.22	0.16	0.43	0.41	0.02	0.59	0.23	0.28	0.07	0.06	0.51	0.54	SO3	0.34	0.65
SrO	0.00	0.00	0.01	0.00	0.02	0.02	0.00	0.00	3.45	0.00	0.00	0.00	0.00	0.05	SrO	0.41	0.12
U3O8	9.95	1.88	9.19	19.87	2.67	12.76	6.51	14.71	21.99	5.89	0.01	18.35	23.72	14.12	U3O8	14.30	4.74
Subtotal	36.47	33.27	17.84	35.40	7.37	21.09	19.45	20.32	42.08	9.29	0.19	21.90	32.27	22.53	Subtotal	29.97	12.43
Balance	1.20	0.18	2.09	0.37	4.19	0.14	0.26	0.19	0.23	0.44	1.75	0.00	0.18	1.62	Balance	1.44	8.76
Waste Loading (wt%)																	
Low-T	21	19	26	35	31	17	38	65	51	33	35	58	64	61	Low-T	45-50	33
High-T	21	19	26	46	40	25	43	84	64	39	41	60	73	61	High-T	62	50
Limit	P	P	Cr	Crystal	P?	Fe	Na	P	Others	Na	Na	Others	P	P	Limit	P	Crystal

(zirconia phase, spinel formation, etc.). Again, this preliminary information cannot be used for final flowsheet development. Without knowing the mass of waste oxides in each tank farm it is not possible to predict the average waste loading for this blending scenario. For conservative estimates, a 25 wt% waste loading is assumed. The WHC is currently evaluating which waste composition(s) should be used for flowsheet development.

Compounds or elements that require special treatment in the off-gas system:

> Tritium, mercury, carbon-14, and iodine that cannot be incorporated into glass at 1150°C must be captured in the off-gas system and sent out as a secondary waste stream. Carbon-14 will probably be released to the atmosphere as long as the Clean Air Act standards are met.
>
> Chlorine, fluorine, tellurium, technetium, cesium, cadmium, and ruthenium are partially soluble in the glass but require special considerations in the off-gas treatment system for recycle. These are discussed in Sections 1.D (incorporation of semi-volatiles) and 4.B (off-gas system requirements).

Noble metals: rhodium, palladium, ruthenium are virtually insoluble in the reference borosilicate glass and all other glasses expected from blended Hanford Site wastes. Their accumulation can cause premature failure of the melter due to electrical short circuiting at concentrations as low as 0.1 wt% in the glass (Larson 1989). Designs completed at KfK show that a steeply sloped (75°) bottom that allows the particles to be drained can prevent accumulation and settling of noble metals. The Japanese run the bottom of their melter at a cooler temperature, heating it only just before pouring through the bottom drain. It is not clear whether or not noble metals are a concern for the Hanford HLW melter. The "All-Blend" composition (Larson 1989) has only 0.07 wt% total noble metals ($Rh_2O_3 + PdO + Ru_2O_3$). At 50% waste loading the noble metals concentration will be 0.04 wt%, and at 25% loading the concentration will be only 0.02 wt%. Even if the noble metals accumulate, they may not cause melter failure before other components fail. Calculations performed by extrapolating a model that was developed for the HWVP melter design and the NCAW glass predict a 2 cm/year accumulation of RuO_2 on the floor of the melter. If this prediction is correct, electrical models would be needed to determine if this settled layer would cause an electrical disturbance.

Spindels: for several of the Hanford Site Wastes, spinels (iron, chrome, nickel compounds) are the first crystals to form in the NCAW glass on cooling. The Waste Acceptance Preliminary Specifications (WAPS) do not specify a limit for the amount of crystalline material allowable in the glass produced (Larson 1989). The concern regarding spinels (or any crystalline phase) is that the crystals will either reduce the durability of the waste form or affect the operation of the melter by filling the melt cavity with crystals. There are two ways to deal with spinel formation:
1) design a melter that is compatible with crystals and ensure that they do not affect the glass durability, or 2) formulate the glass to minimize crystal formation. Glass development for the "All-Blend" waste minimizes crystal formation. Devitrification tests are conducted for each composition for 24 h at 100°C below the expected bulk glass temperature. The acceptance criterion is that the resulting glass must have less than 0.1 wt% crystals.

Acceptable glass properties — The acceptable glass physical properties (WHC 1992) for the previous HWVP NCAW glass are shown in Table 1.4.

Table 1.4. Acceptable Glass Property Ranges for NCAW Glass

Property	Lower Bound	Upper Bound
Redox: Fe^{+2}/Fe^{+3}	0.005	0.3
Viscosity at 1150°C (Pa-s)	2	10
Liquidus Temperature (°C)	N/A	1050
Electrical Conductivity at 1150°C (S/cm)	0.18 (ρ=6 Ω-cm)	0.5 (ρ=2 Ω-cm)

- The redox (ferrous-to-ferric-iron ratio) is controlled because overly oxidized glass tends to foam in the melter, and overly reduced glass tends to precipitate metals and spinels.

- The viscosity is controlled because glass above 10 Pa-s (100 poise) does not mix well, and production is reduced; thin or inviscid glasses increase refractory corrosion.

- The maximum liquidus temperature is set 100°C below the average melter temperature so that crystals do not accumulate in the melter, although this may not be a problem if the crystals do not settle to the melter floor or if the bottom drain removes the crystals.

- Electrical conductivity is controlled to allow joule heating of the glass. The electrical conductivity limits are not firm, because they depend on the distance between the melter electrodes (melter geometry). A melt that is too conductive will exceed the current limit for the Inconel electrodes, thereby increasing the corrosion rate to localized heating at the electrode surfaces.

Ability to handle slurry feeds — The low-temperature, joule-heated melter can be either dry- or liquid-fed. Early melter testing at PNL was done with calciners coupled to these melters, but the use of liquid feeding avoids problems associated with the calciners. Depending on the size of the melter, adequate coverage of the melt surface may require more than one feed nozzle. Significant work has been done to develop feed nozzles that do not clog. Current feed nozzle designs include water cooling to avoid plugging. The nozzles can also be water flushed when the feed is shut off so that the feed does not dry in the nozzle.

C. Incorporation of Semivolatiles

Several elements and compounds are partially soluble in the glass and require special considerations in the off-gas treatment system for recycle. Table 1.5 shows melter decontamination factors (DFs) for elements with DFs below 300. The DF of an element is defined as its mass flow rate into the melter divided by its mass flow rate in the off-gas stream (e.g., a DF of 100 means that 99% of the element is retained in the glass and 1% is lost to the off-gas stream). The DFs shown in Table 1.5 were determined for liquid-fed melters operating at 1150°C. The concentration of each compound in the "All-Blend" waste is also shown in Table 1.5. The strategy for removing /recycling these components in the off-gas system will be discussed in Section 4.B.

Volatile losses from a liquid-fed melter are believed to be affected by certain parameters; for example, cold cap coverage, plenum temperature, and feed/glass composition. Because of its high specific activity, cesium is of particular interest. Depending on glass composition, it can volatilize

Table 1.5. Melter Decontamination Factors

Oxide	Wt% Oxide in Waste	Melter DF	Reference
CdO	0.091	7.5	2
Cl	0.033	6.6	1
Cs_2O	0.012	83	1
F	0.555	9.2	1
HgO	0.008	1.3	3
Rb_2O_3	0.007	290	4
Rh_2O_3	0.013	29	5
Ru_2O_3	0.047	10	2
SO_3	0.341	6.4	1
SeO_2	0.024	58	2
Tc_2O_7	0.021	2.5	3
TeO_2	0.003	11	2

as Cs metal, or as Cs_2O, CsOH, or other compounds (IAEA 1982; Erlebach 1960). If chloride is present in the feed, Cs volatility will increase substantially (Burkholder and Allen 1987). CsCl is assumed to be the primary volatile species in this case. The addition of technetium increases volatility through formation of $CsTcO_4$. On addition of Tc to a feed, Cs losses increased from 2-5% (without Tc) to 18% (Baumgartner 1984).

D. Ability to Handle Insoluble and Conductive Compounds

See Section 1.B.

E. Waste Loading

Waste loading is the weight percent of waste (as oxides) in the final glass. Waste loading determines both the required production rate of the melter and the quantity of glass that will be produced. The quantity of glass produced from the tank wastes is important for several reasons: 1) The costs to place canisters in the federal repository are high; an estimated $2 billion can be saved by increasing the waste loading of Hanford Site glass(es) from 25 wt% to 45 wt% (Merrill and Chapman 1993); 2) The first U.S. repository has a limited allocation for HLW canisters. DOE-RW is currently evaluating the impact of the increased number of canisters resulting from TPA changes.

The design basis for the HWVP design with NCAW glass at 1150°C was 25% to 28% waste loading. The remainder of the glass was 3% recycled oxides and 69% frit. Initial experiments indicate that this waste loading can easily be achieved for the "All-Blend" waste at 1150°C. The extent and method of blending is not well known, but it is expected that tank wastes with problem constituents will be blended when practical to reduce impacts to the melter. Some of the tanks have high concentrations of problem compounds, such as Cr_2O_3 and P_2O_5. The waste loading will be lower than 20% if these wastes cannot be diluted by blending with the contents of other tanks. For calculational purposes, the waste loading assumed for the 1150°C melters is 25%. The impact on melter production rate will be discussed in Sections 3 and 4.

2. Control Product Quality

For reasons stated in Section 1, the waste form for the LTCM is assumed to be borosilicate glass.

A. Product Quality

Expected progress in glass development and results of previous glass formulation work conducted at Hanford, Savannah River, and West Valley suggest that this melter will not have problems with durability, phase separation, crystallinity, and homogeneity. Glass development ensures that the final waste form is more durable than Savannah River Environmental Assessment (EA) glass when tested with the Product Consistency Test (PCT) and the MCC-1 leach test.

B. Waste Homogenization Capabilities

The former reference melter (DWPF design) had a residence time of two days, which ensured proper dissolution and mixing of the waste and glass. In the new plant melter, this can be controlled by design of the melter depth. The pressure of undissolved feed in the glass is unlikely, because the convection cells are slow and do not provide a path for the feed to leave the melter before melting.

C. Analytical Requirements for Quality Acceptance

To be determined.

D. Minimum and Optimum Residence Time

The two-day residence time of the DWPF design provided a dampening effect for any feed variations, so that fluctuations in feed composition were diluted by the large volume of glass in the melter. The drawbacks of a long residence time are: 1) insoluble particles have a longer time to settle to the melter floor; 2) glass holdup requires larger handling equipment to remove a failed melter full of glass; 3) the radiation source term in the event of an accident would be larger. Therefore, it is not clear what the "optimum" residence time would be.

At a constant production rate per melter surface area, the residence time is a function of the melter depth. Without a sloped bottom, this melter technology has no significant requirements for depth, only that enough depth is provided so that the current density limit (10 A/in^2) for the electrodes is not exceeded. Current density limits will be a problem only if the glass is conductive or the electrodes are close together.

E. Unpredictable Evaporation (Segregation) of Glass Components

This melter operates continuously under very steady conditions, so that process upsets are rare. Increased feed volatility would be a problem only during startup after a feed outage; that is, when slurry is fed onto an open, hot glass surface. This is seldom done, and when it is, water is first fed to the melter to cool the upper glass surface.

3. Develop Technology on Schedule

This category deals mainly with the maturity of the technology. The LTCM technology was the baseline for the Hanford Site HLW vitrification plant before the recent change in scope. This mature technology has been tested since the early 1970s for the vitrification of HLW. The only adaptations necessary for the current Hanford Site plant are an increase in production capacity (or addition of parallel melter lines) and a change in feed composition.

A. Ability to Meet TPA Milestones(a)

The amount of technology development already completed suggests that this technology would allow the DOE to meet its TPA milestones if sufficient funds were available.

B. Demonstrated Scale of Operation

This technology has been demonstrated under nonradioactive conditions at several locations in the US, including

- the Scale Glass Melter (SGM) at Savannah River (1.2 m^2, 45 kg/h)
- the West Valley Nuclear Services (WVNS) melter (2.15 m^2, 45 kg/h)
- the Liquid-Fed Ceramic Melter (LFCM) at PNL (1.05 m^2, 50 kg/h)
- and the Pilot-Scale Ceramic Melter (PSCM) at PNL (0.76 m^2, 22 kg/h)

This technology has also been demonstrated with radioactive samples in

- the PAMELA melter in Belgium (30 kg/h, 1.4 m^2, 8 MCi vitrified)
- the Radioactive LFCM at PNL (7 to 20 kg/h, 0.5 m^2, 22 MCi vitrified).

The 2.5 m^2 DWPF melter is currently undergoing shakedown testing with nonradioactive simulants.

C. Availability of Data or Access to Data to Allow Evaluation for Melter System Technology Assessment and Melter System Candidate Selection

Access to data is not a problem.

D. Magnitude/Amount of Technical Development Required

Technology development would involve selecting a melter geometry, building scaled melters (if they do not already exist), and conducting testing on the new feed formulations. The large increase in production rate over the previous HLW designs would require substantial scale-up work if only one or two melters are planned for the plant. This would include designing a bottom

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(a) Final melter selection by the end of 1998, plant startup by 2009, completion of campaigns by 2028.

drain that can control glass pouring at rates up to 1200 kg/h (assuming that maximum pour rates will be twice the average production rate). Designing plenum heaters that can span increased melter width may also be a problem (if the heaters are hung horizontally in the melter, similar to the DWPF design).

As with any of the melters being evaluated, the tank-waste characterization and glass development efforts will be significant. This technology may rely more heavily on development of blending strategy and glass composition than some of the other technologies being evaluated.

E. Additional Technical Development Required for Deployment

To be determined

F. Probability of Technical Success Within Schedule and Resource Constraints

Meeting the TPA milestones appears to be possible with this melter technology. The resource constraints will not defer technology development, although deployment and operation may prevent problems.

G. Processing Rate

As stated, the assumed processing rate for the LTCM is 40 kg/h•m^2. This may be optimistic. Extensive plenum heating is usually required to meet this production rate. On average, most production rates during melter runs at PNL were closer to 30 kg/h•m^2. Assuming 17,000 MT of waste oxides, 25% waste loading, 19 years of plant operation, and a 60% total operating efficiency (TOE),[a] the required processing rate would be 16.3 MT/day for a melter or melters with a total processing area of 17 m^2. For example, the glass pool geometry for a single, 16 MT/day melter would be 3 m x 6 m (assuming a 2:1 aspect ratio). If two melter lines are used, the glass surface would be 2 m x 4 m (8 m^2).

H. Extent of Mock-ups and Test Facilities Required

Existing testing facilities include but are not limited to

- the K-6 ft melter at KfK in Germany (0.88 m^2)
- the Advanced-B Melter (0.53 m^2) at PNC[b] Tokai
- the Integrated DWPF Melter System (IDMS) melter (0.29 m^2) at Savannah River
- the Small-Scale High-Temperature melter (SSHTM) (0.21 m^2) operated at 1150°C at PNL
- the 1/10th scale melter (0.25 m^2) at PNL

(a) This was the assumed operating efficiency of the HWVP, including melter replacement every three years.

(b) Power-Reactor and Nuclear Fuel Development Corporation.

- the PSCM (0.76 m^2) at PNL
- the LFCM (1.05 m^2) at PNL
- the Pilot-Scale High-Temperature Melter (PSHTM) (2 m^2) operated at 1150°C at PNL
- the Duramelter™ 100 (0.13 m^2) at GTS Duratek
- the Duramelter™ 300 (0.33 m^2) at GTS Duratek.

I. Necessity for New Inventions

New inventions would be required for items not previously considered for HLW vitrification and for items requiring significant modification to existing designs because of the increased melter size. This would depend on how many parallel lines of melters would be used in the plant. Use of only one line would require new feed distribution systems, melter moving equipment, bottom drain, and plenum heaters. The bottom drain for a single melter would have to control glass pouring at up to 1200 kg/h (assuming that maximum pour rates will be twice the average production rate). Designing plenum heaters that can span the increased melter width may also be a problem (assuming that the heaters are hung horizontally, similar to the DWPF design). None of these modifications or inventions seems impossible.

4. Integration with Process and Facility — *This section was provided by Fluor Daniel, Inc.*[1]

5. Control and Maintenance of Process and Facility

This section includes a discussion about the ability of the melter technology to allow safe and efficient operation of the vitrification facility. Low-temperature, joule-heated melters have demonstrated remote operation capability in radioactive environments in Russia (the Mayak plant), Belgium (the PAMELA plant), and the United States (the Radioactive Liquid-Fed Ceramic Melter [RLFCM] at PNL). Similar systems have been designed, but not operated, in Japan (Tokai) and the U.S. (West Valley, HWVP, and Savannah River).

A. Ease of Control

As stated above, the capability of this technology in remote operating environments has already been demonstrated, but requires special measures, including temperature measurement in the glass, plenum space, discharge area(s), refractories, and cooling water circuits. The most difficult parameter to control is the amount of cold cap coverage. The feed rate must be controlled so that the melt pool is not completely flooded with feed because bridging of the cold cap will cause gas release. Control of cold cap coverage is usually based on nonradioactive experience and plenum temperature measurements. Remote infrared (IR) viewing cameras have been designed to monitor cold cap coverage, but have not been implemented.

Melter plenum pressure is usually maintained at a slight vacuum to control contamination of the process cells. A diaphragm-operated valve (DOV), with continuous feedback from the plenum pressure measurement, provides dynamic control.

B. Remoteability

Special design features are required for remote melter operation. Before discussing these features, the term "remote environment" must first be defined. The DWPF and HWVP were canyon remote facilities, designed so that all maintenance was done by crane and impact wrench, i.e., without manipulators. All access was from the top, because horizontal movement was difficult. The current facility configuration calls for a valve corridor, which is described in the Fluor Daniel, Inc. report.

C. Reliability

The reliability is measured by the TOE, the total number of hours that the melter operates divided by the total number of hours that the melter is in place, which includes the time required for melter changeout. For the HWVP, the assumed TOE of 60% was reached by assuming that the melter was on-line 70% of the time and that it required a six-month changeout every three years. This was believed to be conservative, because on-line efficiencies greater than 85% have been regularly attained during melter runs. In practice, efficiencies will probably be less than 70% during the first year of operation. After the problems have been worked out of the process, the on-line efficiency will probably exceed 70%. The average on-line efficiency of the PAMELA plant was 85% [88% for the Low Enriched Waste Content (LEWC) campaigns and 80% for the High Enriched Waste Content (HEWC) campaign].[2] For the most recent LFCM test conducted at PNL (Perez et al. 1994) the on-line efficiency was > 98%.

D. Maintainability

A failure modes and effects analysis (FMEA) was conducted for the West Valley vitrification system in 1987 (Westsik et al. 1987). This analysis identified 19 items that had a high failure frequency or a medium failure frequency with lengthy repair times. Most were either external to the melter system (feed pump) or were easily repaired or replaced (feed nozzle, thermowells, dip tubes, or TV system). Identified items whose failure could require replacement of the melter or significant repair periods included failure of the bottom electrode due to noble metals accumulation and glass-discharge plugging.

E. Estimated Lifetime

The minimum melter lifetime of the HWVP melter was two years, and the expected lifetime was three to five years. The most likely scenario for an early melter failure was expected to be an accumulation of noble metals on the melter floor with resultant short circuiting of the lower set of electrodes. This was determined for the NCAW feed, which has eight times the concentration of noble metals as the current blended waste. It is not clear whether the lower concentration of noble metals will be a problem in the melter. If it is believed to be a problem, a sloped-bottom design could be incorporated with supporting design and development work. Information on sloped-bottom variations of this melter is included as an appendix to this data package.

F. Ability to Confine Radioactive Materials

A vacuum is kept on the melter plenum and overflow (glass discharge) section to minimize the risk of airborne release of radionuclides to the vitrification cell. The accumulation of deposits (e.g., cesium) in the off-gas line can be controlled by using a film cooler to quench and dilute the hot gas leaving the melter, or by regularly cleaning the off-gas line with either a reamer or an air "blaster."

The melter is equipped with an emergency off-gas line to provide backup vacuum during shutdown of the primary off-gas system.

A significant source of radioactive materials is from maintenance of equipment. This does not appear to be directly related to the melter technology.

G. Potential for Radioactive Source Buildup and Achievement of As Low As Reasonably Achievable (ALARA)

Off-gas treatment is discussed in the Fluor Daniel, Inc. report.[1]

The bottom drain can be used to drain the glass from the melt cavity at the end of the melter life. This may be optimistic; melter failure could prevent drainage of the glass from the melter. This is an unresolved problem for most of the melters being considered. Because of the required size of this melter (if only one or two melter lines are used), the glass/radiation source remaining in the melter after failure could be substantial.

Another potential cause of radioactive-source buildup is the migration of cesium into the fused cast refractory. This suggestion has not been substantiated with data and is being investigated by analyzing the refractory blocks from the Radioactive LFCM at PNL.

H. Sealing and Containment Relative to Melter

Sealing the melter to prevent inleakage to the off-gas system and outleakage to the melter cell has always been a significant challenge in the design of remote melters. Metal bellows are provided for sealing the canister to the melter during glass pouring. Packing materials are used to seal all flanged connections such as the melter lid, off-gas pipes, and lid penetrations. Leakage is a significant concern because of the large size of this melter.

I. Modular Design Concepts that Simplify Replacement or Repair

This melter design is not modular except for the supporting systems (e.g., canister handling). The Fluor Daniel, Inc. Report evaluates melter disposal costs as a function of melter size.

J. Refractory Life

These melters usually have multiple layers of refractory inside a water-cooled containment box (see Figure 1.1). The glass-contacting refractory is usually a high chrome fused-cast ceramic (either Carborundum Monofrax K-3[a] or a chrome AZS[b]). Because the fused-cast refractories have a relatively high thermal conductivity, they are backed with refractories that have decreasing thermal conductivities and glass corrosion resistance. The use of high-chrome glass-contacting refractories is a particular area of deviation from the commercial glass industry, in which high-chrome refractories are avoided except in high-wear areas (e.g., throat blocks) because of the strong coloring effect of chrome (one exception to this is the fiberglass industry). The HLW melters can have chrome refractories throughout the melter because the color of the product glass is not important.

At 1050°C to 1150°C, reported corrosion rates for carborundum K-3 in contact with borosilicate glass were 10 to 20 μm/day at the melt line, and less than 10 μm/day below the glass surface. The K-3 corrosion rate measured during a rebuild of the PSCM at PNL was 4 to 8 μm/day (Larson 1989a). The fused cast refractory in the previous HWVP/DWPF design was 12 in. thick. At a maximum corrosion rate of 20 μm/day, the expected refractory life would be approximately 40 years.

The melter plenum refractory is usually a castable refractory, such as Carborundum Alfrax-66.[c] The refractory is supported by either ceramic or Inconel hangers. Failure of the plenum refractory has mainly been associated with improper hangers or inadequate allocation for thermal expansion (Larson 1989b).

K. Electrode Life/Replacement (Barnes and Larson 1981)

This melter has side- and bottom-entering electrodes made of Inconel-690. Barnes and Larson (1981) found a maximum corrosion rate of 3 μm/day for the Inconel-690 electrodes in the PSCM at PNL after three years of operation. The submerged electrodes experienced little corrosion, but Inconel in the plenum space of melters has shown severe damage from halides and sulfates in the feed stream (Dierks 1980). Therefore, the Inconel electrodes in most melters are submerged. Most Inconel items that are exposed to off gases (thermowells and bubblers) are remotely replaceable.

Large current densities must be avoided to minimize corrosion of Inconel electrodes. The maximum current density for Inconel-690 in this type of melter is 10 A/in^2 (1.6 A/cm^2). The normal design limit is 5 A/in^2 (0.8 A/cm^2).

(a) Carborundum Monofrax K-3: 60% Al_2O_3, 27% Cr_2O_3, 6% MgO, 4% Fe_2O_3, 2% SiO_2.
(b) Sorg ER-2161-RT: 32% Al_2O_3, 26% Cr_2O_3, 26% ZrO_2, 13% SiO_2.
(c) Carborundum Alfrax-66: 96% Al_2O_3, 4% CaO.

L. Ability to Safely Handle Organics

It is planned that all organics will be destroyed in the plenum space of the melter. The plenum space generally operates at 650°C when plenum heaters are used. It is not clear if the plenum gases come to equilibrium temperature before leaving the melter. Because of this uncertainty, destruction and removal efficiencies (DREs) are usually demonstrated for organic materials expected in the feed. The DRE for the LFCM (with plenum heaters) was recently determined for formic acid (or formate ion) as a preliminary indication of the DRE for organics in general. The destruction of formate was at least 99.8% efficient for feeds containing 37 g/L to 46 g/L formate (Perez et al. 1994). Similar tests have been completed at Savannah River to prove the DRE for the DWPF melter.

M. Operational Simplicity

Except for the variability of the cold cap, this melter technology does not operate dynamically. There are very few moving parts, and process dynamics are very slow because of the large time constant of the glass pool. Also see Section 5.A.

N. Estimated Lifetime

See Section 5.E.

O. Estimated Downtime to Repair

Replacement of the HWVP melter was estimated to take six months. Replacement times for various melter-related items was estimated for the West Valley melter (Westsik et al. 1987). See Table 1.6. The WVNS plant is canyon remote with limited manipulator access.

6. Minimize Total Cost — *This section was provided by Fluor Daniel, Inc.*[1]

Table 1.6. Replacement Times for Melter Components

Item	Repair Time
Thermowell replacement	1 day
TV camera replacement	8 h
Dip tube (level measurement) replacement	1 day
Overflow heater replacement	2 days
Overflow heater connection replacement	3 days
Film cooler replacement	2 days
Feed nozzle replacement	1 day
Electrode failure	high
Inner refractory cooling system failure	high
Canister load cell replacement	2 days

Endnotes

1. Fluor Daniel, Inc. August 1994. "Alternative Melter Systems Assessment 20 Metric Tons per Day HLW Glass Production." Prepared under contract #04-436404 with Westinghouse Hanford Company.

2. Letter from C.C. Chapman, "Technical Exchange Between PAMELA and the West Valley Demonstration Project," April 14, 1987.

Data Package 1, Appendix A

Low-Temperature, Joule-Heated, Ceramic-Lined Melter with a Sloped Bottom

This appendix to the data package for the low-temperature, joule-heated ceramic-lined melter describes the design option of a sloped melter bottom. Information contained in this appendix was obtained for the Japanese, German, and Chinese designs, which are the same as described in the original data package, except that they have sloped bottoms. The format of this appendix differs from that of the data package in that only those sections that differ from the original data package are included. Two reports, which are included as attachments, provide significant summary information on melter development and experiences from Germany, Japan, and China.

The sloped-bottom melter design evolved as a result of problems experienced with noble metals accumulation. Noble metals (palladium, rhodium, and ruthenium) have a very low solubility in glass-forming melts; they tend to settle out and agglomerate on the melter floor. They are also corrosive to melter refractories, and are excellent conductors of electricity. When sufficient noble metals accumulate, the highly conductive layer tends to cause electrical shorting of electrodes that are near the floor. To remediate.these electrical problems, either the noble metals must be removed or the melter must be replaced. Significant impacts on plant operation and costs resulting from replacing the melter have driven the study of options for removing the accumulated sludge layers. One melter design feature that has been proven to help remove sludge layers from the melter floor is a sloped bottom, which allows the sludge to flow downward and out the bottom drain (Elliott et al. 1994).

The "All-Blend" composition[1] contains only 0.07 wt% total noble metals (Rh_2O_3 + PdO + Ru_2O_3). At 50% waste loading. the noble metals concentration in the glass would be 0.04 wt%, which is far less than the levels up to 1.4 wt% tested in Germany and Japan (Elliott et al. 1994).

One concern with incorporating a sloped bottom in the design of a large melter is that the depth and glass holdup will increase beyond reason. Basic operating parameters for the sloped-bottom melter technology are presented in Tables A.1.1 through A.1.3. Each table provides sizing information for melters with different slopes; the dimensions refer to the internal melt cavity. The bases for most of these numbers are explained in Data Package 1. As noted in the tables, the wide variety of melter sizes required depends on the number of melter lines chosen and the slope of the melter floor. The glass depth in the tables refers only to the vertical distance from the melt surface to the bottom drain, and does not take into account the additional height of the plenum space. One melter with a 75° sloped bottom would probably be too deep, and appropriate depth would require several melters in parallel. To determine the most appropriate configuration, an optimization must be made between melter size, melter capacity, the number of melters required, and longtime operation (potential noble metals problems). An optimized design would then have to be tested on a small scale and improvements made before designing the next scale melter. This should take into account the extensive experience of KfK, PNL, Power Reactor and Nuclear Fuel Development Corporation (PNC) and Commissariat A L'Énergie Atomique (CEA). It was suggested that with our low concentration of noble metals, a 75° bottom is probably not necessary, but a sloped bottom should still be used (possibly 45°).[2]

Table A.1.1. Operating Parameters for Low-Temperature, Joule-Heated, Ceramic-Lined Melter(s), 45° Sloped Bottom

Specific Glass Production Rate	40 kg/h•m^2			
Waste Loading in Glass	25 wt%			
Oxide Loading in Slurry	500 g/L			
Number of Melter Lines	1	2	3	4
Glass Surface Area (m^2)	17.0	8.5	5.7	4.3
Square Surface Area Dimension (m)	4.1	2.9	2.4	2.1
Glass Depth (m)	1.9	1.3	1.0	0.9
Glass Production Rate (MT/day)	16.3	8.2	5.4	4.1
Glass Production Rate (kg/h)	681.0	340.0	227.0	170.0
Slurry Feed Rate (L/h)	1362.0	680.0	454.0	340.0
Glass Residence Time (hours)	43.0	30.0	25.0	21.0
Glass Holdup(a) (MT)	29.3	10.3	5.6	3.7

(a) Assumes a molten glass density of 2500 kg/m^3.

To calculate the melter dimensions shown in the tables, the glass surface area geometry was assumed to be square. However, this is not necessarily the best choice for some of the larger melters, such as the 4.1 m x 4.1 m melter. It is generally assumed that at some point the melter cavity geometry would become rectangular because of facility constraints. If this assumption is applied to the melters shown in Tables A.1.1 through A.1.3, the glass pool surface area geometries would be longer and narrower with increasing melter size. However, this presents an even more challenging problem. It is assumed that the bottom drain geometry does not change (become longer and narrower) to match the changing glass pool surface area geometry. Therefore, two of the four walls become less steeply sloped because of the greater horizontal distance they must extend inward to meet with the bottom drain. For example, for a 45° sloped

Table A.1.2. Operating Parameters for Low-Temperature, Joule-Heated, Ceramic-Lined Melter(s), 60° Sloped Bottom

Specific Glass Production Rate	40 kg/h•m^2			
Waste Loading in Glass	25 wt%			
Oxide Loading in Slurry	500 g/L			
Number of Melter Lines	1	2	3	4
Glass Surface Area (m^2)	17.0	8.5	5.7	4.3
Square Surface Area Dimension (m)	4.1	2.9	2.4	2.1
Glass Depth (m)	3.3	2.3	1.8	1.5
Glass Production Rate (MT/day)	16.3	8.2	5.4	4.1
Glass Production Rate (kg/h)	681.0	340.0	227.0	170.0
Slurry Feed Rate (L/h)	1362.0	680.0	454.0	340.0
Glass Residence Time (hours)	74.0	53.0	43.0	37.0
Glass Holdup (MT)	50.7	17.9	9.7	6.3

Table A.1.3. Operating Parameters for Low-Temperature, Joule-Heated, Ceramic-Lined Melter(s), 75° Sloped Bottom

Specific Glass Production Rate	40 kg/h•m^2			
Waste Loading in Glass	25 wt%			
Oxide Loading in Slurry	500 g/L			
Number of Melter Lines	1	2	3	4
Glass Surface Area (m^2)	17.0	8.5	5.7	4.3
Square Surface Area Dimension (m)	4.1	2.9	2.4	2.1
Glass Depth (m)	7.1	4.9	3.9	3.3
Glass Production Rate (MT/day)	16.3	8.2	5.4	4.1
Glass Production Rate (kg/h)	681.0	340.0	227.0	170.0
Slurry Feed Rate (L/h)	1362.0	680.0	454.0	340.0
Glass Residence Time (hours)	160.0	113.0	92.0	80.0
Glass Holdup (MT)	109.2	38.6	21.0	13.6

floor in a melter with a 17 m^2 surface area, if the maximum length were 2.5 m for one wall, the melt pool surface would be 2.5 m x 6.8 m. Two of the four sloped walls could be 45°, but the other two would be about 19° because of the greater distance they extend inward. This may not be steep enough to avoid the accumulation of sludges. The only way to increase the slope of these two walls is to have a longer and narrower bottom drain opening. Unfortunately, this bottom drain design would be more likely to accumulate sludge layers.

1. Process Range of Composition

   B. Range of Waste Handling Capabilities

   In Data Package 1, Table 1.2 shows an upper bound of 0.25 wt% total noble metals in the glass for the NCAW. Although this limit was developed for the NCAW, it may provide a good indication of what would be acceptable for a flat-bottom melter. The current "All-Blend" waste composition has only 0.07 wt% total noble metals (or 0.04 wt% total noble metals in the glass assuming 50% waste loading), which is significantly lower than the upper bound. Thus, a sloped bottom melter might not be necessary to remove sludge layer accumulations because accumulation may not be a problem. Testing must be done to verify this. Although the "All-Blend" waste composition has only 0.07 wt% total noble metals, different tank waste blending scenarios will probably result in varying concentrations of noble metals. The expected upper and lower limits are not known, but WHC is currently working on determining them. The successful results obtained from wastes processed at much higher noble metals concentrations suggest that a properly designed and optimized sloped-bottom melter will be able to handle the relatively low concentrations of noble metals expected in the Hanford Site waste. Attachments 1 and 2 provide additional information on testing and results.

3. Develop Technology on Schedule

This category deals mainly with the maturity of the technology. The low-temperature, joule-heated, ceramic-lined melter technology was the baseline for the Hanford Site HLW vitrification plant before the recent change in scope. It is a mature technology that has been tested since the early 1970s for the vitrification of HLW.

Attachments 1 and 2 provide details on testing with sloped-bottom melters and the facilities available for further testing. Extensive research has shown this design option to be beneficial in the removal of accumulated sludge layers (including noble metals) from the melter floor.

B. Demonstrated Scale of Operation

This sloped-bottom technology has been demonstrated nonradioactively at several locations, including:

- K-W2 Melter at KfK, Germany (45° bottom, 1.4m^2, 31 kg/h)
- K-6-(prime) Melter at KfK, Germany (60 to 75° bottom, 0.88m^2, 18 kg/h)
- K-W3 Melter at KfK, Germany (60 to 75° bottom, 1.4m^2, 38 kg/h)
- C-melter at PNC, Japan (25° bottom, 0.3m^2)
- Advanced B-melter at PNC, Japan (45° bottom, 0.53m^2)
- Mock-up Melter III at PNC, Japan (45° bottom, 0.66m^2, 8.8 kg/h)
- Large-Scale Melter at Japan Nuclear Fuel Service (JNFS), Japan (50 to 53° bottom, 2.2m^2, 44 kg/h).

C. Availability of Data or Access to Data to Allow Evaluation for Melter System Technology Assessment and Melter System Candidate Selection

Data obtained from Germany, Japan, and China.

D. Magnitude/Amount of Technical Development Required

As mentioned, this technology successfully removes sludge layers of accumulated noble metals, but further testing is required to determine the most appropriate configuration for the Hanford Site HLW plant. An optimization must be made between melter size, melter capacity, the number of melters required, and longtime operation (potential noble metals problems). An optimized design would then have to be tested on a small scale and improvements made before designing the next scale melter.

5. Control and Maintenance of Process and Facility

E. Estimated Lifetime

Processing of noble metals in a joule-heated melter can significantly shorten the lifetime of the melter because of electrical short-circuiting through a conductive layer of settled noble metals. The sloped-bottom melter design will help resolve this problem by allowing the noble metals to be removed through the bottom drain.

F. Refractory Life

As discussed, settled layers of noble metals can cause short-circuiting of the electrodes by providing a path of least resistance through the layer. This causes higher temperatures near the melter floor, which significantly increases the amount of corrosion to the refractory.

Endnotes

1. Letter from R.W. Powell of WHC to J.M. Creer of PNL, "Double-Shell Tank/Single-Shell Tank Waste Blend Composition for High-Level Waste Vitrification Process Testing." May 1994.

2. Telephone conversation between W. Grünewald (KfK, Germany) and M. Elliott (PNL) on August 16, 1994.

ATTACHMENT 1 TO DATA PACKAGE 1, APPENDIX A

Melter concepts for vitrification of high level waste in Europe and Japan

- Summary -

Dr. Roth
W. Tobie
W. Grünewald

KfK/PNL - contract No. 125818-A-I1
Supplement 3

Japan

Development of vitrification process in Japan (PNC)

Melter development and tests carried out in the Engineering Test Facility (ETF) for Joule-heated Ceramic Melters

Table 3

Structure of A-Melter	
Designed	1978
Constructed	1988
Operation time	2600 d
Produced waste glass	58 to
Volume of model solution	- *
Number of drain outs	1489
Electrodes	3 pairs (Mo); 1 pair (SnO_2) with water-cooled shafts
Electrodes form	rod-shapes
Melter refractory	- *
Capacity	min. 100 l - max. 200 l
Power consumption	55 kW (stand-by)
Melting surface	- *

* data not available

Rectangular chamber with refractory blocks and stainless steel casing. Two separated zones - melting zone and drain out zone -, flat bottom and direct heated platinum bottom drain nozzle.

Table 6

Structure of Advanced B-Melter	
Designed	1984
Constructed	1985
Operation time	700 d
Produced waste glass	28 to
Volume of model solution	7.7 m^3 (incl. Noble metals)
Number of drain outs	333
Electrodes	- *
Electrodes main	1 pair Inconel 690 aircooled plates
Electrodes auxiliary	1 pair Inconel 690 plates
Electrodes riser	Inconel 690 rod-shaped
Melter refractory	Cr_2O_3-Al_2O_3 fused-cast block Al_2O_3-ZrO_2-SiO_2 sintered block Al_2O_3-SiO_2 cast block
Capacity	300 l
Power consumption	55 kW (stand-by)
Melting surface	0.53 m^2

* data not available

Rectangular chamber with refractory blocks and stainless steel casing. Sloped bottom (57.5° and 45°) and indirectly heated Inconel 690 bottom drain nozzle. Resistance-heated overflow system. Microwave heating-up (30-35 kW) and boosting (20-25 kW).

Melter development and test carried out in the Mock-up Test Facility (MTF) for Joule-heated Ceramic Melters

Table 7

Structure of Mock-up I-Melter	
Designed	1982
Constructed	1983
Operation time	290 d
Produced waste glass	18.4 to
Volume of model solution	37 m^3 (partly with noble metals)
Number of drain outs	91
Electrodes	1 pair Inconel 690, aircooled plates
Melter refractory	- *
Capacity	120 l
Power consumption	- *
Melting surface	- *

* data not available

Rectangular chamber with refractory blocks and stainless steel casing. Flast bottom and 4 bottom drain nozzles in different heights located in the corners of the melting chamber.

Table 8

Structure of Mock-up II-Melter	
Designed	1984
Constructed	1987
Operation time	713 d
Produced waste glass	35 to
Volume of model solution	41 m^3 (partly with noble metals)
Number of drain outs	136
Electrodes	1 pair of Inconel 690 aircooled plates
Melter refractory	-*
Capacity	180 l
Power consumption	55 kW (stand-by)
Melting surface	-*

* data not available

Rectangular chamber with refractory blocks and stainless steel casing. Sloped bottom (7.5°) and 3 bottom drain nozzles in different heights. Separate chamber for glass level detection.

Table 9

Structure of Mock-up III-Melter	
Designed	1986
Constructed	1988
Operation time	still in operation
Produced waste glass	17 to (till 1990)
Volume of model solution	17 m^3 (partly with noble metals)
Number of drain outs	- *
Electrodes main	1 pair of Inconel 690 aircooled plates
Electrodes auxiliary	1 pair of Inconel 690 plates
Melter refractory	- *
Capacity	330 l
Power consumption	- *
Melting surface	0.61 m^2

* data not available

Rectangular chamber with refractory blocks and stainless steel casing. Sloped bottom (55° and 45°) and indirectly heated Inconel 690 bottom drain nozzles. Separate chamber for glass level detection.

Table 10

Composition of the Tokai Vitrification Facility HAWC simulate vitrified in the Mock-up Test Facility with Mock-up III-Melter

Element	Oxide yield g/l
H^+	6.754
Na	47.704
P	0.793
Fe	8.377
Cr	2.189
Ni	2.202
K (*2)	0.289
Cs	4.559
Sr	1.542
Ba	2.884
Zr	6.422
Mo	5.795
Mn (*2)	0.857
Ru	4.275
Pd (*1)	2.788
Ag	0.087
Cd	0.103
Sn	0.069
Se	0.103
Te	0.768
RE	-

Oxide	Oxide yield g/l	Oxide yield (wt%)
-	-	-
Na_2O	64.458	41.702
P_2O_5	1.817	1.176
Fe_2O_3	11.977	7.749
Cr_2O_3	3.207	2.075
NiO	2.802	1.813
K_2O	0.348	0.225
Cs_2O	4.847	3.136
SrO	1.824	1.180
BaO	3.220	2.083
ZrO_2	8.675	5.612
MoO_3	8.694	5.625
MnO_2	1.356	0.877
RuO_2	5.629	3.642
PdO	3.297	2.075
Ag_2O	0.093	0.060
CdO	0.117	0.076
SnO_2	0.088	0.057
SeO_2	0.144	0.093
TeO_2	0.961	0.622
RE	31.104	20.123
	154.568	100.001

*1 Rh replaced by Pd

*2 Tc replaced by Mn, Rh replaced by K

Composition of the glass fiber cylinders type PF 798 used for the vitrification of Tokai Vitrification Facility HAWC simulate

Table 11

Glass fiber type PF 798	
Oxide	wt%
SiO_2	62.3
B_2O_3	19.0
Al_2O_3	6.7
Li_2O	4.0
CaO	4.0
ZnO	4.0

Table 12

Calculated composition of the glass product PO 789 generated for HAWC simulate SW17 and glass fiber cylinders type PF 798

Oxide	Glass type PO 789 wt%
Glass frit	
SiO_2	46.60
B_2O_3	14.20
Al_2O_3	5.00
Li_2O	3.00
Na_2O	-
K_2O	-
CaO	3.00
ZnO	3.00
BaO	-
SUB TOTAL	74.80
Waste	
Na_2O	10.00
P_2O_5	0.30
Fe_2O_3	2.04
Cr_2O_3	0.10
NiO	0.23
Rb_2O	0.11
Cs_2O	0.75
SrO	0.30
BaO	0.49
ZrO_2	1.46
MoO_3	1.45
Tc_2O_7	Mn 0.37
RuO_2	0.74
Rh_2O_3	0.14
PdO	0.35
Ag_2O	0.02
CdO	0.02
SnO_2	0.02
SeO_2	0.02
TeO_2	0.19
Y_2O_3	0.18
La_2O_3	0.42
CeO_2	0.87
Pr_6O_{11}	0.42
Nd_2O_3	0.37
Sm_2O_3	0.29
Pm_2O_3	Nd 0.31
Eu_2O_3	0.05
Gd_2O_3	0.02
Actinide	Ce 2.47
SUB TOTAL	25.20
TOTAL	100.00

Viscosity (950°C):	361.5 dPas
Viscosity (1150°C):	40.6 dPas
El. Resistivity (1150°C)	6.65 Ωcm

TVF-Melter

TVF-Melter has Mock-up III Melter design and had the following design requirements :

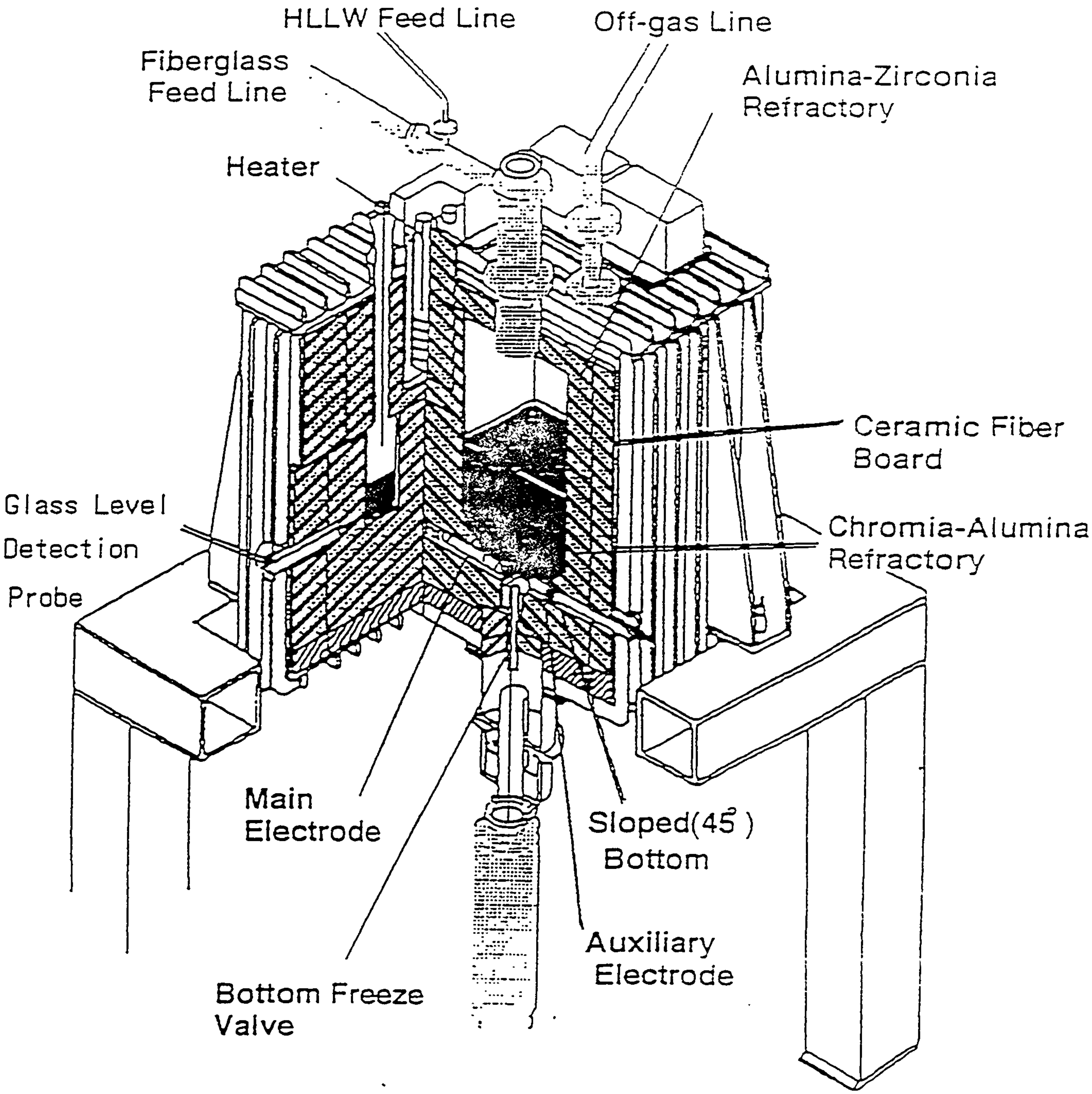
Melter temperature : 1100°C±50°C (max. 1250°C)
Production rate : 8.8 kg glass/hr
Feed rate : Conditioned HLLW 15 l/h (150 g Oxide/l)
and fiber glass additive 6.6 kg/hr
Discharge frequency : Every 34 hr (~ 300 kg/batch)
Operation lifetime : 5 years

The melter data of the final design were :

Outside dimension : 1.9 m x 1.9 m x 2.3 m (w x d x h)
Melting surface area : 0.66 m^2 (0.8 m x 0.83 m)
Glass pool volume : Max. 350 l
Floor : Sloped 45°
Electrode : Main electrode : 1 pair Inconel 690 plates
Auxiliary bottom electrode : 1 pair Inconel 690 rods
Refractory : Glass contact : Monofrax K.3
Superstructur : Sintered Al_2O_3-ZrO_2
Back-up insulation : Mullite
Heating up : 10 SiC heating elements with Inconel jackets
Glass drain : Induction-heated bottom drain nozzle (freeze valve)
Feed line : Glass additive, HLLW, water
Off gas line : Main and back-up line to first scrubber
(submerged bed scrubber)

A drawing of the TVF-Melter structure and its process control for plenum temperature operation is given in Fig. 4.

Most likely the low mode temperature method (bottom temperature kept at ~ 850 °C) will be used for the TVF vitrification, because it has a high efficiency regarding drain out of noble metals.



TVF MELTER STRUCTURE

Fig. 4

Fig. 5

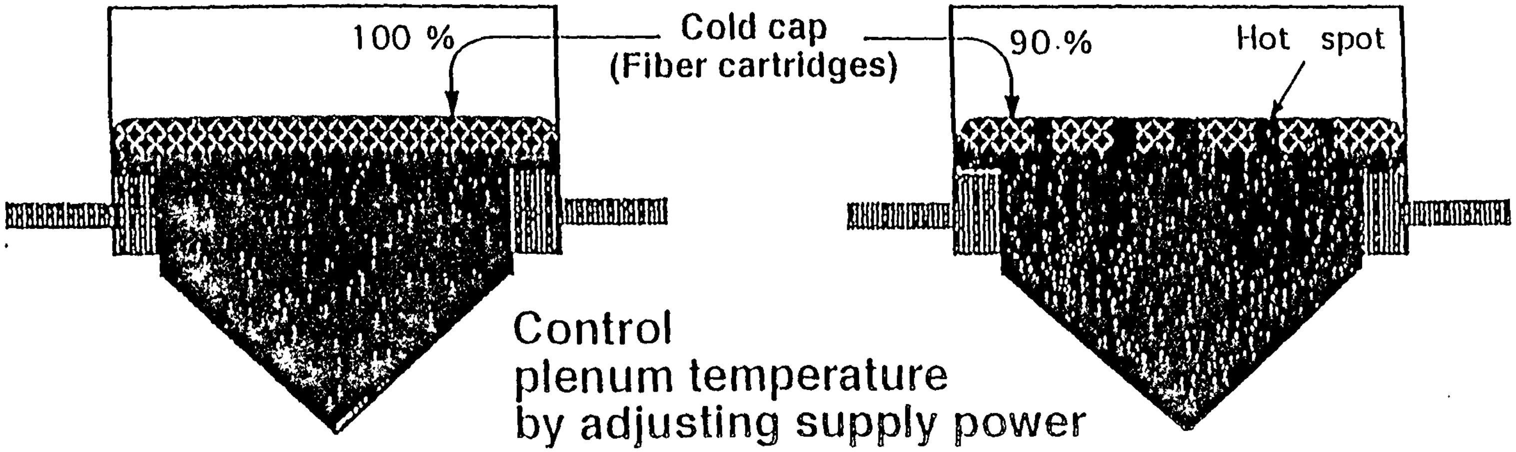
PROCESS CONTROL FOR THE MELTER OPERATION

(1) Low Plenum Temp. Operation

- about 300°C in Plenum space
- No Glass surface (almost 100 % Cold cap coverage)
- No pressure surge (due to Fiber cartridge)

(2) High Plenum Temp. Operation

- 400-500°C in Plenum space (Exposure of glass surface)
- Expect high Melt rate
- Increment of Particle release
- Difficult to control bottom temp.



Control
plenum temperature
by adjusting supply power

Operational conditions of the Mock-up III Melter for low mode temperature method

Obtained in a test run with Mock-up III Melter in the Mock-up Test Facility (MFT)

Feeding rate : 10-12 l/h TVF-simulate SW17
Feeding method : Glassfiber cylinders type PF798
Glass production rate : 10-12 kg/h
Glass pool temperature : 1150 - 1220 °C
Main electrodes temperatures : 800 - 900 °C aircooled (~ 40 Nm^3/h)
Auxiliary electrodes temperature : 800 - 900 °C
Total power comsumption : 45 - 50 kW
Melter plenum temperature : 300 - 500 °C
Melter underpressure : 80 - 100 mmWc
Melter surface : 0.61 m^2

Cold test status of Tokai Vitrification Facility (TVF)

The TVF was constructed from 1988 to middle 1992. The inspection and check for function and performance of equipment and systems are now under work.

Three test runs were scheduled and performed, one of them fully noble metal simulated. The total amout of glass product produced during the three test runs is about 22 to. The hot test operation was scheduled for April this year, but due to some license problems they couldn't go on with the schedule.

It is most likely that the hot operation, scheduled in autumn 1995, will be postponed also.

Large Scale Melter

The large scale melter designed for the Japan Nuclear Fuel Service (JNFS) K-facility (K-facility for vitrification) is based on the TVF-melter. The design throughput is nominal about 44 kg glass/hr and maximal about 52 kg glass/hr. The large scale melter was constructed in 1990-1991 at PNC and operated in Nov. 1991 with HLLW simulant. A microwave system for both heating up and boosting was not designed. For start up SiC heating elements were used.

Specification of Large Scale Melter :

Type	:	Liquid-fed ceramic melter
Outside Dimension	:	2.34 m x 2.74 m x 2.66 m (w x l x h)
Melting cavity	:	Internal dimension 1.46 m x 1.51 m Melting surface are 2.2 m^2
Floor	:	Sloped 49.6°/53.3°
Electrode	:	Main electrode : 1 pair *MA690 plater (* equivalent to Inconel 690/Ni-Cr alloy) Auxiliary bottom electrode : 1 pair MA690 rods
Heating up	:	SiC heating elements
Glass drain	:	Induction heated bottom drain nozzle (freeze valve) and subsidiary drain nozzle in the glass level detection chamber
Feed line	:	Glass fiber cylinders, glass beads, HLLW, water

The HLLW to be vitrified with the large scale melter will be produced by reprocessing of PWR reactor spent fuel with a burn up of 45000 MWd/tU and a specific power of 38 MW/tU.

The performed test run, mentioned above, was divided into a lowly simulated waste feed test and a highly simulated waste feed test. In the lowly simulated test run (without noble metals) about 7 to of glass beads and 5 to of glass fiber additives were vitrified. In the highly simulated test run (130 kg RuO_2, 80 kg PdO) about 5 to of glass beads and 7 to of glass fiber additives were vitrified. The waste feeding time was about 380 hr for 21 m^3 of lowly simulated HLLW and about 450 hr for 20 m^3 of highly simulated HLLW. The target compossition of the glass product for highly simulated HLLW is given in table 13.

Table 13

Oxides Glass Additives	wt%
SiO_2	46.72
B_2O_3	14.22
Na_2O	6.25
Al_2O	5.04
Li_2O	3.01
CaO	3.01
ZnO	3.01
Total	**81.26**
Na_2O	3.74
P_2O_5	0.17
Fe_2O_3	1.55
Cr_2O_3	0.29
NiO	0.25
K_2O	0.10
Cs_2O	0.69
SrO	0.24
BaO	0.44
ZrO_2	1.61
MoO_3	1.21
MnO_2	0.57
CoO	–
RuO_2	0.87
PdO	0.51
Ag_2O	0.02
CdO	0.03
SnO_2	0.03
SeO_2	0.02
TeO_2	0.15
R.E	6.15
Total	**18.74**

Germany

HLLW Programmes in the FRG

1. HAWC-WAW (Start 1983)

   for industrial vitrification (Wackersdorf)
   280 - 400 m^3/year

2. HAWC-WAK (Start 1987)

   for vitrification of high level waste stored at Karlsruhe WAK-site
   85 m^3 max

3. HEWC (Start 1985)

   for vitrification of high level waste stored at Belgoprocess site, Mol
   800 m^3

4. LEWC (Start 1979)

   for active demonstration of the liquid-fed ceramic melter process by vitrification of 50 m^3 LEWC-waste

1. HAWC-WAW

Basic Data

Average Burn-up	40 000 MWd/to
Specific Volume	800 l/t
Salt	131 g/l
Oxide Residue	64 g/l
HNO_3	5 M/l
Density	1.2 kg/l
Cooling time	7 years
Specific Activity	600 Ci/l approx.
Amount per Year	280 - 400 m^3 max

Design Data

HAWC	66 l/h
Feed	72 l/h
Glass Product	30 kg/h
Waste Glass Loading	15 Wt%
Can Dimension	430 dia, 1350 high
Cans per Year	290 - 415
Glass per Year	116 - 166 to max
Operation days	190 - 270 per year

Active Vitrification Facility WAW

Design Company	Nukem (Member of the KWU-guided Consortium for WAK design and construction)
Design Basis	INE-Mock-up Facility V-W1 and PAMELA
Status	Programme stopped in 1989 because no reprocessing will be performed in Germany
Number of lines	Two independent vitrification lines

INE-Mock-up Facility V-W1

Construction	1983 - 1986	
Melter	K-W1 (flat bottom)	
Operation	1st Campaign	Febr. 1987, 16 m³ HAWC-Simulate
	2nd Campaign	May 1987 30 m³ HAWC-Simulate
	3rd Campaign	Sept. 1987 31 m³ HAWC-MAWC-Simulate
Melter Exchange	K-W1/K-W2 (45° bottom) Nov./Dec. 1987	
Noble Metal Campaigns	1st Campaign	Apr. To May 1988 33 m³ HAWC-Simulate
	2nd Campaign	Jan. To March 1989 30 m³ HAWC-Simulate

Element/ Ion	Referenz g/1	△ g/1
34 Se	0.08	-
37 Rb	0.5	-
38 Sr	1.2	-
39 Y	0.7	-
40 Zr	5.2	0.20
41 Nb	-	-
42 Mo	4.6	0.51
43 Tc	1.1	0.09
44 Ru	2.2	1.23
45 Rh	0.5	0.20
46 Pd	1.9	0.23
47 Ag	0.03	0.06
48 Cd	0.12	0.03
49 In	-	-
50 Sn	0.04	0.03
51 Sb	-	-
52 Te	0.5	0.15
53 I	-	-
55 Cs	3.7	-
56 Ba	2.6	-
57 La	1.8	-
58 Ce	3.6	-
59 Pr	1.7	-
60 Nd	6.2	-
61 Pm	0.04	-
62 Sm	1.3	-
63 Eu	0.2	-
64 Gd	0.2	-
65 Tb	-	-
66 Dy	-	-
92 U	3.0	0.21
93 Np	0.7	-
94 Pu	0.04	0.02
95 Am	0.7	-
96 Cm	0.05	-
14 Si	0.06	-
24 Cr	1.1	-
25 Mn	0.1	-
26 Fe	3.7	-
27 Co	-	-
28 Ni	0.4	-
29 Cu	-	-
30 Zn	-	-
82 Pb	-	-
83 Bi	-	-
11 Na	-	-
12 Mg	-	-
13 Al	-	-
19 K	-	-
20 Ca	-	-
80 Hg	-	-
F^-	-	-
Cl^-	-	-
SO_4^{2-}	-	-
PO_4^{3-}	-	-

△ : Portion of each element in g/l HAWC assumed to end-up in the dissolver residue

HAWC-WAW

Reference Composition
for noble metal campaign
at INE, March 1988

Preliminary Composition of the Glass Frit and Glass Product for the Noble Metals Campaign, March 1988

	Frit Wt%	Glass product Wt%
SiO_2	53.3	46.2
B_2O_3	18.8	16.3
Al_2O_3	3.0	2.6
MgO	2.1	1.8
CaO	5.6	4.8
Li_2O	3.9	3.4
Na_2O	9.7	8.4
TiO_2	3.6	3.1
HAWC-Oxides	-	13.4
Viscosity		
1150°C	-	50 - 60 dPas
950°C	-	400 - 500 dPas
Spec. el. resitance		
1150°C	-	5.5 Ωcm

2. HAWC-WAK

Basic Data

Total HAWC-volume	86 m^3
Total Activity	26.1 Mio. Ci
Specific Activity	303 Ci/l
Oxide Residue	92 g/l
Oxide Loading in Glass Product	16 Wt%
Total Glass Production	49.5 to
Specific Activity of the Glass Product	527 Ci/kg
HNO_3	4 M/l
Noble Metals Content in HAWC	
Ru	2.232 g/l
Rh	0.580 g/l
Pd	1.270 g/l

Options

Vitrification	In PAMELA, 1991
Problem	Transport Licence of the HAWC
Melter	K-6, designed by INE with 60 - 75° bottom inclination

Reference composition of the HAWC-WAK, status March 1993. Composition of the HAWC-simulate used for the fourth long-term noble metals test run D6 in May/June 1993

Element (Ion)	HAWC-Reference composition 1)				HAWC-Simulate used for the D6 test run		
	Element/Ion g/l	Oxide	Oxide yield g/l	Oxide yield wt %	Element/Ion g/l	Oxide yield g/l	Oxide yield wt %
34 Se	0.062	SeO_2	0.087	0.096	0.062	0.087	0.106
37 Rb	0.286	Rb_2O	0.313	0.371	- 1)	- 1)	- 1)
38 Sr	0.791	SrO	0.935	1.035	0.791	0.935	1.140
39 Y	0.575	Y_2O_3	0.731	0.808	0.575	0.731	0.894
40 Zr	2.196	ZrO_2	2.966	3.281	2.196	2.966	3.028
41 Nb	-	Nb_2O_5	-	-	-	-	-
42 Mo	3.375	MoO_3	5.064	5.602	3.375	5.064	6.194
43 Tc	0.913	Tc_2O_2	1.355	1.499	- 2)	- 2)	- 2)
44 Ru	2.232	RuO_2	2.939	3.251	2.232	2.939	3.595
45 Rh	0.579	Rh_2O_3	0.714	0.790	-	-	-
46 Pd	1.272	PdO	1.464	1.619	1.272	1.464	1.791
47 Ag	0.113	Ag_2O	0.121	0.134	-	-	-
48 Cd	0.083	CdO	0.095	0.105	-	-	-
49 In	-	In_2O_3	-	-	-	-	-
50 Sn	0.058	SnO_2	0.074	0.082	0.058	0.074	0.091
51 Sb	0.011	Sb_2O_3	0.013	0.014	-	-	-
52 Te	0.523	TeO_2	0.653	0.723	0.523	0.653	0.799
53 I	-	-	-	-	-	-	-
55 Cs	3.137	Cs_2O	3.326	3.679	3.137	3.326	4.067
56 Ba	2.327	BaO	2.598	2.875	2.327	2598	3.178
57 La	2.050	La_2O_3	2.405	2.660	2.050	2.405	2.942
58 Ce	3.011	CeO_2	3.699	4.092	3.011	3.699	4.524
59 Pr	1.417	Pr_2O_3	1.658	1.834	1.417	1.658	2.028
60 Nd	5.059	Nd_2O_3	5.900	6.528	6.313	7.362	9.005
61 Pm	0.004	Pm_2O_3	0.004	0.005	- 3)	- 3)	- 3)
62 Sm	1.121	Sm_2O_3	1.300	1.438	- 3)	- 3)	- 3)
63 Eu	0.129	Eu_2O_3	0.149	0.164	- 3)	- 3)	- 3)
64 Gd	0.385	Gd_2O_3	0.444	0.491	0.385	0.444	0.543
65 Tb	-	Tb_2O_3	-	-	-	-	-
66 Dy	-	Dy_2O_3	-	-	-	-	-
92 U	5.731	U_3O_8	6.758	7.476	-	-	-
93 Np	0.459	NpO_2	0.506	0.559	-	-	-
94 Pu	0.183	PuO_2	0.208	0.230	-	-	-
95 Am	0.425	Am_2O_3	0.468	0.518	-	-	-
96 Cm	0.017	CmO_2	0.019	0.021	-	-	-
14 Si	-	SiO_2	-	-	-	-	-
24 Cr	1.860	Cr_2O_3	2.718	3.007	1.860	2.718	3.324
25 Mn	0.215	MnO_2	0.341	0.377	1.128	1.789	2.188
26 Fe	7.058	Fe_2O_3	10.091	11.163	7.058	10.091	12.343
27 Co	-	CoO	-	-	-	-	-
28 Ni	1.284	NiO	1.635	1.808	1.284	1.635	2.000
29 Cu	0.015	CuO	0.018	0.020	0.015	0.018	0.022
30 Zn	0.009	ZnO	0.011	0.012	0.009	0.011	0.013
82 Pb	0.003	PbO	0.003	0.003	0.003	0.003	0.004
11 Na	18.310	Na_2O	24.682	27.305	18.310	24.682	30.189
12 Mg	0.410	MgO	0.680	0.752	0.410	0.680	0.831
13 Al	0.057	Al_2O_3	0.108	0.119	0.057	0.108	0.132
19 K	0.217	K_2O	0.261	0.289	0.503	0.605	0.740
20 Ca	0.353	CaO	0.494	0.546	0.353	0.494	0.604
F^-	0.019	F^-	0.019	0.021	0.019	0.019	0.023
Cl^-	0.014	Cl^-	0.014	0.015	0.014	0.014	0.017
P	1.027	P_2O_5	2.353	2.603	1.027	2.353	3.098
HNO_3	4 M	-	-	-	4 M	-	-
		Σ	90.391	100.00		81.757	100.00

1) Rb portion replaced by K
2) Tc portion replaced by Mn
3) Pm, Sm and Eu portions replaced by Nd

Technology Program

Melter Technique	INE
Glass Frit Development	INE / HMI, Berlin

Melter Technique

Prototype Melter	K-6'
Active Melter	K-6, final design 1994
Basic Requirement	- Melter must be able for use in the PAMELA cell - 60 - 75° bottom inclination due to the significant amounts of noble metals in the HAWC-WAK
Prototype Melter Tests	At INE (VA-2 facility)
Start-up	Nov. 1988
Cans	430 dia, 1350 high
Glass Draining System	Bottom drain, overflow
Test Programm	Until 1993
Total Amount of Noble Metal (in 88 m^3 existing HAWC-WAK waste)	Ru 196 kg Rh 51 kg Pd 112 kg

2. HEWC-Programm

Basic Data

Stored Volume (3 Tanks)	742 m^3 total
Activity	5.3 - 9.5 Ci/l
Salt	280 g/l
Oxide Residue	100-110 g/l
Specific Elemente	High Al-Content Sulphur Mercury
HNO_3	0.5 M

Technology Programm

Start-up	Sept. 1985
Tests with HEWC-Simulate	INE (VA-2 Facility)
Flass Frit Development	HMI/Berlin

Active HEWC-Vitrification

Start-up	Oct. 6, 1986
HEWC-Volume Vitrified	860 m^3 (Aug. 1991)
Total Glass Product	412 to
Programm Schedule	1986 - 1991/92
Cans	300 dia, 1200 high (Oct. 86 - June 88) 60 l, total 939 430 dia, 1350 high, 150 l, total 698

Active HEWC

Element	Concentration		
	Tank 258-1	Tank 258-2	Tank 540-12
Al	54.4	50.6	41.4
B	0.0044	0.037	0.029
Ca	0.13	0.04	0.02
Ce	0.059	0.043	0.039
Cr	0.062	0.015	0.087
Fe	2.49	1.4	1.23
Hg	2.23	2.40	2.61
La	0.038	0.028	0.024
Li	0.003	0.001	0.006
Mg	0.37	0.30	0.30
Mn	0.049	0.033	0.057
Mo	0.083	0.059	0.044
Na	0.46	0.213	1.82
Nd	0.125	0.092	0.079
Ni	0.083	0.083	0.033
Pd	0.01	0.02	0.006
Rh	0.007	0.008	0.009
Ru	0.059	0.039	0.035
Se	0.107	0.091	0.077
Si	0.020	0.014	0.02
SO_4	8.4	5.0	3.5
Sr	0.0281	0.0206	0.0166
Tc	0.047	0.027	0.031
Ti	0.007	0.007	0.007
U	0.05	0.015	0.11
Zr	0.120	0.139	0.132
Amount	168 m^3	118	456
Activity	9.5 Ci/l	6.9	5.3

Main Points to be tested

Hg	Behaviour during processing
Al	Influence of Al_2O_3-rich calcines on melting into the glass pool
Waste Glass Loading	Maximum possible waste glass loading
Glass	Canister glass quality assurance Opimum melt viscosity for process and glass draining

Test runs performed at INE

Inactive HEWC Test Runs	Nov. 1985 Feb. 1986 Dec. 1986 March 1987
Total Volume of Vitrified Simulate	40 m^3
Waste Glass Loading	Up to 24.7 Wt%
Glass Frit Tested	SM 527 SM 539
Glass Frit Selected Finally	SM 539
Average Throughput Capacity	30 l/h, K-2 melter
Programm Termination	Sept. 1987

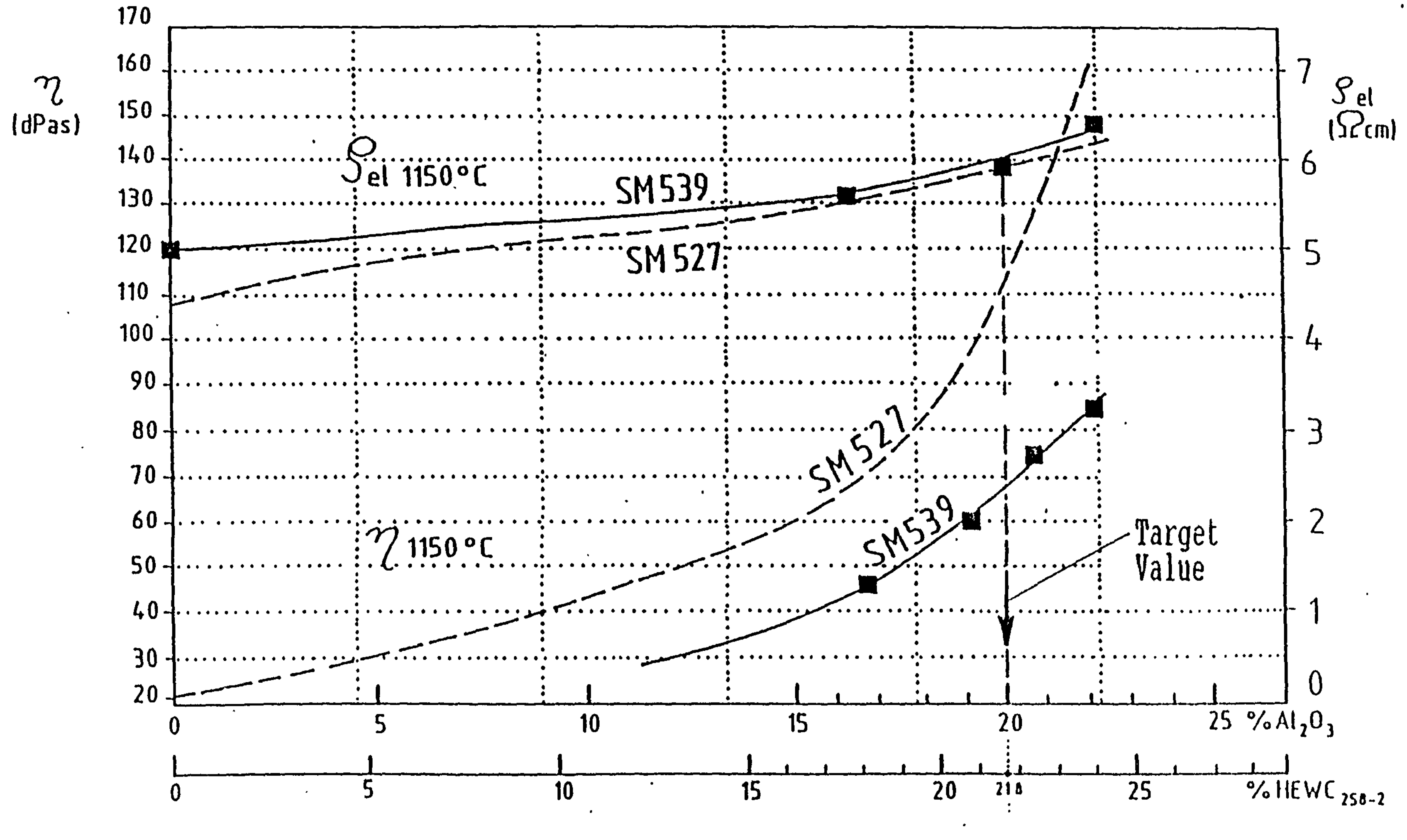
PAMELA Operation

Glass Frit	SM 539
Throughput Capacity	22 - 25 l/h
Mercury	Ends-up in the Evaporator condensate (will be bituminized)
Glass Blocks	Stored on Site
Waste Glass Loading	22 Wt%

Glass Frit Composition

used for active HEWC vitrification

	Oct. 1986 - June 1987 SM 527	Further used SM 539
SiO_2	50 Wt%	45
B_2O_3	28	33
Na_2O	11	10.5
Li_2O	4	4.5
CaO	5	6.5
TiO_2	2	-
HEWC-Oxides	22 Wt%	22



Influence of Waste Glass Loading on Glass Melt Properties for HEWC Vitrification

SM 527	Initial Glass Frit used in PAMELA Oct. 1986 - June 1987
SM 539	Further used Glass Frit

4. LEWC

Inactive Technology Programm	Started 1979 Terminated 1983
Active LEWC-Vitrification	Started Oct. 1985 Finished 1986

Final Data

Vitrified Activity	α $0.35 * 10^5$ Ci β $0.75 * 10^7$ Ci
Number of Glass Blocks	442 (via bottom drain)
Number of Vitromet Blocks	100 (via overflow drain)
Amount of Glass	77.8 to
Glass Storage	On Site
Process Availability	88%
Noble Metals Processed	Ru 63.2 kg Rh 14.2 kg Pd 9.6 kg
PAMELA Melter Condition	Approximately 40% of the noble metals accumulated on melter floor, especially ruthenium

Vitrification runs for HLLW-simulate at INE, Karlsruhe

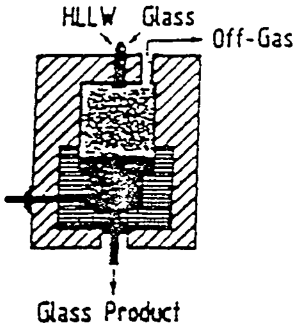
Date	Plant	Ceramic melter	Designation of operation runs	Amount of vitrified waste (l)	Type of HLLW	Type of glass frit	Produced waste glass (t)
9/76 - 2/78	VA-0	K-O		18000		VG 38-2	4.0
2/78 - 2/78	VA-1	K-1	1 - 35	560	LWR-2c	VG 98-2	0.123
4/78	VA-1	K-1	E 1	1700	LWR-2c	VG 98-2	0.260
	VA-1	K-1	E 2	1548	426 l/t	VG 98-2	0.560
	VA-1	K-1	E 3	2027	426 l/t	VG 98-2	0.445
	VA-1	K-1	E 4	2280	426 l/t	VG 98-2	0.520
	VA-1	K-1	E 5	2427	426 l/t	VG 98-2	0.702
	VA-1	K-1	E 6	2159	426 l/t	VG 98-2	0.700
	VA-1	K-1	E 7	163	426 l/t	VG 98-2	0.060
	VA-1	K-1	E 8	119	426 l/t	VG 98-2	0.045
	VA-1	K-1	E 9	2950	426 l/t	VG 98-2	1.307
	VA-1	K-1	E 10	830	426 l/t	VG 98-2	1.365
	VA-1	K-1	E 11	742	426 l/t	VG 98-2	1.334
	VA-1	K-1	E 12	681	426 l/t	VG 98-2	0.250
	VA-1	K-1	E 13	670	426 l/t	VG 98-2	0.171
4/79	VA-1	K-1	S1	1255	426 l/t	VG 98-2	0.580
				Σ 20111			Σ 6.422
10/80	VA-2	K-2	V 1-5	500	H_2O/Glas	VG 98-2	0.100
10/80	VA-2	K-2	V 6-10	810	H_2O/Glas	VG 98-2	0.200
	VA-2	K-2	V 11-20	1680	H_2O/Glas	VG 98-2	0.690
	VA-2	K-2	V 21-24	640	H_2O/Glas	VG 98-2	0.830
	VA-2	K-2	V 25-29	2560	LEWC	DC 16	2.960
	VA-2	K-2	V 30	1020	LEWC	DC 16	0.800
	VA-2	K-2	V 31	190	LEWC	DC 16	0.060
	VA-2	K-2	V 32	670	LEWC	DC 16	0.600
	VA-2	K-2	V 33	4800	LEWC	DC 16	5.800
	VA-2	K-2	V 34	2000	LEWC	VG 98/12	1.500
4/82	VA-2	K-2	V 35	5500	LEWC	SH 58 FR	5.100
				Σ 20370			Σ 18.640
3/83	VA-3	K-3	P-1	350	LEWC	SM 513	0.956
	VA-3	K-3	P-2	4010	LEWC	SM 513	4.085
	VA-3	K-3	P-3	2680	LEWC	SM 513	2.988
	VA-3	K-3	P-4/I	3830	LEWC	SM 513	4.001
	VA-3	K-3	P-4/II	3890	LEWC	SM 513	4.022
7/83	VA-3	K-3	P-4/III	4330	LEWC	SM 513	4.942
				Σ 19090			Σ 21.994
6/84	VA-2	K-2	V 100	-	-	SM 513	0.394
	VA-2	K-2	V 101	150	H_2O	SM 513	0.048
	VA-2	K-2	V 102	570	H_2O/Glas	VG 98/12/ SM 513	0.198 0.733
	VA-2	K-2	V 103	2180	HAWC	VG 98/12	
	VA-2	K-2	V 104	1670	HAWC *	VG 98/12	0.555
7/84	VA-2	K-2	V 105	1680	HAWC *	VG 98/12	0.607
				Σ 6250			Σ 2.535
11/85	VA-2	K-2	V 110	1060	HEWC	SM 519	0.505
			V 111	7320	HEWC	SM 519	3.540
2/86	VA-2	K-2	V 112	7000	HEWC	SM 521	2.855
12/86	VA-2	K-2	V 113	10280	HEWC	SM 527	5.307
4/87	VA-2	K-2	V 114	5921	HEWC	SM 540FR	2.923
				Σ 31581			Σ 15.130
10/84 - 1/85	PAMELA	K-3	I		H_2O/Glas	SM 513	
2/85 - 3/85	PAMELA	K-3	II	14700	LEWC	SM 513	14.900
6/85 - 7/85	PAMELA	K-4	III	6500	LEWC	SM 513	10.000
8/85 - 9/85	PAMELA	K-4	IV	2000	act. LEWC (blended)	SM 513	2.600

Date	Plant	Ceramic melter	Designation of operation runs	Amount of vitrified waste (l)	Type of HLLW	Type of glass frit	Produced waste glass (t)
10/85 - 8/86	PAMELA	K-4		49000	act. LEWC	SM 513	78.000
10/86 - 9/91	PAMELA	K-4 K-5		860000	act. HEWC	SM 540	411.700
				Σ 909000			Σ 489.700
12/87	VA-2	K-2	V 115	3804	HAWC-WAK	SWA752FR	2.114
2/87	V-W1	K-W1	W 1	15700	HAWC	VG 98 12.2	5.500
5/87 - 6/87	V-W1	K-W1	W 2	33700	HAWC	VG 98 12.2 Li	13.800
9/87- 9/87	V-W1	K-W1	W 3	25360	HAWC	VG 98 12.2 Li	7.100
				Σ 74760			Σ 26.400
4/88 - 5/88	V-W1	K-W2	W 4	33100	HAWC *	VG 98 12.2 Li	12.800
1/89 - 3/89	V-W1	K-W2	W 5	30000	HAWC *	VG 98 12.2 Li	12.200
				Σ 63100			Σ 25.000
5/90 - 6/90	VA-WAK	K-6'	D1	5000	HAWC-WAK	SM752 FR	2.500
6/90	VA-WAK	K-6'	D2	10300	HAWC-WAK *	SM752FR	5.800
4/91	VA-WAK	K-6'	D3 **	-	-	-	-
6/91	VA-WAK	K-6'	D4	9600	HAWC-WAK *	SM752FR	5.600
2/92 - 3/92	VA-WAK	K-6'	D5	15400	HAWC-WAK *	GGWAK1	8.700
5/93 - 7/93	VA-WAK	K-6'	D6	15900	HAWC-WAK *	GGWAK1	9.300
				Σ 56200			Σ 31.900
7/92	VA-WAK	ESM	U 1	2600	NCAW		1.080
7/92 - 8/92	VA-WAK	ESM	U 2	14200	NCAW *		6.423
				Σ 16800			Σ 7.503
3/93	V-W1	K-W3	C1	24800	BVPM-simulate	BVPM-frit	14.900
11/93	V-W1	K-W3	C2	20100	BVPM-simulate	BVPM-frit	13.100
				Σ 44900			Σ 28.000

* incl. Noble metals

** Check overflow system

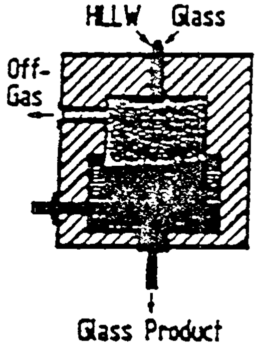
Melter Type	K-1	K-2	K-3	K-4 / K-5	K-W1	K-W2	K-6'	K-W3	ESM
Vitrification Plant	VA-1 (INE) Basic Test Facility	VA-2 (INE) Engineering Test Facility	VA-3 (INE) PAMELA-Mock-up	PAMELA (DWK/Mol) Active Demonstration Plant)	V-W1 (INE) Wackersdorf Mock-up	V-W1 (INE) Wackersdorf Mock-up	VA-2 PAMELA-Mock-up	K-W1 BVPM-Mock-up	VA-2 (Modified)
Waste Type	HAW, 426 l/h (Simulate)	LEWC, HEWC, HAWC (Simulate)	LEWC (Simulate)	LEWC, HEWC	HAWC (Simulate)	HAWC (Simulate incl. noble metals)	HAWC-WAK (Simulate incl. Noble metals)	BVPM (Simulate incl. noble metals)	NCAW (Simulate incl. Noble metals)
Design Throughput	20 - 25 l/h	30 - 40 l/h	30 l/h	30 l/h	72 l/h	72 l/h	34 l/h	60 l/h	20 l/h
Glass Production Rate	15 - 20 kg/h	20 - 30 kg/h	30 kg/h	30 kg/h	31 kg/h	31 kg/h	18 kg/h	38 kg/h	10 kg/h
Glass Pool Surface	0.36 m^2	0.64 m^2	0.72 m^2	0.72 m^2	1.4 m^2	1.4 m^2	0.88 m^2	1.4 m^2	0.28 m^2
Bottom Geometric	Flat	Flat	Flat	Flat	Flat	45° sloped bottom	60 - 75° sloped bottom	60 - 75° sloped walls	
Glass Pool Volume	70 l	250 l	300 l	300 l	560 l	750 l (max)	420 l (max)	750 l (max)	234 l
Discharge Volume	25 l	50 l	60 l	60 l	150 l	150 l	75 l	150 l	
Start-up Technique	12 Heating Elements	14 Heating Elements	20 Heating Elements	20 Heating Elements	13 Heating Elements	6 Heating Elements	5 + 2 Heating Elements	5 + 2 Heating Elements	4 + 1 Heating Elements
Number of Pairs of Power Electrodes	3 (Rods)	2 (Rods)	4 (Plates)	4 (Plates)	5 (Plates)	4 (Plates)	3 (Plates)	3 (Plates)	2 (Plates)
Glass Draining Systems	Bottom Drain	Bottom drain (2)	Bottom Drain Overflow)	Bottom Drain Overflow)	Bottom Drain Overflow Vacuum Suction	Bottom Drain Overflow	Bottom Drain Overflow	Bottom Drain Overflow	
Glass Pool Refractory	ER 2161 ZAC 1711 ZAC 1681 Supral AR 90	ER 2161	ER 2161	ER 2161	ER 2161	ER 2161	ER 2161	ER 2161	ER 2161
Electrode Material	Molybdenum Tin Oxide	Inconel 690	Inconel 690	Inconel 690	Inconel 690	Inconel 690	Inconel 690	Inconel 690	Inconel 690
Outside Dimensions (L x D x H)	1.4x1.4x1.8m	1.8x1.8x1.9m	2.6x2.0x2.0m	2.6x2.0x2.0m	3.7x2.4x2.3m	3.4x2.2x2.2m	2.7x1.8x2.3m	3.2x1.8x2.5m	
Weight	7 t	9 t	18 t	18 t	31 t	27 t	19 t	31 t	7 t



K-1

First liquid-fed ceramic melter

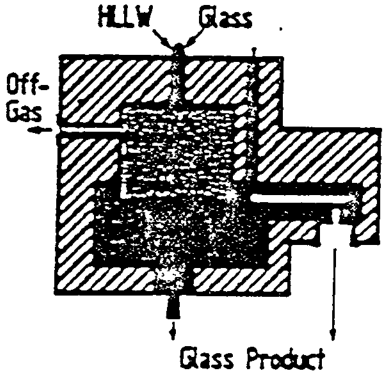
Year of development	1976
Operation	1977-1979
Type of waste	HAW (426 l/t)
Vitrified waste volume	18 m³
Produced waste glass	3 t



K-2

Full-scale melter integrated in an engineering test facility (no remote handling technique)

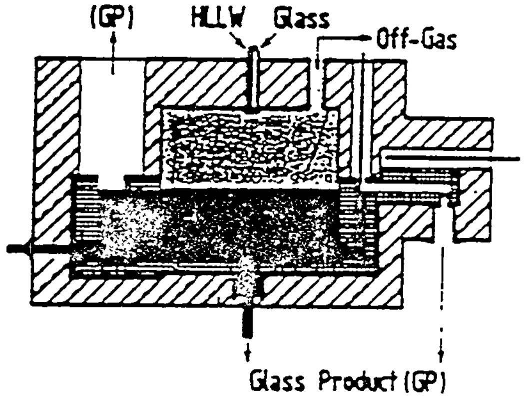
Year of development	1978
Operation	since 1980
Types of waste	LEWC, HEWC, HAWC
Vitrified waste volume	38m³
Produced waste glass	26t



K-3

PAMELA mock-up melter

Year of development	1980
Operation	(KfK/INE) 1983
	(PAMELA) 1985
Type of waste	LEWC
Vitrified waste volume	34m³
Produced waste glass	34t



K-W1

Full-scale test melter for the Wackersdorf vitrification plant (remote handling technique)

Year of development	1984
Operation	Start-up in 1986
Type of waste	HAWC

Ceramic melter types developed at INE

Melter types in the PAMELA-project

K-3 mock-up melter
constructed in 1980

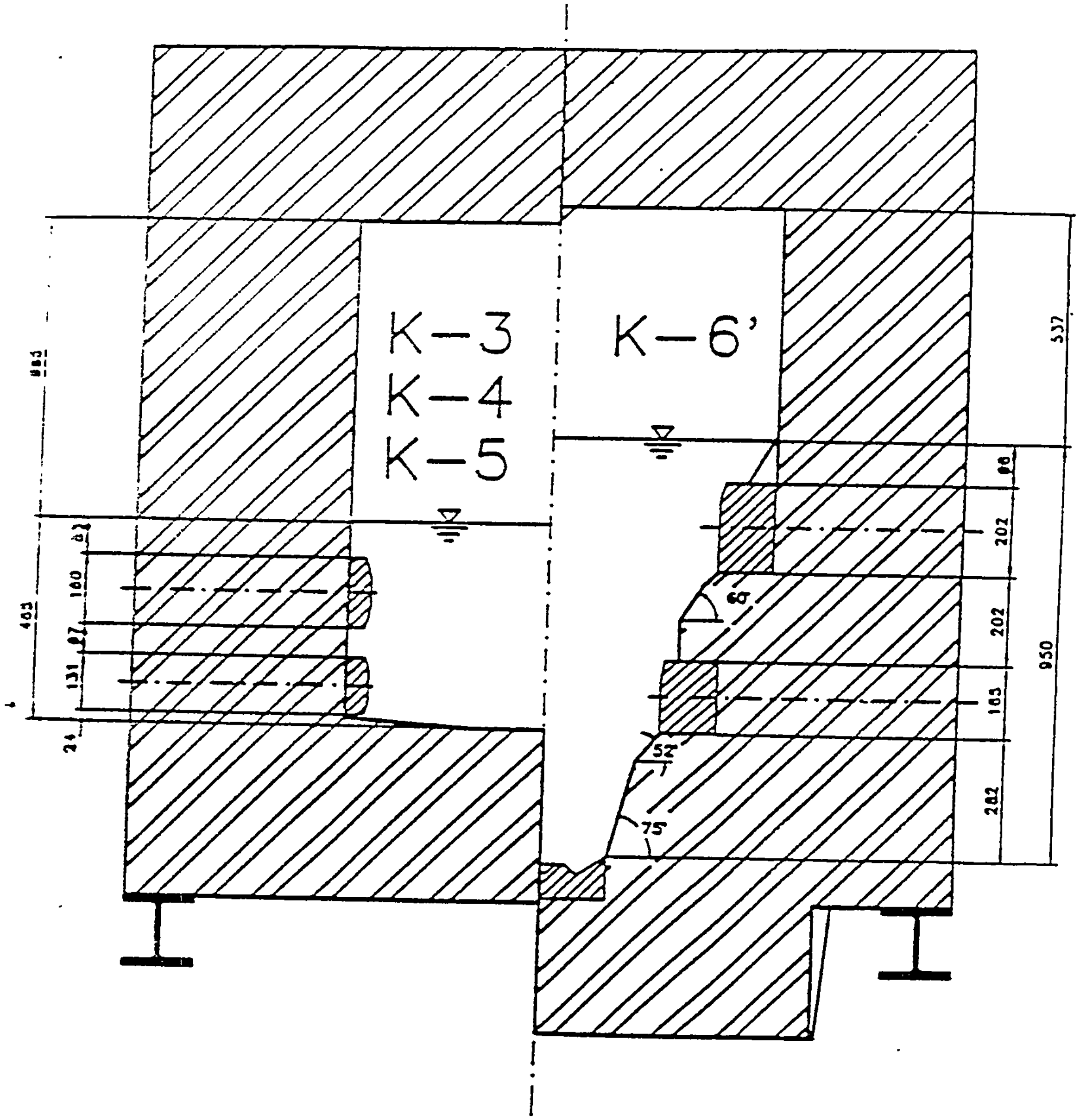
K-4 first radioactive melter
constructed in 1984

K-5 back-up melter
constructed in 1987

K-6 melter for the vitrification of HAWC-WAK containing noble metals
constructed in 1995/96

- outside dimensions as well as supporting connections will be the same as for the melter K-4 and K-5
- glass tank geometry will be changed, based on the experience with the sloped bottom melter K-W2. Bottom inclination 60 - 75°

K-6' non-radioavtive mock-up melter
constructed in 1988
test operation in the VA-2 plant in order to fix the final design of the K-6 melter

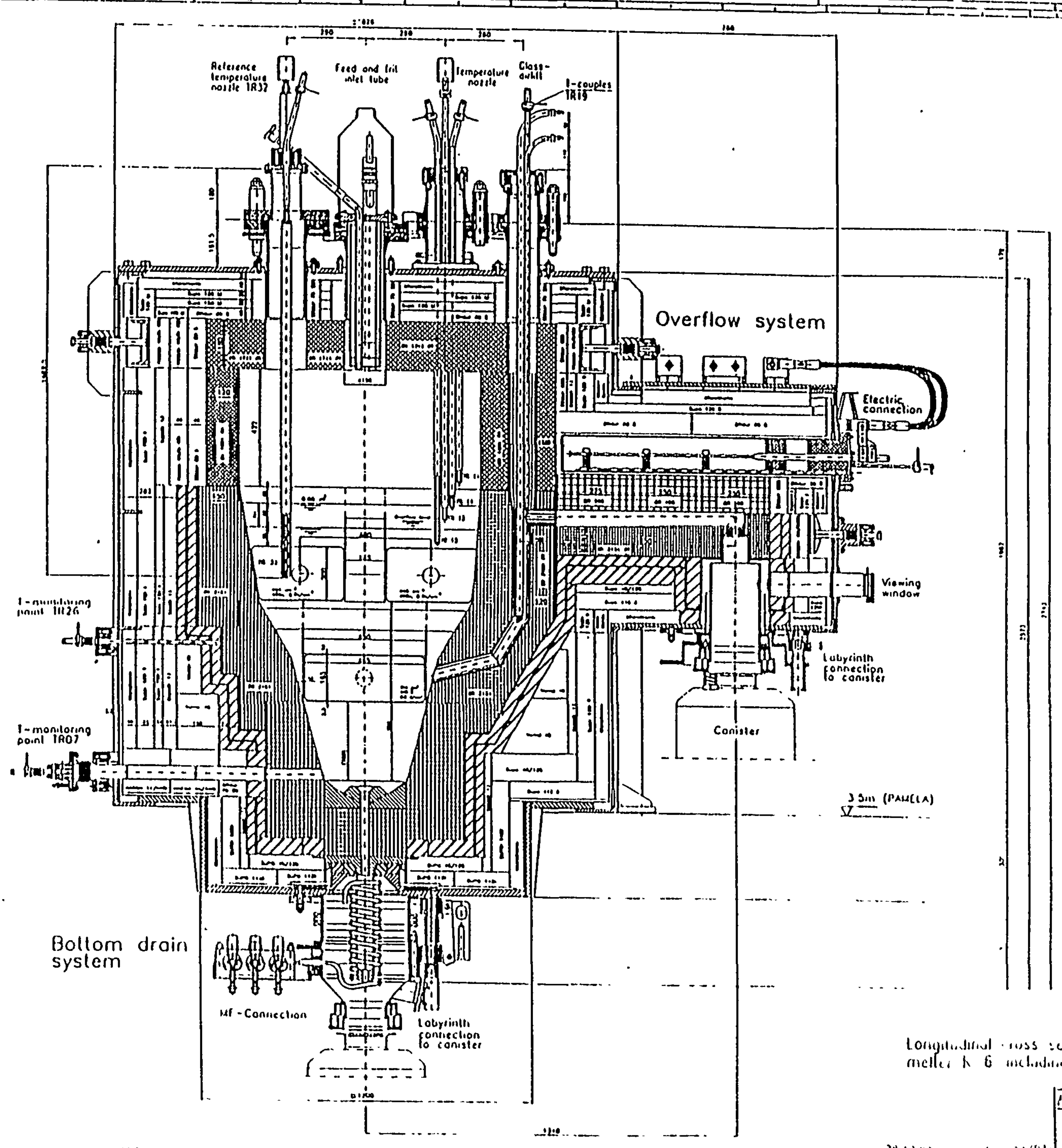


Melter designation	K-3, K-4, K-5	K-6'
Waste type	LEWC, HEWC	HAWC-WAK sim.
Glass pool surface	0.72 m^2	0.88 m^2
Glass pool volume	300 l	ca. 400 l
Discharge volume	60 l (3 x 50 l)	2 x 75 l
Start-up technique	20 MoSi Elements	5 SiC Elements
Containment Height	2.6 m	2.9 m
Total weight	18 to	ca. 20 to

Comparison of PAMELA melter types

Main data and characteristics of the noble metals compatible prototype melter K-6

Parameter/Characteristic	Data/Specification
Design throughput	34 l/h feed 18 kg/h glass production rate
Glass pool surface area	0,88 m^2
Power electrodes	Inconel 690, three main pairs, aircooled, one bottom electrode, not aircooled
Glass pouring systems	Bottom drain, overflow drain
Heating of the overflow systems	By RHF completely
Glass melt level detection	By specially developed device, based on an el. signal
Glass pouring batch	200 kg maximum
Melter power control	By current control and power subcontrol
Glass melt reference temperature	1150-1180 °C (monitored by TR32)
Melter power consumption	100 kW approximately, in total
Glass tank inventory	850 kg to 1050 kg
Number of temperature monitoring points	29
Glass tank and melter plenum ceramic refractories	ER 2161, ER 1681, ER 1711 (supplier SEPR, Avignon, France)
Melter wall insulation	Multilayer ceramics with decreasing thermal conductivity
Melter box	Stainless steel containment box
Melter box dimension	1826 x 2710 x 2262 mm (depth x length x height)
Melter outside dimension	2400 x 3370 x 2743 mm (depth x length x height)
Melter weight including 1040 kg of glass and transportation device (950 kg)	19236 kg (containment 3660 kg, ceramics 12442 kg, subcomponents like electrodes etc. 634 kg, nozzles, bus bars 510 kg)
Start-up heating	By five SiC-heating elements (melter plenum) By two $MoSi_2$-heating elements (glass overflow)
Minimum quantity of start-up glass frit	240 kg
Type of start-up glass frit	GG WAK 1, 1350 dPas (950°C); 102 dPas (1150°C) 27 Ωcm (950°C); 9.4 Ωcm (1150°C)
Couplings for el. power supply of power electrodes	Special design, combined for supply of power and electrode cooling air
Off gas pipe	Through melter plenum side wall
Design underpressure in melter while operating	20 mm WS
Inleakage rate (at design underpressure)	20 Nm^3/h



Longitudinal cross section through the prototype melter K 6 including the overflow system

Melter development in the Wackersdorf Project

K-W1 First full-scale test melter for the Wackersdorf vitrification plant
(remote handling technique included)

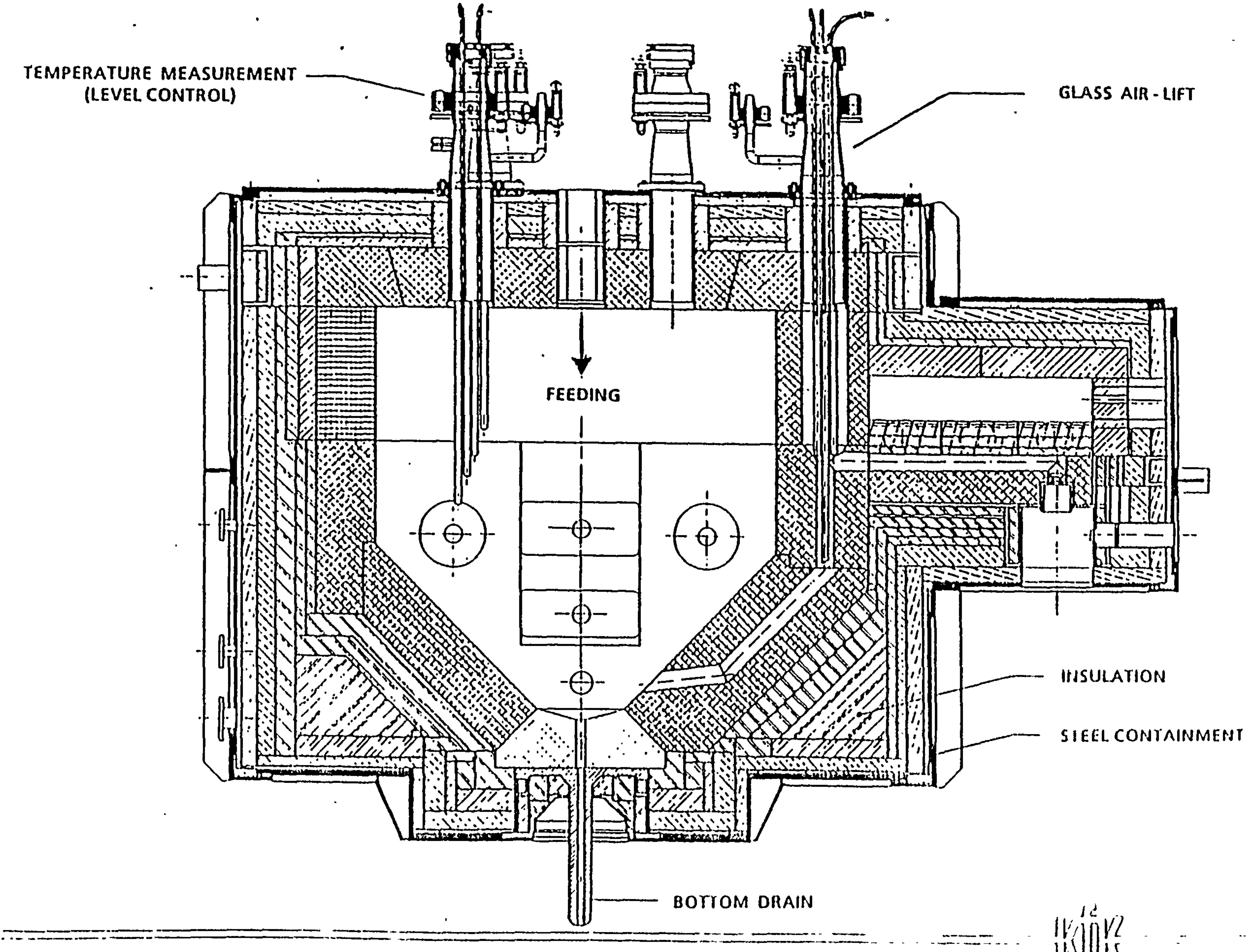
Year of development	1984
Operation	1987
Type of waste	HAWC, HAWC/MAWC
Vitrified waste volume	78 m^3

K-W2 Non-radioactive mock-up melter replacing K-W1 melter
Noble metal behaviour and especially lifetime aspects are to be considered

Construction	1987
Start-up	1988
Operation	1988 - 1991

Melter data K-W2

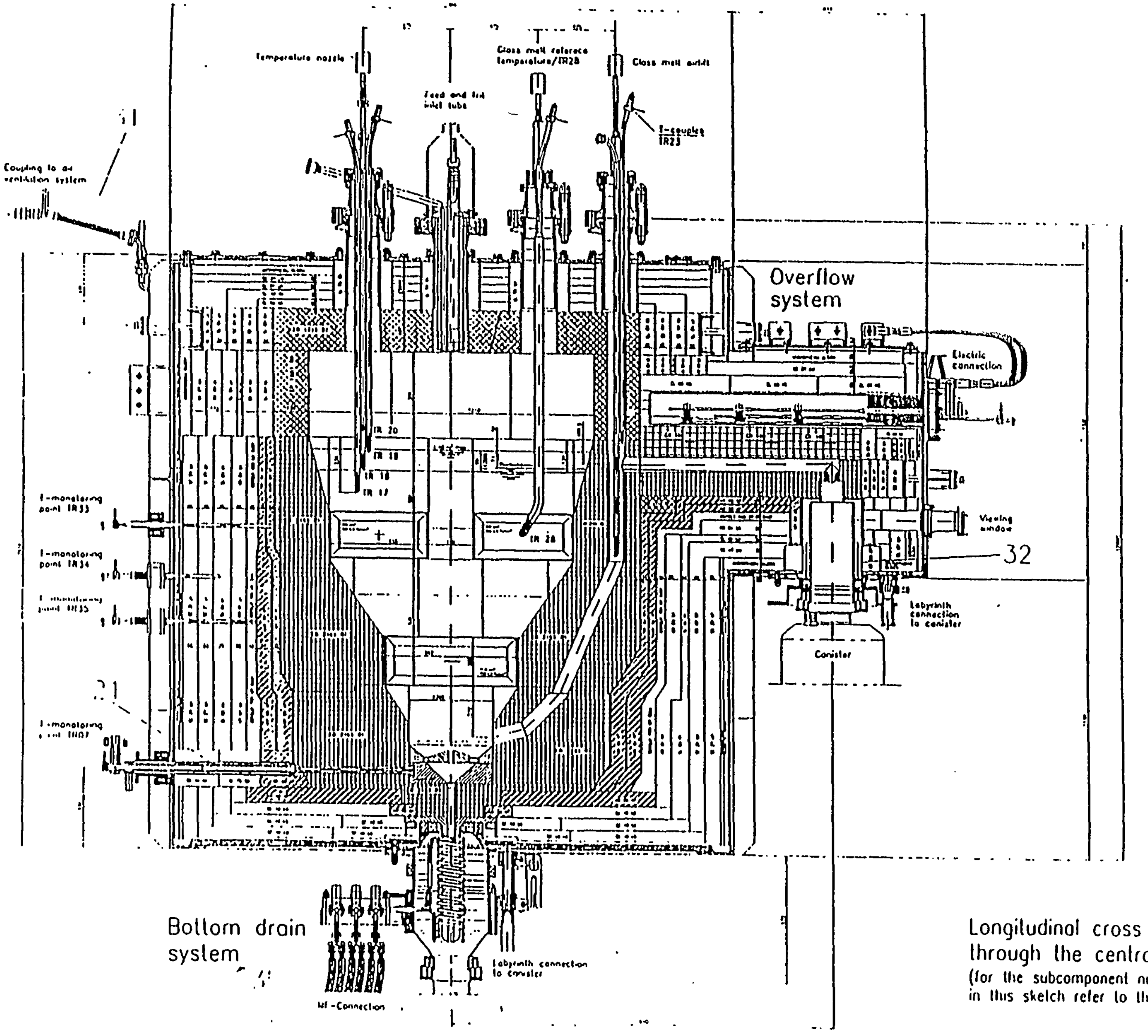
Design feed rate	72 l/h
Design glass production rate	31 kg/h
Glass pool temperature	1150°C
Glass pool surface	1.4 m^2
Glass tank volume	600 - 750 l
Pairs of electrodes	4
Total electrode surface	2500 cm^2
Power input (at design feed rate)	90 - 100 kW
Glass draining	Bottom drain, overflow drain
Discharge volume	150 l
Off-gas leaving	vertically
Start-up system	6 SiC-elements
Glass pool refractory	ER 2161 (30% Cr_2O_3)
Containment	Stainless steel
Outside dimensions	3.4 m x 2.2 m x 2.2 m
Weight	27 to



MELTER K-W2 (VERTICAL CROSS SECTION)

Main data and characteristics of the noble metals compatible BINE Vitrification Plant Mock-up melter (BVPM)

Parameter/Characteristic	Data/Specification
Design feed throughput	60 l/h feed 38 kg/h glass production rate
Guaranteed feed throughput	45 l/h 26.9 kg/h glass
Glass pool surface area	1.4 m^2
Power electrodes	Inconel 690, three main pairs, aircooled, one bottom electrode, not aircooled
Glass pouring systems	Bottom drain, overflow drain
Heating of the overflow systems	By RHF completely
Glass melt level detection	a) By specially developed device, based on an el. signal b) By temperature nozzle, monitoring TR18 and TR19
Glass pouring batch	400 kg maximum
Melter power control	By current control and power subcontrol
Glass melt reference temperature	1150-1180 °C (monitored by TR28)
Melter power consumption	110 kW approximately, in total including overflow
Glass tank inventory	1600 kg to 1900 kg approximately
Number of temperature monitoring points	37 (including start-up monitoring points)
Glass tank and melter plenum ceramic refractories	ER 2161, ER 1681, ER 1711 (supplier SEPR, Avignon, France)
Melter wall insulation	Multilayer ceramics with decreasing thermal conductivity
Melter box	Stainless steel containment box
Melter box dimension	1826x3198x2516 mm (depth x length x height)
Melter outside dimension	2603x3588x3200 mm (depth x length x height)
Melter weight including 1700 kg of glass and transportation device (900 kg)	30 700 kg (containment 4500 kg, ceramics 21500 kg, subcomponents like electrodes etc. 1000 kg, nozzles, bus bars 500 kg)
Start-up heating	By five SiC-heating elements in the melter plenum By two MoSi$_2$-heating elements (glass overflow)
Minimum quantity of start-up glass frit	300 kg
Type of start-up glass frit (B-VPMS glass frit)	608 dPas (950°C); 55 dPas (1150°C) 23.1 Ωcm (950°C); 8.3 Ωcm (1150°C)
Couplings for el. power supply of power electrodes	Special design, combined for supply of power <u>and</u> electrode cooling air
Off-gas pipe	Vertical, through melter lid
Design underpressure in melter while operating	20 mm Wc
Inleakage rate (at design underpressure)	20 Nm^3/h



Longitudinal cross section of the VPM melter through the central melter plane
(for the subcomponent numbers 21, 32, 35 and 37 given in this sketch refer to the list given in fig 3 8)

ATTACHMENT 2 TO DATA PACKAGE 1, APPENDIX A

Preliminary Melter Performance Assessment Report

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3.0 Review of Literature

This section contains a review of literature related to noble metals relevant to the melter performance assessment. The general chemistry of noble metals precedes discussions of international vitrification studies on the behavior of noble metals in glass.

3.1 General Chemistry of Noble Metals

Platinum-group metals (or noble metals) are characterized by the common property of general chemical inertness. The group is comprised of ruthenium, osmium, rhodium, iridium, palladium, and platinum. Of these, Ru, Rh, and Pd originate from the fission of ^{235}U and are present in Hanford neutralized current acid waste (NCAW), a product from the reprocessing of spent fuel from nuclear reactors. Upon its discharge from a reactor, the following radioactive noble metal isotopes are present in the spent fuel, in addition to stable isotopes:

Isotope	Half Life	Stable Decay Product
^{103}Ru	39.3 days	^{103}Rh
^{106}Ru	372.6 days	^{106}Pd.
^{102}Rh	2.9 years	^{102}Ru
^{103m}Rh	56.1 min	^{103}Rh
^{107}Pd	6.5 E+06 years	^{107}Ag

Ruthenium-103 and ^{103m}Rh decay to stable ^{103}Rh within one year. Rhodium-102 decays to stable ^{102}Ru after approximately 30 years. This increase in stable Ru is largely offset by the decay of ^{106}Ru that becomes stable ^{106}Pd after 10 to 20 years. No appreciable decay of ^{107}Pd occurs in 10^3 years.

There are also small quantities of shorter half-life isopotes of Ru and Rh in fuel discharged from the reactor. These isotopes decay quickly. The amount of these isotopes is small ($< 10^{-1}$ g/T) compared to the stable Ru isotopes that are present. Thus, the isotopic distribution of noble metals is nearly constant over time. Ruthenium remains by far the most predominant noble metal.

The NCAW contains several times as much Ru as Rh or Pd, and therefore the chemistry of Ru is of most interest to the Hanford Waste Vitrification Project (HWVP). The chemistry of Ru is complex, in part because it has eight possible valence states. Metallic Ru has a melting point of 2310°C and a boiling point of 3900°C, both of which are higher than temperatures reached in high-level waste storage tanks or in the reference HWVP melter. At approximately 800°C, Ru oxidizes in air to form RuO_2.

The reprocessing of nuclear fuel yields wastes that contain many different species of Ru. Nitro and nitrato complexes of nitrosylruthenium are the most common and are mainly Ru (III) nitrosyl derivatives (Fletcher and Martin 1955), such as trinitrato nitrosylruthenium $[RuNO(NO_3)_3(H_2O)_2]$ or sodium tetranitro nitrosylruthenium, $Na_2[RuNO(NO_2)_4OH]$. It is difficult to predict the distribution of Ru among the numerous possible complexes in high-level wastes.

3.1.1 Separation of Noble Metals from HLW Solutions

Various methods for separating Ru from high-level wastes have been examined. One involves separating the noble metals and Tc from insoluble residues in the waste (MacCragh 1972) by means of various reaction and heating cycles. Another uses electrolytic separation to remove Pd, Rh, Tc, and Ru from PUREX acid waste (Carlin et al. 1975). In this process, approximately 60% of the Ru was removed. A third method removes Pd, Tc, Rh, and Ru by passing PUREX (Plutonium-Uranium Extraction) waste through carbon beds containing various organic compounds that selectively remove each of the noble metals and the Tc (Moore 1974). Distillation of ruthenium tetroxide (RuO_4) using an air stream and/or strong oxidants has been effective in removing up to 99% of the Ru from aqueous waste streams (Eaton et al. 1950; Goryunov et al. 1960). Separation methods may have different efficiencies depending on the form in which the noble metal is present. This can complicate separation efforts, as the distribution of noble metal species is sometimes not apparent and can change as the waste solution conditions change. Substantial work has also been done on extraction of various noble metal complexes from solution by organic solvents or by use of ion exchange resins or Fe powder (Nikitina et al. 1969; Bruchertseifer and Koch 1971; Bol'shakov et al. 1970; Mezhov et al. 1972; Blum et al. 1972). However, such methods may not be applicable to waste solutions, which contain many different species of noble metals and may be much more complex than the experimental solutions.

3.1.2 Solubility in Glass

The noble metals fed to a melter have limited solubilities in glass. The solubility limit in silicate glasses is approximately 0.05 wt% for Rh and approximately 0.03 wt% for Pd (Volf 1984). The solubility of Ru is only 0.01 wt% in silicate glasses containing <25 mol% Na_2O, but can be as high as 0.25 wt% when Na_2O exceeds 25 mol% (Mukerji 1972). Schreiber et al. (1991) found that the solubility of noble metals in waste glass is redox controlled. The large amounts of iron present in waste glasses prevent noble metals from appreciably dissolving in the glass. The iron dampens out most efforts to increase noble metal solubility by oxidizing the melt. In a glass melter, the preponderance of noble metals will remain as particles of metal or oxide in the glass, or a fraction (primarily in the case of Ru) may volatilize.

3.1.3 Volatility

Ruthenium has the potential to be highly volatile in a melter environment. Ruthenium tetroxide is believed to be the primary volatile Ru compound. Its formation and volatility are dependent on a number of variables, including presence of oxidants or reductants in the waste, concentration of O_2, and temperature. Small quantities of RuO_4 can be formed at relatively low temperatures (up to 130°C); however, this generally does not lead to significant losses of Ru. At temperatures above 130°C, volatilization increases dramatically if oxidizing conditions exist (IAEA 1982). Reductants in the melt or an inert atmosphere drastically diminish the extent of Ru volatilization. Volatile forms of Ru other than RuO_4 can form in a melter or in melter off gas. Ruthenium can also form volatile RuNO species by reaction with NO_x.

Much of the work in characterizing Ru volatilization addressed waste calcining and melting rather than a liquid-fed ceramic melter such as the reference HWVP melter. The oxidizing conditions of waste calcining and melting result in volatilization losses of up to 80% of the total Ru (IAEA 1982). Volatilization from a liquid-fed ceramic melter is not so substantial because the oxygen content is lower. Losses of volatile Ru from liquid-fed melters have been reported as 13% to 26% (Klein et al. 1983) and 3% to 15% (Klein et al. 1985).

Volatile Ru must be removed from the off-gas system to prevent discharge of radioactive materials as well their accumulation in melter off-gas lines. At temperatures above 100°C, RuO_4 is unstable and can decompose to oxygen and RuO_2, which plates out on off-gas piping. The deposited RuO_2 can act as a catalyst for further Ru deposition.

3.1.4 Removal of Ru from Off Gas

May et al. (1958) described removal of Ru from the gaseous phase by nitric acid. The efficiency of removal depends on the Ru species present, Ru and nitric acid concentrations, temperature, and air flow rate through the scrubber. Off-gas streams from liquid-fed ceramic melters contain more Ru in solid particulate form than do off-gas streams from calciners, where the Ru is primarily in the gas phase (Klein et al. 1985). A packed bed dust scrubber operating at 90°C to 95°C removed volatile Ru species leaving a liquid-fed melter as submicron aerosols (Klein et al. 1983). During this test, RuO_2 deposits accumulated in the solution and on the packing.

Volatile RuO_4 can be adsorbed to various materials. Silica gel was 99.9% efficient in removing Ru as RuO_4, as droplets, and as particles (Gill and Wisehart 1954). The Ru can be eluted in water at 60°C to 70°C (Newby et al. 1960). Other solid materials that adsorb RuO_4 include ferric oxide, soil, and clay.

As mentioned, numerous methods exist for removing Ru and other noble metal complexes from aqueous streams. These methods could be considered for treating off-gas scrub solutions or other secondary waste streams.

3.1.5 High-Level Waste Simulant Process

Because noble metal behavior is often dependent on the chemical species present, it would be desirable to know the species present in the actual tank waste and in the waste simulants used in melter testing. Because this information is not available, the processes by which each is created will be compared. Then the representativeness of the simulant preparation process can be evaluated, although the exact distribution of species is not known.

Spent reactor fuel is reprocessed via the PUREX process. The major steps in this process are summarized as follows:

1. The spent fuel is removed from the cladding and dissolved in hot HNO_3.
2. N_2O_4 is added to adjust the oxidation state of Pu for more efficient extraction.
3. Plutonium and U are extracted by tributyl phosphate (TBP) and normal paraffin hydrocarbons (NPH). A small fraction of Ru is extracted along with the P and U.
4. The remaining aqueous high-level waste is concentrated by evaporation to approximately 7M HNO_3.
5. A reductant is added to the waste to lower the HNO_3 concentration to approximately 2 to 4M.
6. The waste is neutralized with NaOH before storage in tanks.

This procedure cannot be precisely followed in preparation of simulated waste for melter tests. The feed preparation steps are summarized as follows:

1. The major components (in the form of nitrates) are blended.
2. The solution is neutralized, washed, and decanted.
3. The slightly soluble chemicals are added.
4. The minor components (including noble metals as nitrates) are slurried and neutralized.
5. The minor component slurry is washed with 0.1M NaOH and decanted.
6. The minor component slurry is mixed with the major component slurry.

Differences between these two processes could cause the noble metals in the simulated melter feed to exist in a different form than in the actual NCAW. Differences in temperature or HNO_3 concentrations and the addition of N_2O_4 and reductants to the PUREX waste can account for differences in oxidation state or complexed form. However, in both cases, the primary component, Ru, would be expected to be present mostly as a mixture of nitro and nitrato complexes of nitrosyl Ru. Distribution of the complexes changes on neutralization.

Another possible difference between actual waste and simulant is that noble metals precipitated with the minor components of the simulant could be more concentrated than if they were precipitated with all the components, both major and minor. However, in gradient furnace testing (GFT) of simulants, noble metals were concentrated into identifiable particles of approximately 10 μm or less, regardless of whether the noble metals were precipitated with the major components or with the minor components.

None of these differences is expected to lead to significant differences between noble metal behavior in glass melts with actual and simulated feeds; however, the expectation must be confirmed.

3.2 Vitrification Studies at Savannah River

The U.S. Department of Energy's Defense Waste Processing Facility (DWPF), where high-level radioactive waste will be vitrified into a durable borosilicate glass, is located at the Savannah River Site (SRS) in South Carolina. The DWPF is the first such production facility in the United States. Its melter design was completed in 1982, before the effects of noble metals accumulation on melter operation were known. Calculations of refractory corrosion rates predict a melter life of 2 to 3 years. A schematic of this melter design is shown in Figure 3.1. The Integrated DWPF Melter System (IDMS) was later designed as a pilot-scale test facility for the DWPF. Before testing with the IDMS, two short-term noble metals campaigns with a 1/100th scale mini-melter revealed a need for extended noble metals testing. Numerous test runs with the IDMS melter addressed the designs of the DWPF feed preparation system, offgas system, and the melter itself.

The DWPF melter design shown in Figure 3.1 has a cylindrical melt cavity with a shallow-disk bottom and is lined with Monofrax K-3 ceramic refractory. The total melter cavity volume is 193 ft^3 (5.5 m^3) with an average glass volume of 87.7 ft^3 (2.5 m^3). Two sets of water cooling systems keep the temperature of the melter exterior lower than 50°C. Two pairs of plate Inconel 690 electrodes are used to maintain the glass melt temperature at 1150°C, with each pair supplying an average of 80 kW during normal operation. During routine glass pouring, an induced vacuum causes the glass to overflow the riser and flow through the pour spout into stainless steel canisters. The riser/pour spout heater maintains the glass exit temperature at 1100°C. The melter is designed with a production rate of approximately 103.4 kg/hr. A bottom drain is used to remove residual glass from the melter after operations are complete [Gutmann (1988); SRS, unpublished, endnote 1].

The IDMS engineering-scale melter (schematic in Figure 3.2) is prototypic of the DWPF melter. It was designed with a melt surface area of 0.29 m^2 (approximately 1/9th of the DWPF surface area), and a melt volume of 0.20 m^3. The decrease in melt surface area was achieved by adding a second 12-inch layer of K-3 refractory to the lower inside walls of the melt tank of a DWPF melter, reducing the inner diameter from 48 inches to 24 inches. The design production rate of this smaller melter is therefore about 1/9 that of the DWPF melter, or 11 kg/h. Two pairs of electrodes maintain the melt temperature at around 1150°C by providing 35-kW power. All other design features of the IDMS melter, such as materials of construction, drain systems, and cooling and heating systems, are essentially the same as the DWPF melter design (Hutson et al. 1991; Hutson 1992).

Before testing was initiated with the IDMS melter, two campaigns were done with a 1/100th scale mini-melter between March and June 1989. Specific information about the mini-melter design is currently unavailable. The two main objectives were to determine a) the impact of noble metals on the behavior of the vitrification system and b) the need for further testing. In the first campaign (LNM), feed was processed with the expected low concentrations of noble metals, producing 215 pounds of glass in approximately 2 weeks. The second campaign (HNM) used feed with high noble metals concentrations, representing the worst case; 310 pounds of glass were produced in about 3 weeks. The noble metals concentrations are presented in Table 3.1 as a weight percent of the dry sludge in the feed.

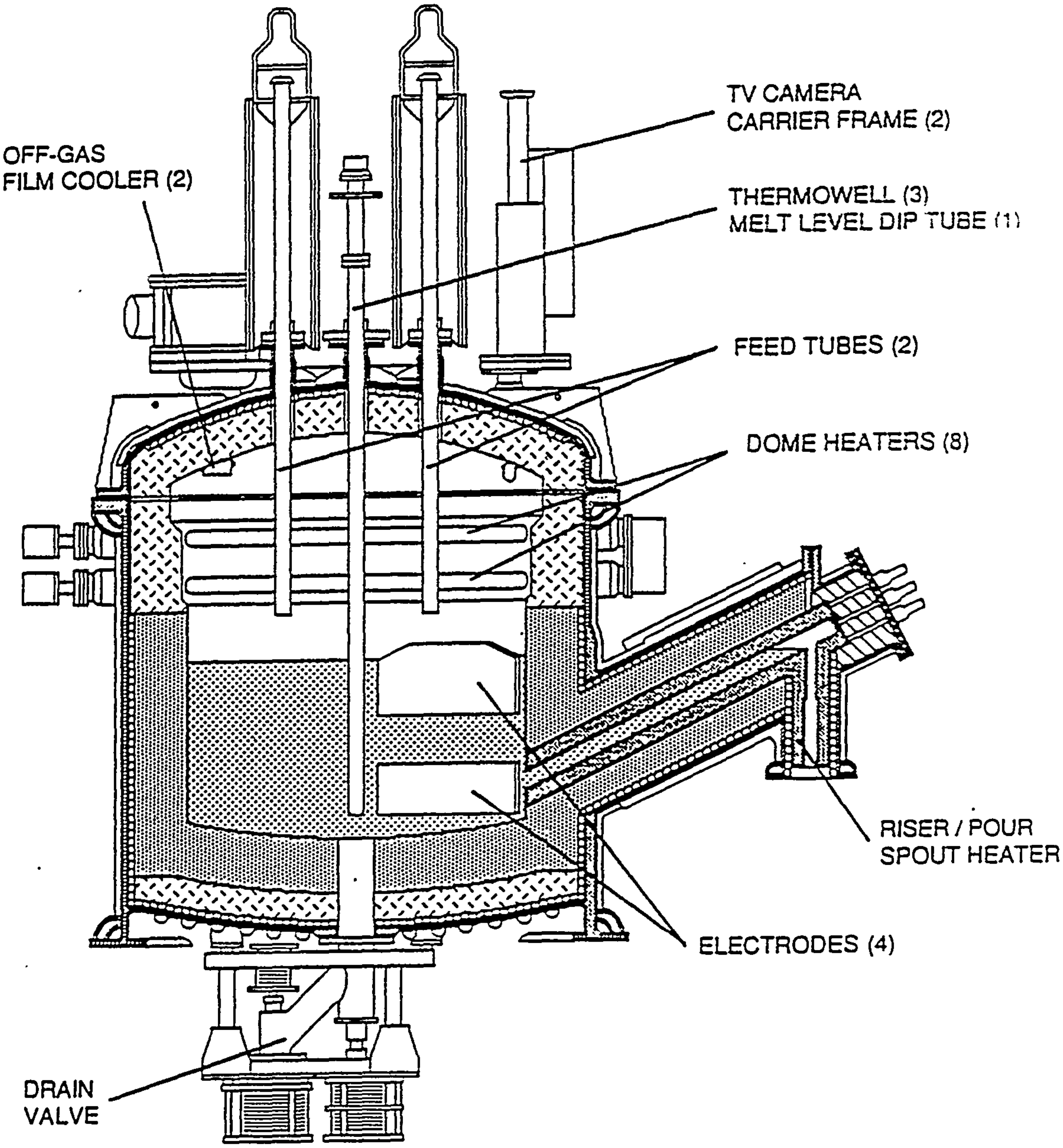

Figure 3.1. DWPF Melter Design (Gutmann 1988)

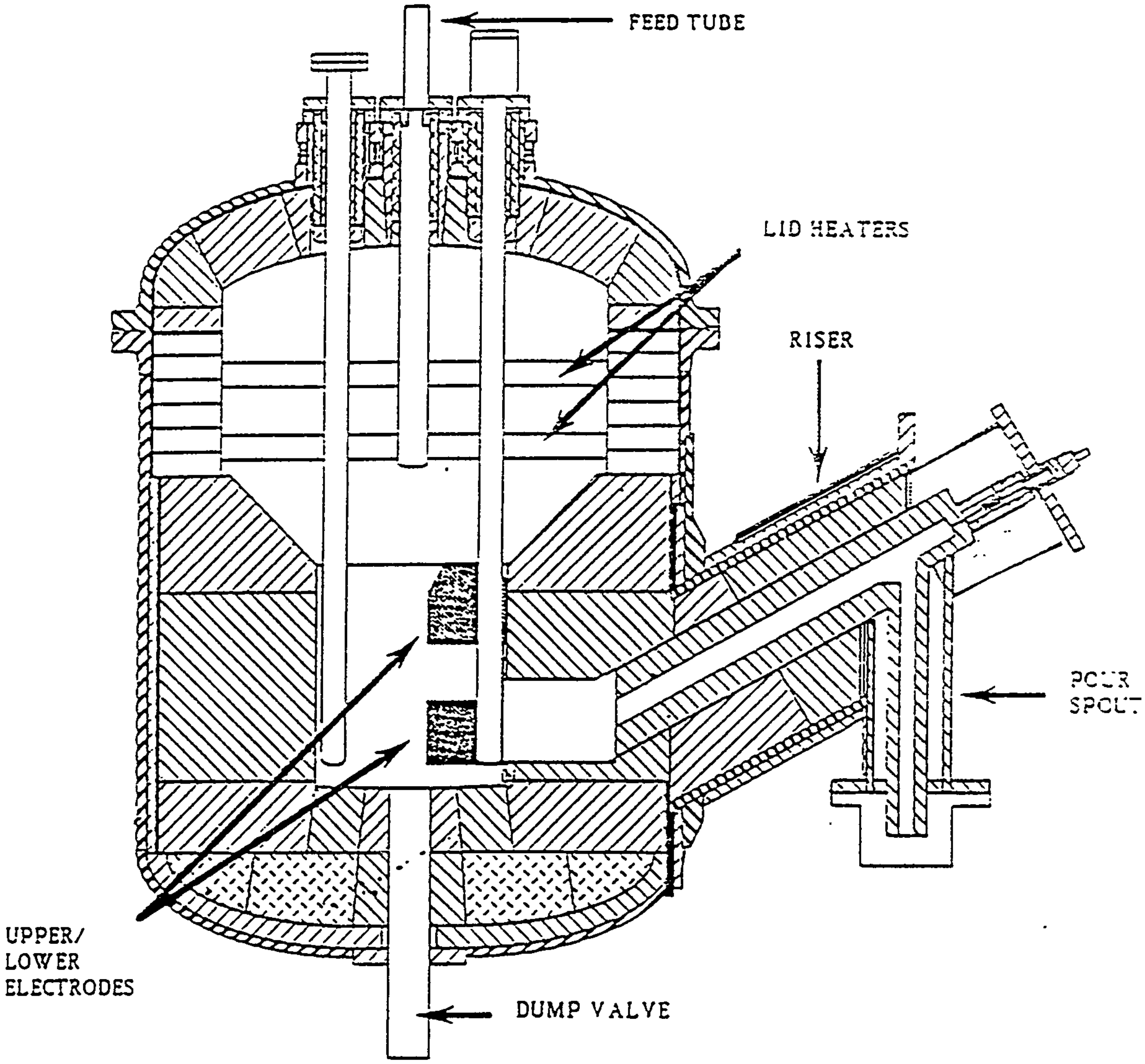

Figure 3.2. IDMS Melter Design (Hutson and Smith 1992)

During operation of the mini-melter, no decline in electrical resistance due to noble metals was detected, and the electrodes displayed no adverse effects from noble metals. The glass product contained noble-metal particles of approximately 5 μm, and no problems were experienced with the glass pouring system. When the melter was dismantled after the campaigns, metal nuggets containing Ru, Rh, Pd, Te, and Se were found on the melter floor.[a] Unlike the experience of Germany, Japan, and PNL, needle-like crystals of Ru were not present in the glass product or on the melter floor.

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[a] Information on the form or oxidation state of noble metal particles was not provided.

Table 3.1. Noble Metals Concentrations (Allen 1989) (wt% dry sludge solids)

Noble Metal	LNM Campaign	HNM Campaign
PdO	0.046	0.046
RhO_2	0.025	0.025
RuO_2	0.135	0.458
Total	0.206	0.529

An overall noble metals mass balance indicated that 15% to 20% of the noble metals in the feed accumulated in the melter during each campaign. The observations during these two runs led to the decision to perform additional campaigns with the IDMS melter to further investigate the behavior of noble metals [Allen (1989), unpublished, endnote 10; Nakaoka and Strachan (1990), unpublished, endnote 2; Kruger, unpublished, endnote 3].

Nine IDMS campaigns were proposed to investigate the effects of mercury and noble metals on melter operation. To date, a total of 14 runs have been completed, with one planned for early 1994. Table 3.2 shows the target compositions of the three simulated sludges used in these campaigns (unpublished, endnote 4). The sludges are referred to as Blend, PUREX (high iron, low viscosity), and HM (high aluminum, high viscosity). Three campaigns were completed with the Blend sludge, four campaigns with the HM sludge, and five with the PUREX sludge. (Two additional runs for the HWVP are discussed later in this section.) As shown in Table 3.2, the PUREX and HM sludges contained the same amounts of noble metals. The original PUREX sludge formulation had a much lower noble metals content, but additional noble metal compounds were added to the feed in all PUREX campaigns to match the concentrations in the HM sludge (Hutson, et al. 1991; Hutson 1993).

The first two IDMS noble metals campaigns were conducted between June 1990 and March 1991. Their main purpose was to verify that hydrogen would evolve as a result of the noble metal-catalyzed destruction of formic acid during feed preparation. The Blend sludge simulant, shown in Table 3.3, was used in these runs, referred to as Blend 1 (BL1) and Blend 2 (BL2). A glass frit (Frit-202) was also added to the feed; its composition is shown in Table 3.4. Addition of noble metal compounds to achieve the desired concentrations in sludge preceded frit addition; these quantities are shown in Table 3.5. Campaigns BL1 and BL2 produced, respectively, 2809 and 4368 pounds of glass (Hutson et al. 1991).

The BL1 and BL2 runs were preceded by an IDMS campaign that did not include noble metals in the feed. Data from that run indicated that the glass pool resistances between the upper electrodes and lower electrodes remained relatively constant. When noble metals were introduced during BL1 and BL2, a slight change in the ratio of upper electrode resistance to lower electrode resistance suggested that any accumulation of noble metals had little effect on the electrical characteristics of the glass (Hutson et al. 1991).

Approximately 2 months after BL1 was initiated, a glass sample that was taken 1 to 2 inches above the melter floor showed no signs of noble metals accumulation. After completion of the BL2 run, a second glass sample was taken from approximately the same location. Although Pd and Rh were not

Table 3.2. Target Compositions of Simulated Sludges (wt% elemental dry basis)

Element	Blend	PUREX	HM
Ag	0.014	0.014	0.014
Al	6.860	3.936	8.966
Ba	0.302	0.271	0.129
Ca	1.540	2.133	0.839
Cr	0.042	0.256	0.150
Cs	0.006	0.002	0.019
Cu	0.161	0.133	0.043
Fe	20.600	24.486	13.611
Group B (Nd)	0.170	0.231	2.342
Hg	1.588	0.102	3.263
K	0.284	0.260	0.163
Mg	0.141	0.147	0.277
Mn	4.800	4.226	4.202
Na	4.190	6.376	5.552
Ni	1.880	2.607	0.828
P	0.071	0.048	0.027
Pd	0.045	0.079	0.079
Pb	0.440	0.315	0.151
Rh	0.018	0.038	0.038
Ru	0.100	0.217	0.217
Se	0.002	0.002	0.002
Si	3.900	1.033	4.318
Sr	0.000	0.021	0.242
Te	0.022	0.022	0.022
Zn	0.332	0.250	0.035
Zr	0.127	2.589	1.363.

detected in this sample, Ru needles of 5 to 15 microns in length were found in 20 to 40 micron clusters. Samples of the BL1 glass product contained RuO_2 needles, usually less than 5 microns long and frequently associated with Fe/Mn/Cr/Ni spinels. BL2 glass product samples contained RuO_2 needles up to 5 microns, 20-micron Ru/spinel clusters, and 2-micron spherical aggregates of Pd/Rh and Pd/Ru (Hutson et al. 1991).

The next two campaigns (Blend 3 and HM1) were performed to investigate hydrogen generation during non-noble metal cold testing and did not include noble metals or mercury; they produced about 4751 pounds of glass using Frit-202 as the glass former. The next four runs used high levels of noble metals to determine maximum amounts of hydrogen generation expected during actual radioactive operation of the DWPF. These four runs included two with the PUREX simulant (PX1 and PX2), and two with the HM simulant (HM2 and HM3). They produced about 14,160 pounds of glass, using

Table 3.3. Blend Sludge Characterization (Hutson et al. 1991)

Elemental Analysis by ICP - Microwave Dissolution

Element	Count	Mean	StDev	% RSD	Units
Ca	64	1.547	0.109	7.046	wt%
Cu	64	0.160	0.012	7.475	wt%
Mg	64	0.141	0.027	19.054	wt%
Mn	64	4.784	0.276	5.776	wt%
Pb	64	0.435	0.037	8.581	wt%
Zn	64	0.332	0.017	5.257	wt%
Zr	64	0.142	0.115	81.509	wt%
Fe	64	20.918	1.267	6.055	wt%
Na	64	4.280	0.542	12.661	wt%
Nd	64	0.179	0.120	67.202	wt%
Ni	64	1.873	0.114	6.060	wt%
Ti	64	0.007	0.003	40.480(a)	wt%
Cr	64	0.048	0.036	76.071	wt%
P	64	0.069	0.010	14.838	wt%

Elemental Analysis by ICP - Na_2O_2 Fusion

Element	Count	Mean	StDev	% RSD	Units
Mg	68	0.163	0.041	25.167	wt%
Al	68	6.863	0.292	4.254	wt%
Ba	68	0.302	0.013	4.382	wt%
Fe	68	20.194	0.872	4.318	wt%
Li	68	0.002	0.001	50.003(a)	wt%
Ti	68	0.011	0.009	79.215(a)	wt%
B	68	0.004	0.002	41.421(a)	wt%
Si	68	3.901	0.181	4.631	wt%

Ionic Analysis by IC

Ion	Count	Mean	StDev	% RSD	Units
Nitrite	68	13472.044	373.414	2.772	mg/L
Nitrate	68	1361.985	41.851	3.073	mg/L
Sulfate	68	772.426	43.642	5.650	mg/L
Cl	66	1084.288	84.063	7.753	mg/L
F	66	845.212	298.095	35.269	mg/L

(a) Indicates components which are most likely not present in the Blend sludge. Measurements shown are the baseline value.

Table 3.4. Frit-202 Composition (Hutson et al. 1991)

Component	Specified wt%	Actual wt%
SiO_2	77.0 ± 1.0	76.6
Na_2O	6.0 ± 0.5	6.1
B_2O_3	8.0 ± 0.5	6.7
Li_2O	7.0 ± 0.5	7.7
MgO	2.0 ± 0.25	1.9
Al_2O_3	< 1.89	0.45
Fe_2O_3	< 0.29	0.04
Mn	< 0.2	n/a
Ni	< 0.2	n/a
Cr	< 0.1	n/a
Pb	< 0.1	n/a
TiO_2	< 0.15	0.09
F	< 0.05	0.01
Cl	< 0.05	0.01

Table 3.5. Noble Metals Quantities Added in Campaigns BL1, BL2 (Hutson et al. 1991)

		Compound (grams)		Element (grams)	
Element	Compound Added	BL1	BL2	BL1	BL2
Ru	$RuCl_3$, 42 wt% Ru	1617.4	1617.0	679.3	679.1
Rh	$Rh(NO_3)_3$ solution, 4.933 wt% Rh	2871.5	2871.9	141.7	141.7
Pd	$Pd(NO_3)_2$ solution, 8.769 wt% Pd	4040.5	4037.0	354.3	354.0

Frit 202. An accumulation of noble metal deposits was first detected on the melter floor near the completion of these runs, when the melter began showing the first signs of changes in electrical behavior. Specific information about noble metals retention and glass product composition for the first six runs is currently not available (Hutson 1993).

Because of similarities between the DWPF and HWVP melter designs, the IDMS facility was then used to process and characterize a waste sludge simulant known as the Hanford neutralized current acid waste (NCAW '91). Two noble metals campaigns completed between November 1991 and February 1992 are referred to as HWVP1 and HWVP2.

The melter feed for the HWVP campaigns was prepared by first combining a mixed hydroxide slurry with primary trim chemicals to obtain a waste simulant that was deficient in noble metals. Noble metal compounds were then added in the amounts shown in Table 3.6. Frit, formic acid, and other chemicals were then added to the feed mixture to produce a simulant nearly identical to NCAW '91. The frit used in the runs was specified by PNL; its composition is shown in Table 3.7. The final compositions of the waste simulant feeds used in the HWVP campaigns are shown in Tables 3.8 and 3.9 (Hutson 1992).

Table 3.6. Noble Metals Quantities (Hutson 1992)

		Compound (grams)		Element (grams)	
Element	Compound Added	HWVP1	HWVP2	HWVP1	HWVP2
Ru	$RuCl_3$, 42 wt% Ru	4445.0	4445.0	1866.9	1866.9
Rh	$Rh(NO_3)_3$ solution, 4.933 wt% Rh	10482.5	10482.3	517.1	517.1
Pd	$Pd(NO_3)_2$ solution, 8.769 wt% Pd	7334.0	7334.0	643.1	643.1

Table 3.7. Frit Composition (Hutson 1992)

Component	Specified wt%	Actual wt%
SiO_2	72.26	73.135
B_2O_3	20.45	18.902
Li_2O	7.29	6.972
Na_2O	--	0.359
CaO	--	0.088
Fe_2O_3	--	0.039
TiO_2	--	0.103
ZrO_2	--	0.039
Al_2O_3	--	0.189
BaO	--	0.016
K_2O	--	0.031
ZnO	--	0.078

Table 3.8. HWVP1 Waste Simulant Feed Composition (Hutson 1992)

Component	Oxide	Elemental Wt%	Measured Oxide Wt%	Corroded Oxide W%	NCAW'91 Oxide Wt%
Potassium	K_2O	0.14	0.18	0.18	0.07
Cesium	Cs_2O	0.73	0.84	0.17	0.17
Aluminum	Al_2O	1.33	2.74	2.74	2.75
Barium	BaO	0.05	0.05	0.05	0.05
Boron	B_2O_3	3.98	13.94	12.98	13.91
Cadmium	CdO	0.79	0.98	0.98	1.00
Calcium	CaO	0.23	0.36	0.36	0.24
Cerium	CeO_2	0.21	0.27	0.27	0.18
Chromium	Cr_2O_3	0.06	0.09	0.12	0.08
Copper	Cuo	0.07	0.09	0.08	0.07
Germanium	GeO_2	BDL	BDL	BDL	<0.01
Iron	Fe_2O_3	4.88	7.59	7.11	8.12
Lanthanum	La_2O_3	0.20	0.26	0.26	0.19
Lead	PbO	0.13	0.15	0.15	0.18
Lithium	Li_2O	2.31	5.41	4.81	4.96
Magnesium	MgO	0.08	0.15	0.15	0.12
Manganese	MnO	0.43	0.60	0.60	0.65
Molybdenum	MoO_3	0.11	0.18	0.19	0.16
Neodymium	Nd_2O_3	1.81	2.30	2.30	1.00
Nickel	NiO	0.43	0.59	0.59	0.66
Niobium	Nb_2O_5	BDL	BDL	BDL	<0.01
Palladium	PdO	0.07	0.09	0.09	0.03
Phosphorus	P_2O_5	0.06	0.16	0.16	0.38
Praseodymium	Pr_2O_3	0.15	0.19	0.19	0.04
Rhodium	Rh_2O_3	0.04	0.05	0.05	0.03
Rubidiium	Rh_2O_3	BDL	BDL	BDL	0.02
Ruthenium	Ru_2O_3	0.13	0.17	0.17	0.11
Samarium	Sm_2O_3	0.10	0.12	0.02	0.02
Selenium	SeO_2	0.03	0.05	0.05	<0.01
Silicon	SiO_2	21.23	49.45	49.45	52.04
Silver	Ag_2O	0.04	0.04	0.04	0.03
Sodium	Na_2O	4.97	8.77	7.90	7.83
Strontium	SrO	0.02	0.02	0.02	0.03
Tantalum	Ta_2O_5	BDL	BDL	BDL	<0.01
Tellurium	TeO_2	ND	ND	ND	0.03
Tin	SnO	0.02	0.02	0.02	<0.01
Titanium	TiO_2	0.09	0.15	0.15	0.19
Yttrium	Y_2O_3	0.02	0.03	0.03	0.02
Zinc	ZnO	0.11	0.16	0.15	0.10
Zirconium	ZrO_2	2.55	3.75	3.75	4.31

Table 3.9. HWVP2 Waste Simulant Feed Composition (Hutson 1992)

Component	Oxide	Elemental Wt%	Oxide Wt%	NCAW '91 Oxide Wt%
Potassium	K_2O	0.08	0.09	0.07
Cesium	Cs_2O	0.10	0.11	0.17
Aluminum	Al_2O_3	1.36	2.68	2.75
Barium	BaO	0.05	0.06	0.05
Boron	B_2O_3	3.99	13.43	13.91
Cadmium	CdO	0.80	0.95	1.00
Calcium	CaO	0.27	0.39	0.24
Cerium	CeO_2	0.11	0.14	0.18
Chromium	Cr_2O_3	0.05	0.08	0.08
Copper	CuO	0.07	0.09	0.07
Germanium	GeO_2	0.02	0.03	<0.01
Iron	Fe_2O_3	5.08	7.59	8.12
Lanthanum	La_2O_3	0.12	0.15	0.19
Lead	PbO	0.18	0.20	0.18
Lithium	Li_2O	2.29	5.15	4.96
Magnesium	MgO	0.10	0.18	0.12
Manganese	MnO_2	0.41	0.55	0.65
Molybdenum	MoO_3	0.11	0.17	0.16
Neodymium	Nd_2O_3	0.88	1.08	1.00
Nickel	NiO	0.45	0.60	0.66
Niobium	Nb_2O_5	BDL	BDL	<0.01
Palladium	PdO	0.01	0.01	0.03
Phosphorus	P_2O_5	0.03	0.07	0.38
Praseodymium	Pr_2O_3	0.04	0.05	0.04
Rhodium	Rh_2O_3	0.01	0.01	0.03
Rubidium	Rb_2O_3	BDL	BDL	0.02
Ruthenium	Ru_2O_3	0.04	0.05	0.11
Samarium	Sm_2O_3	0.02	0.02	0.02
Selenium	SeO_2	BDL	BDL	<0.01
Silicon	SiO_2	24.00	53.63	52.04
Silver	Ag_2O	0.04	0.05	0.03
Sodium (ICP)	Na_2O	5.79	8.16	7.83
Strontium	SrO	0.03	0.04	0.03
Tantalum	Ta_2O_5	0.01	0.02	<0.01
Tellurium	TeO_2	NA	NA	0.03
Tin	SnO	0.01	0.02	<0.01
Titanium	TiO_2	0.09	0.16	0.19
Yttrium	Y_2O_3	0.02	0.02	0.02
Zinc	ZnO	0.10	0.13	0.10
Zirconium	ZrO_2	2.66	3.75	4.31

Melter operation began with the transfer of approximately 490 gallons of HWVP1 simulant feed to the melter feed tank. However, approximately 300 gallons of residual waste simulant (containing noble metals) from a previous melter run remained in the feed tank. The first batch of HWVP1 simulant was therefore mixed with the residual simulant in the melter feed tank before pumping to the melter. The HWVP1 campaign produced approximately 3390 pounds of glass, and some residual waste simulant remained in the melter feed tank following the run. The HWVP2 campaign was initiated by transferring approximately 550 gallons of simulant to the melter feed tank, where it was mixed with the residual HWVP1 simulant. During this campaign, the average feed rate was about 25.4 lb oxides/h, producing a total of 4561 pounds of glass. As before, approximately 300 gallons of waste remained in the melter feed tank at the completion of the run (Hutson 1992).

Samples of the feed material and the glass product for both campaigns were obtained and analyzed for noble metals content by Monarch Analytical Laboratories, an independent laboratory. Analysis results of samples obtained at steady state (after 2 to 3 melter turnovers) during each campaign were used to calculate steady state noble metals retentions; all noble metals not accounted for in the product were assumed to have remained on the melter floor. The steady state retention values were then used in calculating overall retentions for each campaign (Hutson 1992). Table 3.10 shows the results of these calculations. As noted in the table, negative retention values for Pd during the HWVP2 campaign suggest that more Pd was discharged than was fed. The actual reason is not known, but there are three possible explanations. Tables 3.8 and 3.9 show that the HWVP1 feed had a greater Pd content than the HWVP2 feed (0.09 wt% versus 0.01 wt%). Since a significant amount of the HWVP1 feed remained in the melter feed tank at the end of the first campaign and was then combined with the first batch of HWVP2 feed, it is possible that more Pd was fed than was reported. That would have occurred if the HWVP2 feed was analyzed before it was mixed with the residual waste in the tank. A second possible explanation is that a significant amount of Pd from the HWVP1 campaign remained in the melter cavity at the end of the run, was removed with the HWVP2 glass product, and was included in the material balance for the HWVP2 campaign. The third possible explanation is analytical error in measuring noble metals the glass and feed samples.

Table 3.10. Noble Metals Retentions in HWVP Campaigns (Hutson 1992)

	Steady State Retention, %		Overall Campaign Retention, %	
Element	HWVP1	HWVP2	HWVP1	HWVP2
Ru	13.1	12.7	17.7	17.5
Rh	15.1	9.2	20.6	9.7
Pd	3.4	-8.1	1.9	-7.6

Periodically during and after the HWVP campaigns, glass samples were taken about 3 to 5 cm above the melter floor, analyzed for noble metal content, and examined with a scanning electron microscope (SEM). Table 3.11 shows the analysis results for those samples. Before feeding of the HWVP1 simulant, a sample taken above the melter floor showed evidence of mainly RuO_2 crystals and Ni/Mn Fe/Cr spinels accumulated on the melter floor in previous runs. A sample taking during the campaign contained the same noble metal and spinel compounds, as well as individual Pd particles. Finally, a sample taken after completion of the run contained the same types of deposits plus some Rh. All HWVP1 glass samples were obtained through the feed tube port at the center of the melter floor (Hutson 1992).

During the HWVP2 campaign, glass samples were obtained from both the center feed tube port and the borescope port located near the face of one electrode. A comparison of the analysis results of samples taken from the two locations shows that an uneven layer of noble metals had accumulated on the melter floor, with a higher concentration of Ru in the samples taken from the borescope port, which was near the outside edge of the melter cavity. Therefore, convective currents may act to move the RuO_2 from the melter center toward the outside edges. Also, the presence of RuS_2 in samples taken from the outside edge of the melter floor suggests that the temperature near the edge may be lower than the bulk glass temperature; RuS_2 decomposes at temperatures >1000°C (Hutson 1992, 1993).

Four additional campaigns with the IDMS melter, using Frit-202 as the glass former, were conducted primarily to justify a change in the feed preparation system from formic acid to nitric acid addition. One run used the HM simulant (HM4), and the remaining three used the PUREX simulant (PX3, PX4, and PX5). During HM4 and PX3, approximately 8334 pounds of glass was produced. Quantities of glass produced during PX4 and PX5 are currently not available.

Table 3.11. Analysis of Melter Floor Samples (Wt%) from HWVP Campaigns (Hutson 1992)

Sample:[(a)]	Before HWVP1	During HWVP1	After HWVP1	After HWVP2	After HWVP2	After HWVP2	After HWVP2
Location:	Feed Tube	Feed Tube	Feed Tube	Feed Tube	Borescope	Feed Tube	Borescope
Element	Date: 10/15/91	12/4/91	12/18/91	2/18/92	3/6/92	3/27/92	4/20/92
Ru	4.68	0.42	6.20	2.02	9.67	5.53	12.60
Rh	0.41	0.03	0.30	0.02	0.27	–	0.18
Pd	0.07	0.02	0.01	0.33	0.08	–	0.09

(a) Values in wt%.

Feed and glass product samples were analyzed during the first twelve IDMS campaigns to estimate overall retentions of noble metals. Approximately 43,542 pounds of glass produced during these twelve campaigns contained an average of 0.039 wt% Ru, 0.009 wt% Rh, and 0.021 wt% Pd.[a] Table 3.12 shows the overall mass balances and the resulting retentions of noble metals. The negative value for "% Retained" of Pd is most likely a result of analytical error.

The overall experience of IDMS noble metals melter campaigns has been similar to the experience of Germany, Japan, and PNL (see Sections 3.3, 3.4, and 3.6). Tests performed with a 1/100th scale mini-melter resulted in an overall noble metals retention of 15% to 20% during the production of 525 pounds of glass; changes in electrical resistance of the glass were not detected during the runs. Subsequent campaigns with noble metals were done with the IDMS 1/9th scale melter. During initial operation of that melter, changes in electrical behavior were not detected due to noble metals; however, after the completion of approximately six campaigns, the melter began showing signs of changes in electrical behavior, and an accumulation of noble metals was detected. Two campaigns using an HWVP simulant feed also showed retention of noble metals: 0% to 2% for Pd, 10% to 21% for Rh, and 18% for Ru. Analysis of samples taken from varying locations on the melter floor suggested an uneven layer of accumulated noble metals. Convective currents within the melter may have been moving the particles toward the outside edges of the melter floor. Overall noble metals retentions for twelve IDMS campaigns were estimated from analyses of feed and glass product samples during the runs. Overall, 35% of Ru, 21% of Rh, and 0% of Pd was retained during the twelve campaigns.

3.3 Vitrification Studies in Germany

In 1976, Germany began developing a vitrification program for treating radioactive wastes. Much of the initial work centered around treating radioactive waste generated from reprocessing fuel elements at the Eurochemic plant in Mol, Belgium. Two wastes were produced and subsequently vitrified at the Mol plant, 50 m^3 of low enriched waste concentrate (LEWC) and 760 m^3 of high enriched waste concentrate (HEWC). The LEWC had a high concentration of noble metals that settled in the melter to form a conductive layer on the melter floor, leading to processing difficulties in the melter. Realizing the problems caused by noble metals in melters, Germany developed a program to evaluate the glass chemistry of noble metals and the effect of noble metals on glass performance.

Table 3.12. Noble Metals Mass Balance (Hutson 1993)

Element	Quantity Fed, lb	Quantity Poured, lb	% Retained
Ru	26.05	16.90	35.1
Rh	5.10	4.02	21.2
Pd	8.93	8.95	- 0.2

(a) These values represent the overall glass product compositions, calculated from the total glass and total noble metals poured during the twelve campaigns. Two of the campaigns, however, did not include noble metals in the feed simulant as previously mentioned.

3.3.1 K-1 Melter

The first small-scale liquid-fed ceramic melter (LFCM), designated K-1, was developed at Kernforschungszentrum Karlsruhe (KfK) at the Institut für Nukleare Entsorgungstechnik (INE) in 1976, and was later operated from 1977 through 1979 at the VA-1 test facility. The primary purpose of this melter was to test refractory and electrode materials. The waste processed was a simulant of high-activity waste (HAW), producing 18 m^3 of glass during 1500 hours of operation and 17,500 hours of idling. The actual composition of the waste simulant processed is not certain. The melter design specifications included a throughput of 20 to 25 L/h, a glass production rate of 15 to 20 kg/h, a glass pool surface area of 0.36 m^2, and a glass pool volume of 70 L. There were three pairs of electrode rods made of molybdenum and tin oxide, and the melter bottom was essentially flat. The refractory was made of four different materials (ER-2161, ZAC 1711, ZAC 1681, and Supral AR 90), one material on each wall. Figure 3.3 shows a schematic of the melter design (Grünewald, Koschorke, and Roth 1986).

Following operations, the melter was examined for corrosion. The ER-2161 fused-cast ceramic refractory material showed the least amount of material loss. This refractory, composed of 28 wt% Cr_2O_3, 28 wt% Al_2O_3, 30 wt% ZrO_2, and 14 wt% SiO_2, lost approximately 10 to 20 mm of thickness over 2.5 years of operation, and was subsequently chosen as the material to be used in later melter designs. Also, the molybdenum electrodes were highly corroded after 2.5 years of operation, with

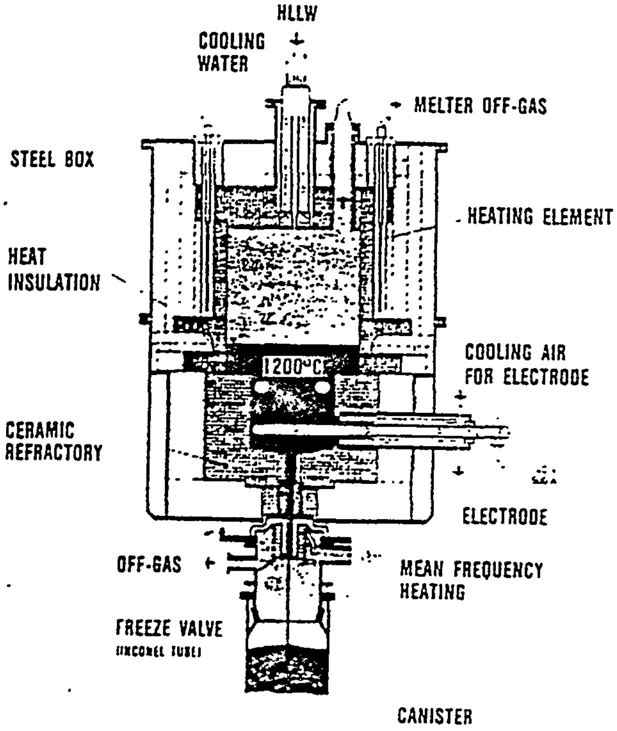


Figure 3.3. K-1 Melter Design (Weisenburger, Grünewald, and Koschorke 1979)

the upper set showing twice as much corrosion as the lower set. The more extensive corrosion occurred in the upper set because those electrodes were partially exposed. Frequently the electrodes had to be pushed through the melter walls, a very difficult task (Grünewald, Koschorke, and Roth 1986; Weisenburger 1980).

3.3.2 K-2 Melter: KfK-INE

The K-2 melter was developed in 1978 and began operating in 1980 at the VA-2 test facility at KfK. The primary purpose of this melter was to test melter equipment, including cooling systems, the offgas system, and the melter bottom drain. The melter was designed as a scale-up of K-1, with a glass pool surface area of 0.64 m^2, a glass pool volume of 250 L, a throughput of 30 to 40 L/h, and a glass production rate of 20 to 30 kg/h. It had two pairs of electrode rods made of Inconel 690. As with the K-1 melter, the refractory material was ER-2161 fused-cast ceramic. The K-2 melter design is shown in Figure 3.4. The wastes processed, in the form of nitric acid feeds, were simulants of LEWC, HEWC, and high activity waste concentrate (HAWC). Figure 3.5 shows relative compositions and activities of these three actual wastes, and Figure 3.6 provides compositions of the actual glass products generated (Grünewald, Koschorke, and Roth 1986).

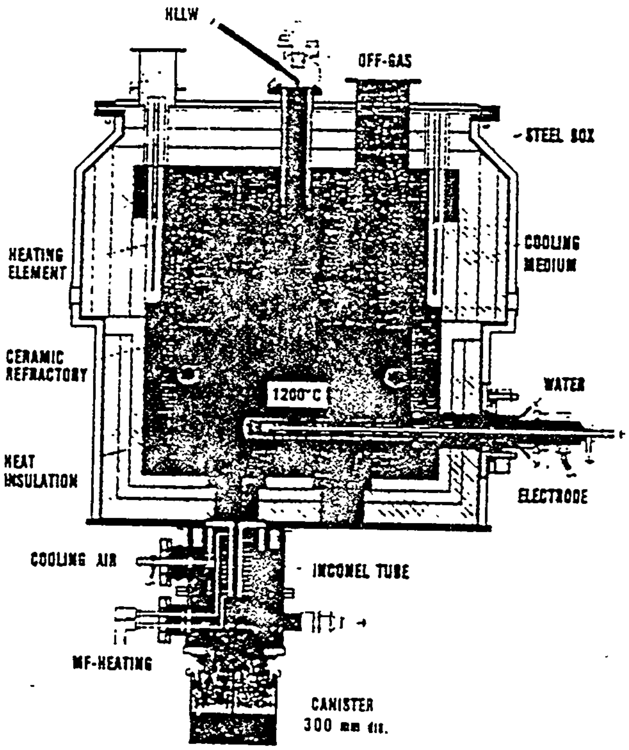
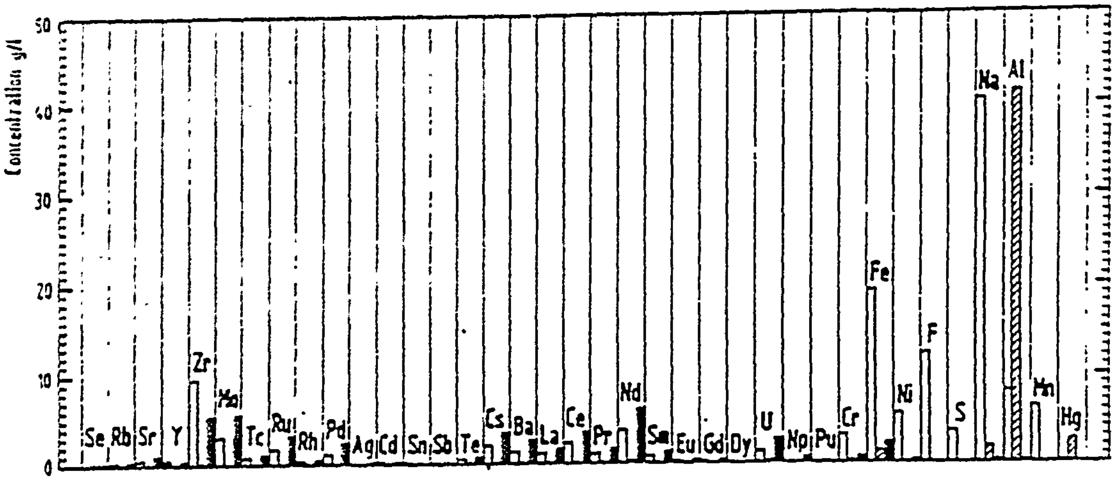


Figure 3.4. K-2 Melter Design (Weisenburger, Grünewald, and Koschorke 1979)

Feed - Composition		□ LEWC - Mol	▣ HEWC - Mol *	■ HAWC - Wackersdorf
Specific Activity	Ci/l	165	9	608
Density	g /cm³	1.27	1.3	1.2
Oxide Yield	g /l	180	100	66
Free Nitric Acid	M/l	2.2	0.5	5
Volume	m³	49 (total)	757 (total)	372 (annually)



*Data refer to Tank-Composition 540-12

Figure 3.5. High-Level Liquid Waste Types (Grünewald, Koschorke, and Roth 1986)

Glass Product	□ LEWC - Glass	▩ HEWC - Glass	■ HAWC - Glass
Waste - Loading, Weight-%	11	24.7	15
Viscosity at 1150 °C, dPas	50	74	55
Electr. Resistivity at 1150 °C, Ωcm	4.3	3.7	3.8

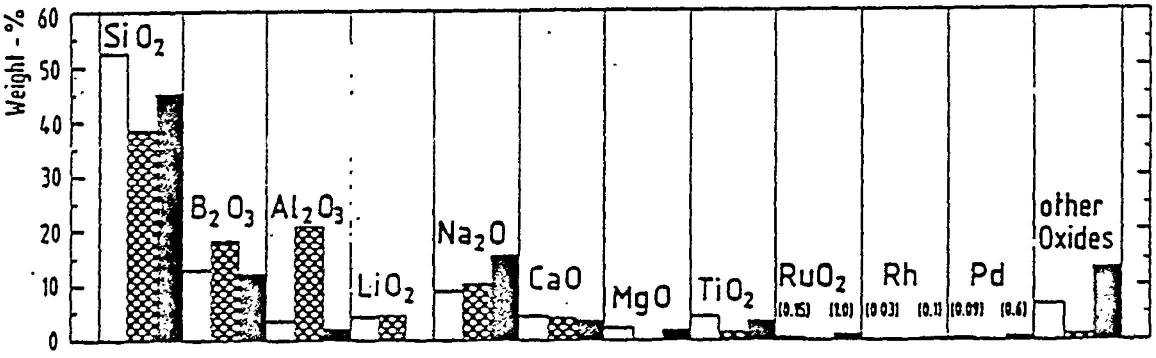


Figure 3.6. Glass Product Compositions for the K-2 Melter Operation (Grünewald, Koschorke, and Roth 1986)

During testing of the K-2 melter, 5.5 m^3 of HAWC simulant was vitrified, producing about 2.5 metric tons of glass. Waste simulant was fed at an average rate of 15 L/h, along with glass beads ranging in size from 0.1 to 1.25 mm in diameter. The average glass production rate was 34 kg/h. The glass product form, known as VG 98/12.2, was a borosilicate glass previously developed from the parent formulation VG 98/12. Of the noble metals fed during this test, 67% of Ru and 63% of Pd accumulated on the melter floor in the form of RuO_2 and Pd-tellurides. The flat melter floor and a slightly elevated drain hole prevented these particles from draining. The RuO_2 crystals were smaller than 1 μm, and the Pd tellurides were about 5 μm in diameter. The settled layer of noble metals had an increased viscosity and a decreased resistivity compared to the bulk glass. Although the electrodes did not fail during the operation, a decrease in electrical resistance was observed between the bottom electrodes (Pentinghaus 1986).

3.3.3 K-3 Melter

As part of the mock-up facility VA-3 at KfK, the K-3 melter was developed and later used as a test melter for the PAMELA plant. It was designed by combining operating test results for materials and equipment from the previously tested K-1 and K-2 melters. After the design was completed in 1980, it was put into operation in 1983 at KfK. Figure 3.7 shows a schematic of the melter design. The design features included a throughput of 30 L/h, a glass production rate of 30 kg/h, a glass pool surface area of 0.72 m^2, and a glass pool volume of 300 L. There were four pairs of air-cooled electrode plates made of Inconel 690, two lower and two upper sets. Their arrangement in the melter cavity is shown in Figure 3.8. The refractory material was ER 2161, and the melter plenum was surrounded by a ceramic refractory (ZAC 1681, composed of 51% Al_2O_3, 33% ZrO_2, 16% SiO_2). Twelve heating elements made of $MoSi_2$, shown in Figure 3.9, were used as an external heat source during startup of the melter. In addition to a bottom drain system for glass removal, this melter also had a glass overflow system used in the production of glass beads. During the tests, a total of 34 m^3 of LEWC simulant waste was vitrified, producing 37 metric tons of glass. At KfK, 19 m^3 of simulant was first processed in three campaigns, and another 15 m^3 was then processed at PAMELA in 1985 (Grünewald, Koschorke, and Roth 1986; Weisenburger 1980).

3.3.4 K-4 Melter

The PAMELA vitrification plant, located in Dessel, Belgium at the Eurochemic site, was designed with an LFCM referred to as K-4. Its design was based on the K-3 melter with only a few modifications. After construction was completed in late 1984, the melter was put into hot operation in October 1985 following 1 year of cold test campaigns. The melter operated in four campaigns from October 1985 to May 1988 (Buelt, unpublished, endnote 5).

The K-4 melter, shown in Figure 3.10, is essentially the same design as the K-3 melter. It has outside dimensions of 2 x 2 x 2.6 m (l x w x h) and is lined with the ER 2161 refractory. Four pairs of electrode plates (two upper and two lower) made of Inconel 690 provide the joule heating. These plates are air cooled to maintain the electrode temperature below 1120°C. At a maximum, the upper electrodes consume 55 kW and the lower electrodes consume 20 kW. Two outlets from the melter for removing the glass product include a bottom drain for the glass blocks and an overflow for the production of glass beads. The bottom of the melter is essentially flat, with approximately a 4° slope (Wiese, Höhlein, and Weisenburger 1986).

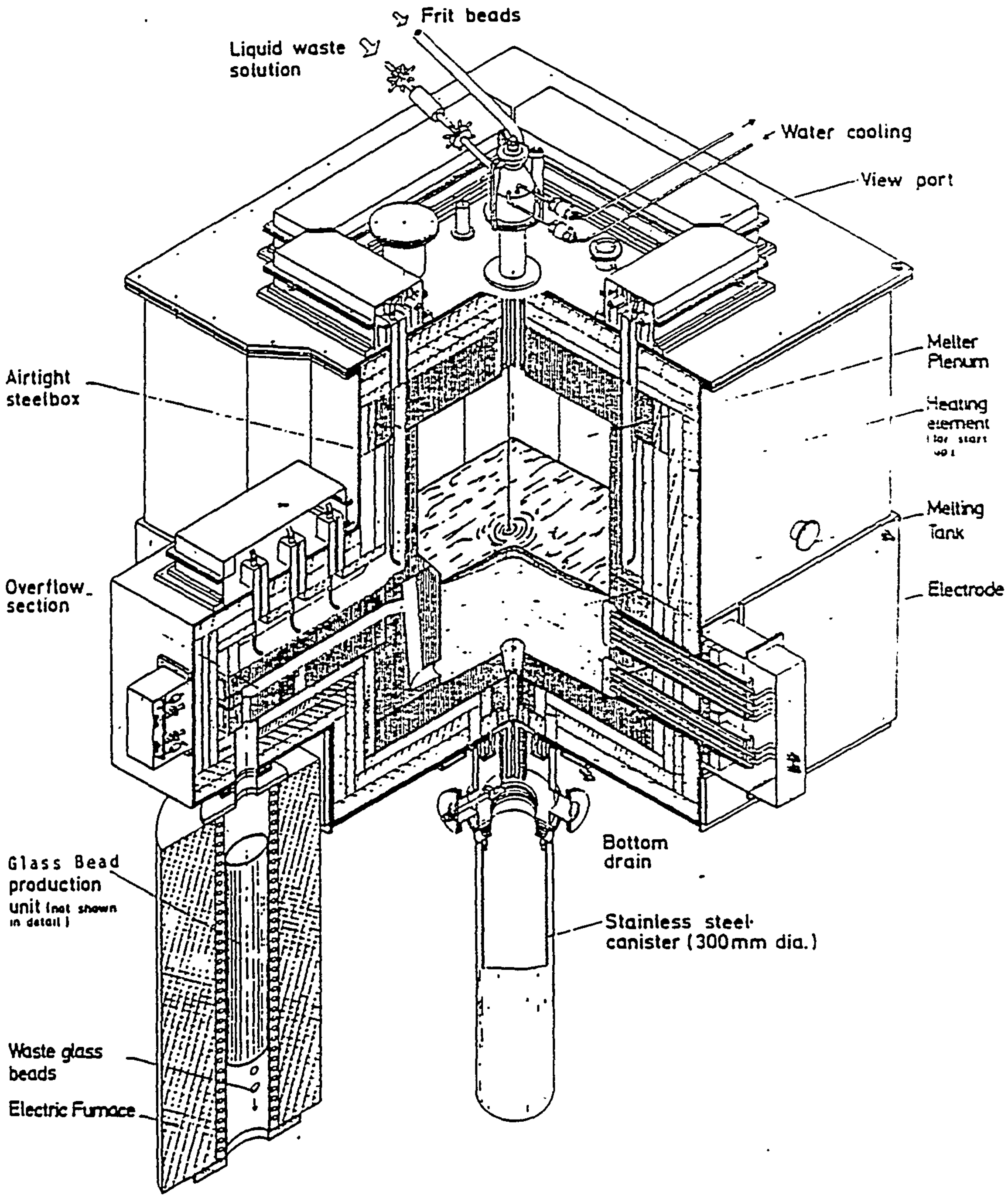


Figure 3.7. K-3 Melter Design (Weisenburger 1980)

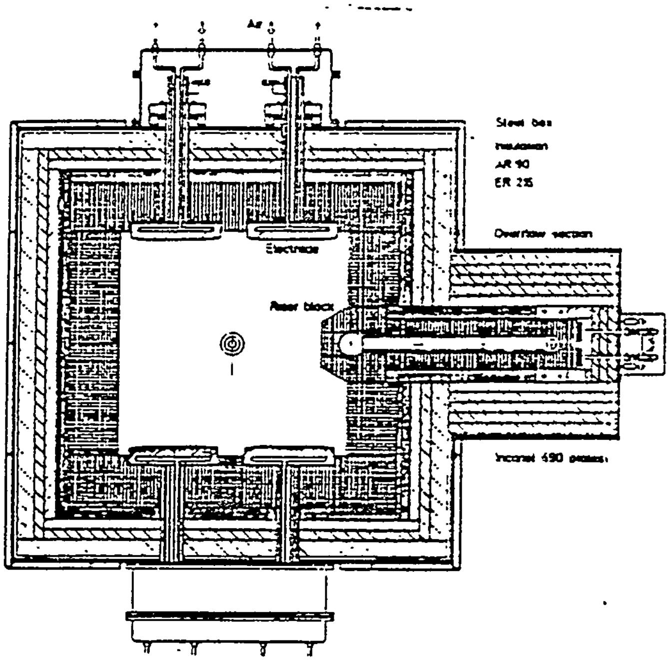


Figure 3.8. K-3 Melter Cavity, Horizontal Cross-Section (Weisenburger 1980)

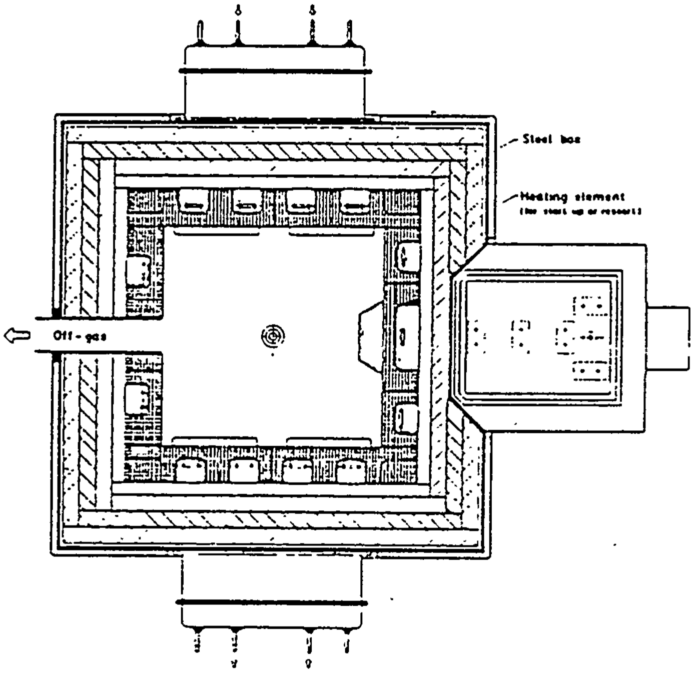


Figure 3.9. K-3 Melter Plenum, Horizontal Cross-Section (Weisenburger 1980)

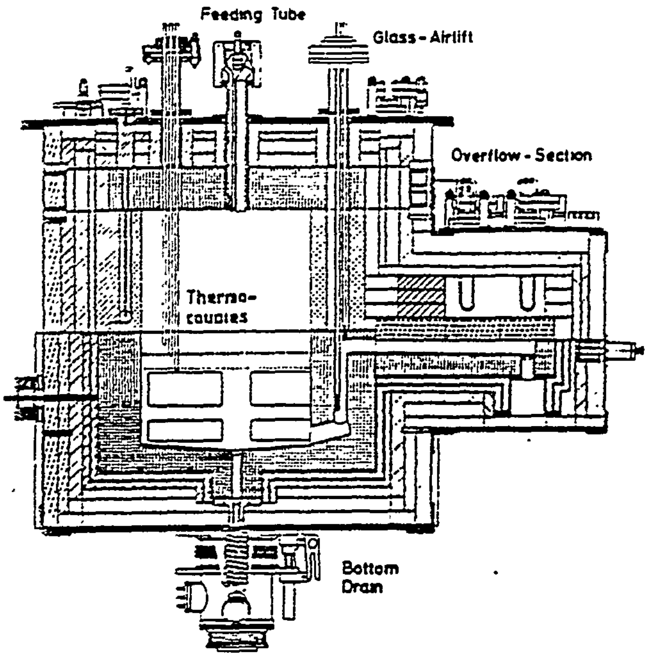
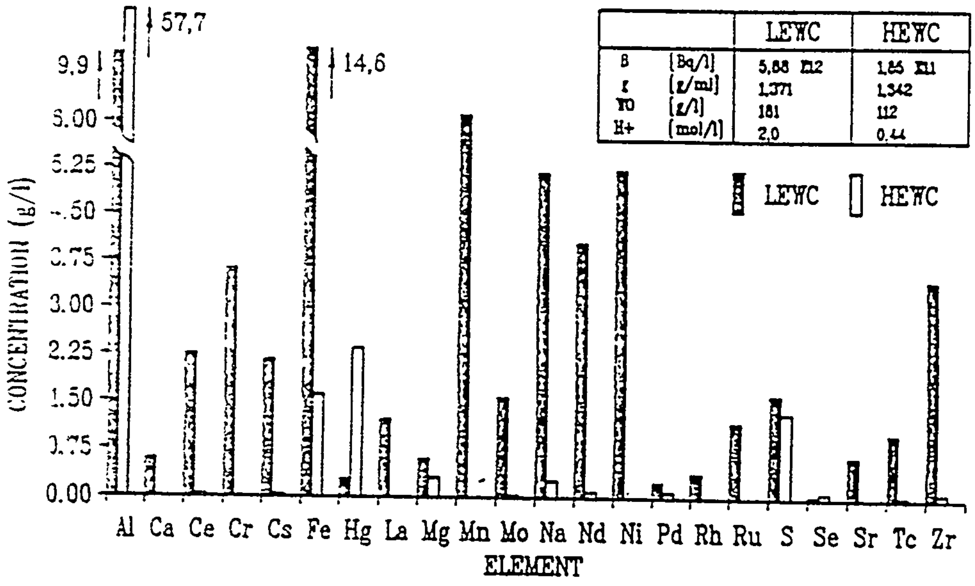


Figure 3.10. K-4 Melter Design (Höhlein et al. 1986)

Two types of high-level waste solutions vitrified at PAMELA include approximately 50 m^3 LEWC and 800 m^3 HEWC. Their compositions and relative activities are shown in Figure 3.11. Because of the high sulfur content of the LEWC, the waste glass loading was limited to 11 wt% on an oxide basis; however, the HEWC glass waste content varied between 21 and 25 wt% on an oxide basis. The melter was designed to have a throughput of 30 kg/h for the LEWC and 12 kg/h for the HEWC glass (Wiese and Ewest 1988).

During the first year of operation, 47 m^3 of LEWC was vitrified, producing 467 glass blocks in stainless steel canisters and 100 Vitromet canisters. Vitromet is produced by incorporating glass marbles in a metallic matrix. The LEWC, containing 8 x 10^6 Ci and significant amounts of noble metals, was fed continuously at a rate of 20 to 30 kg/h for the glass block canisters, and 12.2 kg/h for the Vitromet canisters. Glass frit in the form of 2-mm-diameter glass beads was fed batchwise at a rate of 6 pulses per hour. In the 47 m^3 of waste feed, there were about 90 kg of noble metals (Pd, Rh, Ru), of which 64.4 kg was Ru (Wiese and Ewest 1988; Buelt, unpublished, endnote 5).

After the first year, the throughput capacity dropped from 30 kg/h to 20 kg/h. A sample taken from the melter bottom showed areas of Ru concentration 80 times higher than the concentrations in the bulk glass. An overall noble metals balance, shown in Figure 3.12, shows that approximately 67% of the noble metals accumulated on the melter floor to form a layer approximately 5 cm deep. This layer had an electrical resistance about 3 times lower, and a viscosity about 5 times higher, than that of the bulk LEWC glass at 1150°C. Because the settled sludge layer was significantly more conductive than the bulk glass, the current field and electric potential in the melter was affected, as shown in Figure 3.13, where the density of lines represents the density of current and potential [Weisenburger (1989) unpublished, endnote 11; Wiese and Ewest (1988)].



		LEWC	HEWC
B	[Bq/l]	5,88 E12	1,85 E11
ρ	[g/ml]	1,371	1,342
TO	[g/l]	181	112
H+	[mol/l]	2,0	0,44

Figure 3.11. Composition of LEWC and HEWC (Wiese and Ewest 1988)

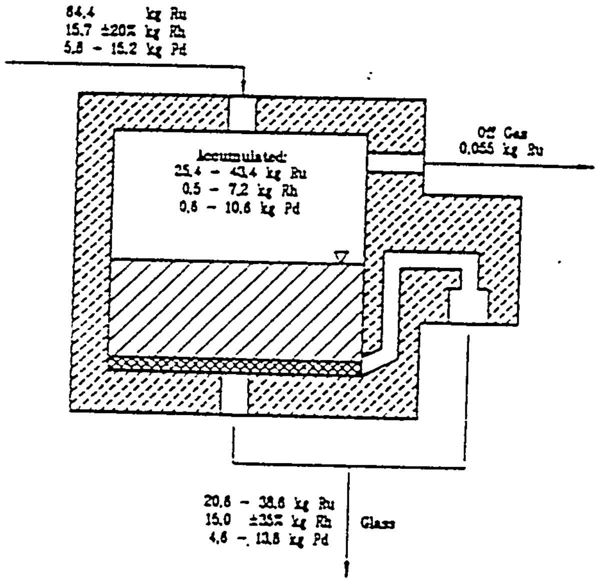


Figure 3.12. Noble Metals Balance (Weise and Ewest 1988)

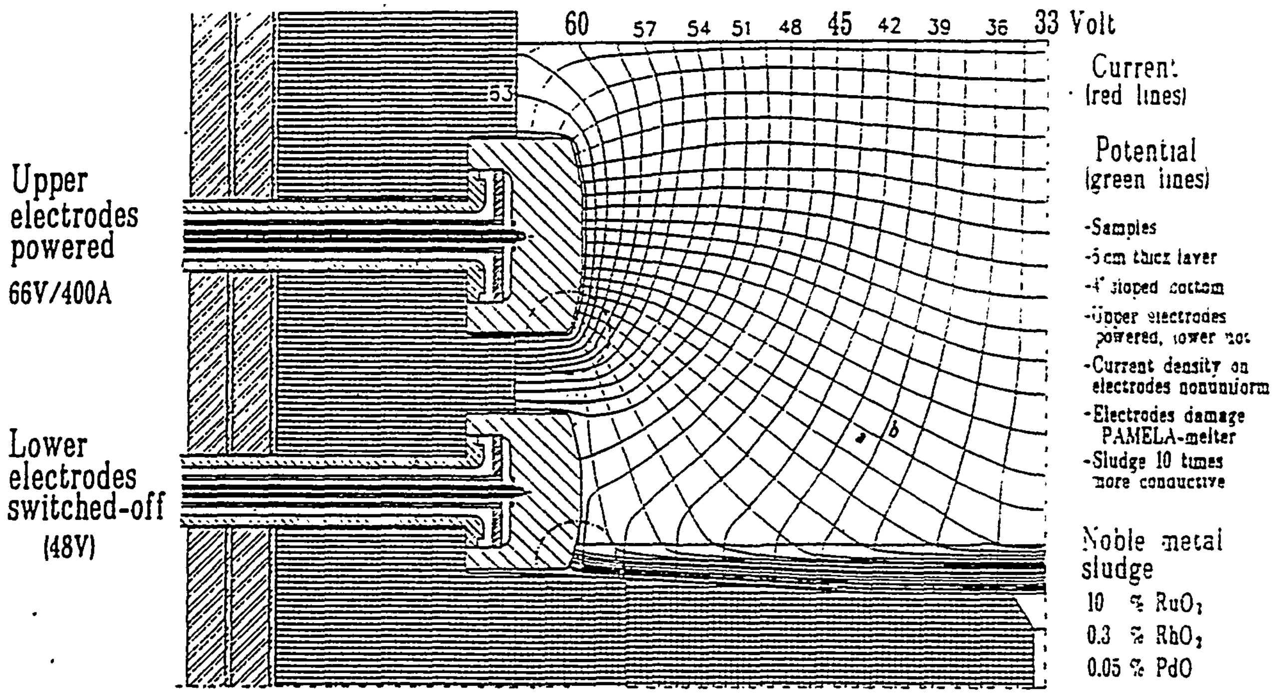


Figure 3.13. K-4 Melter Electric Potential and Current Field [Weisenburger (1989), unpublished, endnote 11]. Current density shown by line density.

Approximately 215 m^3 of HEWC was also processed by the K-4 melter during the last campaign. Compared to the LEWC waste, the HEWC was significantly less radioactive, containing 4 x 10^6 Ci activity, with considerably fewer noble metals. The glass frit used for the HEWC was SM 539 (see Table 3.13 for the composition). This frit was chosen over the SM 527 frit listed in the table because of its lower viscosity at 1150°C of 50 dPa·s compared to 120 dPa·s (Wiese and Ewest 1988).

During the entire melter operating period of 2-2/3 years, four electrode failures were observed. Some believe the failure was caused by the short circuiting through the highly conductive settled sludge layer of noble metals; others think the failures resulted from the asymmetry of the melter, which caused the current to flow off center and create a transfer of current from one pair of electrodes to an adjacent pair. This theory is supported by the fact that three of the four failures occurred with the top electrode (Buelt, unpublished, endnote 5).

In November 1986, the bottom drain of the K-4 melter failed, as shown in Figure 3.14. The suspected cause of the failure was an accumulation of heavy metal oxides on the floor. The overflow system then failed in May 1988, leading to the melter's shutdown and replacement with the K-5 melter (Buelt, unpublished, endnote 5; Tobie and Weisenburger 1990).

Table 3.13. Composition of Glass Frit, wt% (Wiese 1988)

	Former Glass Frit (SM 527)	New Glass Frit (SM 539)
SiO_2	50.0 ± 0.5	45.5 ± 0.5
B_2O_3	28.0 ± 0.5	33.0 ± 0.5
Na_2O	11.0 ± 0.3	10.5 ± 0.3
Li_2O	4.0 ± 0.1	4.5 ± 0.1
TiO_2	2.0 ± 0.2	–
CaO	5.0 ± 0.2	6.4 ± 0.2

3.3.5 K-5 Melter

After the K-4 melter failed at PAMELA, the K-5 melter was installed. During operation of the K-5 melter at PAMELA, there were some disturbances in the glass flow rate from the bottom drain assumed to have been caused by a sludge accumulation on the melter floor. Additional tests were performed in a glass laboratory in Dessel, Belgium, to investigate the cause of these disturbances, and to attempt to reduce the amount of Al_2O_3 accumulated on the melter floor. The compound Sb_2O_3, known as a refining agent in the glass industry, was tested in glass melts to determine its effects on accumulation of alumina sediment on the melter floor. The simulated inactive waste was made from 80 wt% SM 539 FR glass frit (see Table 3.13) and 20 wt% waste oxides of HEWC from tank 540-12. The waste/frit mixtures were melted in corundum crucibles for 4 hours, allowed to cool to room temperature, and then cut in half (De, Wiese, and Demmonie 1990).

Results showed that with less than 1 wt% Sb_2O_3 in the melt, the accumulation of glass decreased considerably after 4 hours of melting. After 5 hours, the sediment layer disappeared completely, resulting in a completely homogeneous glass. The Sb_2O_3 acts to "stir" the molten glass by producing oxygen that moves upward through the glass. The remaining Sb becomes totally dissolved in the glass and has almost no effect on viscosity, crystallization, and aqueous corrosion. There is, however, an observed decrease in electrical conductivity. Although these tests do not directly involve noble metals, the use of a chemical reagent to react and agitate the glass melt may become useful in future noble metals tests (De, Wiese, and Demmonie 1990).

3.3.6 K-W1 Melter

In 1984, KfK began developing a melter, designated K-W1, for use in the German reprocessing plant, WA-Wackersdorf (WAW). This plant was to be constructed by Deutsche Gesellschaft zur Wiederaufarbeitung von Kernbrennstoffen (DWK) to reprocess 500 tons of spent fuel from light water reactors. The reprocessing plant was expected to produce 370 m^3/yr of HAWC. This waste was projected to contain high concentrations of noble metals. Although the Wackersdorf plant was never completed, the insight gained during the melter development at KfK was very useful.

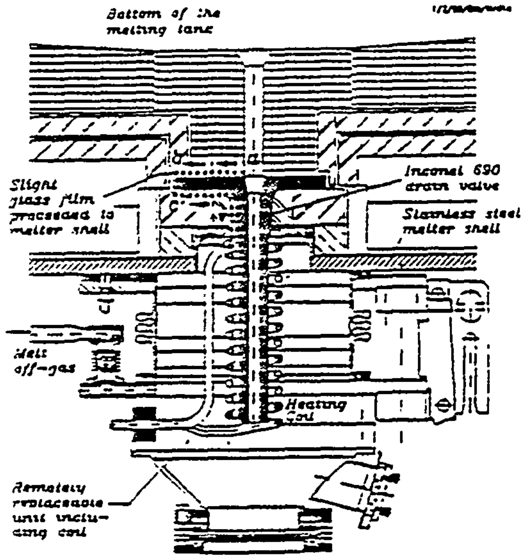


Figure 3.14. Bottom Drain of the K-4 Melter. Glass Leakage Detected at Point 'd' (Tobie and Weisenburger 1990)

The K-W1 melter was designed to be a full-scale test melter for the WA-Wackersdorf vitrification plant, and was operated in the V-W1 mock-up test facility at KfK. It was put into operation in 1986 after its construction was completed in 1984. The waste processed by this melter was a simulant of HAWC. Its design features included a glass pool surface area of 1.4 m^2, a design throughput of 72 L/h, a glass production rate of 31 kg/h, and a glass pool volume of 560 L. There were five pairs of electrode plates made of Inconel 690, and the refractory material was ER 2161. The design permitted three methods of glass removal, including a bottom drain, an overflow, and vacuum suction. The major change in this melter design was in the electrode arrangement relative to the geometry of the glass pool (Grünewald, Koschorke, and Roth 1986).

3.3.7 K-W2 Melter

A large-scale melter, designated K-W2, was designed and constructed in 1986-1988, and began operating in April 1988 at KfK. HAWC simulant was processed in this melter during two campaigns (W4 and W5) in 1988 and 1989. This melter was very similar in design to the K-W1 melter, with a glass pool surface area of 1.4 m^2, a design feed rate of 72 L/h, and a glass production rate of 30 kg/h. A major modification to the design was the 45° sloped melter floor. Shown in Figures 3.15 and 3.16 are detailed sketches of the melter design [Weisenburger (1989), unpublished, endnote 11].

During test runs for both campaigns, numerous samples of glass were obtained from the molten glass stream pouring from the bottom drain. In addition, samples were taken from a canister that had been sliced, as well as from the sediment on the melter floor collected after completion of the runs. The content of noble metals was analyzed by optical emission spectroscopy of an inductively coupled plasma (ICP) and by x-ray fluorescence (XRF) analysis. Viscosity measurements were taken using a platinum spindle immersed in the melt. Also, the electrical resistance of each sample was determined

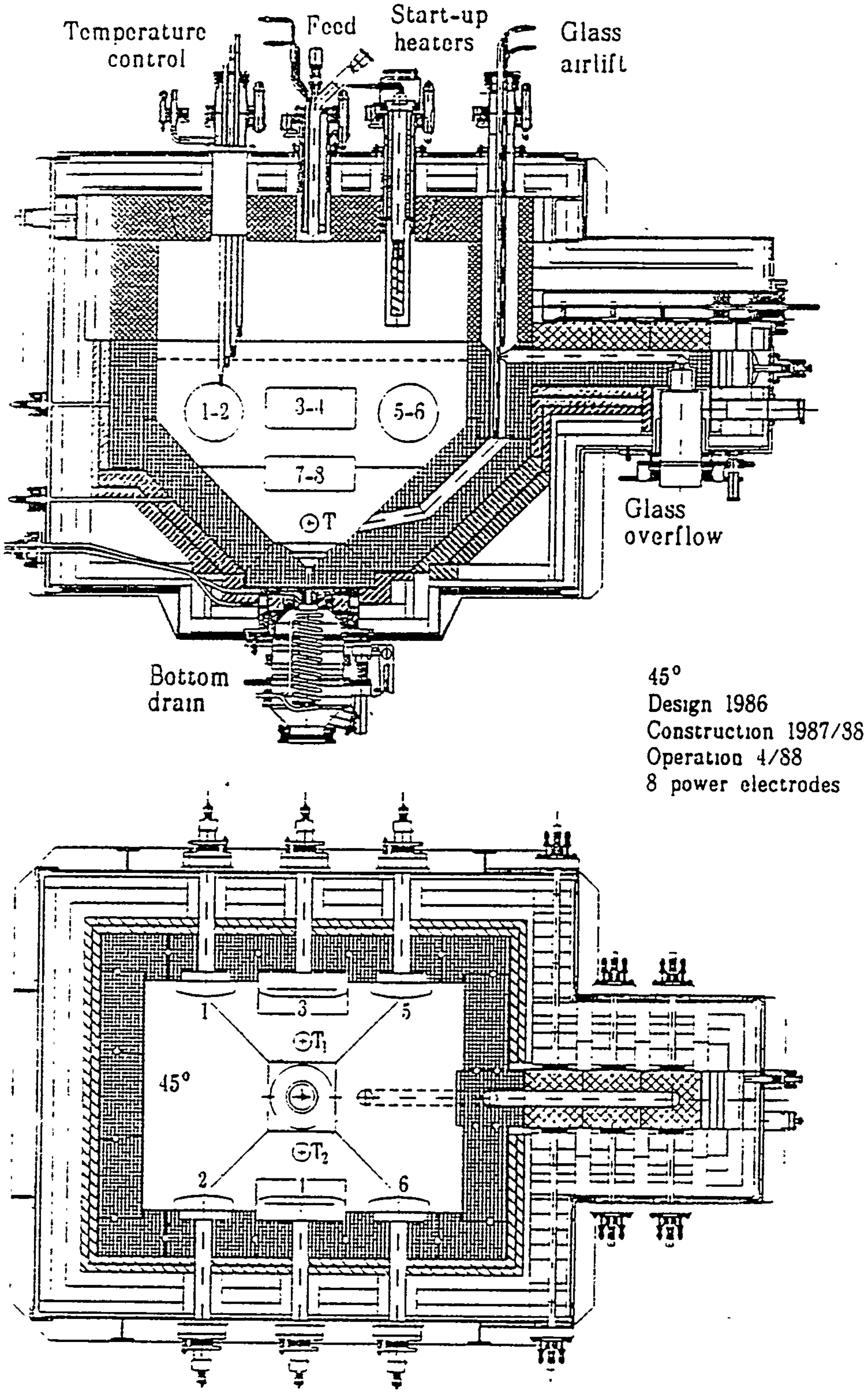


Figure 3.15. K-W2 Melter Design - View 1 [Weisenburger (1989), unpublished, endnote 11]

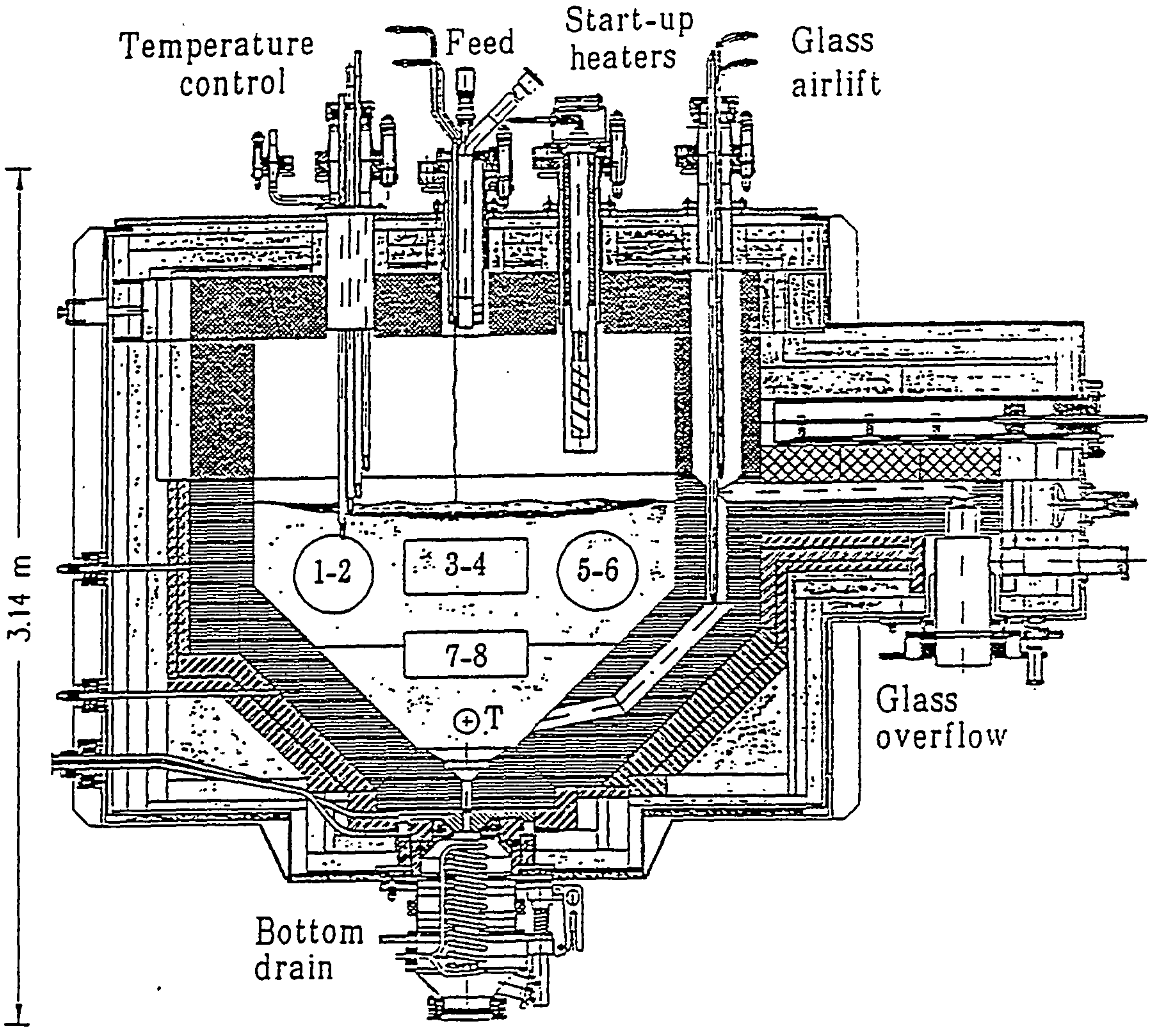


Figure 3.16. K-W2 Melter Design - View 2 [Weisenburger (1989), unpublished, endnote 11]

by measuring the resistance between two Pt electrodes inserted in the side walls of a small ceramic cell. A transmission electron microscope was used to identify the chemical composition of the noble metal particles (Krause and Luckschelter 1991).

The first campaign, W4, took place from April 14 to May 26, 1988. The primary purpose of this campaign was to identify the effects of noble metals on melter operation, and to determine the efficiency of noble metals removal with the bottom drain. Approximately 33 m^3 of high-level liquid waste (HLLW) simulant containing 157 kg noble metals (2.2 g/L Ru, 1.9 g/L Pd, 0.5 g/L Rh) was vitrified to form 13.2 metric tons of glass at an average production rate of 22 kg/h. Table 3.14 shows the compositions of both the reference waste solution and the HLLW waste simulant used in this campaign. The melter was operated with an average waste feed rate of 55 L/h, and the required power input of 75 to 90 kW was supplied by the upper electrodes only. The 13.2 metric tons of glass product contained an average of 0.69 wt% RuO_2, 0.45 wt% Pd, and 0.12 wt% Rh [Grünewald and Roth (1989), unpublished, endnote 12; Weisenburger (1989), unpublished, endnote 11].

Table 3.14. Composition of the Reference Solution and the HLLW Simulant Used in Campaign W4 (Krause and Luckschelter 1991)

Element/Ion	DWK Reference Solution, g/L	HLLW Simulant, g/L
^{34}Se	0.08	0.08
^{37}Rb	0.5	0.5
^{38}Sr	1.2	1.2
^{39}Y	0.7	0.7
^{40}Zr	5.2	5.2
^{42}Mo	4.6	4.6
^{43}Tc	1.1	--
^{44}Ru	2.2	2.2
^{45}Rh	0.5	0.5
^{46}Pd	1.9	1.9
^{47}Ag	0.03	0.03
^{48}Cd	0.12	0.12
^{50}Sn	0.04	0.04
^{52}Te	0.5	0.5
^{55}Cs	3.7	3.7
^{56}Ba	2.6	2.6
^{57}La	1.8	1.8
^{58}Ce	3.6	3.6
^{59}Pr	1.7	1.7
^{60}Nd	6.2	6.4
^{61}Pm	0.04	--(a)
^{62}Sm	1.3	1.3
^{63}Eu	0.2	--(b)
^{64}Gd	0.2	0.2
^{92}U	3.0	--
^{93}Np	0.7	--
^{94}Pu	0.04	--
^{95}Am	0.7	--
^{96}Cm	0.05	--
^{14}Si	0.06	0.06
^{24}Cr	1.1	1.1
^{25}Mn	0.1	0.1
^{26}Fe	3.7	3.7
^{28}Ni	0.4	0.4
Free HNO_3	5 mol/L	5 mol/L
Total HLW-oxide concentration	64 g/L57 g/L	

(a) Pm replaced by 0.04 g/L Nd.

(b) Eu replaced by 0.19 g/L Nd.

During routine glass pouring with the bottom drain throughout the campaign, 55% to 62% of the noble metals were removed. At the end of the campaign, the melter was flushed with noble metal-free glass and completely drained, increasing the noble metals removal efficiency to 67% to 93%. Figure 3.17 shows the locations of noble metals residue in the melter after the melter was completely drained [Weisenburger (1989), unpublished, endnote 11].

The second campaign, W5, ran from January 22 to March 11, 1989. Objectives of this campaign included determining the effects of air bubbling in the melter on the settled sludge layer, as well as proving that removing Rh from the waste simulant had no effect on the size and sedimentation of noble metal particles on the melter floor. Approximately 30 m^3 of simulated waste was processed. This simulant had the same composition as the W4 simulant (see Table 3.14), except Rh was not included. This simulated waste, fed at a rate of 45 to 50 L/h, contained about 123 kg noble metals (2.2 g/L Ru, 1.9 g/L Pd), and produced about 12.8 metric tons of glass at an average production rate of 20.3 kg/h. The 12.8 metric tons of glass product contained about 0.60 wt% RuO_2 and 0.48 wt% Pd. Heating was supplied by the upper electrodes with a power of 75 to 85 kW, while the power from plenum heating was 15 kW [Grünewald and Roth (1989), unpublished, endnote 12; Weisenburger (1989), unpublished, endnote 11].

The use of air bubbling in the melter greatly increased the removal efficiency of the noble metals, however, it was not effective enough to completely prevent noble metals from accumulating. During routine glass pouring, the removal efficiency increased from 66% to 88% for Ru, and for Pd the efficiency increased from 74% to over 100% (assuming an analytical error). The use of air bubbling also allowed the noble metals to be removed in the glass overflow system with the same efficiency as with the bottom drain. Based on these results, it was determined that the 45° slope was not steep enough to completely drain the settled sludge layer, and that the floor in the next melter design should have a greater slope [Weisenburger (1989), unpublished, endnote 11].

Glass samples taken during campaign W4 were analyzed using methods previously discussed and were found to contain between 0.5 and 16.5 wt% noble metals. The electrical resistance of these samples decreased significantly at noble metals contents greater than 2 wt%, and glass viscosity increased greatly at noble metals contents greater than 3.5 wt%. A semi-logarithmic plot shows a linear relationship such that as the noble metals content increases, viscosity increases, and electrical resistance decreases (Figure 3.18). Viscosity measurements taken as a function of shear rate indicate that the noble metals sludges behave very similarly to pseudoplastic liquids. Figure 3.19 shows this typical behavior of the noble metals sludge. These viscosity measurements also demonstrate that the flow behavior of accumulated noble metals depends on the size and morphology of the particles. As the size of particles increases, especially with the RuO_2 needles, the viscosity increases and the sludge behaves more like a pseudoplastic, non-Newtonian liquid (Krause and Luckschelter 1991).

Texture analyses performed on glass samples taken from both campaigns found that the noble metals existed mainly as needle-like RuO_2 particles and spherical $PdRh_xTe_y$particles. In the glass product, the RuO_2 particles were agglomerates of small grains with a few needle-shaped particles up to 100-μm long, as shown in Figure 3.20. Samples taken from the melter bottom, however, contained mostly clusters of long needle-shaped RuO_2 particles up to 500 μm long as shown in Figure 3.21. With an increase in melting time, these particles become more compact and granular, with the RuO_2 needles enclosing the $PdRh_xTe_y$ sphere (Krause and Luckschelter 1991).

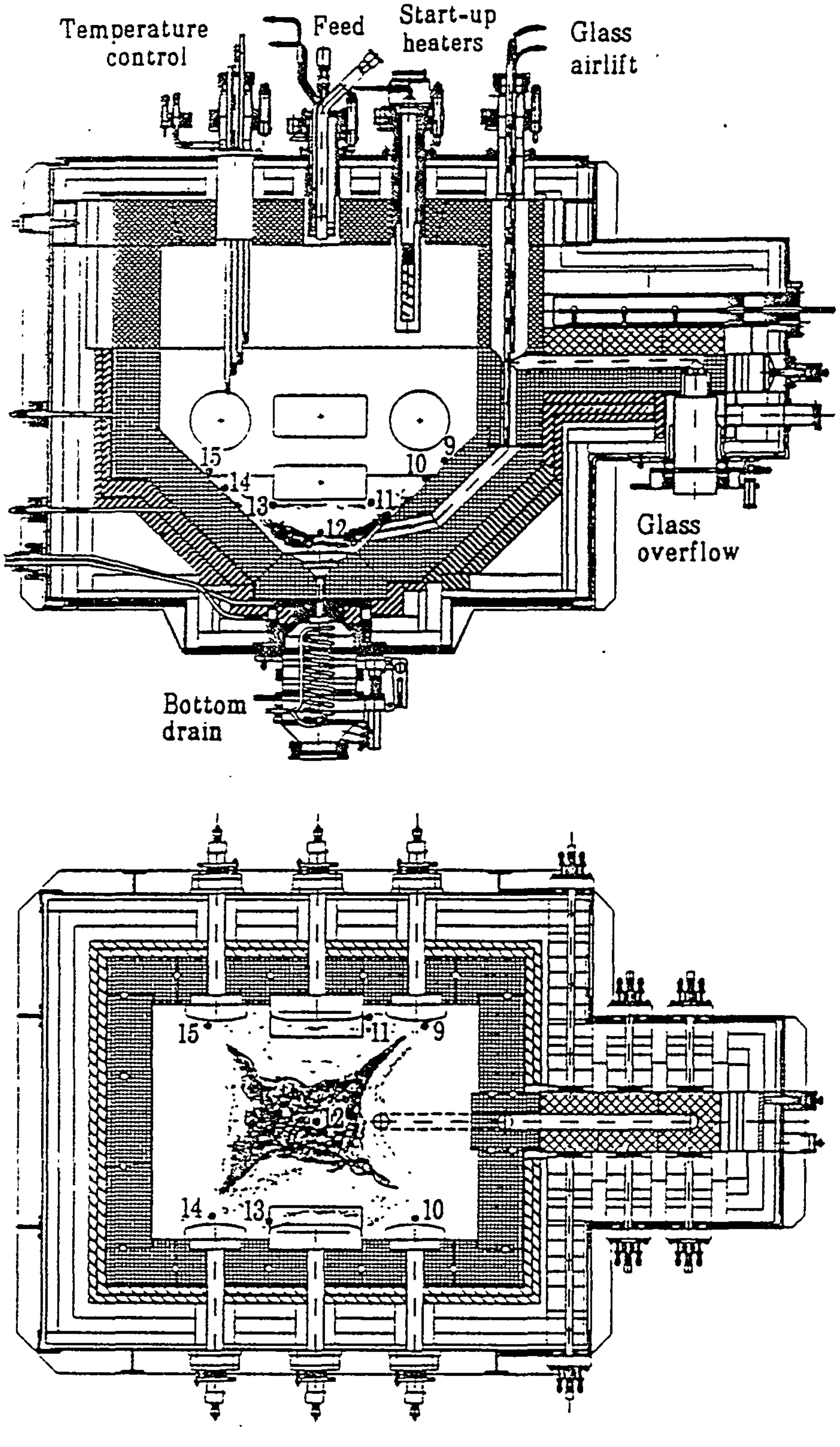


Figure 3.17. Residue in Melter K-W2 After Campaign W4 [Weisenburger (1989), unpublished, endnote 11]

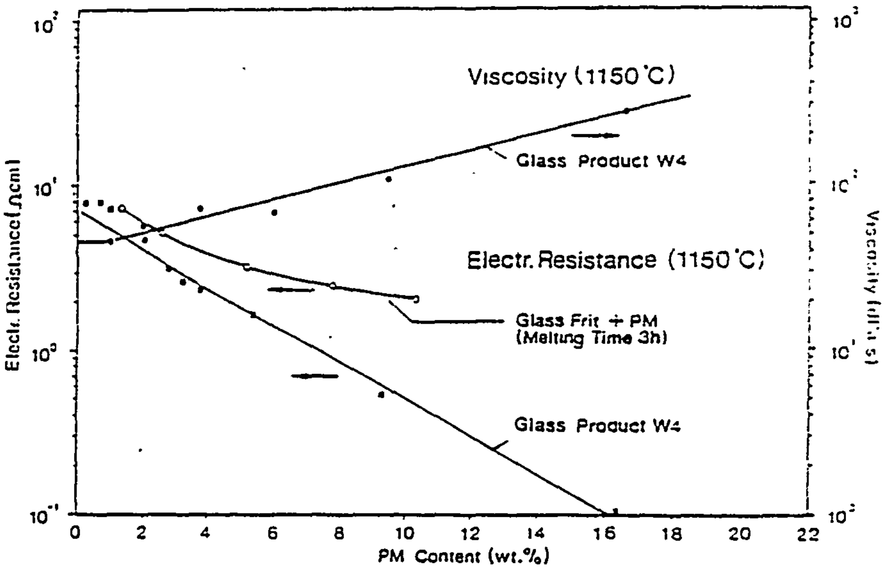
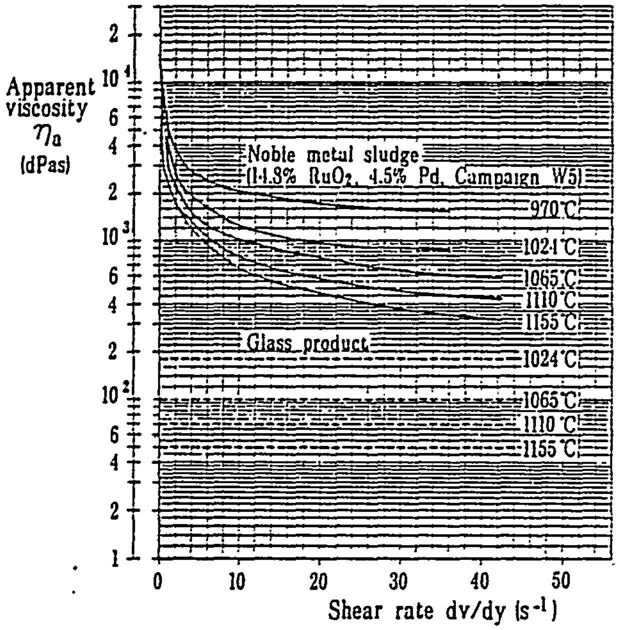


Figure 3.18. Dependence of Viscosity and Electrical Resistance on Noble Metals Content (Krause and Luckschelter 1991)



-Sludge non-Newtonian fluid, η (T,Sr)
-10-100 times higher viscous, removal difficult
-Accumulation tendency
-Data measured by a rotary viscosimeter

Figure 3.19. Viscosity Dependence on Shear Rate and Temperature [Weisenburger (1989), unpublished, endnote 11]

Figure 3.20. RuO_2 Particles in the Glass Product after Campaign W5 (Krause and Luckschelter 1991)

Figure 3.21. RuO_2 Particles in the Melter Bottom after Campaign W5 (Krause and Luckschelter 1991)

To characterize the shape of the noble metal particles, the form factor parameter was defined as

$$F = 4\ A/\pi\ D^2$$

where F = form factor
A = area
D = diameter.

A value of F = 0 corresponds to a circle, and F = 1 corresponds to a line or needle. There appears to be a relationship between the RuO_2 particle form factor and the diameter of the $PdRh_xTe_y$ spheres, where the mean diameter of the $PdRh_xTe_y$ spheres increases as the RuO_2 form factor decreases. In campaign W5, where the Rh was left out, the mean diameter of the $PdTe_y$ spheres was slightly larger than spheres from W4 campaign samples (Krause and Luckschelter 1991).

Analysis of noble metal particles also revealed a dependence of Rh content on time. In campaign W4 samples, the RuO_2 particles had high contents of Rh, whereas the $PdRh_xTe_y$ particles had lower Rh contents. When air bubbling was introduced later in campaign W4, this observation was reversed. The RuO_2 particles then had a low content of Rh and the $PdRh_xTe_y$ particles had higher Rh contents. This reversal was believed to be a direct result of the mobilization of particles from the sediment, allowing the particles to remain in the melter for a longer period of time. Therefore, as the noble metals residence time increased, the fraction of Rh in the $PdRh_xTe_y$ particles also increased. Another correlation was found to exist between the $PdRh_xTe_y$ particle diameter and the Rh content in W4 glass samples, where the sphere diameter increases by a factor of about 1.5 with increasing Rh content. Finally, a plot of RuO_2 form factor versus Rh content revealed a nearly linear relationship of decreasing form factor with increasing Rh content. Based on these results, it was concluded that the omission of Rh in the W5 campaign had no effect on the size and sedimentation of noble metal particles (Krause and Luckschelter 1991).

Through extensive laboratory-scale tests on noble metals, it was determined that the formation of RuO_2 needles depends on the existence of other compounds in the waste feed stream. To obtain a high proportion of long RuO_2 needles, there must be significantly more $NaNO_3$ and MoO_3 than RuO_2 in the mixture, and the ratio Na_2O/MoO_3 must be greater than 2. Figure 3.22 shows an example of the crystals obtained when these conditions are met. These laboratory tests also concluded that the RuO_2 needle formation can be decreased by creating a reducing environment in the melt, or by using glass frit powder (grain <500 μm) instead of glass beads. These results, however, have not yet been tested and verified in a full-scale melter system (Krause and Luckschelter 1991).

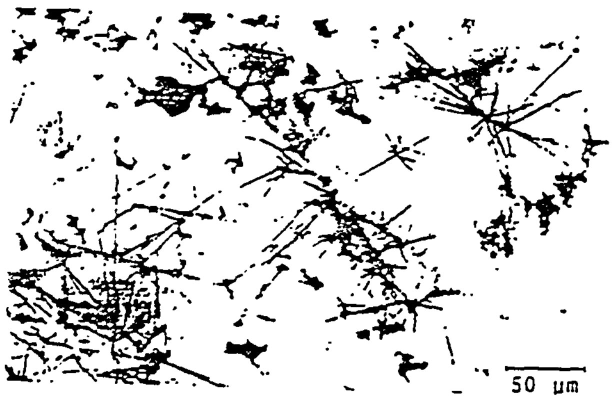


Figure 3.22. RuO_2 Needles Formed from a Mixture of Glass Frit, MoO_3, Alkalinitrate, and RuO_2 (Krause and Luckschelter 1991)

3.3.8 VA-WAK K-6 Melter

In 1988, the construction of a new mock-up facility, VA-WAK, was started at KfK. The facility included an advanced glass melter designated K-6. This facility began operating on June 4, 1990, with the primary objective of achieving an overall melter lifetime of 5 years. The melter, shown in Figures 3.23 and 3.24, incorporated improvements to the K-4 PAMELA melter--specifically, an increase in glass pool surface area from 0.74 to 0.88 m^2, and a melter floor with a 75° sloped settling chamber. The walls between the two sets of electrodes above the settling chamber were sloped at 60°, with vertical walls above the main electrodes. Two pairs of main electrodes were used to maintain the bulk glass temperature at 1150°C, and power input from another set of electrodes was supplied to the lower section of the melter (settling chamber) to maintain a temperature sufficient for glass drainage at 1050°C to 1100°C. Two methods of glass removal included an induction-heated bottom drain valve as well as an overflow system. The bottom drain design shown in Figure 3.25 was improved to prevent glass leakage. For comparison, the previous design from the K-4 melter is shown in Figure 3.14 (Tobie and Weisenburger 1990).

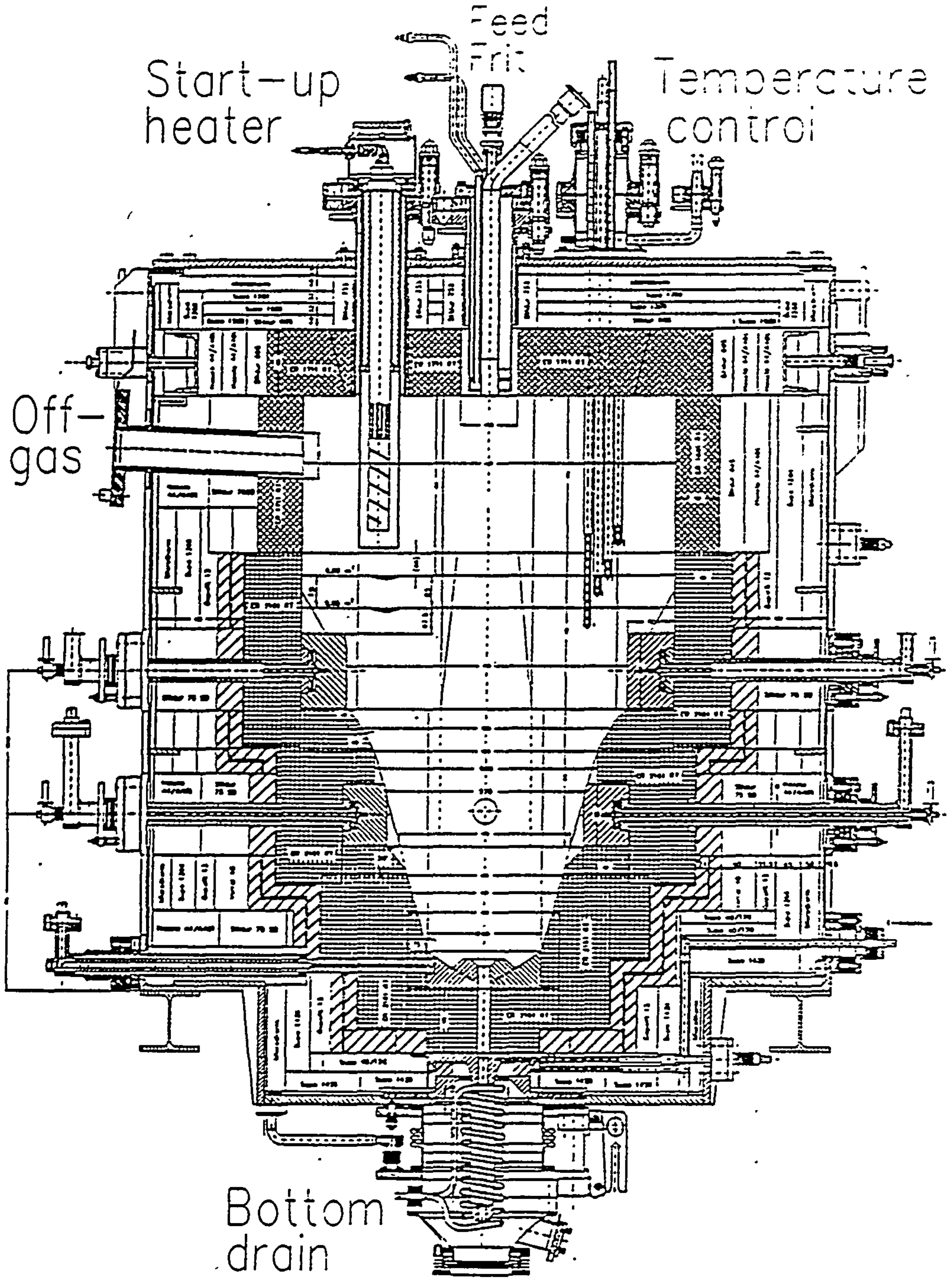


Figure 3.23. K-6′ Melter Design, Cross Section [Weisenburger (1989), unpublished, endnote 11]

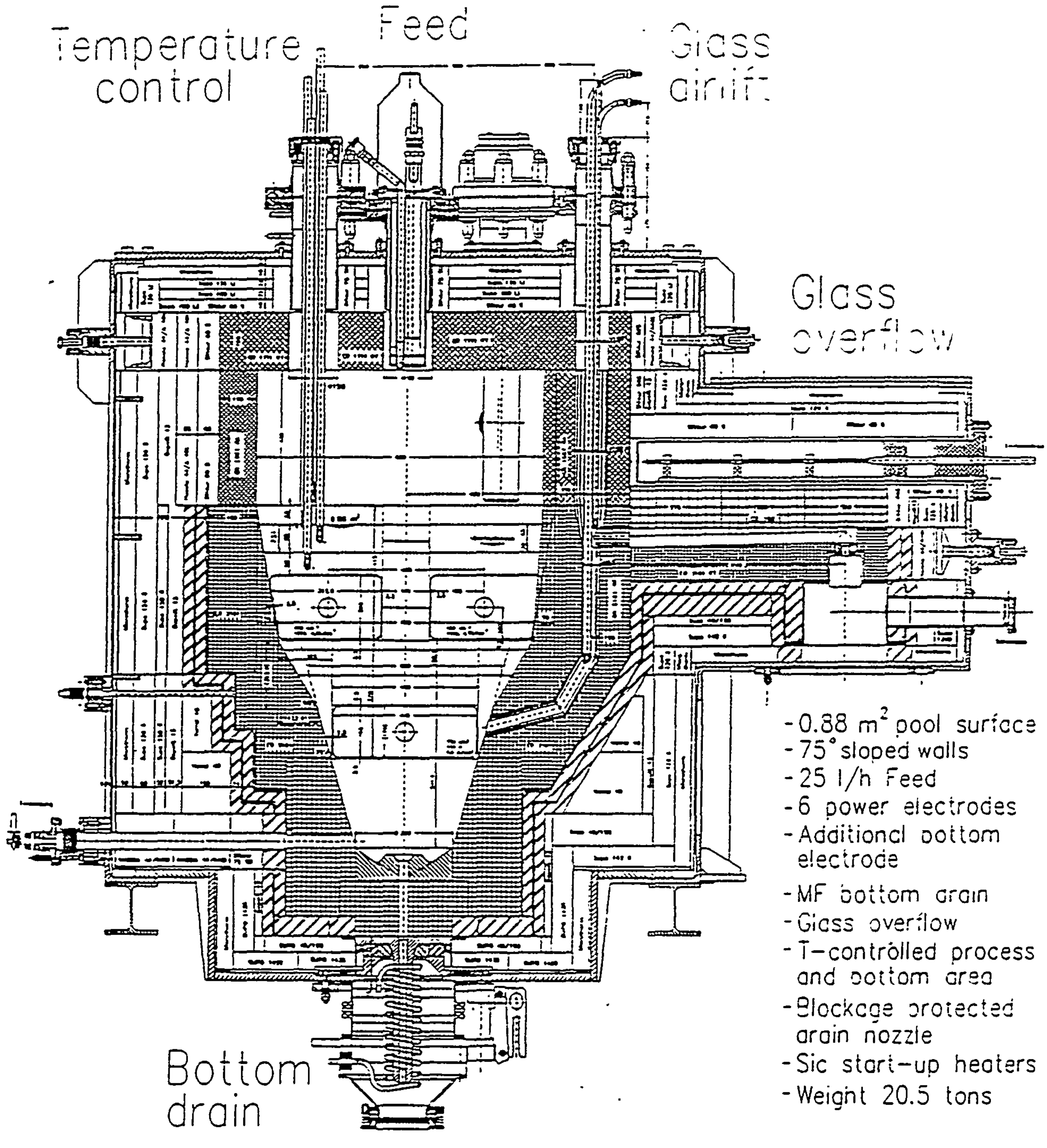


Figure 3.24. K-6´ Melter Design, Longitudinal Cross Section [Weisenburger (1989), unpublished, endnote 11]

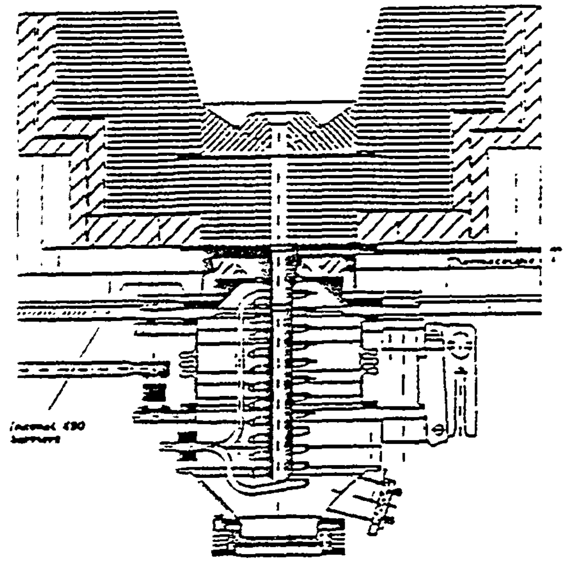


Figure 3.25. Advanced Bottom Drain Design for K-6' Melter (Tobie and Weisenberger 1990)

Table 3.15 compares the actual HAWC waste composition and the simulant feed solution processed in the K-6´ melter. In general, this waste has a high specific radioactivity, a high sodium content, and significant noble metals concentrations. The glass product waste loading was approximately 17 wt%, with 1 wt% noble metals in the glass (Tobie and Weisenburger 1990). During test runs, the K-6´ melter was operated 24 hours/day with a 24-L/h feed rate. Although the waste simulant was fed to the melter continuously, frit was added batch-wise in the form of 1-mm glass beads. During operation, the plenum temperature was around 650°C, about 150°C higher than usual. At the inlet to the dust scrubber, the off gas temperature was 250°C to 260°C, with an outlet temperature of 76°C to 82°C. Pouring occurred about every 12 hours at an average rate of 50 kg/h, for a total of 200 kg of glass. Approximately 15 samples were taken from the pour stream during a pour. At the tip of the bottom drain, the average temperature was 1010°C (Kruger, unpublished, endnote 6; Sevigny, unpublished, endnote 7).

Test results from operating this melter showed that the noble metals accumulated on the melter floor as expected, but were then drained from the melter during pouring with the bottom drain. As a result, no decrease in electrical resistance between the lower electrodes was detected during the run. Samples analyzed at PNL indicated that the noble metals were primarily in the form of RuO_2 needles and Pd-Te globules. A yellow phase in the glass product was believed to be a sodium molybdate salt with a high concentration of Ru and Pd. Based on all test results, it was concluded that the highly sloped walls of the melter bottom were sufficient to remove noble metals through the bottom drain (Kruger, unpublished, endnote 6; Sevigny, unpublished, endnote 7).

An additional set of tests performed with the K-6´ melter investigated the efficiency of noble metals removal using the bottom drain system versus the overflow system. In each test, the melter was operated continuously for approximately 500 hours with regular glass pouring. The first test

Table 3.15. Composition of Simulant HAWC Waste Used in K-6´ Melter (Tobie and Weisenburger 1990)

	HAWC-WAK		Simulant
Constituent	Element, g/L	Oxide, g/L	Oxide, g/L
Major Fission Products			
34 Se	0.08	0.11	0.11
37 Rb	0.46	0.50	–
38 Sr	0.9	1.06	1.06
39 Y	0.7	0.89	0.89
40 Zr	6.2	8.38	8.38
42 Mo	4.6	6.90	6.90
43 Tc	1.0	1.57	–
44 Ru	3.0	3.95	3.95
45 Rh	0.83	1.02	–
46 Pd	1.8	2.07	2.07
47 Ag	0.1	0.11	–
48 Cd	0.07	0.08	–
52 Te	0.8	1.0	1.0
55 Cs	3.0	3.18	3.18
56 Ba	2.3	2.57	2.57
57 La	2.0	2.35	2.35
58 Ce	3.1	3.81	3.81
59 Pr	2.0	2.34	2.34
60 Nd	5.3	6.18	6.35
62 Sm	1.2	1.39	1.39
63 Eu	0.16	0.18	–
64 Gd	0.8	0.92	0.92
Actinides			
92 U	6.2	7.31	–
93 Np	0.3	0.34	–
94 Pu	0.2	0.23	–
95 Am	0.15	0.16	–
Corrosion Production			
24 Cr	1.3	1.9	1.9
25 Mn	0.17	0.27	0.27
26 Fe	5.2	7.44	7.44
28 Ni	1.2	1.83	1.83
29 Cu	0.8	1.00	1.00
30 Zn	0.1	0.12	0.12
82 Pb	0.1	0.11	0.11
Process Chemicals and Others			
11 Na	16.0	21.6	21.6
12 Mg	0.2	0.33	0.33
13 Al	0.2	0.38	0.38
19 K	0.4	0.48	0.73
20 Ca	0.4	0.56	0.56
PO_4^{3-}	0.6	0.45	0.45
HNO_3	5.3 M	–	5.3 M
Total Oxide Yield	–	95.4	78.0
Radioactivity (β/γ)	515 Ci/L	–	–

was performed with glass pouring through the bottom drain system only; however, the second test was conducted using the overflow system. In addition, air sparging was used to help suspend the noble metal particles in the second test, with an air flow rate of 200-300 L/h introduced to the glass melt. Test results showed that 89.7% of the Ru fed was discharged from the melter with the bottom drain system; however, only 58.6% of the Ru fed was discharged with the overflow system and air sparging, indicating that air sparging is inadequate for avoiding noble metals accumulation (Grünewald et al. 1993).

3.3.9 Summary of Vitrification Development in Germany

Table 3.16 summarizes data obtained on melter development in Germany. Test results showed that the accumulation of noble metals can be greatly decreased by increasing the slope of the melter floor. When using a flat-bottom melter with a bottom drain, approximately 65% of the noble metals fed were retained in the melter. However, with a 75°/60° sloped melter floor, net deposits of noble metals were not detected by measuring changes in electrical resistance at the end of each pour through the bottom drain. After comparing two systems for glass pouring, the bottom drain was found to be more efficient than the overflow system in discharging noble metals. For Ru, retention was 10.3% using the bottom drain and 41.4% with the overflow system. Air sparging was also tested to determine its effects on noble metals accumulation. With a melter having 45° sloped floor, agitating the molten glass resulted in a decrease of Ru retention from 38% to 24%, and a decrease of Pd retention from 45% to 3%. However, in tests with a 75°/60° sloped floor, it was found that air sparging was not effective enough at suspending noble metal particles to allow discharge through the overflow system. A thorough investigation of the behavior of noble metal deposits and a complete analysis of the individual particles was also performed, and the conclusions were made that the removal of Rh from the simulant waste stream has no effect on the size and sedimentation of other noble metals. Also, general relationships were found between noble metal content and electrical, rheological, and morphological behavior of the accumulated sludge layer.

3.4 Vitrification Studies in Japan

In 1966, Japan began generating nuclear power, which has since becom the major source of electricity in that country. By 2000, it is estimated that 40% of the total power generated in Japan will come from nuclear power. The first nuclear fuel reprocessing plant, Tokai Reprocessing Plant (TRP), has been operating since 1977. This plant had produced about 300 m^3 of HLLW as of 1988, storing the waste in tanks onsite. In 1980, the Japan Atomic Energy Commission (JAEC) issued a policy for the treatment and disposal of HLLW, stating that the HLLW should be vitrified to form a borosilicate glass using a joule-heated LFCM. After storage for 30 to 50 years, the glass will be disposed of in a deep geological formation. As a result of this and other policies, Power Reactor and Nuclear Fuel Development Corporation (PNC) has been actively developing technology for use in Japan's first vitrification plant, the Tokai Vitrification Facility (TVF) (Tsuboya and Tsunoda 1988).

Table 3.16. Summary of Germany's Melter Development

Melter	Characteristics	Campaign/Run	Dates	Noble Metals Retention
K-1/VA-1	0.36 m^2 area, bottom drain, flat bottom	18 m^3 glass	1977-1979	Data not available
K-2/VA-2	0.64 m^2 area, bottom drain, flat bottom	2.5 tons glass	1980-	57% for Ru 53% for Pd
K-3/VA-3	0.72 m^2 area, bottom and overflow drain, flat bottom	22 campaigns, 37 tons glass	1983-1985	Data not available
K-4/ PAMELA	0.72 m^2 area, bottom and overflow drain, 4° sloped bottom	LEWC campaign, 77.8 tons glass	1/85-12/86	67% total
K-4/ PAMELA	0.72 m^2 area, bottom and overflow drain, 4° sloped bottom	HEWC campaign, 248.3 tons glass	1/86-1/89	Data not available
K-5/ PAMELA	(a)		1987-	Data not available
K-W1/V-W1	1.4 m^2 area, bottom drain, overflow, vacuum suction, flat bottom		1986-	Data not available
K-W2	1.4 m^2 area, bottom drain, overflow, vacuum suction, 45° sloped floor	Campaign W4, 13.2 tons glass	4/88-5/88	38% for Ru 45% for Pd 41% for Rh
K-W2	1.4 m^2 area, bottom drain, overflow, vacuum suction, 45° sloped floor, air bubbling	Campaign W5, 12.8 tons glass	1/89-3/89	24% for Ru 3% for Pd
K-6′	0.88 m^2 area, bottom drain, 75°/60° sloped floor	8.5 tons glass	6/90 - present	10.3% for Ru
K-6′	0.88 m^2 area, overflow system, 75°/60° sloped floor, air sparging	5.5 tons glass	6/90 - present	41.4% for Ru

(a) Assumed to be the same as the K-4 design.

3.4.1 Melters A, B, and C: PNC

In January 1978, vitrification testing began at the Engineering Test Facility (ETF), operated by PNC. The purpose of these tests was to obtain experimental data from the processing of HLLW generated by the Tokai Reprocessing Plant. Specifically, vitrification equipment, including the melter, the offgas system, and the canister handling system, was studied. Seventeen campaigns were completed by the end of 1981 using three joule-heated LFCMs: Melter A, Melter B, and Melter C (Okamoto et al. 1982).

Melter A was designed as a two-chamber vessel with a separate melt chamber and a vertical riser. The surface area in the melt chamber was 0.3 m^2. Glass was poured with an overflow system, where the glass flowed out the bottom of the melt chamber, into the riser, and out the overflow into a canister. Originally, the rod-shaped side-entering electrodes were made of molybdenum, but were later replaced with Inconel 690 electrodes. Tests with this melter and Melter C showed that the molybdenum electrodes wear 55 to 72 times faster than the Inconel 690 electrodes. The other two melters used in the ETF tests, designated Melter B and Melter C, had a glass-melting capacity of 80 L/day. These melters were joule heated with a melting temperature of 1200°C. Melter B had a melting volume of 260 L, with a surface area[a] of 0.59 m^2, whereas Melter C had a volume of 145 L with a surface area of 0.3 m^2. For glass pouring, Melter B had a resistance-heated overflow nozzle made of Inconel 600 and Pt, whereas Melter C had a high-frequency heated bottom drain nozzle made of Inconel 601. The electrodes in Melters B and C were side entering and made of molybdenum, but the Melter C electrodes were later replaced with Inconel 690 rods. All three melters had an alumina zirconium silica (AZS) glass contact refractory. Melters A and C were operated from 1978 to 1984, and Melter B was operated from 1980 to 1983 [Okamoto et al. (1982); Bonner (1982), unpublished, endnote 13].

Through the end of 1981, 51.3 metric tons of glass product was produced over a total in-service operating period of 1406 days for the three melters. The glass was a borosilicate glass with an approximate waste loading of 29 wt%. Before feeding to the melter, the waste was first denitrated with formic acid and then concentrated. The exact composition of the waste is not known, nor is it known if the waste contained noble metals. During melter operation, the molybdenum electrodes showed significant corrosion in Melters B and C of 0.81 g/h and 1.06 g/h, respectively. As previous laboratory-scale tests indicated, the Inconel 690 electrodes showed a much higher resistance to corrosion, with a rate of about 0.05 g/h (Okamoto et al. 1982).

3.4.2 Mock-Up Test Facility: PNC

Test results from the ETF operations were used to develop the melter for the Mock-up Test Facility (MTF), which was constructed in March 1982 by PNC and operated until 1983. The melter's two-chambered design was similar to that of the ETF Melter A. This melter, shown in Figure 3.26, was a joule-heated ceramic melter with a glass production capacity of 280 kg/d. Electrode plates made of Inconel 690 provided the heat required for glass melting at 1150°C to 1200°C. The melter design included an AZS glass contact refractory, a glass-melting volume of 160 L, and both an overflow and a bottom drain system for glass discharge (Sasaki et al. 1984).

During the fifth campaign of the MTF melter, approximately 12 m^3 of simulated HLLW was vitrified, producing 3.5 metric tons of glass product. Tables 3.17 and 3.18 show the compositions of the simulated waste and the glass frit. Although the actual glass product compositions were not provided, calculations showed an expected composition as listed in Table 3.19. Noble metals that accumulated on the melter floor caused a change in the melter temperature distribution and was noticed for the first time in melter development. Analysis revealed that the deposits contained RuO_2 and metallic alloys (Pd-Te and Ru-Rh). The average density of the noble metals layer was 3.45 g/cm^3, significantly higher than the average glass product density of 2.80 g/cm^3. To help prevent the accumulation of noble metals, mechanical stirring or air sparging was suggested for future designs [Sasaki et al. (1984); Brouns (1984), unpublished, endnote 14].

(a) Another source described Melter B as having a surface area of 0.45 m^2. It is uncertain which value is more accurate.

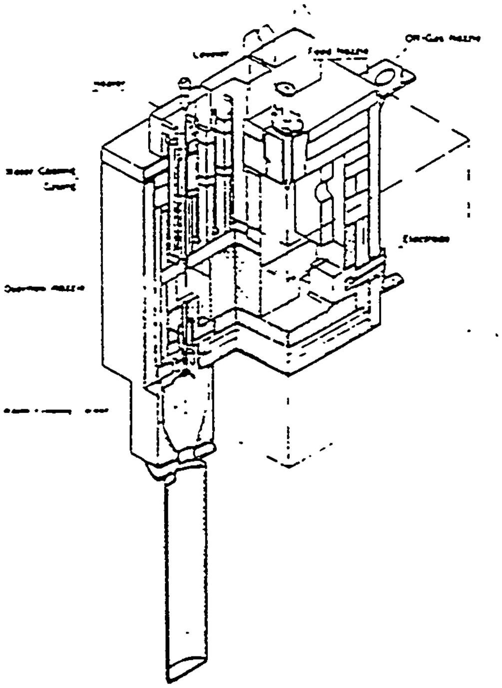


Figure 3.26. MTF Mock-up Melter Design (Sasaki et al. 1984)

3.4.3 Advanced-B Melter: PNC

After operation of the B and C melters at the ETF, the design was modified to become the Advanced-B Melter design. The purpose of this new design was to study the use of microwave heating for melter startup. A cross section of the design is shown in Figure 3.27; features include a 45° sloped melter floor, a melting surface area of 0.53 m^2, a glass volume of 300 L, and Cr_2O_3-Al_2O_3 fused-cast refractory. A 915-MHz microwave heating device with a maximum capacity of 50 kW was installed. After approximately 86 hours of operation, the glass temperature in the melter reached 700°C. Although melter startup using the microwave system was successful, maintenance problems led to the decision not to use this system in future designs [Brouns (1987), unpublished, endnote 15].

Three noble metals campaigns were performed with the Advanced-B Melter from November 1985 to August 1986. A total of 21.6 kg RuO_2 and 10.2 kg PdO was fed to the melter in the three campaigns. Based on data taken from the second campaign, it was assumed that 16.8 wt% of the RuO_2 fed and 0.2 wt% of the PdO fed would be volatilized. This prediction does not assume, however, that these compounds volatilize as oxides. Subtracting the quantities of noble metals assumed to be volatilized from the original amounts fed yielded the net amount incorporated in the glass. The net value was then used to calculate the melter drainage efficiency. At the end of operation, the glass product samples were analyzed and the melter was found to have an average drainage efficiency of 82% for RuO_2 and >100% for PdO (assumed to be an analytical error) [Brouns (1987), unpublished, endnote 15].

Table 3.17. Composition of the Simulated HLLW

Components		Concentration (g/L)
Na_2O		30.40
P_2O_5		0.90
Fe_2O_3		6.20
Cr_2O_3		0.30
NiO		0.70
Rb_2O		0.34
Cs_2O		2.27
SrO		0.91
BaO		1.49
Y_2O_3		0.55
La_2O_3		1.29
CeO_2		2.62
Pr_2O_3		1.23
Nd_2O_3		
Pm_2O_3	Nd_2O_3	4.20
Sm_2O_3		0.89
Eu_2O_3		0.14
Gd_2O_3		0.07
ZrO_2		4.45
MoO_3		4.41
Tc_2O_7		1.14
(MnO_2)		
RuO_2		2.25
Rh_2O_3		0.43
PdO		1.06
Ag_2O		0.04
CdO		0.06
SnO_2		0.05
Sb_2O_3		—
TeO_2		0.57
SeO_2		0.06
UO_3		
NpO_2		
PuO_2		7.51
(CeO_2)		
Am_2O_3		
Cm_2O_3		
Total		76.53 g/L

Table 3.18. Composition of Glass Frit (Sasaki et al. 1984)

Composition	Wt%
SiO_2	60.20
Li_2O	4.00
ZnO	4.05
B_2O_3	18.93
BaO	4.05
Al_2O_3	4.73
CaO	4.05
Others	Under 1.0

3.4.4 Chemical Processing Facility

In December 1982, laboratory-scale hot vitrification tests were started in the Chemical Processing Facility (CPF) located near the Tokai Reprocessing Plant. Radioactive HLLW from the TRP was processed, but the actual waste composition is not known. The melter was a small-scale joule-heated ceramic melter, shown in Figure 3.28. As of 1987, 11 runs were successfully completed. In the sixth run, about 1.5 L of waste glass was produced with a radioactivity of 3,700 Ci (Sasaki et al. 1984; Tsuboya and Tsunoda 1988). At this time, additional information on the melter design, test results, and relevance of the melter design to behavior of noble metals is not available.

3.4.5 Small-Scale Melters

In 1983, PNC performed vitrification tests with the MTF melter, as previously discussed in Section 3.4.2, and concluded that noble metals (Ru, Pd, Rh) tend to accumulate on the melter floor as a result of their low solubility in the molten glass. To help develop an improved melter design that would prevent accumulation of noble metals, two small-scale melters with sloped floors were later tested. As shown in Figure 3.29, one melter had a 30° sloped floor with a 41° sloped sidewall, and the other had a 45° sloped floor with a 58° sloped sidewall. Both melter designs included one pair of electrode plates made of Inconel 601, a glass contact refractory made of AZS, a melter cavity surface area of 0.054 m^2, and a resistance-heated drain nozzle made of Inconel 601. The 30° sloped melter had a high glass capacity of 11.3 L, whereas the 45° sloped melter had a 12.6-L glass capacity. Glass temperatures were monitored by thermocouples inserted through the melter lid (Igarashi and Takahashi 1991).

Two batches of high-level waste simulants were fed to the melters, one containing noble metals and the other without noble metals. The target compositions of the two glass products are shown in Table 3.20. The melters were operated batch-wise, with a melting time of about 24 hours from feeding to draining. For each melter, the simulant without noble metals (P0699) was melted first for reference, then the simulant with noble metals (P0686) was processed. Multiple batches of each simulant were processed, and approximately 8 kg of cullet was added to the melter after each previous melt was completely drained. A resistance heated drain nozzle made of Inconel 601 was used to control the glass

Table 3.19. Expected Glass Product Composition (Sasaki et al. 1984)

Component	wt%
SiO_2	45.00
B_2O_3	14.20
Li_2O	3.00
CaO	3.00
ZnO	3.00
BaO	3.49
Al_2O_3	3.60
Na_2O	10.00
P_2O_3	0.30
Fe_2O_3	2.04
Cr_2O_3	0.10
NiO	0.23
Rb_2O	0.11
Cs_2O	0.75
SrO	0.30
ZrO_2	1.46
MoO_3	1.45
MnO_2	0.37
RuO_2	0.75
Rh_2O_3	0.14
PdO	0.35
Ag_2O	0.02
CdO	0.02
SnO_2	0.02
SeO_2	0.02
TeO_2	0.19
Y_2O_3	0.18
La_2O_3	0.42
CeO_2	3.34
Pr_6O_{11}	0.42
Nd_2O_3	1.38
Sm_2O_3	0.29
Eu_2O_3	0.05
Gd_2O_3	0.02
Total	100.00

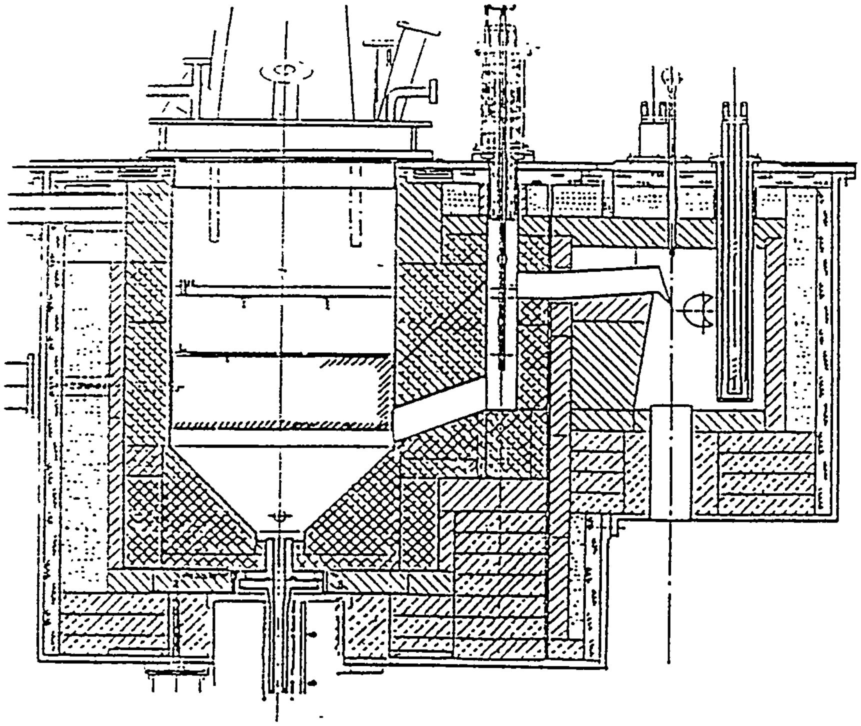


Figure 3.27. Advanced-B Melter Cross Section [Brouns (1987), unpublished, endnote 15]

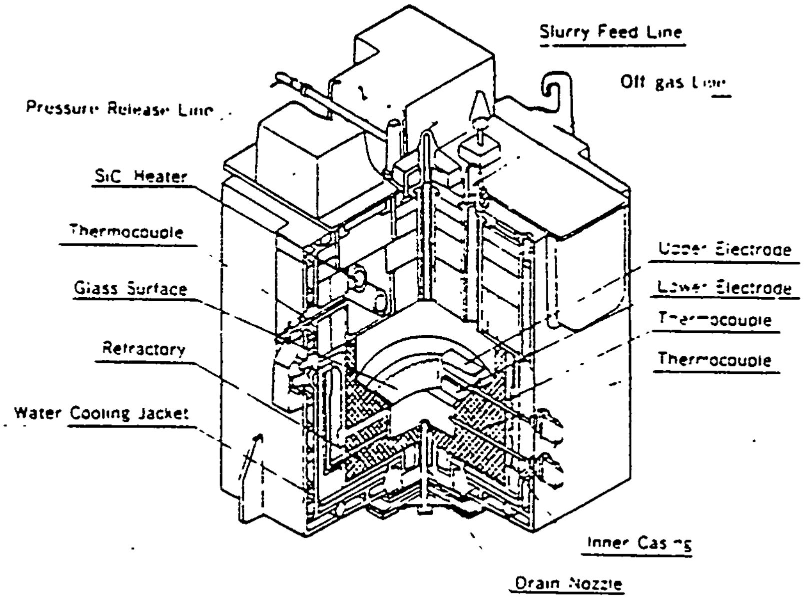
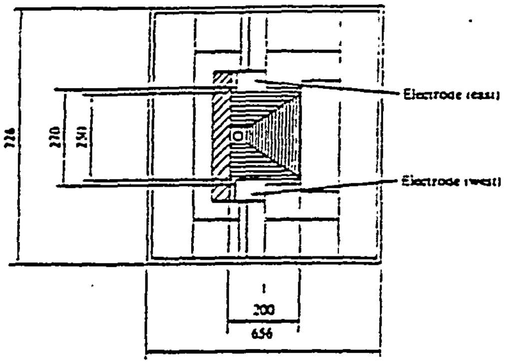
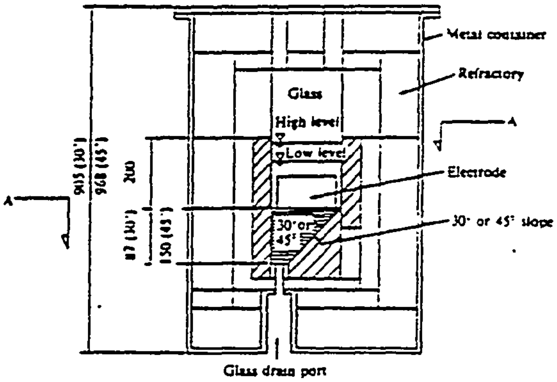


Figure 3.28. CPF Melter Design (Sasaki et al. 1984)



(a) horizontal cross section at A-A



(b) vertical cross section

Figure 3.29. Design of Sloped-Floor Melter (Igarashi and Takahashi 1991)

pour rate between 12 to 20 kg/h. Samples of the molten glass were taken during each pour and analyzed for noble metal content by XRF. To examine the accumulation of noble metals, the melters were allowed to cool with a small amount of glass inside, and were cut vertically through the sloping floor (Igarashi and Takahashi 1991).

Figure 3.30 shows the operating results for the melter with the 30° sloped floor. While the power and electrode temperature were kept relatively constant during operation with noble metals, the glass temperature on the melter floor gradually increased as the electrode resistance decreased. This indicates an accumulation of noble metals on the melter floor was providing a much higher electrical conductivity than that of the surrounding molten glass (Igarashi and Takahashi 1991).

Operating results for the melter with the 45° sloped floor are shown in Figure 3.31. The power and electrode temperature were kept relatively constant during operation, except for batches 8 and 9, in which the power was changed deliberately. During operation, the electrode resistance and glass temperature did not fluctuate significantly as a result of noble metals. Therefore, no effects of noble metals accumulation on the melter floor were observed (Igarashi and Takahashi 1991).

Table 3.20. Target Compositions of High-Level Waste Glasses (Igarashi and Takahashi 1991)

Component	Glass P0699	P0686
Glass Batch		
SiO_2	45.00	45.00
B_2O_3	14.20	14.20
Al_2O_3	3.60	3.60
Li_2O	3.00	3.00
Na_2O[a]	10.00	10.00
CaO	3.00	3.00
ZnO	3.0	3.00
BaO[a]	3.49	3.49
Simulated Wastes		
K_2O	0.86	–
SnO_2	–	0.02
Fe_2O_3	2.78	2.04
Cr_2O_3	0.10	0.10
NiO	0.58	0.23
P_2O_3	0.30	0.30
SrO	0.30	0.30
ZrO_2	1.46	1.46
MoO_3	1.45	1.45
TeO_2	0.19	0.19
CoO	0.14	–
Y_2O_3	0.18	0.18
La_2O_3	0.42	0.42
CeO_2	3.34	3.34
Pr_6O_{11}	0.42	0.42
Nd_2O_3	1.38	1.38
Sm_2O_3	0.29	0.24
MnO_2	–	0.37
Rb_2O	–	0.11
Cs_2O	–	0.75
Eu_2O_3	0.05	0.05
Gd_2O_3	0.14	0.02
RuO_2	–	0.74
Rh_2O_3.	–	0.14
PdO	–	0.35
Ag_2O	–	0.02
CdO	–	0.02
SeO_2	–	0.02

(a) Na_2O and BaO contents include an amount from the waste.

Upon examination of the sedimentation layers after the melters cooled, the maximum thickness of noble metals in the 30° sloped-floor melter and the 45° sloped-floor melter was 40 mm and 20 mm, respectively. Figures 3.32 and 3.33 depict the relative locations of the sediments in relation to the melter bottom. Although a layer of noble metals did accumulate on the floor of the 45° melter, it had no observed effect on electrode resistance or glass temperature. Most likely, the electrodes were too far from the sediment layer to permit electrical conduction through the layer (Igarashi and Takahashi 1991).

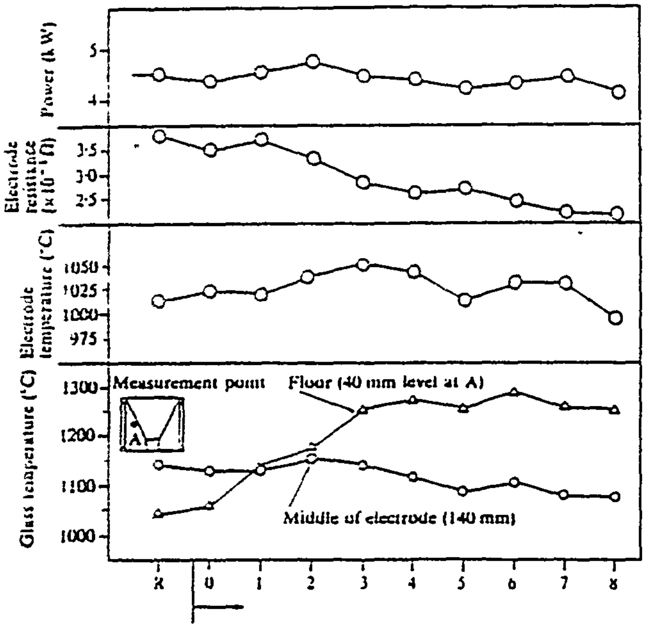


Figure 3.30. Operating Results for Melter with 30° Sloped Floor (Igarashi and Takahashi 1991)
R Reference Batch (No Noble Metals)
0 Glass with Noble Metals
1-8 Batches with Noble Metals

Analysis of the sediments showed that the noble metals existed as needle-shaped RuO_2 particles, ranging in size from 5 to 12 μm, round Pd-Te alloy particles with a size of 15 to 20 μm, and Ru-Rh-Pd alloy particles of 5 to 10 μm. Drain efficiency (the mass of noble metals drained divided by the mass of noble metals fed) was calculated for each batch processed. The estimated overall drain efficiency for the 30° sloped-floor melter was 20% for RuO_2 and 35% for Pd. For the 45° sloped-floor melter, the estimated overall drain efficiency was 70% for RuO_2 and 90% for Pd. The authors concluded that the 45° sloped floor melter was effective in draining the noble metal sediment. However, subsequent tests with noble metals conducted at PNC indicated that a 70% drainage efficiency was insufficient for successful long-term melter operation, and additional tests were required to improve the melter design. These tests were performed with the Mock-up Melter III as described later in this report (Igarashi and Takahashi 1991).

3.4.6 Pilot-Scale LFCM: IHI

Ishikawajima-Harima Heavy Industries (IHI) designed and constructed a pilot-scale LFCM based on technology developed by PNC. A physical modeling test was conducted to develop a melter design that would avoid accumulation of noble metals on the melter floor. Copper powder was used as a simulant in tests of three-electrode melters with sloped floors to determine temperature distributions and convection flow patterns, as well as noble metal precipitation. In a two-electrode melter, the fluid on the melter floor is poorly heated and therefore is not stirred by natural convection. In a three-electrode

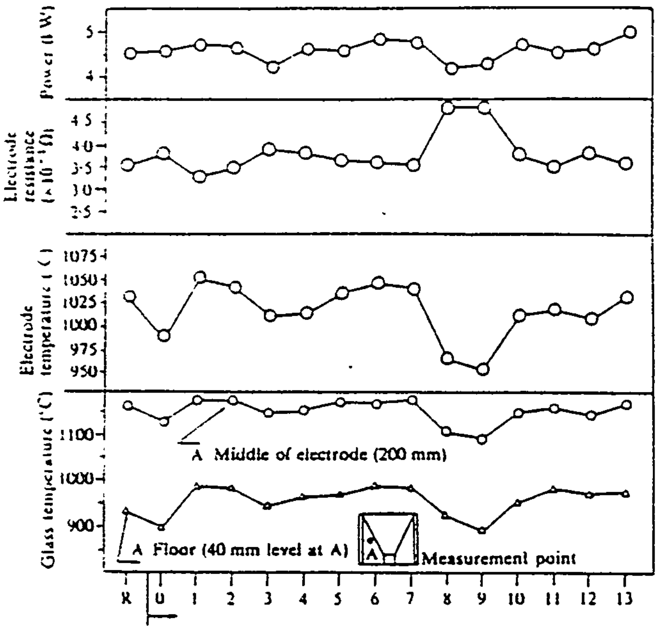


Figure 3.31. Operating Results for Melter with 45° Sloped-Floor (Igarashi and Takahashi 1991)
R Reference Batch (No Noble Metals)
0 Glass with Noble Metals
1-13 Batches with Noble Metals

melter, temperature distribution should be uniform during operation. Results of the modeling tests also showed that the stirring of noble metals from natural convection should prevent electrical shorting between the electrodes in a three-electrode system with a sloped bottom (Asano et al. 1986).

Figure 3.34 is a schematic of the IHI pilot-scale melter in which the basic design is based on results of the physical modeling tests. Design features included a molten glass surface area of 0.25 m^2, a molten glass volume of 93 L, a liquid waste throughput of 150 L/day, and a glass production rate of 70 kg/day. Two main electrodes and one bottom electrode, made of Inconel 690, were included in the design. Glass was poured every 24 hours from the melter through the bottom drain system. To help in the removal of accumulated noble metals, the melter floor was designed with a 45° and 53° sloped bottom (Sakai et al. 1989; Asano et al. 1988).

Three simulated waste streams were processed during the melter operation: two with and one without noble metals. Five campaigns in 1987 produced about 2.3 metric tons of glass. In the second campaign, a thermocouple-well detected a 20- to 30-mm sedimentation layer of noble metals on the melter floor. After complete drainage of the melter, no noble metals sediment was detected on the bottom electrode (Asano et al. 1988).

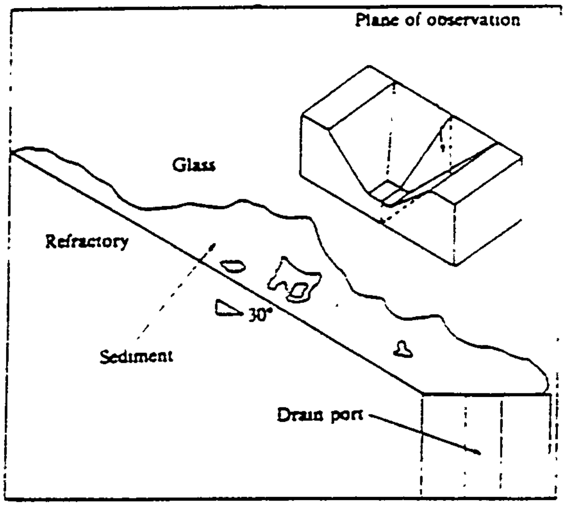


Figure 3.32. Noble Metals Layer in 30° Sloped-Floor Melter (Igarashi and Takahashi 1991)

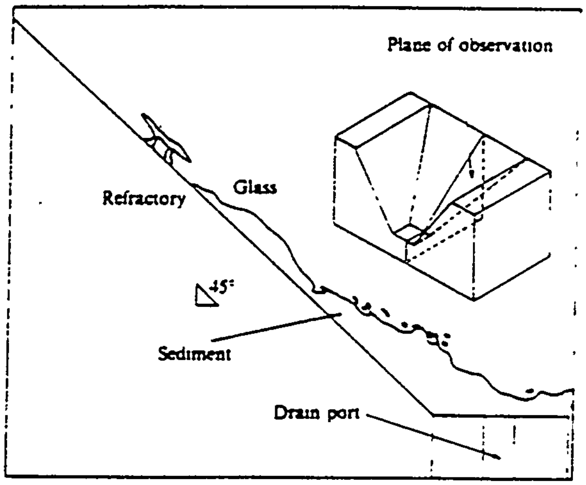


Figure 3.33. Noble Metals Layer in 45° Sloped-Floor Melter (Igarashi and Takahashi 1991)

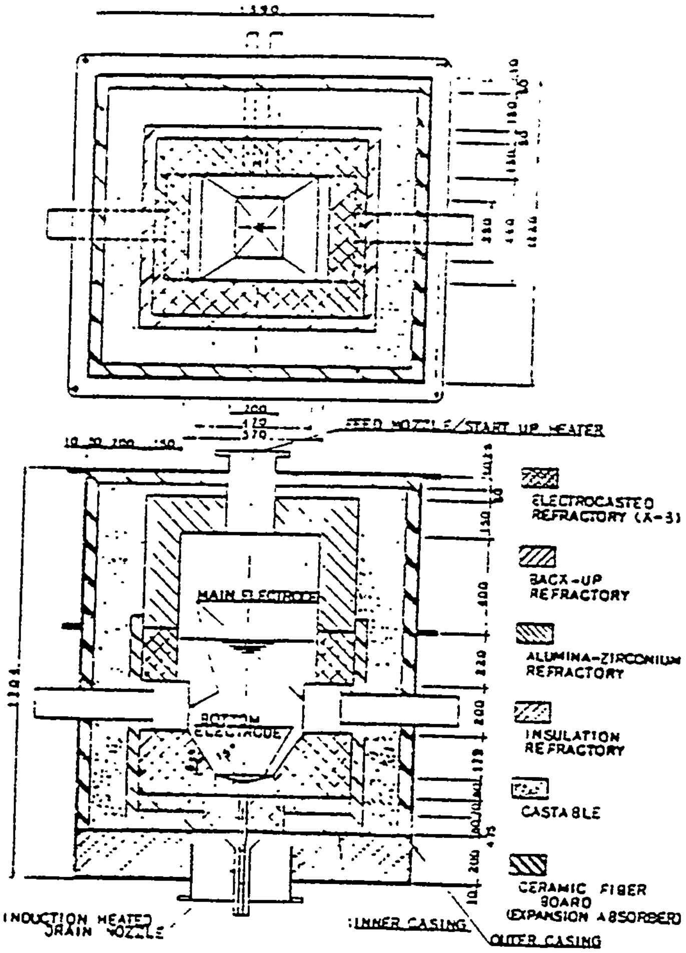


Figure 3.34. Pilot-Scale LFCM Design (Sakai et al. 1989)

3.4.7 Tokai Vitrification Facility: PNC

In 1984, PNC completed the detailed design of the Tokai Vitrification Facility (TVF), which will process HLLW from the Tokai Reprocessing Plant. Construction was completed in April 1992, and the plant is currently under test operation. Several improvements and design decisions for the TVF were made based on previous operating test results. To decrease the volatilization of Ru during melting, a denitration process of the HLLW with formic acid was investigated. However, the process was too difficult to operate and the investigators decided to remove volatilized Ru in the offgas system. To reduce the entrainment of particulates in the offgas, cylindrical glass fiber was selected as the glass additive to be used in the melter. This material reduces the particulate entrainment by one-tenth compared to glass beads (Sasaki et al. 1986).

The LFCM designed for the TVF is shown in Figure 3.35. Design features of this melter include a melting surface area of 0.66 m^2, a maximum glass pool volume of 350 L, an operating temperature of 1050°C to 1150°C, a two-zone induction-heated bottom freeze valve for draining, a glass contact refractory made of Monofrax K-3®, and a 45° sloped floor. Full-scale melter tests of 3 to 8 days, completed in 1986, confirmed that a 45° sloped floor would prevent accumulation of noble metals; more than 90% of the noble metals were drained from the melter during normal operation. Two pairs of electrodes made of Inconel 690 are used: a main pair and an auxiliary pair on the melter bottom. HLLW is fed at a rate of 15 L/h (150 g oxide/L) with fiber glass additive at 6.6 kg/h. Cylinders (70 mm diameter x 70 mm length) of the additive are soaked in the HLLW before feeding; the fibers have a maximum liquid holding capacity of 4 mL/g. The final glass production rate is about 8.8 kg/h with a 25 wt% waste loading (Yoshioka et al. 1989; Torata et al. 1988; Sasaki et al. 1986).

3.4.8 Mock-Up Melter III: PNC

A full-scale mock-up melter for the TVF was constructed in 1987 and began operating in 1988. This Mock-up Melter III is the same size and has the same design as the TVF melter shown in Figure 3.35. During the first four campaigns (16 to 19), 12.4 m^3 of simulated HLLW was vitrified.

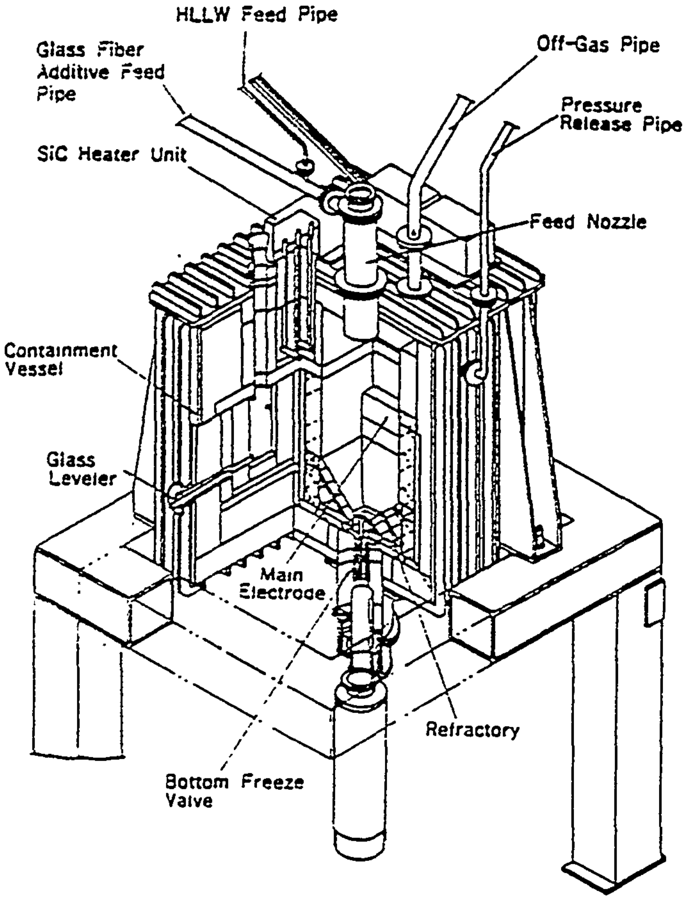


Figure 3.35. TVF Melter Design (Uematsu 1986)

producing 8 metric tons of glass product. In campaign 19, 3.7 m^3 of processed simulated waste included 24.2 kg RuO_2, 10.5 kg PdO, and 3.6 kg Rh_2O_3. The glass composition was about 0.9 wt% RuO_2, 0.34 wt% Pd, and 0.11 wt% Rh.[a] During campaigns 16 to 18, no deposits of noble metals were detected. However, during campaign 19, the electrical resistance decreased approximately 20% between the main electrodes and an approximate 35% decrease was detected between the bottom electrodes. At the end of the campaign, an accumulation of noble metals was present on the melter floor [Chapman (1989), unpublished, endnote 16; McElroy (1989), unpublished, endnote 17; Yoshioka and Takahashi 1990].

Although full-scale melter tests completed in 1986 showed that regular glass draining could remove >90% of noble metals fed to a melter, the remaining 10% could cause problems in melter operation over time. Additional tests performed with Mock-up Melter III investigated a way of decreasing the accumulation of noble metals on the melter floor. In two campaigns (20 to 21), power to the bottom electrodes was adjusted to maintain an internal electrode temperature of 800°C. It was thought that the increased viscosity of colder glass near the melter bottom would significantly slow the settling rate of noble metals particles. The glass temperature near the melter bottom was 800°C to 950°C during periods when pouring did not occur, but it climbed to 900°C to 1050°C during glass pouring (Yoshioka and Takahashi 1990).

Table 3.21 shows the amounts of noble metals fed and the resulting glass compositions for campaigns 20 and 21. Electrical resistance between the main electrodes did not change significantly during melter operation. Resistance between the bottom electrodes dropped as noble metals were fed to the melter, but rose to its original value after each batch was poured. As shown in Figures 3.36 and 3.37, the efficiency of noble metals discharge improved significantly in the 20th campaign, in which the bottom melter temperature was reduced. For RuO_2, the average drainage efficiency went from 57% in campaign 19 to 83% in campaign 20. At the end of campaign 21, a balance of noble metals, shown in Figure 3.38, indicated that less than 1% of the total noble metals fed to the melter actually remained in the melter. The investigators concluded that the method of melter operation used in campaigns 20 and 21 effectively prevents accumulation of noble metals accumulation (Yoshioka and Takahashi 1990).

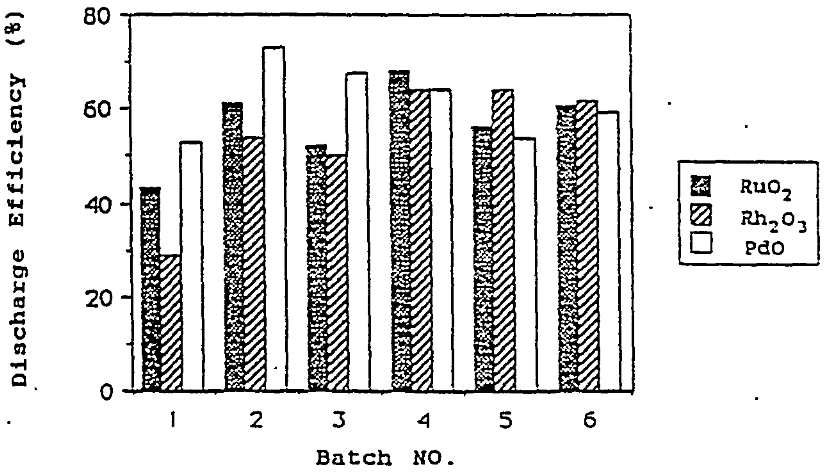
3.4.9 Large-Scale LFCM: PNC

PNC designed a new, large-scale LFCM, and construction was completed in September 1991. Although the design was based on the TVF melter, it was considerably larger with a melting surface area of 2.2 m^2 (compared to 0.66 m^2). Figures 3.39 to 3.41 show sketches of the actual design. Two pairs of electrodes made of MA690 were used. The MA690 is equivalent to Inconel 690/Ni-Cr alloy. The melter bottom had a 49.6°/53.3° sloped floor with a bottom drain freeze valve [Igarashi (1992), unpublished, endnote 18].

(a) An additional source also provided information on noble metals processed in campaign 19, however, the amounts reported of noble metals fed in the waste simulant were lower by 11-20%. The values given here are assumed to be more accurate because they are the most current.

Table 3.21. Noble Metals Amounts and Glass Compositions (Yoshioka and Takahashi 1990)

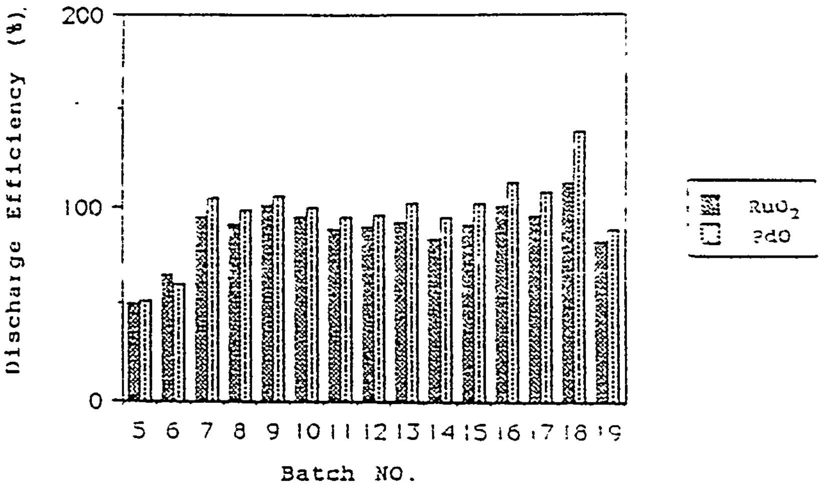
Campaign Number	Noble Metal	Feed Amount (kg)	Content in Feed (g/L)	Content in Glass (wt%)
20	RuO_2	40.8	5.6	0.84
	PdO	22.9	3.2	0.53
	Rh_2O_3	–	–	–
21	RuO_2	41.6	5.6	0.84
	PdO	17.7	2.2	0.37
	Rh_2O_3	1.3	1.0	0.17



Discharge Efficiency of Noble Metals during the Melter Runs (19th Campaign)

Figure 3.36. Noble Metals Discharge Efficiency During Campaign 19 [Chapman (1989), unpublished, endnote 16]

A total of 40.9 m^3 of simulated HLLW was processed in the large-scale melter, producing 30,309 kg glass at an average rate of 44 kg/h. Two waste streams were vitrified: 19.7 m^3 containing noble metals (133.7 kg RuO_2 and 78.5 kg PdO) and 21.2 m^3 without noble metals. Tables 3.22 and 3.23 show target compositions of the glass products. At the end of operation with the waste stream containing noble metals, the melter floor contained residual noble metals, including 0.11 kg RuO_2 and 0.07 kg PdO, 0.08% retained and 0.09% retained, respectively [Igarashi (1992), unpublished, endnote 18].



Discharge Efficiency of Noble Metals during the Melter Runs (20th Campaign)

Figure 3.37. Noble Metals Discharge Efficiency During Campaign 20 [Chapman (1989), unpublished, endnote 16]

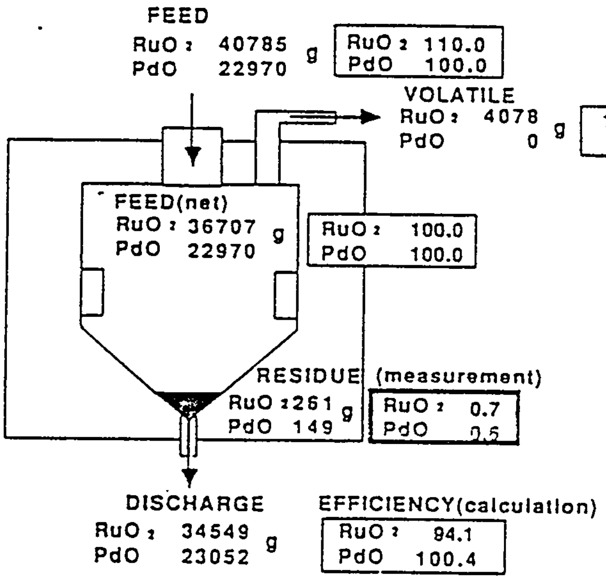
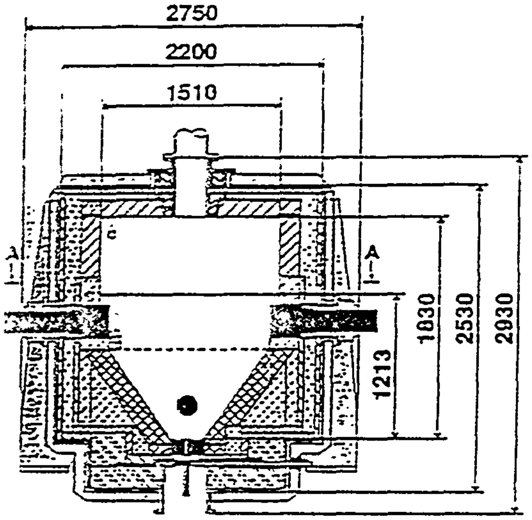
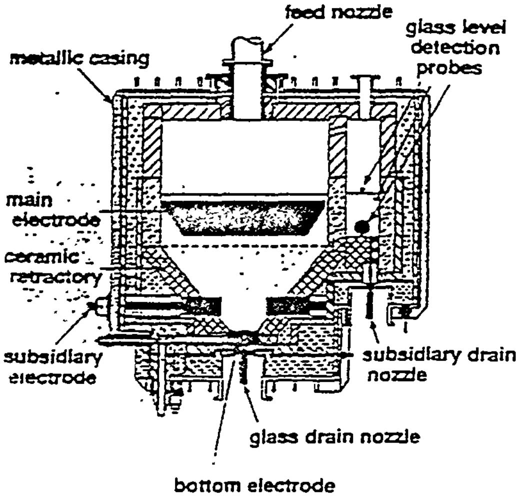


Figure 3.38. Noble Metals Balance After Campaign 21 (Yoshioka and Takahashi 1990)



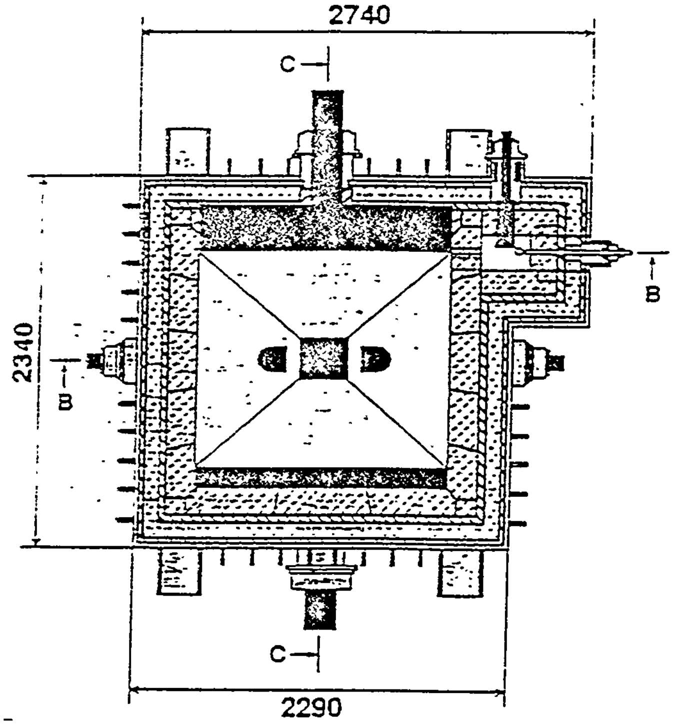
Large-scale Melter
(C-C vertical section)

Figure 3.39. Large-Scale Melter, C-C Vertical Cross Section [Igarashi (1992), unpublished, endnote 18]



Large-scale Melter
(B-B vertical section)

Figure 3.40. Large-Scale Melter, B-B Vertical Cross Section [Igarashi (1992), unpublished, endnote 18]



Large-scale Melter
(A-A horizontal section)

Figure 3.41. Large-Scale Melter, A-A Horizontal Cross Section [Igarashi (1992), unpublished, endnote 18]

Several tests were later completed to determine the effects of temperature and Na_2O content on the length of RuO_2 crystals. Changing the melting temperature from 1000°C to 1200°C resulted in an increase of RuO_2 crystal length from 0 to 8 μm . Increasing Na_2O content from 5% to 15 wt% increased the RuO_2 crystal length from 0 to 6 μm [Igarashi (1992), unpublished, endnote 18].

Table 3.24 provides a summary of data on melter development in Japan. In general, the accumulation of noble metals decreases as the slope of the melter floor increases. With a 30° sloped floor, retention of RuO_2 and of PdO were approximately 80% and 65%, respectively. Increasing the slope to 45° decreased the retention of noble metals, with values of 12.5% to 43% for RuO_2 and 0% to 39% for PdO. In addition to increasing the slope of the melter floor, a method of glass cooling near the melter floor proved successful in limiting deposition of noble metals. The cold, viscous glass near the bottom acts as a barrier to particles of noble metals. The noble metals therefore remain in the molten glass above the layer of cold glass. A decrease in the bottom electrode temperature to 800°C resulted in a decrease of noble metals retention from 43% to 17% for RuO_2, and from 39% to 3% for PdO. As mentioned earlier, it was recommended that mechanical stirring or air sparging be incorporated into future designs. It appears that tests using these methods have not been completed. Therefore, information on the effects of glass stirring is currently not available.

Table 3.22. Target Composition of Glass Product With Noble Metals [Igarashi (1992), unpublished, endnote 18]

	Oxides	wt%
Glass Additives	SiO_2	46.72
	B_2O_3	14.22
	Na_2O	6.25
	Al_2O	5.04
	Li_2O	3.01
	CaO	3.01
	ZnO	3.01
	Total	81.26
Waste	Na_2O	3.75
	P_2O_5	0.17
	Fe_2O_3	1.55
	Cr_2O_3	0.29
	NiO	0.25
	K_2O	0.10
	Cs_2O	0.69
	SrO	0.24
	BaO	0.44
	ZrO_2	1.61
	MoO_3	1.21
	MnO_2	0.57
	CoO	–
	RuO_2	0.87
	PdO	0.51
	Ag_2O	0.02
	CdO	0.03
	SnO_2	0.03
	SeO_2	0.02
	TeO_2	0.15
	R. E.	6.25
	Total	18.75

Replacements: Rb → K, Tc → Mn, Rh → Pd Gd, Y, Sb, La, Ce, Pr, Nd, Sm, Eu, Actinides → Rare earth mixture (RE)

Table 3.23. Target Composition of Glass Product Without Noble Metals [Igarashi (1992), unpublished, endnote 18]

	Oxides	wt%
Glass Additives	SiO_2	46.72
	B_2O_3	14.22
	Na_2O	6.25
	Al_2O	5.04
	Li_2O	3.01
	CaO	3.01
	ZnO	3.01
	Total	81.26
Waste	Na_2O	3.75
	P_2O_5	0.17
	Fe_2O_3	2.42
	Cr_2O_3	0.29
	NiO	0.63
	K_2O	0.10
	Cs_2O	0.69
	SrO	0.24
	BaO	0.44
	ZrO_2	1.61
	MoO_3	1.21
	MnO_2	0.57
	CoO	0.13
	RuO_2	–
	PdO	–
	Ag_2O	–
	CdO	0.03
	SnO_2	0.03
	SeO_2	0.02
	TeO_2	0.15
	R. E.	6.26
	Total	18.74

Replacements: Ru → Fe, Pd → Ni, Rb → K, Tc → Mn, Rh → Co
Gd, Y, Sb, La, Ce, Pr, Nd, Sm, Eu, Actinides → Rare earth mixture (RE)

Table 3.24. Summary of Japan's Melter Development

Melter	Characteristics	Campaign/Run	Dates	Noble Metals Retention
ETF - A	0.3 m^2 area, overflow drain, flat bottom		1978-1984	N/A
ETF - B	0.59 m^2 area, overflow drain, flat bottom		1980-1983	N/A
ETF - C	0.3 m^2 area, bottom drain, flat bottom		1978-1984	N/A
MTF Mock-up	160 L volume, overflow & bottom drain, flat bottom	5 Campaigns Total	1982-1983	First detected noble metals, data not available
Advanced-B	45° floor, 0.53 m^2 area, bottom drain	Campaign #1	11/85-12/85	12.5% for RuO_2, 0% for PdO
Advanced-B	45° floor, 0.53 m^2 area, bottom drain	Campaign #2	5/86-6/86	27.5% for RuO_2, 0% for PdO
Advanced-B	45° floor, 0.53 m^2 area, bottom drain	Campaign #3	7/86-8/86	13.9% for RuO_2, 0% for PdO
CPF	bottom drain	11 Runs Total	12/82-1987	Data not available
Small-Scale	30° floor, 0.054 m^2 area, bottom drain	8 Batches Total	Estimated 1983-1984	80% for RuO_2, 65% for Pd
Small-Scale	45° floor, 0.054 m^2 area, bottom drain	13 Batches Total	Estimated 1983-1984	30% for RuO_2, 10% for Pd
Pilot-Scale IHI	0.25 m^2 area, 45°/53° floor, bottom drain	5 Campaigns, 2.3 tons glass	1987	Data not available
Mock-up II	Data not available		1984-1986	Data not available
Mock-up III	0.66 m^2 area, 45° floor, bottom drain	Campaign 16, 2.6 tons glass	2/88-3/88	Reported no accumulation
Mock-up III	0.66 m^2 area, 45° floor, bottom drain	Campaign 17, 1.1 tons glass	6/88	Reported no accumulation
Mock-up III	0.66 m^2 area, 45° floor, bottom drain	Campaign 18, 1.8 tons glass	7/88	Reported no accumulation
Mock-up III	0.66 m^2 area, 45° floor, bottom drain	Campaign 19, 2.5 tons glass	1/89	43% for RuO_2, 39% for PdO
Mock-up III	0.66 m^2 area, 45° floor, bottom drain, 800°C bottom electrodes	Campaign 20, 5.6 tons glass		17% for RuO_2 3% for PdO
Mock-up III	0.66 m^2 area, 45° floor, bottom drain, 800°C bottom electrodes	Campaign 21		< 1%
Large-Scale	2.2 m^2 area, 49.6°/53.3° sloped floor, bottom drain	30.3 tons glass	1991 -	0.08% for RuO_2, 0.09% for PdO

3.5 Vitrification Studies in England

In the late 1970s, the Atomic Energy Research Establishment-Harwell in Oxfordshire, England, began to take an interest in the joule-heated ceramic melter (JCM) process. Harwell developed a final design after studying various concepts developed from observation of U.S. melter designs; a schematic is shown in Figure 3.42. KTG Ltd, a company that specialized in glass-making furnace and construction, built a full-scale JCM melter and delivered it to Harwell in March 1982. Because of its unique design, it was expected that this melter would remain in operation more than five years (Morris 1985; Morris et al. 1986b).

During installation of the full-scale JCM in August 1982, financial difficulties canceled the project. Harwell then designed a one-third scale JCM, which was similar to the full-scale JCM except for its smaller size. It had a melting cavity of 0.2 m x 0.2 m compared to the full-scale melter cavity of 0.6 m x 0.6 m. Construction of the new melter was completed in October 1982. Design features of the one-third scale melter, shown in Figure 3.43, included a pair of Inconel 690 electrode plates that were supported from above and stood on the melter floor. This electrode configuration was chosen to minimize current density at the electrode. The melter cavity was constructed from Monofrax K-3 bricks. A vertical pipe was installed to withdraw the glass product using suction through the top of the melter into small 10-L canisters. The tip of the glass removal pipe was about 10 mm above the melter floor (Morris 1985; Morris et al. 1986a, 1986b).

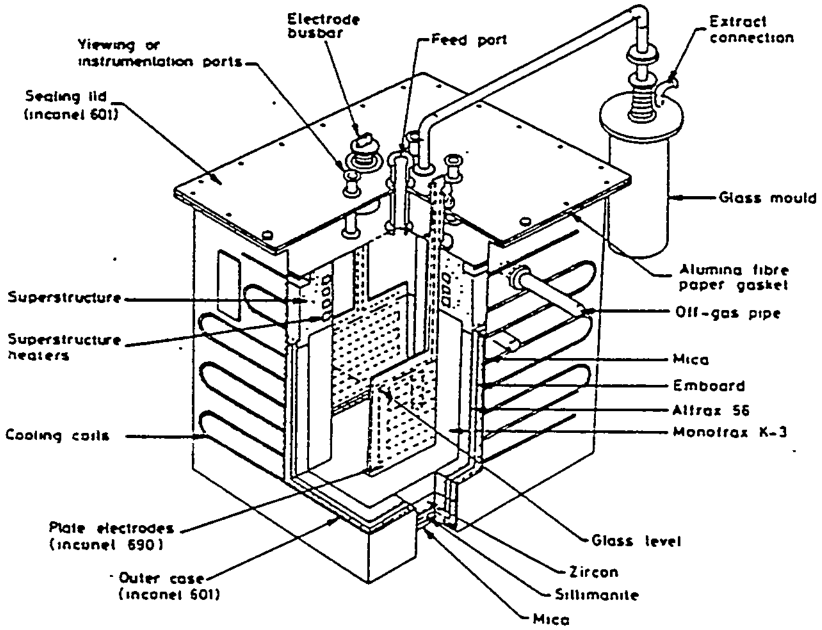


Figure 3.42. Full-Scale JCM Design (Morris 1985)

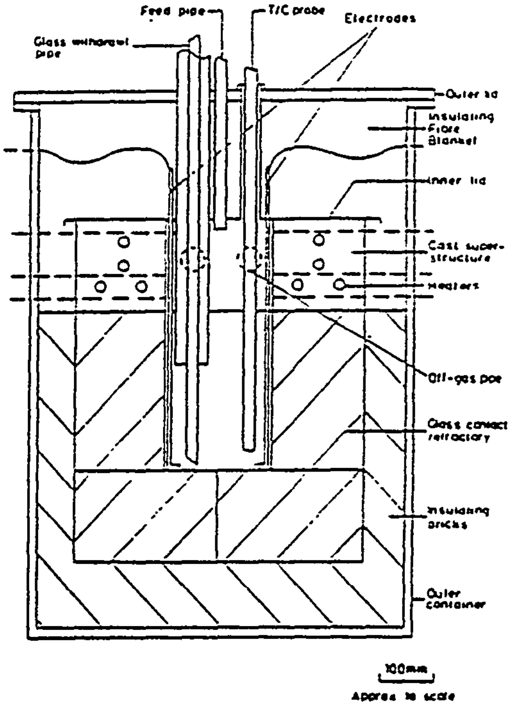


Figure 3.43. One-Third JCM Design (Morris et al. 1986b)

During 10 months, the one-third scale JCM operated approximately 6000 hours, but was idling at 1000°C most of that time. During operation, 7 canisters were filled in 64 hours of pouring, with an average glass quantity of 16.7 kg/canister. The melter feed usually consisted of 75 wt% M9 frit and 25 wt% Magnox calcine; compositions are shown in Tables 3.25 to 3.27. At times, the Magnox calcine was replaced with an LWR simulant. After 7 months of operation, the electrical resistance between the electrodes had noticeably dropped. The melter power supply became current limited about a month later, causing the idling temperature to fall below 1000°C. When the cold, viscous melt could no longer be poured (at 850°C), the melter was shut down and cooled; it was dismantled in February and March 1984 (Morris et al. 1986b).

Table 3.25. M9 Frit Composition (Morris et al. 1986b)

Oxide	wt%
Na_2O	11.0
Li_2O	5.4
B_2O_3	29.5
SiO_2	54.1

Table 3.26. Waste Simulant Compositions (Morris et al. 1986b)

	Wt% as Oxide	
Element	Magnox	LWR
Total fission products	39.16	3.4
Total actinides	0.2	1.4
Al	20.0	–
Fe	10.6	2.7
Cr	2.2	0.7
Ni	1.4	0.5
Mg	24.8	–
Zn	1.7	–
Gd	–	31.3

Examination of the melter electrodes showed localized corrosion in the lower sections, with material weight losses of 14.6% and 4.2% from the two electrodes. In two places corrosion had penetrated completely through the electrodes. Samples of the electrodes taken from areas of minimal corrosion showed evidence that the slow corrosion was a result of oxidation of Cr to Cr_2O_3. However, a large quantity of Ru (average concentration 15.8 wt%) was found near areas of high corrosion. The glass target composition was only 0.6 wt%. A layer (estimated at < 10 mm thick) on the melter floor contained a high concentration of Ru. Further examination of the bottom of the electrodes showed signs of melting, indicating localized, excessive heating of the glass, which accelerated the rate of electrode corrosion. Separate tests showed that the high Ru concentrations did not directly affect the electrode corrosion. It was concluded that, because deposition of Ru cannot be prevented, a new melter capable of removing the sediments as they are formed should be designed (Morris et al. 1986b).

3.6 Vitrification Studies Conducted at PNL

Noble metals have been included in glass development studies since some of the earliest waste solidification and vitrification work at PNL. The insolubility of noble metals in glasses was observed at those early stages and was also known from the literature; however, the effect this insolubility could have on melter operation was not known. Early work focused on waste-form durability and leaching behavior rather than processing concerns. As the processing concerns related to noble metal insolubility in glasses became known, studies became focused on determining particle agglomeration mechanisms, settling behavior, and related subjects.

Early work at PNL (Mendel et al. 1977, Ross et al. 1978) addressing low-melting (< 1100°C) borosilicate waste glasses used several high-level waste simulants and glass-forming frits. Melts were conducted at laboratory-scale (~ 100g). The simulant preparation and melting procedures are not well

Table 3.27. Waste Simulant Compositions (Morris 1985)

Highly Active Liquid Waste Simulates Oxide Concentrations g/L

Oxide	Magnox	LWR
55 l/te U		
160 l/te U		
Ag_2O	–	0.11816
Al_2O_3	51.53083	–
BaO	4.11682	9.15526
CdO	–	0.29701
Co_3O_4	–	–
Cr_2O_3	3.18885	2.04618
Cs_2O	7.62374	13.67646
Fe_2O_3	25.99508	7.57757
In_2O_3	–	8.7e-03
K_2O	–	–
Li_2O	–	–
MgO	51.25580	–
MoO_3	13.84362	25.50500
Na_2O	–	–
NiO	2.08229	1.27252
Rb_2O	1.03275	1.85912
Sb_2O_3	–	0.07183
SeO_2	–	0.36537
SnO_2	–	0.31740
SrO	2.82749	4.96692
TeO_2	1.78952	2.75170
Y_2O_3	1.69149	2.92086
ZnO	2.26311	–
PO_4	4.54545	0.47000
RuO_2	7.15273	13.69264
ZrO_2	13.28438	24.71940
Gd_2O_3	–	87.02262
La_2O_3	3.80140	7.09008
CeO_2	8.65360	16.14004
Pr_6O_{11}	3.77048	7.03241
Nd_2O_3	12.51679	23.34536
Sm_2O_3	2.16339	4.03499
RE_2O_3	30.90567	57.64288
Totals	225.12964	256.45760

All oxides in the HALS are present as the nitrate form except CdO, In_2O_3, MoO_3, Sb_2O_3, SeO_2, SnO_2, and TeO_2.

described; however, frit and waste compositions are available in the references. The waste glasses designated 77-107, 77-260, and 72-68 contained phases high in Pd and Ru. X-ray diffraction (XRD) studies identified the Ru species as RuO_2.

A detailed analysis was performed for glass 72-68. The XRD analysis showed tetragonal RuO_2 crystals (lattice constants $a_o = 4.5$ Å, $c_o = 3.1$ Å) after melting at 1000°C. These crystals comprised [illegible] wt% of the glass, but did not exceed approximately 1 µm in size. They were not visibly altered after [illegible] year at 700°C. The product glass contained Pd at 1.0 wt% with a maximum particle size of [illegible] µm and a [illegible]00-µm Rh particle. The observed increase in concentration of Rh toward the top of the sample was presumed to have been caused by particles rising with bubbles.

Later, work was done at PNL to examine the recovery of noble metals from fission product waste (Jensen et al. 1983). Investigators found that adding a metal oxide and a reducing agent to the waste and glass-formers permits recovery of most of the noble metals. The reducing agent reduces the metal oxide to pure metal, which then acts as a "scavenger" to collect the noble metals. The metals fall to the bottom of the melter, from where they can be drained, separated, and purified. Investigators proposed that the metal mixture could be drained from the bottom of a melter through a freeze valve. The freeze valve concept had been tested using glass but required evaluation for use in draining molten metals.

Laboratory studies were performed to determine the efficiency of this process in noble metal recovery. A mixture of simulated waste, glass-formers, a scavenger oxide, and a reducing agent was melted in a porcelain crucible at 1100°C for 2 hours. The melts were then poured onto a steel plate, where the metal nodule, if formed, would separate from the glass. The metal and glass were then analyzed to determine recovery of the noble metals by the scavenger metal. Various metal oxides and reducing agents were evaluated. In general, 70% to 100% of the palladium, 70% to 100% of the rhodium, and 30% to 70% of the ruthenium could be recovered. At that time, the motivation for noble metal recovery was economic, and was not related to melter operational concerns.

After it became known that the noble metals had the potential to form a sludge that would interfere with melter operation, tests were done to obtain a preliminary characterization of noble metals in simulated HWVP glass [Geldart et al. (1987), unpublished, endnote 19]. These tests included crucible melts and a continuous liquid-fed minimelter (LFMM) run, all using the reference HW-39 waste and frit. The noble metals were added as the oxides RuO_2, PdO, and Rh_2O_3 with average particle sizes of approximately 15 µm, 5 µm, and 2 µm, respectively. The noble metal oxide concentrations in the glass were as follows:

RuO_2	0.16 wt%
PdO	0.05 wt%
Rh_2O_3	0.05 wt%

The crucible melts were performed to determine the effects of redox state, temperature, duration of melt, and noble metal concentration on the behavior of noble metals in the melt. Ferrous/ferric (Fe^{-2}/Fe^{-3}) ratios studied were 0.0, 0.03, 0.27, and 0.65. Temperatures studied were 940°C, 1100°C, and 1170°C. The various melt durations were 2.4, 24, and 240 hours, and total noble metal concentrations used were 0.26, 2, and 11 wt% of the total glass oxides. An increased Fe^{+2}/Fe^{+3} (redox) ratio caused a decrease in the number of spinel crystals present in the glass product; however, the degree to which this occurred depended on the reducing agent used. For example, no spinels were observed at a Fe^{+2}/Fe^{+3} ratio of 0.27 when formic acid was the reducing agent. However, when sugar was the reducing agent, spinels were present at a Fe^{+2}/Fe^{+3} ratio of 0.65. At higher Fe^{+2}/Fe^{+3} ratios, noble metal particles were of high purity, with little mixing of elements. It appears likely that the particles were not metallic, but that is not stated in the report. Increases in temperature enhanced the settling rate of agglomerated particles and therefore decreased the number and size of particles suspended in the melt. Increases in duration of the melt caused increases in the size of particle observed in the melt and in the amounts of settled particles. The only apparent effect of increasing concentration of noble metals was to increase the total number of particles and agglomerates.

Most of the agglomerated particles observed in these crucible melts were < 10 µm. Some of the particles were alloys of Ru, Rh, and Pd, with traces of Cu, Fe, Ni, and Cr. Palladium was observed alloyed with Te in some cases. XRD analysis showed particles that were pure RuO_2 and RhO_2. Particles were seen adhering to bubbles, and some noble metals had accumulated at the surface of the melts.

The mini-melter test was conducted to create more representative melter conditions than the crucible melts. The LFMM is a laboratory-scale continuously fed melter. It consists of an Inconel crucible with an overflow tube where glass is discharged. The crucible is located in a furnace, as shown in Figure 3.44. The cross section of the Inconel crucible is shown in Figure 3.45. Liquid feed was fed to the LFMM at a rate of between 180 and 300 mL/h. The reference HW-39 feed was used. The glass depth was approximately 10 cm. The temperature at the bottom of the crucible varied from 1095°C to 1150°C, and the temperature at the top was 660°C to 1030°C.

The discharged glass was analyzed by XRF, SEM/EDAX, and ICP. The results showed mostly submicron Ru and Pd particles. A core sample taken upon completion of the LFMM test revealed a 0.5 cm metal nodule at the bottom of the crucible, which was mostly an alloy of all three noble metals. Numerous other metal nodules were found at the bottom of the melt, many of which were under the tip of an Inconel thermowell. The thermowell is believed to have caused the precipitation of noble metals, possibly by oxidation of chromium in the Inconel and corresponding reduction of the noble metals. The chromium concentration in the discharged glass was higher than the target concentration; thus, some of the Inconel may indeed have oxidized. The behavior of noble metals in the LFMM may not be representative of their behavior in the HWVP, because the noble metals were added as oxides rather than as soluble nitrates or other complexes. In addition, redox conditions could not be accurately controlled in the LFMM. The expected range of Fe^{+2}/Fe^{+3} ratios (from crucible melts) was 0.0 to 0.3. Actual values obtained in the LFMM were 0.18 to 0.51, again, a likely result of oxidation of the Inconel.

Because the method of noble metal particle agglomeration was not well understood, an effort was made to generate ideas on how such agglomeration might occur. Rough calculations (Hrma, unpublished, endnote 8) assuming that all particles in a typical glass melt are micron-sized RuO_2 particles evenly spaced throughout the melt showed that settling of individual particles cannot account for the

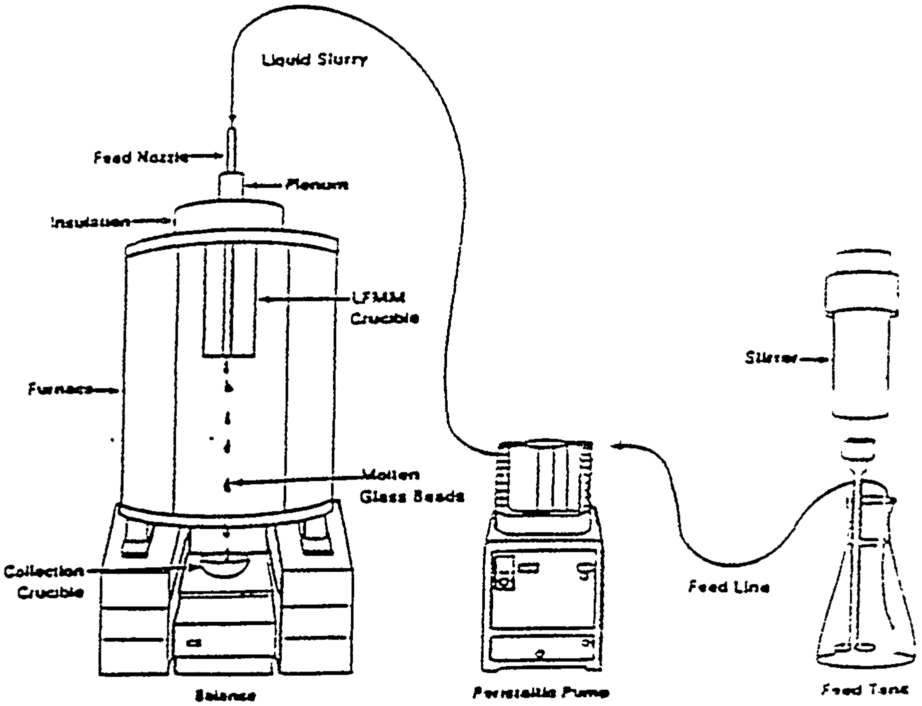


Figure 3.44. Schematic of Experimental Apparatus Used in LFMM Studies

sludges formed on melter floors. Furthermore, it was believed that the individual particles could not significantly agglomerate solely due to random collisions in the melt. The proposed mechanism was shear-induced agglomeration at the cold cap-melt interface.

A relatively simple model was created to determine if agglomeration rates caused by shear could be significant (Lessor et al., unpublished, endnote 9). Results indicated that shear-induced agglomeration could be significant, especially when combined with other agglomeration mechanisms, such as electric field interaction, hydrodynamic interaction, and bubble phenomena.

Additional crucible studies were performed to examine agglomeration and settling of noble metal particles, particularly RuO_2 (Cobb and Hrma 1990). Glass with a total noble metal oxide concentration of 0.45 wt% (0.27 wt% RuO_2, 0.09 wt% PdO, 0.09 wt% Rh_2O_3) was mixed as oxide particles < 100 μm and was melted at 1150°C for 95 minutes. The glass was then cooled, crushed, and disc-milled, and a portion was remelted at 1150°C for 25 minutes. The samples were then heated in alumina crucibles at 1050°C for 15 minutes, 2 hours, 6 hours, 14 hours, 64 hours, or 140 hours, and the product glasses were examined by optical microscopy. In addition, two samples were heated in platinum crucibles for 16 and 64 hours. The RuO_2 was initially present as particles approximately 1 μm in diameter.

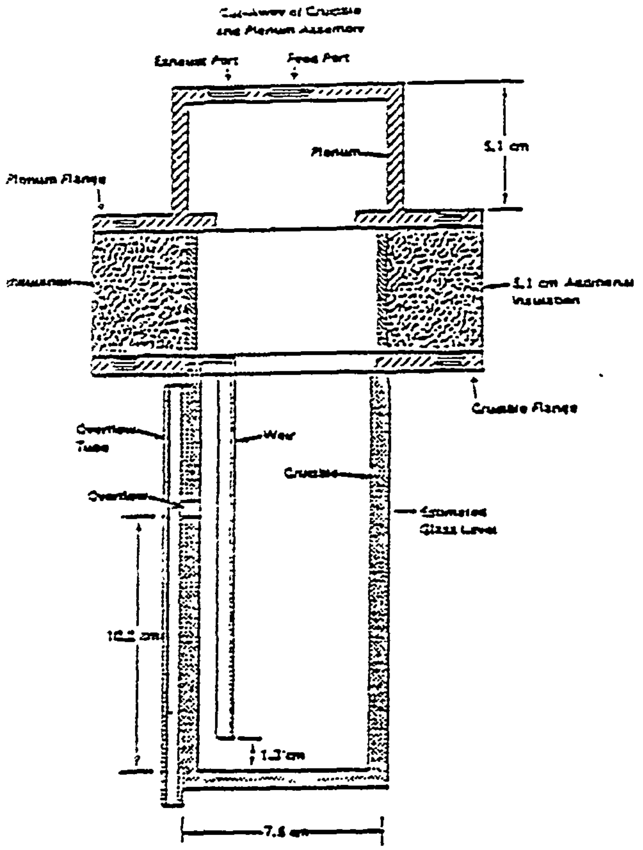


Figure 3.45. Cross Section of the Inconel Crucible Used in the LFMM Studies

Examination of the glasses indicated that much of the agglomeration occurred in the melt meniscus, where velocity gradients would be expected to be greatest. The 2-hour sample showed agglomerates of up to 50 μm dispersed throughout the melt, although most particles were only 1 to 2 μm. Agglomerates were present mainly in the upper half of the 14-hour melt, whereas at 16 hours agglomerates were again dispersed throughout the melt. In melts conducted for longer than 14 hours, a layer of large agglomerates covered the bottom of the crucible. The 64-hour melt contained a 3.5- x 1.5-mm agglomerate beneath the center of the upper melt surface and smaller particles of metallic Rh and Pd.

Calculations using Stoke's law estimate that a spherical RuO_2 particle with a diameter of 1 μm would settle 1 cm in 278 days. Therefore, agglomeration must precede settling. Because the mechanism for agglomeration was velocity-induced shear, particularly in the crucible meniscus, these results cannot be directly correlated to noble metal behavior in a melter. Therefore, it was necessary to examine agglomeration in a representative melter environment.

3.7 Endnotes(a)

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Data Package 1, Appendix B

Low-Temperature, Joule-Heated, Ceramic-Lined Melter: Evaporator Coupled to Melter

During the June meeting, it was suggested that the size of the LCTM could be reduced by evaporating the feed before adding it to the melter. The suggestion was to put a vertical wiped-film evaporator (WFE) directly above the melter such that the dried solids would fall onto the melt pool surface. This appendix provides sizing information for evaporators for various configurations of the LTCM. During the course of putting together the other data packages, it was suggested that the other melters could also benefit from the use of an evaporator. Information on dry-fed versions of the CCM, stirred melter, and Pochet melter were included in the respective data packages, but information on evaporators for these configurations was not available. Therefore, information on evaporators for the other melter configurations will also be included in this appendix. This appendix will cover only evaporators; calciners are discussed in the CCM data package.

Description of Technology

WFEs, also called agitated thin-film evaporators, can dry liquids down to solid powders; their heating surface consists of one large-diameter tube, which may be either straight or tapered, horizontal or vertical. The outside of the tube is heated with steam, oil, or other high-temperature media, such as Dowtherm. Liquid is spread on the inside tube wall by a rotating assembly of blades that either maintain a close clearance from the wall or actually ride on the film of liquid on the wall. The high rotor speeds (tip speeds of 20 to 40 ft/sec) allow handling of viscous materials. WFEs are used only for the most difficult materials because of their expensive construction (Perry and Chilton 1973).

Evaporators that have been tested for drying HLWs include horizontal WFEs, vertical WFEs, and thermosyphons. The CCM pilot plant in Russia is designed to pre-dry the nitric acid feed down to 20% moisture with a vertical WFE. Testing with WFEs has been done at PNL, and is currently being done at Oak Ridge National Laboratory (ORNL).

Wiped Film Evaporator Work at Pacific Northwest Laboratory

Horizontal and vertical WFEs were tested at PNL in the 1970s for predrying feed before sending it to an in-can melter, a metallic melter, or a ceramic melter. All of this work was done with Purex simulants (various metallic nitrates and oxides in 1 to 3 molar nitric acid). A horizontal WFE with a 5 ft^2 heat transfer area was initially tested (Dierks and Bonner 1975). This evaporator operated at 450 rpm with a tip speed of 22 ft/sec., and water cooled, graphite-to-stellite mechanical seals were used to seal the evaporator. The feed solution was preheated to a few degrees below its boiling point. The feed was concentrated to 50% solids (the consistency of mayonnaise) because the WFE was found to foul at higher solids concentrations, and in some instances, the product had to be pumpable. When the WFE was directly coupled to a continuous metallic melter (1150°C), the frit was added to the evaporator feed. When the WFE was directly coupled to an in-can melter the frit was added to the canister separately. When the evaporator was indirectly coupled to the ceramic melter, the concentrate was collected and later pumped into the melter. For the ceramic melter demonstrations, frit was added both in the evaporator feed and as a separate feed stream to the melter. Feeding a wet evaporator concentrate to a melting system reduced melting capacities to 20% to 50% of those of comparable systems receiving calcined wastes. This reduced melting capacity is assumed to be a result of incomplete drying of the slurries. Clogging occurred when the calciner was coupled directly to a melter. Heat transfer from the melter would calcine the partially dried feed near the exit of the evaporator. This was felt to be a result of incomplete drying of the slurry in the evaporator. Various water-cooled nozzles were tested with limited success.

Two series of tests with PUREX simulants were also completed in pilot plant facilities of two commercial manufacturers of WFEs (McElroy 1975a). These tests were done to determine if a simulated HLW slurry could be evaporated to a free-flowing solid in a single pass through a WFE. These short tests did demonstrate that the slurries could be evaporated to 10% to 20% liquid (free flowing). Processing rates were estimated to be in the range of 2 to 11 L/h•ft^2 of evaporator heat transfer surface. A 0.88 ft^2 horizontal Rototherm Artisan WFE, a 10.8 ft^2 LUWA D-210 horizontal dryer, and a 3 ft^2 LUWA CP-150 vertical WFE were tested with steam and hot oil as heat transfer media. All of the units evaporated the slurry down to a 'dry' product (10% to 20% of about 17 molar nitric acid). Little, if any, denitration was achieved in the evaporators, and the products were 55 wt% to 58 wt% oxide. The vertical WFE operated at 1575 rpm with a 5-hp motor and was tested only with hot oil as a heat transfer medium. The product was a uniform powder that averaged 11 wt% liquid (17 molar nitric acid). It was noted that the vertical WFE had a higher solids buildup on the paddles on the rotor shaft than with either of the two horizontal machines.

Wiped Film Evaporator Work at Oak Ridge National Laboratory

ORNL is currently developing a WFE for concentrating radioactive salt waste. The waste is a sodium nitrate and potassium nitrate supernate containing calcium carbonate, magnesium hydroxide, and aluminum hydroxide solids. All testing so far has been on simulants dried to either a near-dry slurry or a dry powder with a vertical WFE. Drying to a cake causes vibration in the WFE as solids accumulate on the wipers. The contact at ORNL suggested drying the Hanford Site waste to a toothpaste-like consistency because of problems with dusting and carry-over from the melter system if the waste is dried to a powder.[1]

The ORNL WFE is a vertical unit that does not have a lower bearing and is therefore remotely replaceable. It can evaporate 0.5 gpm. It has a 5.4 ft^2 heat transfer area. The evaporator shell is a 10-in sch. 40 pipe that is 2 ft long. The overall unit is 7-to-8-ft tall and 2 ft in diameter (see Figure B.1.1). It uses 150 psi steam as a heating medium and has 0.62 ft^3 of steam jacket volume. They maintain a 30 ft/sec tip speed on the wipers. The unit uses a 7.5 hp electric motor. They use an agitated kettle heater to preheat their feed because sensible heat takes twice as much waste treatment facility (WTF) heat transfer area as does latent heat.

ORNL has not done a lot of testing with high solids concentrations. They are currently testing a solution with 20 wt% suspended solids and plan to test 30% and 40% solutions by October.

They do not have to perform routine maintenance, but they have had some operations problems with the pins on the wiper blades. Two different types of pins have failed during tests. They are now using Ultimet (similar to Stellite) pins that are welded into position. The services required for their unit are 150 psi steam, cooling water for the bearings, and electricity for the motor.

Estimated Increase in Melter Production Rate from Using an Evaporator

The assumed benefit of coupling an evaporator to a melter is that the size of the melter can be reduced because the evaporative heat load is removed from the melter. This brings up a difficult question that has

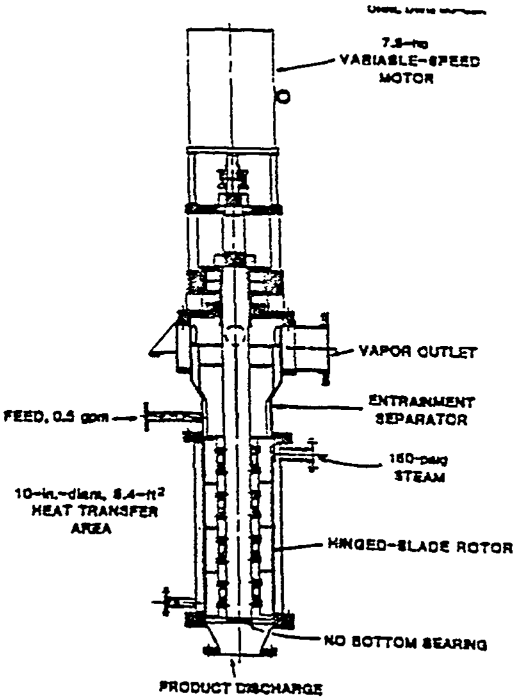

Figure B.1.1. Vertical Wiped Film Evaporator at ORNL

appeared before: what production rate increase should be assumed for dry feeding versus slurry feeding? A rule-of-thumb for production rates in the commercial glass industry is 3 to 5 ft^2/ton/day for dry feeding, which converts to 17 to 28 lb/h•ft^2 (82-135 kg/h•m^2) or an average of 21 lb/h•ft^2 (102 kg/h•m^2). The nominal production rate assumed for slurry-fed HWVP melter was 40 kg/h•m^2 or a factor of 2.5 less than dry-fed commercial glass melters. Obviously, this is a crude approximation because these melters process different glasses at different temperatures.

Ceramic-lined, joule-heated melters for HLW vitrification have been tested using dry feeding. A search of PNL reports was carried out to identify work that would allow a reasonable comparison of melter processing rates for a slurry-fed ceramic melter (SFCM) and a calcine-fed ceramic melter (CFCM). Most of the work was done with calcined feed, not dried feed. Applicable data found in these reports was then used to estimate the required melter surface area for processing 16.3 metric tons of waste glass per day. The following is a brief summary of the data found in these reports, the calculated required melter areas, and an overall discussion of the applicability of these data to a direct comparison of slurry and calcine-fed melter areas.

Table B.1.1 presents glass melt rates reported for a number of tests in thee different melter systems. The glass melt rate for a melter fed with dry material tends to be significantly higher than the corresponding slurry fed rate, especially in the ESCM and LFCM runs, but less so in the calcine-fed ceramic melter /pilot-scale ceramic melter (CFCM/PSCM) runs. This is indicative of factors other than just dry or slurry feeding of the material that influence the process rate. Table B.1.2 presents calculated melter areas required to produce 16.3 MT/day of glass at the feed rates reported in Table B.1.1.

Table B.1.1. Glass Melt Rates for Dry and Slurry Feeding in Several Melter Systems

Melter Run	Feed	Melt Rate (kg/m^2h) Calcine	Slurry	Source
CFCM-7	SRP-TDS-211	74.4	--	PNL-3387
CFCM-8	SRP-TDS-211	51.5	--	PNL-3387
PSCM-4	SRP-TDSF-131	--	35.6	PSCM-4 Run Summary
PSCM-5	SRP-TDSF-165	--	53.0	PSCM-5 Run Summary
LFCM (avg.)	Simulated Hanford waste and	74.0	23.4	PNL-SA-6867
LFCM (max.)	unreacted chemicals	128	33.3	PNL-SA-6867
ESCM (avg.)	Calcined waste and formers or	170	33.2	PNL-SA-6867
ESCM (max.)	HNO_3 slurry of waste and formers	220	48.0	PNL-SA-6867

The above data show that the effect of dry feeding to the joule-heated melter ranges from no change in the production rate to an increase of about 5-fold over slurry feeding. The CFCM/PSCM runs were performed with basically the same melter and the same feeds. The frit in each of the runs was different, but the final glass compositions were similar. These runs show the least difference between dry- and slurry-fed material. Waste slurry was calcined in a spray calciner, mixed with melted glass frit, and fed to the CFCM. The CFCM runs were characterized by numerous foaming incidents, which required stopping the feed and allowing the foam to melt into the glass, thereby greatly reducing the processing rate. Melter control problems were encountered, which likely contributed to the foaming. Additionally, the plenum height in the CFCM was not sufficient to allow full coverage of the melter surface because the dry feed piles up rather than spreads like a slurry. The PSCM rates were among the highest slurry-fed rates, possibly because plenum heating was used to boost the melt rate.

The LFCM dry-fed tests used a purchased batch of oxides, carbonates, and minerals to simulate the waste, and glass formers were added as unreacted chemicals. This mix of dry chemicals was then fed to the melter. Generation of gas from the hydrates, carbonates, and other substances relative to calcined waste/premelted frit was significant, and the gases escaped by percolating through the powdered feed on top of the glass. The melt rate was adversely affected by plugging of gas vents in the cold-cap by feed

Table B.1.2. Melter Area Required for Producing 16.3 MT/d of Glass

Melter Run	Melter Area (m^2) Required for Production of 16.3 MT/d of Glass Calcine-Fed	Slurry-Fed
CFCM-7	9.1	
CFCM-8	13.2	
PSCM-4		19.1
PSCM-5		12.8
LFCM (avg.)	9.2	29.0
LFCM (max.)	5.3	20.4
ESCM (avg.)	4.0	20.5
ESCM (max.)	3.1	14.1

material spread by the solids distributor. Modifications to the solids distributor eliminated this problem, and melt rates at the end of the test were the highest obtained. It was reported that even higher melt rates were thought to be possible. Liquid feeding in the LFCM tests was carried out in tests of short duration (less than 12 h) and may be somewhat less accurate.

The ESCM was the smallest of the melters for which data are reported here (0.27 m^2 versus 0.76 m^2 for the LFCM/CFCM and 1.05 m^2 for the PSCM) and the earliest in operation. The data reported are from two years of operation. Many of the tests were short, one-day tests. Commercial and defense wastes fed over two years of operations included PW-4b, PW-7-2, high fission product waste, a purchased synthetic calcine, and high iron and aluminum Savannah River wastes. A frit used in some of the tests was 72 to 68. During dry feeding, the ESCM typically had about 50% of the melt surface covered and may have operated substantially below its maximum production rate. Although no long term tests appear to have been done in this melter and different feeds/frits were apparently used, the data presented represent the average of many short tests and should be reasonably representative of calcine versus slurry feeding.

Attempts were made to use data that were comparable (e.g., same melter, same feed, same temperature) with the only difference being slurry or calcine feeding. Nevertheless, numerous factors other than dry/slurry feeding have a marked impact on the melt rate. A few of these are discussed below.

1. Some of the data come from rather short operating periods of just a few hours and may not represent the steady-state value.

2. An indirect effect of dry feeding on the bulk glass temperature may enhance the melt rate. The weight of the large feed pile pushes unmelted feed below the glass surface in the center of the pool, resulting in a smaller conduction path, increased resistance, and increased heating. Temperatures were as high as 1280°C in the CFCM runs.

3. Calcined feeds will already be hot as they leave the calciner and will require less energy to melt; however, melt rates of dry feeds not from a coupled calciner are also high.

4. The melt rate can depend on the operating conditions, such as the means of control, cold-cap coverage, and/or plenum heating, which may not be constant from test to test. In the CFCM tests, it was thought that poor control led to much of the difficulties with foaming. In other tests, complete cold-cap coverage prevented venting of gases and reduced the melt rate. The same observation was made with the LFCM when vents were covered by the distributed feed.

5. The melt rate will also depend on the feed. Premelted frit can cause foaming due to entrapment of evolved gases in a viscous melt at the cold cap. The glass formulation and/or glass frit can also have a marked influence on the melt rate. ESCM melts used a glass that was fluid at the higher melting temperatures of these tests. The behavior of the feed may also be different in a dry-fed versus slurry fed system, and this behavior can vary from feed to feed.

6. The melter design can affect the melt rate. The plenum height in the CFCM limited the melt rate, probably by not allowing a sufficient feed pile to completely cover the melt surface.

7. The slurry oxide loading can affect the melt rate, and the oxide loading in the slurry varied greatly among the reported tests.

In summary, past data from several melters operated at PNL shows that the effect of dry-feeding a Joule-heated melter can range from no increase to a five-fold increase in melt rate relative to slurry feeding. However, experience has shown that many other factors other than dry or slurry feeding can also influence the melt rate. These factors have not been carefully controlled in the test data reviewed here; therefore, the increased melt rate should be viewed with caution. Experienced melter personnel agree, however, that dry feeding is likely to result in some measurable increase in the melt rate if all other factors are accounted for.

For purposes of calculation, a production rate of 100 kg/h•m^2 will be assumed for dry-fed melters in this appendix; this is a 2.5X increase in production rate over slurry-fed melters. As stated, this estimate would clearly have to be determined experimentally as a function of feed composition and melter type. Basic parameters for the LTCM with an evaporator are presented in Tables B.1.3 and B.1.4. Table B.1.3 represents the case where the frit is added to the waste at the exit of the evaporator. This allows a more concentrated feed solution (200 g waste oxide/L) to be pumped to the calciner and therefore requires less evaporative capacity. Table B.1.4 represents the case where the frit is added to the feed upstream of the evaporator. The addition of the frit in the waste slurry reduces that allowable concentration of waste down to 125 g waste oxide/L. This results in a larger stream going to the evaporator.

Sizing of Evaporators

LCI Corporation (formerly LUWA) manufactures WFEs. Mr. Bill Glover of LCI was contacted and asked to recommend WFEs to pre-dry the Hanford Site HLW slurry.[2] The first question was how dry the product should be. He said that they do not like to dry to chunks or pastes because they plug their discharge. They prefer to go to a dry and flowable powder. Mr. Glover also stated that melting of hydrates can be a problem, as can early-melting salts that gum up the evaporator. Each salt acts differently; some simply will not process in a WFE. Early melting salts can form a "goo" that clogs the evaporator tube.

Table B.1.3. Operating Parameters for Low-Temperature, Ceramic-Lined Melter with Evaporator (frit added after the evaporator)

Specific Glass Production Rate	100 kg/h•m^2			
Waste Loading in Glass	25 wt%			
Oxide Loading in Slurry to Evaporator	200 g waste oxide/L			
Bulk Glass Temperature	1150°C			
Plenum Temperature	650°C			
Glass Depth[(a)]	0.8 m			
Glass Residence Time	20 h			
Total Operating Efficiency	60%			
Number of Melter Lines	1	2	3	4
Glass Surface Area (m^2/melter)	6.8	3.4	2.3	1.7
Glass Production Rate (MT/day/melter)	16.0	8.0	5.4	4.0
Glass Production Rate (kg/h/melter)	680.0	340.0	230.0	170.0
Slurry Feed Rate to Evaporator (L/h)	850.0	425.0	283.0	213.0
Glass Holdup (MT)	14.0	6.8	4.5	3.4

(a) Assumed based on WHC Phase I study.

Table B.1.4. Operating Parameters for Low-Temperature, Ceramic-Lined Melter with Evaporator (frit added before the evaporator)

Specific Glass Production Rate	100 kg/h•m^2			
Waste Loading in Glass	25 wt%			
Oxide Loading in Slurry to Evaporator	125 g waste oxide/L 500 g total oxide/L			
Bulk Glass Temperature	1150°C			
Plenum Temperature	650°C			
Glass Depth[(a)]	0.8 m			
Glass Residence Time	20 h			
Total Operating Efficiency	60%			
Number of Melter Lines	1	2	3	4
Glass Surface Area (m^2)	6.8	3.4	2.3	1.7
Glass Production Rate (MT/day/melter)	16.0	8.0	5.4	4.0
Glass Production Rate (kg/h•melter)	680.0	340.0	230.0	170.0
Slurry Feed Rate to Evaporator (L/h)	1360.0	680.0	453.0	340.0
Glass Holdup (MT)	14.0	6.8	4.5	3.4

(a) Assumed based on WHC Phase I study.

To go to a paste (to avoid dust carryover to the melter off-gas), we should use a vertical evaporator without exit obstructions should be used. Vertical WFEs operate at a higher speed (30 feet/sec tip speed) and have the advantage of less accumulation; early drying phases fall free. They also have better water boilup rates per surface area. LCI usually estimates 10-20 lb/h•ft^2 water boilup to go to a powder and 30-40 lb/h•ft^2 water boilup to go to a dilute liquid. Vertical WFEs have less control on the amount of dryness because partially dry solids fall free. Horizontal units operate more slowly, and longer residence time provides better control over the product dryness and size. The dryer the product, the lower the specific boilup rate because the heat transfer coefficient is lower when the slurry turns to a solid.

The blades of WFEs need to be replaced every 6 months when used with harsh salts and up to 2 years in less harsh environments. The tube will last indefinitely. The bearing needs to be greased regularly.

The approximate sizes of vertical evaporators required to feed an LTCM are shown in Table B.1.5 (frit added after the evaporator) and Table B.1.6 (frit added before the evaporator). When these evaporators were sized it was assumed that the incoming slurry is preheated to near boiling. If the incoming slurry is cool, the evaporator size will increase. The evaporator sizes were calculated based on an assumed water boilup rate of 25 lb/h•ft^2, which is shown to be optimistic by the specific boilup rates normally used at LCI Corp. As shown in the tables, these evaporators are tall, up to 21 ft, which may cause a head room problem in the melter cell. The diameter of the evaporators may also interfere with the other penetrations on the lid of the melter. The height problem can be resolved by going to a horizontal WFE. Because horizontal WFEs are less efficient, the evaporator size would have to be increased over those shown in Tables B.1.5 and B.1.6.

The WFEs required for a stirred melter(s) are the same as those presented in Tables B.1.5 and B.1.6. Similar information for the CCM is shown in Table B.1.7 (assuming that the frit is added after the calciner). Sizing information was not obtained for CCMs with the frit added before the evaporator, but the evaporator sizes would increase similarly to those in Tables B.1.5 and B.1.6.

Table B.1.5. Evaporator Sizes for the Low-Temperature Ceramic Melter (frit added after the evaporator)

Method of Feeding	Dry			
Concentration of Feed to Evaporator	200 g waste oxide/L			
Slurry Solids	23 wt%			
Solids in Dry Product	90 wt%			
Number of Melter Lines	1	1	2	2
Number of Evaporators per Melter	1	2	1	2
Boil-up Rate per Evaporator (lb/h)	1500	740	740	370
Required Heat Transfer Area (ft^2)	63	32	32	16
Evaporator Height (feet)	19	14	14	9
Evaporator Diameter (inches)	28	21	21	15
Drive (hp)	30	20	20	15

Table B.1.6. Evaporator Sizes for the Low-Temperature Ceramic Melter (frit added before the evaporator)

Method of Feeding	Dry			
Concentration of Feed to Evaporator	125 g waste oxide/L			
Slurry Solids	40 wt%			
Solids in Dry Product	90 wt%			
Number of Melter Lines	1	1	2	2
Number of Evaporators per Melter	1	2	1	2
Boil-up Rate per Evaporator (lb/h)	2600	1300	1300	650
Required Heat Transfer Area (ft^2)	106	50	50	25
Evaporator Height (feet)	21	15	15	14
Evaporator Diameter (inches)	39	27	27	21
Drive (hp)	40	30	30	20

Table B.1.7. Operating Parameters Cold Crucible Melter with an Evaporator

Oxide Loading in Waste Slurry (w/o frit) to Calciner	200 g/L	
Waste Loading in Glass	25 wt%	50 wt%
Number of Melter/Calciner Lines	4	2
Slurry Feed Rate to Each Calciner	250 L/h	500 L/h
Total Glass Production Rate (kg/h)	800	400
Boil-up Rate per Evaporator (lb/h)	440	880
Required Heat Transfer Area (ft^2)	16	36
Evaporator Height (feet)	9	14
Evaporator Diameter (inches)	15	21
Drive (hp)	15	20

The following sections contain information that should be added to the LTCM.

1. Process Range of Composition

As discussed in the introduction, early melting salts can cause sticking and clogging in a WFE. This cannot be predicted without pilot-scale testing. Preliminary information from ORNL is promising.

B. Range of Waste Handling Capabilities

The wide variation in Hanford Site wastes will make it necessary to test a broad range of wastes in a WFE before its acceptance. This would have to be done for any melter technology, but potential sticking problems complicate the issue.

C. Incorporation of Semivolatiles

Passing dry or semi-dry feed through the plenum of the melter is expected to cause increased volatilization and carryover to the off-gas system. This was a significant problem during testing of WFEs with melters at PNL (McElroy 1975b). The carryover can be captured in the off-gas system and recycled to the evaporator, but this will be an additional burden.

2. Control Product Quality

As discussed in the CCM data package, addition of the frit to the waste after the evaporator complicates the qualification of the product glass. The equipment that meters the frit to the melter must be qualified as well as the glass composition. It must be clearly demonstrated that the evaporator does not accumulate waste in a cyclic nature such that the ratio of waste and glass formers varies with time.

D. Minimum and Optimum Residence Time

Because the increased processing rate exceeds that of a slurry-fed melter, the residence time is less, 20 hours versus 50 hours. The 20 hours should be adequate for proper homogenization, but it limits the capability of the system to dampen feed variations. If this is a problem, the melter depth can be increased. The shorter residence time may be an advantage because insoluble particles have less time to settle to the bottom of the melter.

E. Unpredictable Evaporation (Segregation) of Glass Components

It is not clear if the carryover to the off-gas system will be enriched in specific compounds. If so, the recycle will have to be carefully controlled so that the glass composition does not vary.

3. Develop Technology on Schedule

This category deals mainly with the maturity of the technology. The WFE technology is mature. As discussed, WFEs have been demonstrated with ceramic melters, although testing was not extensive. From a survey of the literature, it appears that all testing was done with nitric acid solutions and not alkaline solutions, such as the Hanford Site wastes. The effectiveness of drying Hanford-type wastes with WFEs is yet to be demonstrated. It is not clear whether this is an issue.

E. Demonstrated Scale of Operation

Glass processing rates of 5 to 18 kg/h were demonstrated with a WFE coupled to an in-can melter (McElroy 1975c). Nitric acid feed stocks were used for these experiments.

The Russian CCM pilot plant has a single WFE that supports three CCMs. The WFE can dry nitric acid solutions to 20% moisture (1000 to 1100 kg salt/m^3) to supply three 30 kg/h melters.

F. Magnitude/Amount of Technology Development Required

Technology development needed to determine the effectiveness of drying alkaline slurries with WFE involves answering the questions:

(1) Do early melting salts cause clogging of a WFE with Hanford simulants?

(2) If early melting phases appear, can they be prevented using additives?

If the WFEs are found to be effective in drying Hanford-type wastes, the following questions would have to be answered:

(1) What is the best configuration of WFE and melter (vertical or horizontal WFE, steam heating or oil heating, direct coupling or indirect coupling to the melter, glass formers added before or after the WFE, number of WFEs per melter)?

(2) What is the optimum product dryness to allow good coverage of the melt pool while avoiding extensive dusting and carryover to the off-gas system?

(3) What increase in melter production rate is realized from dry feeding versus slurry feeding?

(4) Does the optimum combination of WFE and melter give a distinct advantage over a liquid-fed melter (is there a space savings, added simplicity, reduced risk, reduced cost, etc.)?

G. Processing Rate

See "Estimated Increase in Melter Production Rate from Using an Evaporator" in the introduction.

H. Extent of Mock-Ups and Test Facilities Required

Pilot-scale testing of WFEs is available at LCI Corporation or ORNL (5.4 ft^2 vertical WFE, 0.5 gpm capacity). It is not clear if there is a facility with a WFE coupled to a melter. If there is not, this could probably be accomplished at any of the melter facilities listed in Data Package 1.

5. Control and Maintenance of Process and Facility

This section includes a discussion of the capability of the melter technology to allow safe and efficient operation of the vitrification facility.

B. Remoteability

Vertical WFEs for remote environments are currently being developed at ORNL and in Russia. This does not appear to be an major issue. Remote horizontal calciners are currently in operation in France and England.

C. Reliability

According to information from ORNL, these units appear to be reliable; however, confirmation by pilot-scale testing remains to be done.

D. Maintainability

The wiper blades on the WFE would have to be adjusted or replaced about every six months. The mechanical seals would probably be serviced at the same time. Automatic lubricators are required for the WFE bearings.

G. Potential for Radioactive Source Buildup and Achievement of ALARA

There will be some buildup of radioactive feed materials in the WFE. If proper control is maintained, this should not be a large source of contamination. Increased maintenance of the wiper blades will also contribute to contamination.

H. Sealing and Containment Relative to Melter

"A pair of water-lubricated, graphite-to-stellite mechanical seals on each end of the rotor shaft effectively eliminates air in-leakage into the evaporator" (Dierks and Bonner 1975).

I. Modular Design Concepts that Simplify Replacement or Repair

Adding a WFE to the melter would make the melter system modular and would reduce the size of the melter (see Tables B.1.3 and B.1.4) and the associated disposal costs.

M. Operational Simplicity

Adding a WFE to the ceramic melter increases the complexity of the system. The WFE increases the number of moving parts in the melter system and increases control requirements.

Endnotes

1. Telephone conversation between M. Boring of ORNL and M. Elliott of PNL. August 2, 1994.

2. Telephone conversation between B. Glover of LCI Corporation and M. Elliott of PNL. August 2, 1994.

Data Package 1, Appendix C

Low-Temperature, Joule-Heated, Ceramic-Lined Melter With Agitation (Bubbling System)

This appendix to the data package for the low-temperature, joule-heated, ceramic-lined melter, describes a melter with a proprietary bubbling system that can be used for melt pool agitation. All information contained in this appendix was obtained from GTS Duratek, and therefore, applies specifically to their own system, the DuraMelter™. In addition to information on Duratek's proprietary bubbling system, information on the balance of their melter design is also included because Data Package 1 did not include it. As with the other appendices, only sections that differ from the original data package are included.

When gathering the information to include in this appendix, we received written answers to most of our questions about the DuraMelter™ system, but the answers were mostly qualitative. We also received copies of a few published papers that provided some additional, general information. During a telephone conversation, we requested references or actual data to support claims being made about the bubbling system (such as production rates, etc.), and were informed that we would first have to sign a non-disclosure agreement.[1] As a result, the information in this appendix is very sketchy and cannot be confirmed with operating data. Efforts are under way to get actual operating data for the DuraMelters™.

Description of Technology

The DuraMelter™ is a completely enclosed joule-heated melter, equipped with lid/plenum heaters (if desired), a bottom drain to completely empty the melt cavity at the end of processing, and a surface sulfate drain to remove undesired fluid second phases, which can collect on the melt surface and exacerbate processing. Normally, glass is discharged through side-exiting risers activated by airlifting. Glass can be poured directly into receiving containers or converted into DuraGems (flattened glass marbles).[2]

The DuraMelters are constructed from the following materials (Bowan 1993a): Inconel 690 electrodes, Monofrax K-3 contact refractory, Zirmul AZS refractory and 95% alumina castable backing the K-3, Inconel housing/interior liner, refractory ceramic fiberboard insulation around the melter, and a 304L stainless steel external shell.

Figure C.1.1 is a schematic of the DuraMelter™ 300, which is a nominal 300 kg glass/day melter that has been used for testing. This melter is similar to previous HLW melter designs except for the horizontal air sparge, the inner Inconel shell, and the lack of a cooling jacket.

Each DuraMelter™ is equipped with a gas bubbling system, as shown in Figures C.1.2 and C.1.3 (Macedo 1994), which consists of one or more multi-orifice Inconel 690 tubes positioned directly between the pairs of electrodes, and lying horizontally near the floor of the melter. In the figures, the Inconel tube is #110, and the bubbles are #107. During operation, the bubbling system produces a line of bubbles that rise up through the molten glass pool between the electrodes. Use of air, enriched air, or oxygen in the system is preferred. Duratek has optimized their bubbling rate by using a feedback loop from a processing variable that could not be disclosed.[3]

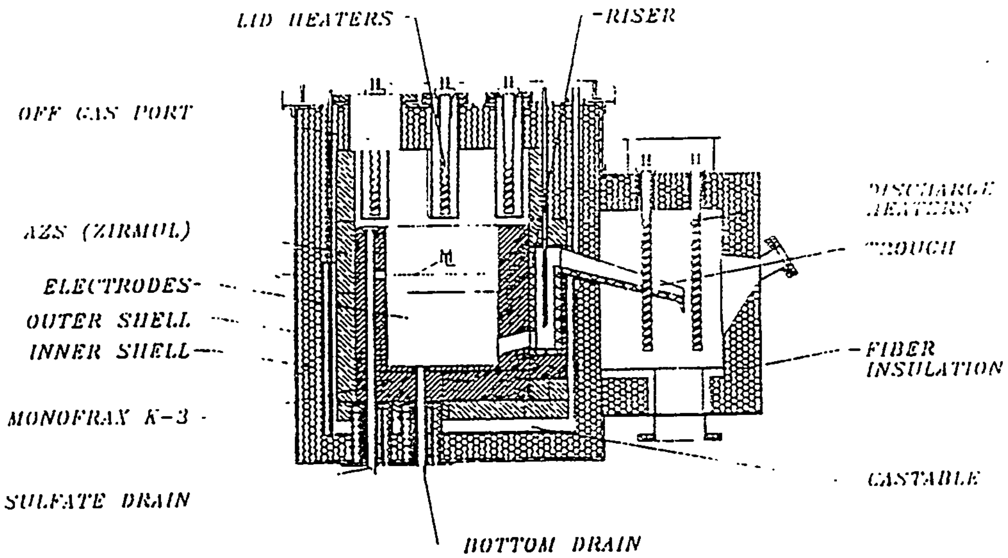

Figure C.1.1. DuraMelter™ 300

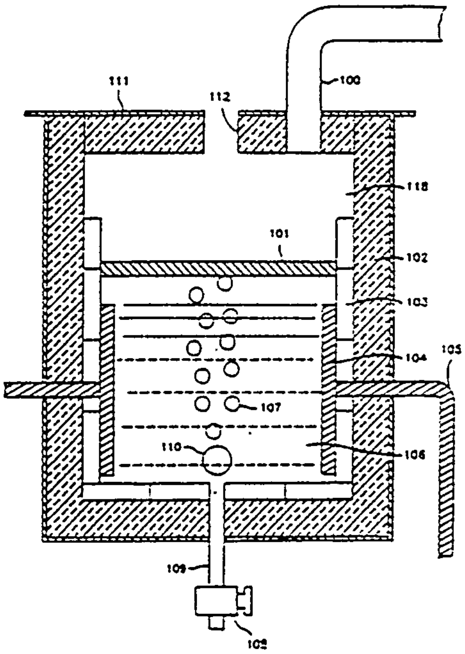

Figure C.1.2. DuraMelter™ Bubbling System, Side View

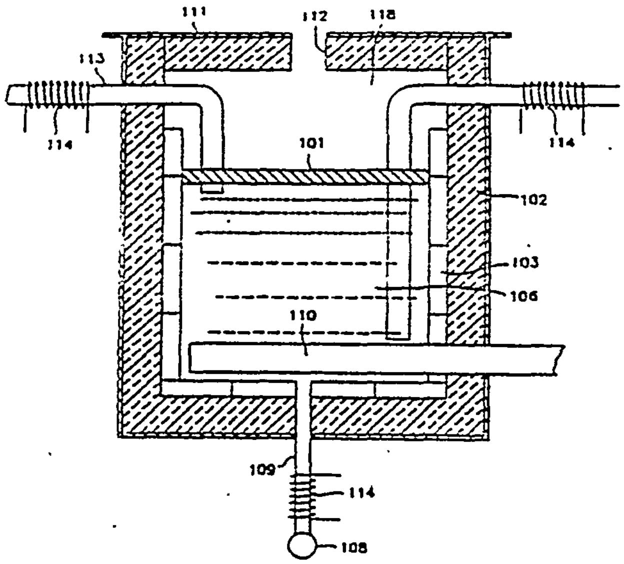

Figure C.1.3. DuraMelter™ Bubbling System, End Sectional View

"A curtain of gas bubbles produced by the tubes in the glass melt will have a volume fraction of gas of 10% to 60%, preferably 15% to 40%, and ideally 20% to 30%. Maximization of the rate of power delivery and an optimized temperature profile are thereby achieved. If there is a region where the bubbles occupy 33% of the volume of the melt, the power will be 50% higher and the additional temperature as well as the effective lower density of this column of glass will give the column of glass an upflow motion" (Macedo 1993).

Using the bubbling system in the melter has three main advantages (Bowan 1993a; Bowan 1993b; Bowan 1994; Macedo 1993):

1. The bubbling creates a vigorous stirring action, which enhances the convection in the melt pool. This has a significant impact on the melter production rate, and also helps to suspend any particles that would normally settle and accumulate on the melter floor, such as noble metals or crystals.

2. Using air or oxygen to produce the bubbles helps control the oxidation state of the melt pool by providing a strong oxidizing condition in the melt and thereby allowing higher concentrations of organics and metallics in the waste stream.

3. The bubbling action can help disrupt a sulfate layer, which might form on the surface of the glass pool and could decrease the electrical performance of the electrode circuit.

More thorough discussions of these advantages are included in the appropriate sections of this appendix.

To produce a glass with 25% waste loading at a production rate of 16 MT/day and a 125 kg/h•m^2 specific process rate requires a total glass surface area of 5.3 m^2 with this technology. This can be accomplished with either one melter or multiple melter lines. For example, the glass pool geometry for a single, 16 MT/day melter would be about 2.3 m x 2.3 m. If two melter lines are used, the glass surface would be 1.6 m x 1.6 m (2.6 m^2). Basic parameters for this melter technology are presented in Table C.1.1.

1. Process Range of Composition

   B. Range of Waste Handling Capabilities

Waste streams that have been tested or will be tested in the DuraMelter™ include mixed waste simulants and asbestos wastes. Table C.1.2 lists some borosilicate glass compositions reported in the literature, and Table C.1.3 shows a typical asbestos waste feed. As indicated in Table C.1.2, the waste sludge used to produce the Fernald Test Glass had a relatively high concentration of magnesium fluoride. The literature and conversations with Duratek do not make it clear which of these compositions have been tested and what the processing rates were, although it is likely that the M Area Sludge has not been processed. These compositions are in addition to those presented in the original Data Package 1.

Acceptable Glass Properties -

- Viscosity and Electrical Conductivity

In addition to the composition shown in Table C.1.2, the data in Table C.1.4 below was presented in the literature for the Fernald Test Glass. They provide acceptable values for

Table C.1.1. Operating Parameters for the DuraMelter™

Specific Glass Production Rate	125 kg/h•m^2	
Waste Loading in Glass	25 wt%	
Oxide Loading in Slurry	500 g/L	
Bulk Glass Temperature	1150°C ± 50°C	
Plenum Temperature	600-900°C	
Glass Depth[(a)]	2.5 m	
Glass Residence Time	50 h	
Total Operating Efficiency	60%	
Number of Melter Lines	1	2
Glass Surface Area (m^2)	5.3	2.7
Glass Production Rate (metric ton/day)	16.0	8.0
Glass Production Rate (kg/h)	667.0	333.0
Slurry Feed Rate (L/h)	1334.0	667.0
Glass Holdup[(b)] (metric tons)	33.3	16.7

(a) Calculated based on a 50 h residence time. This could easily be reduced if a lower residence time is acceptable.

(b) Assumes a molten glass density of 2500 kg/m^3.

Table C.1.2. DuraMelter™ Glass Compositions

Oxide (wt%)	Startup Glass (Bowan 1993a)	Fernald Test Glass (F5-46) (Bowan 1993a)	Savannah River M Area Waste (Bowan 1994)
Al_2O_3	3	4.4	9.51
B_2O_3	16	12.2	11.22
BaO			0.02
CaO		20.8	0.30
Cr_2O_3			0.02
CuO			0.01
Fe_2O_3	12		3.09
K_2O			1.09
Li_2O			3.07
MgO			0.14
MgF_2		15.6	
MnO_2			0.03
Na_2O	16	6.4	13.31
NiO			0.47
P_2O_5			2.48
PbO			0.05
SiO_2	46	33.6	47.18
TiO_2			0.05
U_3O_8			1.93
ZnO			0.23
ZrO_2			6.10
Others (a)	7	7.0	
Total	100	100	100.3

(a) Composition of "others" not specified in references.

viscosity and electrical conductivity. The viscosity and conductivity are lower than in normal HLW glass. The following quote also describes the effects of the gas bubbling on the electrical resistance of the glass melt:

> "By introducing gas bubbles into the melt, which are voids and which will not conduct electricity, one decreases the cross sectional area of the melt through which the current passes, thus increasing the resistance of the melt. If the power supply is arranged to be a constant current supply (rather than constant voltage), the additional resistance will increase the power density and thus the temperature and will form a highly oxidizing hot region into which the waste materials are introduced" (Macedo 1993).

Table C.1.3. Typical Asbestos Waste Feed

Feed Constituent	Wt% of Feed
WASTE	
Water	11.6
Polyethylene	2.9
Chrysotile[(a)]	21.8
Gypsum	8.7
Cement	10.9
Iron	2.2
ADDITIVES	
Silica	19.3
Sodium Carbonate	22.6
TOTAL	100.0

(a) Chrysotile $3MgO*2SiO_2*2H_2O$ comprises about 95% of the asbestos consumed in the United States.

- Redox

"Most high-level nuclear wastes contain a variety of transition metals capable of assuming variable valence states in glass melts. The steady state oxidation state of the melt pool can change suddenly with melt temperature fluctuation or waste feed chemistry shifts. Ideally, through empirical data, the chemistry of the feed is adjusted to a point which yields a melt oxidation state that is tolerant of temperature fluctuations. Absence of this type of control can result in melt foaming (analogous to the foam head on a root beer poured over ice) which can clog or impede gas flow to the off-gas treatment system. The bubbling system in the DuraMelter fixes the oxidation state of the glass pool and makes it completely tolerant of feed chemistry or melt temperature shifts. During an asbestos vitrification demonstration on the DuraMelter™ 1000, whole polyethylene bags of asbestos containing materials were fed to the melter. It was expected that the combustion of the bags would result in a highly reducing melt pool. However, periodic glass samples from the melter discharge were analyzed and all iron in the glass was found to be trivalent."[2]

C. Incorporation of Semivolatiles

"Thermal stabilization processes can volatilize some of the waste components they are trying to capture and stabilize. Vitrification also risks losing some fraction of certain elements which bond weakly in glasses or have low solubility in glasses. Cesium, iodine, chlorine, and technetium are some such species. It is wise to minimize the processing temperature of the glass pool to maximize capture and vitrification of semivolatile species. This limits losses of these components to

Table C.1.4. Viscosity and Electrical Conductivity Data For Test Glass F5-46 (Bowan et al. 1993a)

Temperature (°C)	Viscosity (poise)	Conductivity (s/cm)
1000	13.6	0.03
1150	4.9	0.10

the off-gas treatment system, minimizing secondary waste generation. This was the premise of lower melting temperatures for West Valley and DWPF and remains sound for waste streams containing substantial activity in the form of semivolatiles. Again, the DuraMelter™ operates at a temperature of 1150°C, and we believe this to be the lowest reasonable melting temperature which maintains an economical operating process."[2]

Most LTCMs are operated with a cold cap, which helps minimize the amount of volatilization by providing a protective blanket over the glass pool. The information quoted in Section 1.D suggests that the bubbling system vigorously agitates this melt pool, which could disrupt the cold cap and increase volatilization. Volatilization would also be increased in low-viscosity glasses similar to the glass shown in Table C.1.4. No data has been provided to prove either case.

D. Ability to Handle Insoluble and Conductive Compounds

"Noble Metals: Most high-level nuclear wastes contain noble metals which originate from the fission process. The concentrations of these species vary depending on the history (rate of burn up and length of cool down) of the reactor fuel from which they are generated. Noble metals are those of the platinum group (ruthenium, rhodium, palladium, etc.), which either in the metal or oxide state have poor to nonexistent solubility in most glasses. Since these species are dense and electrically conductive, their presence jeopardizes quiescent operation of joule-heated melters. At the PAMELA facility in Mol, Belgium, a failure stemming from the collection of noble metals on the floor of the melter occurred. The operators of this facility were able to recover and restore operation of this system by sparging the floor of the melter with an air lance. As mentioned earlier, the DuraMelter™ is equipped with a proprietary bubbling system which vigorously agitates the melt pool. This agitation would easily keep noble metal inclusions suspended in the melt bath, allowing them to be discharged with the glass during normal melter operations."[2]

2. Control Product Quality

B. Waste Homogenization Capabilities

The main contributor to product quality that can be improved by the bubbling system is homogeneity resulting from increased agitation and enhanced convection. Further, particles (such as crystals and noble metals) can remain suspended and throughly mixed in the glass melt, rather than settling to the melter floor. The presence of undissolved feed in the glass is more likely than with the non-agitated melter. Convection cells, which are much faster in the agitated melter than in the non-agitated melter, could draw some undissolved feed material down and out of the melter before it has a chance to completely homogenize. This has not been confirmed with any experimental tests.

E. Unpredictable Evaporation (Segregation) of Glass Components

In the "All-Blend" composition, sulfate is not expected to cause a problem because of its relatively low content (0.3 wt% SO_3). However, a wide range of possible waste compositions depend on different tank waste blending scenarios, one or more of which might result in a high sulfate glass that could phase separate and accumulate in the melter. The highest SO_3 concentration reported in Data Package 1, Table 1.3, was 0.59 wt% SO_3. The DuraMelter™ is designed with a special system for removing accumulated layers from the melt pool surface. The following describes how this accumulation might occur, and the DuraMelter™ design feature that could remove it.

> "Once sufficient scum has accumulated to significantly affect operation of the furnace, a cycle is started for scum removal. Feed to the furnace (both waste and other materials such as fluxes) is temporarily halted, causing the temperature at the top of the furnace to rise. It may be necessary to use roof heaters (placed above the melt line of the furnace) to accelerate the process of bringing the temperature above the melt line in the furnace above the decomposition temperature of all the waste (T>900°C). This temperature range will destroy waste in the air and on the surface of the melt.
>
> Once the temperature above the melt line is above the decomposition temperature for all of the waste, one can be sure that all the asbestos in the scum and plenum has been decomposed. At this point a top outlet (an output at a level approximating the melt line) is opened. This will allow for the removal of the scum on the melt. During this operation the furnace could be fed with non-waste material. Skimming the melt can be employed for greater efficiency. Once the scum removal has been accomplished, the upper outlet is closed and normal processing of waste is commenced.
>
> In the present invention, control of sulfate levels in the glass melter is extremely important in order to minimize corrosion. Upon heating, sulfates are expected to accumulate in a supernatant gall layer. Additionally, in the present invention, the bubbling of air through the melter may promote and accelerate the separation of this layer from the main melt. In the presence of high levels of sulfates, which may amount to as much as approximately 10% of the batch composition, this layer can be expected to grow rapidly in thickness during continuous feeding and operation of the melter (Macedo 1993).

3. Develop Technology on Schedule

B. Demonstrated Scale of Operation

"GTS Duratek and its partner, the Vitreous State Laboratory, have extensive experience vitrifying low-level and mixed wastes throughout the U.S. DOE complex. Waste vitrification studies have been conducted on wastes from Weldon Spring, Oak Ridge, Hanford, Fernald, Idaho Falls, and Savannah River."[2]

Duratek has developed the following melters (operating data were not provided to confirm the quoted production rates, which are the design production rates):

- DuraMelter™ 10: 10 kg/day nominal glass production, located at the Vitreous State Laboratory.

- DuraMelter™ 100: 100 kg/day nominal glass production, began testing in early 1993, nearly 1000 kg test glass processed through the system so far (Bowan 1993b), located at the Vitreous State Laboratory.

- DuraMelter™ 300: 300 kg/day nominal glass production, mid-1993 startup, located at Fernald, Ohio, as part of the DOE-sponsored Minimum Additive Waste Stabilization program.[2]

- DuraMelter™ 1000: 1000 kg/day nominal glass production, located at the Vitreous State Laboratory.

- DuraMelter™ 5000: 5 ton/day nominal glass production (15 ton/day maximum with agitation), scheduled to be operational in 1995, will be used to process Savannah River M-Area waste (Bowan 1994).[2]

- DuraMelter™ Pilot-Scale Asbestos Melter: 1.22 m^2 area, 900 kg/day glass production, unsure if actually tested.

G. Processing Rate

"The DuraMelter™ is equipped with a proprietary bubbling system which enhances convective heat transport to the conventional vertical melting process. GTS Duratek has demonstrated production capacities near 3 tons glass/m^2 melter surface/day, with this system. This compares to a design basis of 0.64 ton glass/m^2 melt surface/day for West Valley and 1 ton glass/m^2 melt surface/day for the DWPF. Actual demonstrated production capacities of these systems have been lower."[2]

H. Extent of Mock-Ups and Test Facilities Required

"GTS Duratek manages its pilot plant facility at the Catholic University's Vitreous State Laboratory. This facility is equipped with three DuraMelter™ systems able to conduct actual waste vitrification demonstrations for GTS Duratek's clients. A DuraMelter™ 10 and DuraMelter™ 100 are dedicated to low-level radioactive and mixed waste tests (low dose rate, uranium, technetium, etc.), while the largest (DuraMelter™ 1000) is used for hazardous and simulated waste vitrification studies. This largest unit has an idling melt volume of 1180 liters of glass and a production capacity from two to three tons of glass per day."[2]

The above-quoted production capacity of "...two to three tons of glass per day" for the DuraMelter™ 1000 is believed to have been obtained with the air bubbling system and the nominal 1000 kg/day without air bubbling. No information has been provided to verify this.

5. Control and Maintenance of Process and Facility

J. Refractory Life

The combination of vigorous agitation and a low viscosity glass may significantly increase corrosion of the fused cast refractories and other glass-contacting materials (such as electrodes, thermowells).

K. Electrode Life/Replacement

"Inconel as well as other metals have a current per unit area limit above which significant corrosion occurs. The exact current depends on the temperature of the electrode/melt interface, redox conditions, and the expected furnace life. A typical result obtained is in the range of less than 50A per square inch, preferably less than 20A per square inch, and more preferably less than 10A per square inch. Production rates for this type of furnace can be limited by the rate of power delivery to the melt" (Macedo 1993).

Endnotes

1. Telephone conversation between B.W. Bowan (Duratek) and P. Shafer (PNL) on August 12, 1994.
2. Letter from B.W. Bowan (GTS Duratek) to P. Shafer (PNL) dated June 22, 1994.
3. Telephone conversation between B.W. Bowan (Duratek) and P. Shafer (PNL) on August 12, 1994.

Data Package 2

Low-Temperature, Joule-Heated, Metal-Lined Melter (Stirred Melter)

Description of Technology

The baseline melter is a system proposed by Stir-Melter Inc., which has the following features (see Figures 2.1 and 2.2):

- a melting pot and agitator made of Inconel 690
- a rectangular melt cavity
- a nominal operating temperature of 1050°C
- auxiliary resistance heaters surrounding the melting pot for easy startup
- refractory, insulation, and cooling water panels surrounding the melting pot a water-cooled bottom drain for emptying the melter
- an overflow system for routine glass pouring
- multiple feed stock capability: dry, liquid, or slurry.[1]

Stir-Melter, Inc. recommended that the waste be dried before feeding to the melter and that it be fed separately from the dry glass formers. Although Stir-Melter, Inc. did not specify a drying method, evaporation systems similar to those shown in Data Package 1, Appendix B could be used. The study done by Fluor Daniel, Inc. assumed that concentrated waste slurry is fed separately from the dry glass formers. The Savannah River melter design assumed that the waste slurry and glass formers are mixed before being fed to the melter. The reasons for these assumptions are further discussed in Section 1.B. The information provided in this data package is based on dry feeding of waste and glass formers separately. Selection of combined feeding of waste and glass formers would affect:

1. the feed preparation system (evaporator no longer required)
2. the off-gas system (increased off-gas system capacity with more units),
3. waste form qualification (mixing procedure and results obtained for combining the slurry waste with the dry glass formers)
4. required melter size for a given production rate.

To provide joule heating in the melt, the Inconel™ agitator acts as an electrode by passing current through the glass to the Inconel™ metal pot. The physical properties of Inconel-690 at higher temperatures limit the nominal operating temperature to 1050°C (see Section 1.A). The two zones of

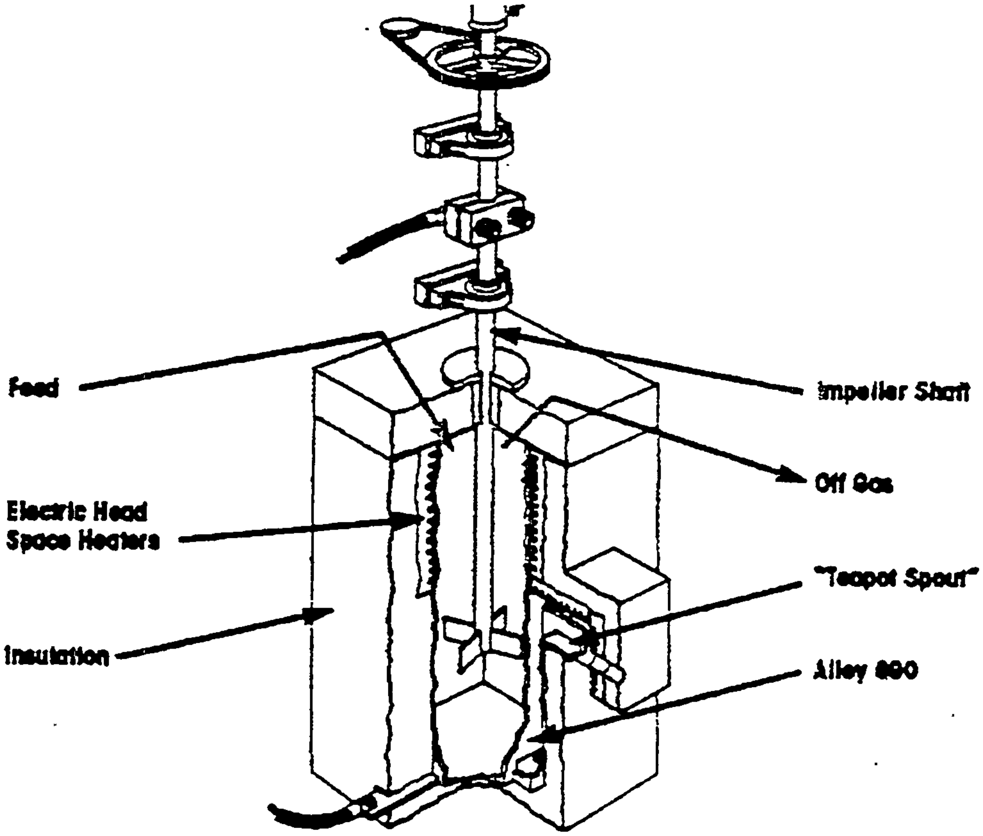

Figure 2.1. Stirred Melter

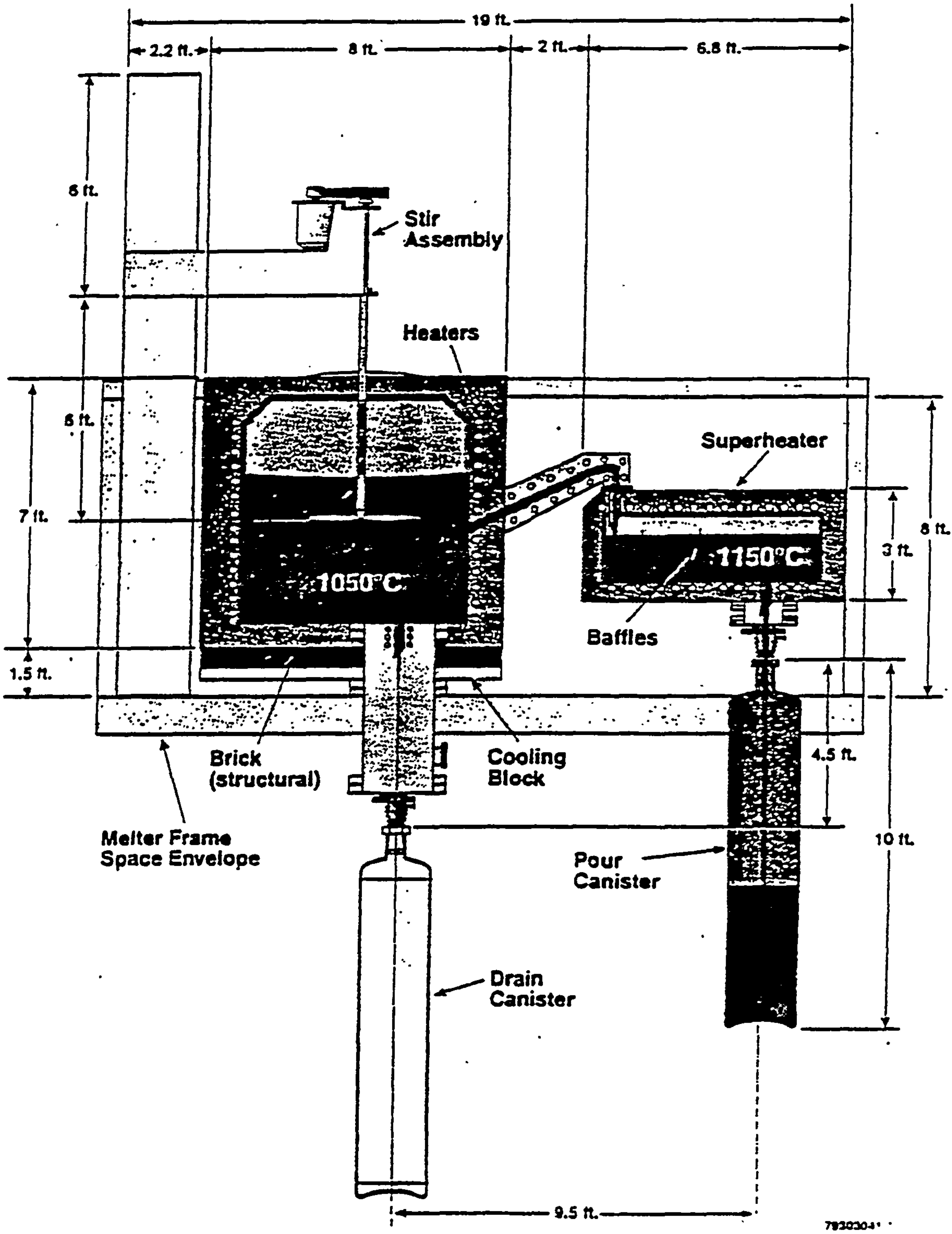

Figure 2.2. Stirred Melter for Savannah River

external resistance heaters surrounding the melter pot are used during startup and for additional temperature control during normal operation. These electric plate heaters are applied to the outside of the melting pot; they are embedded in ceramic with an air gap between the heaters and the pot. The bottom zone provides heat to the glass melt, and the upper zone maintains the required plenum temperature, typically at a minimum of 900°C.[2] Bickford specifies a minimum plenum temperature of 600°C for destroying organics (Bickford 1991).

The double-wall construction of the Inconel™ melting vessel serves as a glass containment system. The outer wall would contain the leaking glass if a breach of the melting tank occurred. Redundant leak protection sensors would alert operators of the breach so that a planned shut-down procedure could be started.[1]

The two systems for glass removal include a bottom drain and a primary glass pouring overflow system. The overflow drain is a continuous, gravity-controlled system. To initiate glass flow at the drain, the water cooling is shut off to allow a plug of frozen glass at the end of the drain to melt. Auxiliary heaters are also located at the bottom and overflow drains to maintain glass flow. If a superheater were added to the melter system (like the reference design for Savannah River), molten glass would flow into the superheater through the melter overflow system. The glass would travel by gravity through serpentine channels built into the superheater to provide a minimum residence time and eventually would reach the pour spout. Four zones of auxiliary resistance heaters would be used to heat the molten glass in the superheater, which would have refractory, insulation, and cooling water panels around the exterior. The superheater would be constructed from Inconel-690 in a box/vault shape.

The 220 kg/h•m^2 assumed specific glass production rate for dry feeding the melter, based on data reported from testing with a 1 ft^2 melter (Bickford 1991), is 5.5 times the assumed production rate (40 kg/h•m^2) for the low-temperature, ceramic-lined, joule-heated melter (LTCM). The specific production rates for stirred melter generally depend on whether the waste is slurry fed or dry fed and on the degree of surface agitation. These production rates and the method for determining the baseline value will be discussed in Section 3.G.

The baseline assumptions presented in this data package (25% waste loading in the glass, 16 MT/day glass production, and 220 kg/h•m^2 specific processing rate) led to suggest that the total glass surface area required for this technology is 3 m^2 (32.3 ft^2). Stir-Melter, Inc. recommended[2] use of four melters, each having a 9 ft^2 (0.836 m^2) surface area and a 3-ft glass pool depth. The same size melter is planned for testing at Savannah River. The 16 MT/day production rate includes an assumed 60% total on-line efficiency. Rounding the number of melters up to obtain the desired production rate provides a total predicted rate that is higher than required and therefore includes more down-time for repairs (approximately 55% on-line efficiency is required).

The baseline system for this data package does not include a superheater, unlike the systems planned for Savannah River and assumed by Fluor Daniel, Inc. Instead, the melter provides a minimum glass residence time of approximately 10 h to ensure good glass quality. Also, the melt pool is divided into two regions. The upper region is intensively mixed, and gas bubbles rise from the lower, unmixed region to produce a more dense and homogeneous glass product. The reason for not including the superheater in the baseline melter system is based strictly on information received from Stir-Melter, Inc. (see Section 8). Tables 2.1 and 2.2 provide basic parameters for both dry feeding (baseline) and slurry feeding (optional) in various melter sizes.

Table 2.1. Operating Parameters for Low-Temperature, Joule-Heated, Metal-Lined Melter(s)

Waste Feeding Method	Dry	Dry	Dry	Dry
Specific Glass Production Rate, (kg/h•m^2)	220	220	220	220
Waste Loading in Glass	25 wt%	25 wt%	25 wt%	25 wt%
Oxide Loading in Waste Slurry	125 g/L	125 g/L	125 g/L	125 g/L
Bulk Glass Temperature	1050°C	1050°C	1050°C	1050°C
Plenum Temperature	1000°C	1000°C	1000°C	1000°C
Glass Depth (nominal)	0.9 m	1.2 m	1.5 m	1.7 m
Glass Residence Time (hours)	10.4	13.9	17.3	19.7
Total Operating Efficiency	60 %	60 %	60 %	60 %
Internal Dimensions(c)	3 ft	4 ft	5 ft	5.7 ft
Number of Melter Lines	4	3	2	1
Glass Surface Area (m^2)	0.84	1.49	2.32	3.03
Glass Production Rate (MT/day)(d)	4.4	7.9	12.2	16
Glass Production Rate (kg/h)	182	328	510	667
Slurry Feed Rate (L/h)	364(b)	656(b)	1020(b)	1334(b)
Glass Holdup(a) (metric tons)	1.9	4.5	8.8	13.1

(a) Assumes a molten glass density of 2500 kg/m^3.
(b) slurry fed to evaporator.
(c) dimensions of molten glass pool, assumes length x width x depth are equal.
(d) production rates are per melter line.

Most of the information in the following sections was supplied by Stir-Melter, Inc., Savannah River Technology Center (SRTC), and Clemson University Research Park. Westinghouse Hanford Company (WHC) contracted Fluor Daniel, Inc. to evaluate the effect of the six candidate melters on the balance of the plant equipment. This study was released as a separate document.[3] The sections of this data package that are covered in the Fluor Daniel, Inc., study are left blank and the reader is referred to the other document as appropriate. Because of similarities between the LTCM and the stirred melter, some of the information provided in this data package is the same or similar to that provided in the data package for the LTCM.

1. Process Range of Composition

For the low-temperature melters, the waste form is assumed to be borosilicate glass. This assumption is based on several reviews (DOE/RL 1990), which recommend borosilicate glass for low-temperature melters because of its durability and processability. In 1981, an independent peer review panel evaluated eight waste forms for the solidification and disposal of HLW:[4] borosilicate glass, SYNROC, porous glass matrix, tailored ceramics, pyrolytic C and SiC coated particles, concrete, metal matrices, and plasma spray coatings. Borosilicate glass was recommended because it immobilizes a wide range of wastes and is insensitive to radiation damage, thermally stable, chemically durable, and processible.

A. Temperature

The maximum operating temperature of these melters is limited by the physical properties of the Inconel-690. The nominal operating temperature, recommended by Stir-Melter, Inc., is not to exceed 1050°C.

Table 2.2. Operating Parameters for Low-Temperature, Joule-Heated, Metal-Lined Melter(s)

Waste Feeding Method	Slurry	Slurry	Slurry	Slurry
Specific Glass Production Rate (kg/h•m^2)	150	150	150	150
Waste Loading in Glass	25 wt%	25 wt%	25 wt%	25 wt%
Oxide Loading in Waste Slurry (DOE/TIC 1981)	125 g/L	125 g/L	125 g/L	125 g/L
Bulk Glass Temperature	1050°C	1050°C	1050°C	1050°C
Plenum Temperature	1000°C	1000°C	1000°C	1000°C
Glass Depth (nominal)	0.9 m	1.2 m	1.5 m	2.1 m
Glass Residence Time (hours)	15.2	20.3	25.4	34.9
Total Operating Efficiency	60 %	60 %	60 %	60 %
Internal Dimensions[(b)]	3 ft	4 ft	5 ft	6.9 ft
Number of Melter Lines	6	3	2	1
Glass Surface Area (m^2)	0.84	1.49	2.32	4.44
Glass Production Rate (MT/day)[(c)]	3.0	5.4	8.4	16
Glass Production Rate (kg/h)	125	224	348	667
Waste Slurry Feed Rate (L/h)	250	448	696	1334
Glass Holdup[(a)] (MT)	1.9	4.5	8.8	23.3

(a) Assumes a molten glass density of 2500 kg/m^3.
(b) dimensions of molten glass pool, assumes length x width x depth are equal.
(c) production rates are per melter line.

> "We have found that there is an operating temperature limit of about 1050°C on the stir melter unit. This temperature limitation is mostly due to the temperature limitation of the Inconel material used to fabricate the melter tank and impeller. At one point, this temperature limit was at 1150°C, but extended times at this temperature caused the impeller to degrade. When the original impeller failed due to excessive temperatures, corrosion from high levels of B and P were also seen. These levels were >20 wt% B_2O_3 and about 1.7 wt% P_2O_5."[5]

This information was confirmed by David Bennert at the Clemson University Environmental Systems Engineering Department, who stated that the actual temperature limit is probably between 1050°C and 1100°C because of stress on the impeller. They have only operated successfully one time at a temperature higher than 1050°C, which was about 1070°C. A test done at 1150°C ended very quickly because of degradation of the impeller, however, it was felt that they may have actually been at a higher temperature (possibly 1220°C because of a bad thermocouple extension wire). Also, the failure may have been attributed to a high boron content in the glass (about 20% B_2O_3).[6]

B. Range of Waste Handling Capabilities

The following waste streams and waste stream simulants have been vitrified by this melter technology (see also Table 2.3):

- Simulated Savannah River Laboratory (SRL) HLW feed

Table 2.3. Glass Compositions Processed with the Stir-Melter™

Oxide (wt%)	Simulated SRL HLW (Richards and Lacsonen 1991)	SGM Feed	Simulated Batch 1 Feed[7] (a)	Simulated SRS M-Area Sludge[7]		Simulated Oak Ridge WETF Sludge[7]		Simulated West Valley HLW (Richards and Jain 1993)
			Target glass (no resin)	20% Borax	15% Borax	45% sludge	40% sludge	
Al_2O_3	3.8		4.82	16.17	19.00	7.59	6.93	6.00
B_2O_3	8.4		7.46	16.45	12.33	15.67		12.89
BaO			0.13	0.02	0.03	0.05	0.04	
CaO	1.6		1.24	1.03	0.54	25.89	27.25	
CeO_2						0.13	0.12	
Cr_2O_3	0.08		0.10	0.04	0.33	0.05	0.04	
Cs_2O			0.08					
CuO	0.21		0.36	0.01	0.02	0.11	0.09	
Fe_2O_3	12.5		12.42	0.92	3.71	2.11	1.49	12.02
K_2O	1.8		3.06	1.06	1.14	0.14		5.00
Li_2O	4.0		4.48				6.06	3.71
MgO	1.0		1.38	0.42	0.22	1.04	1.14	0.89
MnO_2	(MnO) 2.4		2.51	0.31	0.49			1.01
Na_2O	11.6		8.89	21.48	21.73	10.72	8.08	8.00
Nd_2O_3			0.60					
NiO	0.9		0.74	0.72	1.04	0.12	0.10	
P_2O_5	0.05		0.03	3.19	3.79	0.49	0.50	1.20
PbO			0.12	0.10	0.08	0.03	0.02	
RuO_2			0.03					
SiO_2	50.6		50.45	37.54	34.97	35.78	48.10	43.06
SrO	0.02		0.03					
TiO_2	0.8		0.58	0.04	0.04	0.08		0.80
ZnO	0.1		0.09	0.51	0.53		0.02	
ZrO_2			0.4					3.40
Other (b)	0.14							2.02
Total	100		100	100	100	100	100	100

(a) composition not available at the time of writing

(b) composition of "other" not specified in references

- Scale Glass Melter (SGM) feed, which is imulated sludge from the inital Defense Waste Processing Facility (DWPF) vitrification demonstrations at the SRTC

- Simulated Batch 1 feed from DWPF with secium-loaded ion-exchange resin

- Simulated Savannagh River Site (SRS) M-Area sludge with various amounts of hydrous borax additives.

- Simulated Oak Ridge Reservation West End Treatment Facility (WETF) sludge with mixtures of diatomaceous earth, hydrous borax, and a combination of silica, lithium carbonate, and sodium carbonate added

- West Valley high-level waste (HLW) simulants.

The acceptable range of melter feed/glass compositions from the Hanford Waste Vitrification Plant (HWVP) is shown in Table 2.4 (HWVP 1992). This glass contained 25% to 28% waste by weight, which was developed for Hanford Site neutralized current acid waste (NCAW). The NCAW is only a small fraction of the waste to be treated in the current vitrification plant. As shown later in Table 2.6, the NCAW glass must have a viscosity of 20 to 100 poise at 1150°C. At that temperature, it is believed that the ranges shown in Table 2.4 can produce a glass with a viscosity below 100 poise, the upper viscosity limit of the stirred melter (discussed later in this section).

Table 2.4. HWVP Melter Feed Constraints (wt%)

Oxide Component	Lower Bound	Upper Bound
Single-Component Constraints		
SiO_2	46	56
B_2O_3	7	17
Na_2O	7	12.5
Li_2O	2	6
CaO	0	7
MgO	0	5
Fe_2O_3	4	12
Al_2O_3	1	11
ZrO_2	0	10
Others	2	8
Solubility Components		
Cr_2O_3	--	0.5
F	--	1.7
P_2O_5	--	1.0
Sulfur as SO_3	--	0.5
$Rh_2O_3 + PdO + Ru_2O_3$	--	0.25

The actual compositions of the Hanford Site wastes remain to be determined. Initial scoping studies have been completed with various assumptions about the extent of blending that will be possible among the 177 Hanford Site tanks. The first study was done using an "All-Blend" composition that assumed perfect mixing of all 177 tanks. The "All-Blend" waste composition was calculated from tank inventory records, which are only approximate. The Compositional Variability Study (CVS) model developed for the NCAW predicted that this melter technology can produce a glass with 45% to 50% waste loading at 1150°C (which would require a superheater). This has not yet been confirmed experimentally. At 1050°C in the stirred melter, a waste loading of 40% to 45% might be achieved with the "All-Blend" waste composition; this also remains to be confirmed.[8]

A more realistic scenario is that complete blending of all tank wastes will not be possible. The CVS model predicted maximum waste loadings for 15 wastes at 1150°C when only the wastes from each tank farm were blended. The result was high waste loadings for some tank farms and low waste loadings for others, ranging from 17 wt% to 65 wt%. Table 2.5 lists the 15 waste compositions, the "All-Blend" waste (Case C in the table), and the NCAW. The row labeled "Low-T" is the predicted maximum waste loading achievable at 1150°C. The first row shows the limiting constituent in each glass formulation (zirconia phase, spinel formation, etc.). Again, this preliminary information cannot be used for final flowsheet development. These waste loadings may change for the 1050°C stirred melter, but the change is not expected to be significant. The changes will depend on whether the waste stream is high in refractory compounds or high in fluxes. Without knowing the mass of waste oxides in each tank farm it is not possible to predict the average waste loading for this blending scenario. A conservative 25 wt% waste loading is assumed for sizing estimates. WHC is evaluating which waste composition(s) should be used for flowsheet development and will distribute the results to the working group at the August meeting.

Compounds or elements that require special treatment in the off-gas system:

Tritium, mercury, carbon-14, and iodine cannot be incorporated into glass at 1050°C; they must be captured in the off-gas system and sent out as a secondary waste stream. Carbon-14 will probably be released to the atmosphere as long as the Clean Air Act standards are met.

Chlorine, fluorine, tellurium, technicium, cesium, cadmium, and ruthenium are partially soluble in the glass but require special considerations in the off-gas treatment system for recycle. They are discussed in Sections 1.D and 4.B.

Noble Metals: rhodium, palladium, and ruthenium are virtually insoluble in the reference borosilicate glass and all other expected glasses made from Hanford Site blended wastes. Previous tests and studies (Elliott et al. 1994) indicate that accumulation of these metals can cause electrical short circuiting and consequent premature failure of the LTCM (without agitation) at concentrations as low as 0.1 wt% in the glass. The "All-Blend" composition[4] contains only 0.07 wt% total noble metals ($Rh_2O_3 + PdO + Ru_2O_3$), so that at 25% waste loading, the total noble metals concentration would be only 0.02 wt%. Noble metals are not expected to accumulate as much in this melter as in non-stirred melters. The agitation of the glass melt occurs primarily in the upper zone of the melt cavity. Lower fluid velocities in the lower zone allows bubbles to rise, which may provide an opportunity for the noble metals to settle. It has been suggested that sludges could be removed from the bottom of the stirred melter by lowering the agitator into the

Table 2.5. Tank Farm Waste Compositions

	Others Components			Zr-phase		Spinel				Durability			Si	Al			
Oxide	TF-B (Wt%)	TF-T (Wt%)	TF-SX (Wt%)	TF-C (Wt%)	TF-DST (Wt%)	TF-A (Wt%)	TF-AX (Wt%)	TF-TY (Wt%)	TF-BY (Wt%)	TF-S (Wt%)	TF-DSSF (Wt%)	TF-U (Wt%)	TF-TX (Wt%)	TF-BX (Wt%)	Oxide	Case C (Wt%)	NCAW (Wt%)
SiO2	0.76	0.49	9.37	0.06	8.31	0.32	0.57	29.20	5.84	2.13	29.44	18.85	17.33	21.37	SiO2	10.00	4.03
B2O3					0.47		0.00				0.00				B2O3	0.00	0.01
Na2O	52.19	56.03	33.93	10.38	31.98	17.31	51.89	22.29	23.75	69.31	66.00	39.89	30.07	25.14	Na2O	25.30	21.42
Li2O					0.01		0.00								LiO2	0.00	0.00
CaO	0.03	0.00	1.24	9.39	0.79	0.03	2.79	0.00	5.66	0.00	0.62	0.00	0.01	0.12	CaO	2.06	0.79
MgO					0.27		0.00				0.00				MgO	0.08	0.20
Fe2O3	7.93	8.95	12.76	11.00	8.75	59.60	23.52	15.42	9.89	2.70	0.00	2.28	3.91	5.91	Fe2O3	11.00	28.21
Al2O3	1.20	0.66	22.74	7.55	2.65	1.48	1.46	10.06	12.33	13.20	2.00	16.73	15.83	22.98	Al2O3	13.00	9.04
ZrO2	0.22	0.42	0.01	25.85	35.20	0.04	0.05	2.52	0.22	2.93		0.30	0.40	0.33	ZrO2	7.08	15.11
Others	37.67	33.45	19.93	35.77	11.56	21.23	19.71	20.51	42.31	9.74	1.94	21.96	32.45	24.14	Others	31.41	21.19
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	Total	100.00	100.00
Bi2O3	6.43	8.83		0.05				0.33	0.03			0.04	0.05	0.04	Bi2O3	1.95	
CeO2	4.23	5.38	2.07	0.03	0.08	0.48	0.33	1.05	1.99	1.11		2.24	2.76	2.96	CeO2	2.73	0.60
Cr2O3	0.02	0.02	3.92	0.01	0.40	0.00	0.43	0.03	0.00	0.72	0.02	0.19	0.01	0.00	Cr2O3	0.45	0.26
F	0.72	0.50	0.04	1.56	1.43	0.00	0.01	0.04	0.52	0.12	0.07	00.07	0.12	0.17	F	0.56	0.10
La2O3	0.04	0.12			0.66										La2O3	0.43	0.65
MnO2	0.48	1.09	1.67	7.76	0.87	7.18	11.48	0.10	0.41	0.46	0.00	0.21	0.75	0.84	MnO2	1.82	2.14
NiO	0.23	0.03	0.30	5.69	0.47	0.22	0.66	0.00	11.64	0.17	0.00	0.01	0.25	1.25	NiO	2.27	2.30
P2O5	14.20	15.39	0.42	0.28	00.34	0.02	0.02	3.47	1.82	0.54	0.02	0.74	4.10	2.56	P2O5	4.71	0.87
SO3	0.18	0.03	0.22	0.16	0.43	0.41	0.02	0.59	0.23	0.28	0.07	0.06	0.51	0.54	SO3	0.34	0.65
SrO	0.00	0.00	0.01	0.00	0.02	0.02	0.00	0.00	3.45	0.00	0.00	0.00	0.00	0.05	SrO	0.41	0.12
U3O8	9.95	1.88	9.19	19.87	2.67	12.76	6.51	14.71	21.99	5.89	0.01	18.35	23.72	14.12	U3O8	14.30	4.74
Subtotal	36.47	33.27	17.84	35.40	7.37	21.09	19.45	20.32	42.08	9.29	0.19	21.90	32.27	22.53	Subtotal	29.97	12.43
Balance	1.20	0.18	2.09	0.37	4.19	0.14	0.26	0.19	0.23	0.44	1.75	0.00	0.18	1.62	Balance	1.44	8.76

Waste Loading (wt%)

Low-T	21	19	26	35	31	17	38	65	51	33	35	58	64	61	Low-T	45-50	33
High-T	21	19	26	46	40	25	43	84	64	39	41	60	73	61	High-T	62	50
Limit	P	P	Cr	Crystal	P?	Fe	Na	P	Others	Na	Na	Others	P	P	Limit	P	Crystal

melt pool, which should re-suspend any sludge accumulations. It is not clear whether noble metals are a concern for the Hanford Site HLW melter. Finally, if the noble metals do accumulate, they may not cause melter failure before other components fail.

Spinels: for several of the Hanford Site wastes, spinels (iron, chrome, nickel compounds) are the first crystals to form as NCAW glass cools. The Waste Acceptance Preliminary Specifications (WAPS) do not specify a limit for the amount of crystalline material in the glass (Larson 1989). The concern regarding formation of spinels (or any crystalline phase) is that the crystals will either reduce the durability of the waste form or affect the operation of the melter by filling the melt cavity with crystals. The two ways to deal with spinel formation are to design a melter that is compatible with crystals so that they do not affect durability or to formulate the glass so as to minimize crystal formation.

1. This agitator designed into the melter will help keep any crystalline materials suspended in the glass melt and thereby help prevent accumulation on the melter floor. However, agitation does not extend through the entire melt volume, and crystals could settle out in the lower melting zone. As mentioned, a sludge layer might be resuspended into the melt by lowering the agitator to near the melter floor.

> "For the most part, Clemson has been able to produce a consistent quality glass product. This is hampered the most when the drain spout temperature is not kept high enough. This can allow the formation of crystals at the drain spout, depending on glass composition."[5]

David Bennert later explained how they had problems with crystal formation near the drain spout. During processing of WETF feeds, which are primarily calcium-based wastes, one batch was processed with low silica and a consequent high calcium-to-silica ratio. Near the drain, the temperature was about 900°C, and $CaSiO_2$ crystals formed and clogged the drain. This was more of a glass-formulation problem than an operational problem, and the waste being treated was much different from the Hanford Site wastes. Clemson is using a torch on the drain to keep the temperature high enough to prevent clogging and crystal formation. For about six months, Stir-Melter has been operating a new weir-type drain with clamshell heater(s) on their 1/4 ft^2 melter.[6]

2. Glass development for the "All-Blend" waste is directed on minimizing crystal formation. Devitrification tests are conducted for each composition for 24 h at 100°C below the expected bulk glass temperature. The acceptance criterion is less than 0.1 wt% crystals in the glass. As stated, this may not be necessary for the stirred melter. If more crystals are present, waste form development will have to predict their type and quantity and their effect on durability.

Acceptable glass properties: The acceptable physical properties (HWVP 1992) for HWVP NCAW glass are shown in Table 2.6. This information may not be completely applicable to the stirred melter, but no other data is available.

- The redox (ferrous-to-ferric iron) ratio is controlled because overly oxidized glass tends to foam in the melter, and overly reduced glass tends to precipitate metals and spinels. David Bennert explained that they have observed increased impeller attack for wastes containing organics and good melter performance with oxidized glasses at 1050°C. They have tested a system for oxygen sparging into the glass melt, and found that it helps prolong the impeller life. He notes that it is important to stay within the specified range of oxidation state for DWPF.[9]

Table 2.6. Acceptable Glass Property Ranges for NCAW Glass

Property	Lower Bound	Upper Bound
Redox: Fe^{+2}/Fe^{+3}	0.005	0.3
Viscosity at 1150°C (Pa-s)	2	10
Liquidus Temperature (°C)	N/A	1050
Electrical Conductivity at 1150°C (S/cm)	0.18 (ρ=6 Ω-cm)	0.5 (ρ=2 Ω-cm)

- The viscosity is controlled because above 10 Pa-s (100 poise) glass does not mix well and the melter does not operate properly. Thin or inviscid glasses may increase etching or corrosion of the Inconel-690 pot.

> "There is also a viscosity limit of about 100 poise. At viscosities greater than this, we found that the stir melter could not handle the mixing and would not operate properly. We have processed 1) Scale Glass Melter (SGM) Feed, which is simulated sludge from the initial DWPF vitrification demonstrations at SRTC, 2) Simulated Batch 1 Feed for DWPF with cesium loaded Ion Exchange resin, 3) simulated SRS M-Area sludge with various amounts of borax additives, which was how we determine the viscosity limit of the melter, and 4) simulated Oak Ridge Reservation West End Treatment Facility sludge with both borax added and a combination of silica and Li_2CO_3 added."[5]

David Bennert later confirmed that the viscosity limit is about 100 poise. Because prediction of the viscosity during processing is difficult, they are installing a torque meter on their impeller that can act as a viscometer. He also clarified that the SGM Feed processed was glass that had already been melted two to three times by Stir-Melter, and they (Clemson) were simply re-melting the cullet. He was not able to verify the actual composition of this material because changes may have occurred during processing.[6]

- The maximum liquidus temperature is set 100°C below the average melter temperature so that crystals do not accumulate in the melter. Accumulation may not be a problem if agitation prevents settling of crystals to the melter floor or if the crystals are removed through the bottom drain.

- Electrical conductivity is controlled to permit joule heating of the glass. The electrical conductivity limits are not firm, because they are dependent on the distance between the melter electrodes (agitator and melt tank walls). If the melt is too conductive, the current limit will be exceeded for the Inconel™ electrodes, and consequent localized heating at the electrode surfaces will increase the corrosion rate. Electrode current limits are discussed further in Section 5.K.

Ability to handle slurry feeds: The stirred melter can be either dry- or liquid-fed. The baseline is to dry feed the waste separately from the dry glass formers, however either feeding option is equally acceptable. The Fluor Daniel, Inc. study assumed the waste would be slurry fed separately from the dry glass formers. The choice between slurry and dry feeding will remain arbitrary until further testing and evaluation are completed. The dry feeding option was chosen as the baseline for this data package only because it was recommended by Stir-Melter, Inc. An evaporation system similar to that presented in Data Package 1, Appendix B, could be used to dry the waste. As discussed in Data Package 1, reliable nozzles for slurry feeding have been developed.

Slurry can be fed to the stirred melter in different ways. One (preferred by Stir-Melter, Inc.) is to increase the agitation of the melt pool and feed the slurry directly into the vortex. This can exacerbate foaming and off-gas entrainment in the melter, but it also tends to increase the glass production rate. A more conservative approach (preferred by Clemson University) is to slow the agitation and feed the slurry on the outside of the melt pool, closer to the walls. Although the production rate may not be maximized, less foaming and off-gas entrainment may lead to steadier melter operation.[6]

C. Incorporation of Semivolatiles

Volatile losses from a liquid-fed melter appear to be affected by cold cap coverage, plenum temperature, and feed/glass composition. The baseline operation for this melter is without a cold cap (use of a cold cap limits the production rate), which may enhance volatilization of certain species (as compared to a 1150°C ceramic-lined unstirred melter). However, the slightly lower melting temperature could counteract the volatility effects of not having a cold cap. Because of its high specific activity, cesium volatility is of particular interest. The volatility of cesium was discussed in Data Package 1.

Off-gas data are available only for melters operated with a cold cap; therefore semivolatile incorporation for the stirred melter was not estimated. Clemson is initiating studies of off-gas entertainment and volatilization but has not yet reported data.

D. Ability to Handle Insoluble and Conductive Compounds

See Section 1.B.

E. Waste Loading

The waste loading in the glass is defined as the weight percent of waste (as oxides) in the final glass. The waste loading determines both the required production rate of the melter and the quantity of glass that will be produced from the Hanford Site tank wastes. The quantity of glass produced from the tank wastes is important for several reasons, primarily the high costs to place canisters in the federal repository.

The design basis for the HWVP with the NCAW glass at 1150°C was 25% to 28% waste loading, 3% recycle oxides, and 69% frit. Initial experiments indicate that this waste loading can easily be achieved for the "All-Blend" waste at 1150°C (45% to 50%). Waste loading of 40% to 45% may be achieved with the 1050°C stirred melter, although the glass durability may be affected.[8] This has not been proven experimentally. The extent and method of blending are not yet known, but tank wastes with problem constituents will likely be blended whenever practical to reduce impacts to the melter. Some of the tanks have high concentrations of problem compounds, such as Cr_2O_3 and P_2O_5. Waste loading will be less than 20% if the contents of these tanks cannot be diluted by blending with the other tanks. For calculational purposes, 25% waste loading assumed for the 1050°C stirred melter. The impact on melter production rate will be discussed in Sections 3 and 4.

2. Control Product Quality

For reasons stated in Section 1, the waste form for the low-temperature, metal-lined, joule-heated melter is assumed to be borosilicate glass.

A. Product Quality

There may be concerns about product quality because of the melter operating temperature limit of 1050°C. Although the baseline system does not include a superheater (secondary soak tank), one could be added to the melter to increase the glass temperature for any required time. The action of the impeller creates bubbles in the glass melt, the relative amount of bubbles depending on the impeller's speed and the depth in the melt. Clemson University prefers to operate their melter more conservatively, with lower agitation speeds and raising the impeller closer to the surface to provide a larger refining region near the bottom of the tank. This helps minimize both bubble formation and the amount of bubbles remaining in the glass. During normal operations, they achieve a glass product with a theoretical density of approximately 95%.[9] Stir-Melter initially produced glass with a theoretical density of 75% by operating their melter with the agitator deeply submerged in the glass (Richards and Lacsonen 1991). Current information on glass density as a function of feed rate, impeller speed, and impeller level is not available.

Glass durability data is not available at this time.

B. Waste Homogenization Capabilities

This melter is designed with an agitator, which thoroughly mixes the feed into the molten glass. This agitation facilitates dissolution of the waste, which reduces the required residence time to obtain a homogeneous product. The DWPF reference melter had a residence time of two days, but that of the 9 ft^2 stirred melter is 10 to 15 h. Homogeneity can be further controlled by increasing the melter depth and adjusting the depth to which the agitator penetrates the glass pool.

C. Analytical Requirements for Quality Acceptance

The stirred melter system is capable of accepting any qualified feed stream, either dry or liquid. The baseline technology includes an evaporator for drying the waste before it enters the stirred melter. After the waste solution is dried, the dry glass formers are fed separately to the melter. This reduces the amount of water that must be evaporated in the melter, but it also complicates the qualification of the product glass. Glass quality depends on control of the equipment that meters the frit to the melter. However, this method of product qualification is accepted for vitrification of HLWs in other countries. The conventional US method of qualifying the complete batch (glass formers and frit) in one tank is no longer possible. The DWPF in SRS and the West Valley Nuclear Services (WVNS) plant in New York propose mixing all of the feed constituents (waste, recycle, and frit) before acceptance of each batch.

D. Minimum and Optimum Residence Time

The baseline residence time for the stirred melter is about 10 h. Stir-Melter, Inc. suggested that a 2-to-4-h residence time was sufficient for the tests of a one square-foot melter, and a superheater was not required.[2,1]

At a constant production rate per melter surface area, the residence time is a function only of the melter depth. This melter technology has no significant depth requirements except enough depth is provided so that the current density limit for the electrodes is not exceeded (see Section 5.K).

E. Unpredictable Evaporation (Segregation) of Glass Components

This melter operates continuously under steady conditions, so that process upsets are rare. No other information has been provided.

3. Develop Technology on Schedule

This category deals mainly with the maturity of the technology. The low-temperature, joule-heated, metal-lined stirred melter technology has been tested on several waste streams in small-scale melters.

A. Ability to Meet TPA Milestones[a]

Information has not been supplied by the technology proponents.

B. Demonstrated Scale of Operation

This technology has been demonstrated at Clemson University and at Stir-Melter, Inc. on various waste simulants, as explained in Section 1.B, but not on actual radioactive feeds:

- 6 in. x 6 in. melter at Clemson University (no superheater, 2 to 4 lb glass/h, slurry fed) has logged approximately 4500 h[9]
- 1 ft. x 1 ft. melter at Stir-Melter, Inc. (no superheater, 32 lb glass/h, slurry fed, 47 lb glass/h, dry fed)
- 6 in. x 6 in. melter at Stir-Melter, Inc. (no superheater, 10 lb glass/h, slurry waste and dry glass formers fed separately) has logged more than 3000 h at Stir-Melter, Inc. (Stir-Melter, Inc. 1993)
- 3 ft. x 3 ft. melter at Savannah River (with superheater, not tested)

C. Availability of Data or Access to Data to Allow Evaluation for Melter System Technology Assessment and Melter System Candidate Selection

Data has been provided by Savannah River, Stir-Melter Inc., and Clemson University.

(a) Final melter selection by the end of 1998, plant startup by 2009, completion of campaigns by 2028.

D. Magnitude/Amount of Technical Development Required

As with any of the melters being evaluated, the tank waste characterization and glass development efforts will be significant. "It appears that this technology also relies heavily upon waste blending strategy development and glass composition development as do some of the other technologies being evaluated."[1]

This technology needs to be proven over extended periods with melter(s) larger than 1 ft. x 1 ft., the largest stirred melter actually tested to date. This would provide information on corrosion and lifetime of materials, volatility of feed components, production rates, preferred methods of operating, etc. The following is a list of key issues that were identified by Fluor Daniel, Inc. in a study completed for WHC in August 1993:

1. erosion/corrosion resistance of the agitator and melter pot
2. creep resistance of the Inconel-690 pot
3. glass transport system control between the melter and superheater, and pour control from the superheater to the canister
4. process optimization (vertical adjustment of the agitator and foam control)
5. ability to remove agitator, pot, and superheater from the melter frame
6. melter off-gas generation characteristics
7. current density limitations between primary glass melting electrodes
8. waste processing rate
9. agitator/pot seal performance.

The work required to scale up this technology is significant. Extensive testing would be required for the nine items listed above, and possibly others, each time a larger-scale melter is designed and constructed. A 3 ft. x 3 ft. stirred melter has been constructed for testing at Savannah River, but testing has not been initiated. An even larger melter may be required for the Hanford HLW vitrification plant, depending on the method of feeding and the number of parallel melter lines.

The following text was taken from a report written in April 1991, indicating the research and development programs felt necessary to develop a full-scale stirred melter for DWPF:

> "As necessary steps to adapt this technology to the DWPF, the following are recommended (in chronological order):
>
> 1. A Laboratory Stirred Melter capable of processing simulated HLW and possibly non-HLW should be installed in a hood in SRL. This should begin immediately, as it is required to demonstrate melter sealing features and for melter operation studies to support the following recommended programs.

2. Conduct design studies to develop a modular Full-Scale DWPF Stirred Melter design to facilitate repairs and to optimize a method for secondary glass containment.

3. A Full-Scale DWPF Stirred Melter should be designed, built, and tested. The feed and off-gas systems should only be built on the basis of demonstration of connections and sufficient support to allow the stirred melter to operate with simulated HLW feed. It is believed that it will take two to three generations of stirred melter development before the design could be used at DWPF. These generations, however, should be relatively short because they involve changes only to Inconel and thermal insulation, and will not require refractory construction or procurement as was necessary in earlier designs" (Bickford 1991).

E. Additional Technical Development Required for Deployment

This is unknown at this time.

F. Probability of Technical Success Within Schedule and Resource Constraints

The proponents have provided no input with respect to the Hanford HLW vitrification; however the following statement was made regarding the use of the stirred melter as the second generation DWPF design:

> "It was determined that a program for developing the stirred melter for DWPF is clearly needed, and would have a high confidence of making major beneficial impacts on the safe and efficient disposal of HLW at SRS and at other DOE Sites. The high probability of success is based on the fact that small-scale stirred melters have already shown to be feasible and that sufficient technical experience is available through onsite personnel, other DOE Sites, and contractors to develop and demonstrate melters for radioactive waste" (Bickford 1991).

A 3 ft. x 3 ft. stirred melter is currently ready for installation and testing (at Savannah River). This system is similar to the baseline design chosen for this data package, except it includes a superheater to hold the glass at 1150°C for 4 h. Also, the Savannah River design is slurry fed and the waste and glass formers are mixed before feeding.

G. Processing Rate

As stated, the assumed processing rates for the low-temperature, metal-lined, joule-heated melter are 220 $kg/h{\bullet}m^2$ for dry feeding and 150 $kg/h{\bullet}m^2$ for slurry feeding. As will be shown, determining scaled production rate estimates with existing information is difficult.

Testing performed by Stir-Melter, Inc. and sponsored by SRL with simulated HLW slurry in a 1-ft^2 stirred melter (denoted F1) with a slurry feed of 60% water and 40% solids produced a glass with a composition shown in Table 2.3, column #1. Without stirring, the maximum glass output was 1.8 kg/h (19.4 $kg/h{\bullet}m^2$) at 1050°C. This production rate was significantly increased by agitating the melt and minimizing the depth of the agitator in the glass. A maximum glass output of 14.5 kg/h (156 $kg/h{\bullet}m^2$) was reached when the agitator was 15 in. from the bottom of the melter, and density of the glass exceeded 98% (Richards et al. 1991). This is an 8-fold increase in production rate over the unagitated stirred melter at 1050°C, but not necessarily over other comparable melters.

Further testing with a dry feed of similar composition achieved a maximum melting rate of 21.4 kg/h (230 kg/h•m^2) (Richards et al. 1991), a 1.5-fold increase in maximum specific production rate versus that obtained with slurry feeding. Stir-Melter[2] indicated that the design production rate for the Savannah River 9-ft^2 slurry-fed melter is 275 lb/h (150 kg/h•m^2) and we should expect to achieve 500 lb/h (272 kg/h•m^2) when dry feeding, a 1.8-fold increase. This 500 lb/h rate has not been verified with actual data; therefore the observed 1.5-fold increase is used to scale the 9-ft^2 production rate from 150 to 220 kg/h•m^2 for the baseline melter.

H. Extent of Mock-Ups and Test Facilities Required

Existing testing facilities include

- the 1/4 ft^2 stirred melter at Clemson University,
- the 1/4 ft^2 stirred melter at Stir-Melter, Inc., and
- the 1 ft^2 stirred melter at Stir-Melter, Inc. (decommissioned and disassembled)[1]
- the 0.5 ft^2 stirred melter at Stir-Melter, Inc.[1]
- the 9 ft^2 stirred melter at Savannah River

The baseline system chosen for this data package is not actually available for testing; the most likely available system to be used for testing purposes is the 9-ft^2 Savannah River stirred melter.

I. Necessity for New Inventions

This is unknown at this time.

4. Integration with Process and Facility - *This section was provided by Fluor Daniel, Inc.*[3]

5. Control and Maintenance of Process and Facility

This section includes a discussion about the ability of the melter technology to allow safe and efficient operation of the vitrification facility.

A. Ease of Control

Information is currently not available.

B. Remoteability

The agitator/column lift assembly will have the capability to be removed and replaced separately from the remaining melter system. It may also be possible to remove the Inconel 690 melter pot from the remainder of the assembly (Fluor Daniel, Inc. 1993). When the HWVP reviewed the stirred melter concept for increased capacity, it was expected that the entire melter would need to be removed upon melter failure, not just the metal pot.

> "For the most part, the stir melter requires little 'hands-on' operation when operating correctly. Some of the problems that have occurred could have been performed remotely, but would have been more difficult. The biggest concern with operating remotely would be pluggage of the drain tube, because this would be hard to clear remotely." ... " As mentioned earlier, when the stir melter is operating correctly, it can easily be operated remotely. The video camera that has been installed with the unit has greatly aided Clemson in knowing what their operating conditions were and this would be a great advantage in a remote setting. During the demonstrations with the ion exchange feed, loading of the resin did cause some violent reactions because of the large amount of foaming and sparking, so we had to take care to remove the video camera equipment so it wouldn't be ruined. If there was a potential to operate with this type of material, this should be considered."[5]

C. Reliability

The reliability is measured by the total operating efficiency (TOE). The TOE is defined as the total number of hours that the melter operates divided by the total number of hours that the melter is in place, including the time required for melter change out. The assumed TOE for this melter is 60%. Stir-Melter, Inc., Clemson University, and Savannah River have provided no operational data (including operating efficiencies); therefore the assumed 60% TOE may change.

The given production rate of 16 MT/day glass would require 4 melters, each with a 9-ft^2 processing area (as discussed in the introduction). That glass production rate includes a 60% TOE assumption. The total glass production rate actually achieved with 4 melters is slightly higher (17.7 MT/day) than the required value, thus allowing for more down-time for repairs (approximately 55% on-line efficiency actually required). Note that the multiple melter vitrification facility produces 13.3 MT/day even if one of the four melters was off-line for maintenance, thus maintaining the facility's production at ~ 83% of normal.

D. Maintainability

Information in this area has not yet been received.

E. Estimated Lifetime

The minimum melter lifetime of the HWVP melter was two years, and the expected lifetime was three to five years. Estimates of the stirred melter lifetime have not yet been completed because of limited data on reliability of melter components and materials life during processing Hanford HLW feeds.

"Melter Lifetime: The biggest limitation we have seen so far was the corrosion interaction between the impeller and the feed streams. We have had very little corrosion in the tank itself, but did have the problems with the welds."[5]

"To the best of our current knowledge, all components in the design (WV-20) are intended to have a two year life minimum. Experience derived from the WSRC tests may modify the present designs. No items in the present design are anticipated to have a life less than six months" (Stir-Melter, Inc. 1993).

F. Ability to Confine Radioactive Materials

"Glass melter tank failure with subsequent leakage of radioactive waste glass is difficult to predict. Stir-Melter's double wall alloy melt vessel provides glass leak containment."[1]

A vacuum on the melter plenum minimizes the likelihood of airborne release of radionuclides to the vitrification cell. The accumulation of deposits (e.g., cesium) in the off-gas line can be controlled by using a film cooler to quench and dilute the hot off gas leaving the melter or by regularly cleaning the off-gas line with either a reamer or an air "blaster."

Maintainance of equipment is a significant source of radioactive materials; this does not appear to be directly related to the melter technology.

There was a concern raised during the June meeting regarding air in-leakage. The following are two responses received:

"Air Inleakage: During one of the demonstrations recently performed at Clemson, they were able to completely seal the stir melter system, so this does not appear that it would be a great problem."[5]

"Air Inleakage Concern: This is assumed to reference the seal required at the impeller's rotating shaft. An engineered electrically insulated, minimal inleakage, seal system has been developed for the impeller shaft which allows impeller height adjustment within the melt vessel. Since the off-gas system is assumed to pull negative pressure on the melt vessel, a small controlled air inleak is designed into the shaft seal so there is no potential for out-gassing to the outside of the melter."[10]

Also, David Bennert confirmed that improvements have been made to the melter seals on the 6 in. x 6 in. melter at Clemson.[9] Greater improvements may be required for a larger melter.

G. Potential for Radioactive Source Buildup and Achievement of ALARA

Off-gas treatment is discussed in the Fluor Daniel, Inc. report.[3]

This melter has a bottom drain, which can be used to drain the glass from the melt cavity at the end of the melter life. This may be optimistic. Melter failure could occur such that the glass could not be drained from the melter. This is an unresolved problem for most of the melters being considered in this evaluation.

H. Sealing and Containment Relative to Melter

Measures are taken to seal the melter to prevent leakage into the off-gas system and out to the melter cell, a longstanding and significant challenge for designing remote melters. Metal bellows seal the canister to the melter during glass pouring. Packing materials are used to seal all flanged connections such as the melter lid, off-gas pipes, and lid penetrations.

Also see comments in Section 5.F

I. Modular Design Concepts that Simplify Replacement or Repair

The proposed Stir-Melter™ system consists of two modules: the agitator/column lift assembly and the primary melter pot assembly. If a superheater is included in the design, it would also be added as an additional module to the system. The module concept will facilitate removal and replacement of components with a reduction in the number of jumper removal operations (Fluor Daniel, Inc. 1993).

J. Refractory Life

The low-temperature stirred melter does not have refractory, but instead an Inconel™ alloy melting pot that is subject to corrosion. The small-scale melter at the Clemson Research Park was constructed of 0.2-in.-thick Inconel-601 plate. The corner joints of the melting pot were non-structural seal welds, and cracks developed from a mechanical overload caused by bulging side walls on the melter vessel. This bulging was a result of differential thermal contraction between the solid glass and the metal container during cooling. Analysis of the weld joints showed that the failure was a result of loading on the corner welds, which were structurally inadequate, and that corrosion was evident on surfaces exposed to the glass melt or process vapors. The welds have been repaired with Inconel-690 and structural supports have been added to the outside corners.[11]

David Bennert later clarified that although the corner welds had cracked, substantial corrosion had not been present. Although some corrosion was evident, he stated that is was a result of the corner welds cracking, which is not a normal or expected occurrence. The corner welds were repaired, and the vessel continues to be structurally sound.[12] He also stated that tank corrosion is not as important as corrosion on the impeller. He noted further that the Inconel-601 melter currently has about 4500 h logged, and had about 3000 h at the time of the failure.[9] At this time, it is unknown which statements regarding the extent of tank wall corrosion are correct, therefore this issue cannot be resolved. Dennis Bickford of Savannah River might have some additional information. The melter tank for the Hanford HLW vitrification plant will be constructed of Inconel-690, which has greater corrosion resistance and less mechanical strength than does Inconel-601.

In 1991, a program was initiated by the SRS at the request of DOE-HQ to study the use of the stirred melter as a replacement for the existing DWPF melter. This investigation identified several possible problems related to use of the stirred melter, of which the development of "hot spots" was one. It was felt that "hot spots" would result from high localized current densities in sections of the walls that are closest to the agitator, and that this tendency would increase with increasing melter size. It was suggested that changing the melter geometry to a circular cross section would remove this tendency (PRC 1994). At this time, experimental data have not been provided to support the concept that localized "hot spots" are actually a problem, or that the proposed solution of using a round melter tank would resolve it. If a round tank were incorporated, the use of baffles in the tank (to promote mixing) could create an entire set of new problems.[9]

K. Electrode Life/Replacement

This melter has one electrode constructed from Inconel-690, which is also the melt pool agitator. The following information was taken from a report written by Stir-Melter, Inc. for use in the Phase II study:

> "Another concern is the effect of high current densities of the electrode surfaces. For Stir-Melters, this focuses the attention on the impeller since the melter wall has a much larger surface area. In commercial glass melters using molybdenum electrodes, a conventional current loading limit for practical electrode life is about 8 amps/in^2. Tests of alloy 690 in HLW glasses by WSRC have indicated little damage at 25 or more amps/cm^2 (no reference given). This converts to over 160 amps/in^2. Our melting experience with alloy 690 has shown that these surprisingly high numbers may be valid, at least we have only seen slight rounding of sharp corners where current densities are extreme. The WV-20 impeller design will be based on 50 amps/in^2 which is a very conservative number based on our melting experience" (Stir-Melter, Inc. 1993).
>
> "The impeller has been the one piece of equipment that we have had to replace the most due to chemical interaction and the excessive temperature degradation."[5]
>
> "Our WV-1 melter has operated over 3000 h at about 1050°C with no deformation of the blades. In addition, the WV-20 will have a water cooled mild steel shaft. This will significantly reduce the temperatures in the blade roots which are the area of highest stress" (Stir-Melter, Inc. 1993).

L. Ability to Safely Handle Organics

It is planned that all organics will be destroyed in the plenum space of the melter. Two zones of auxiliary heaters in the melter pot are used during startup and for additional temperature control during normal operation. These heaters are electric plate heaters applied to the outside of the melting pot and are embedded in ceramic. The bottom zone provides heat to the glass melt, and the upper zone maintains the temperature in the plenum space at 1000° to 1050°C, with a minimum temperature of 900°C.[2] A second source specifies a minimum plenum temperature of 600°C to destroy organics (Bickford et al. 1991).

M. Operational Simplicity

Information is currently not available.

N. Estimated Lifetime

See Section 5.E.

O. Estimated Downtime to Repair

Information is currently not available.

6. Minimize Total Cost - *This section is provided by Fluor Daniel, Inc.*[3]

7. Minimize Safety and Environmental Risk

A. Plant/worker safety

Information is currently not available.

B. Off-gas - extent of system to remediate off-gas so it can meet site release rates and Clean Air Act of 1955 requirements for radionuclides, etc.

Information is currently not available.

C. High energy issues

Information is currently not available.

D. Criticality

Information is currently not available.

E. Passive shutdown

As discussed in Section 5.J., problems were experienced with the small-scale Clemson University melter when it was cooled down with a full glass load. Bulging of the Inconel-601 tank walls resulted from differential thermal contraction between the solid glass and the metal container. Cracks formed in the corner weld seals, which were later found to be structurally inadequate. Metal tanks constructed in the future will probably be made from Inconel-690.[11,9] The "bulging wall" problem must be addressed. This could be resolved by either increasing the structural integrity with design modifications or by ensuring that melter cooldowns are avoided when the melter is full of glass.

8. Other Risks/Limitations

During the June Technical Advisory Committee (TAC) meeting, several key issues were identified for the various melter technologies that warranted special attention in these data packages. These issues were included in a set of letters sent to the proponents of melter technologies, and the following is the response received from Stir-Melter, Inc.[10]

- **Not Demonstrated to Determine Scale-Up**
  "Alloy Stir-Melter™ Systems are a new developing technology and as such do not have a long history of operation. The significant technical advantages offered by the alloy Stir-Melter™

Systems in terms of low mass, rapid start-stop capability, integral melt vessel construction, and systems sealing capability are sufficient to proceed at this point with experimental studies allowing scale-up development to continue as the concept for the Hanford HLW disposal problem is defined. Note that a 9 ft^2 melter is under construction at Stir-Melter™ for delivery to WSRC in October 1994."

- **Air Inleakage Concern**
  "This is assumed to reference the seal required at the impeller's rotating shaft. An engineered, electrically insulated, minimal inleakage, seal system has been developed for the impeller shaft, which allows impeller height adjustment within the melt vessel. Because the off-gas system is assumed to pull negative pressure on the melt vessel, a small controlled air inleak is designed into the shaft seal so there is no potential for out-gassing to the outside of the melter."

- **Risk of Sludge Forming in Refining Chamber**
  "The refining chamber referred to is Stir-Melter's "superheater." The superheater is purely an artifact of responding to the prescribed need for DWPF glass to be processed at 1150°C for 4 h. Samples of DWPF simulated glass taken from the output of the Stir-Melter™ System have been shown to pass leach tests. The risk noted is eliminated by correct glass formulation and simply removing the superheater from the system."

- **System Corrosion/Abrasion and Lifetime Concerns**
  "The alloy Stir-Melter™ Systems have the capability of operating at significantly lower temperatures than refractory ceramic counterparts. The question of corrosion/abrasion resistance capability requires the input of glass technologists to engineer appropriate glass compositions to meet the leach resistance and melting process requirements. Significant inroads developing such tailored compositions have been made by SRTC in its glass group. Any application for waste glass melting in alloy Stir-Melter™ Systems should start with a *strong experimental* program employing both Stir-Melter™ and SRTC. The concerns over "potential" risks of corrosion and/or abrasion can be addressed with hard data through an applied development program."

- **Operability Concerns; Dynamic Operation**
  "This is assumed to reference the need to spin the impeller within the glass melt. An Inconel-690 impeller and vessel logged 3500$^+$ h operating with a simulated DWPF glass without detectable degradation. Simple, to-the-belt mechanical drive systems of the type used in Stir-Melter™ Systems designs are used routinely in industrial applications without concern."

- **Volatility; Degree of Volatility with No Cold-Cap**
  "Alloy Stir-Melter™ Systems can operate with a cold cap through reduced impeller rotations to yield only four times glass output of an equivalent area joule-heated melter rather than the maximum of ~ eight times the output. If the process requires cold cap, the Stir-Melter™ System size would still be less than a conventional joule-heated melter and the process would run a cold cap or, if required, a "warm" cap. Also note that the lower temperature for melting an "engineered glass" reduces the potential for accelerating the evolution of volatile species."

Endnotes

1. Letter from K. Kormanyos (Stir-Melter, Inc.) to P. Shafer (PNL) dated January 13, 1995.
2. Telephone conversation between K. Kormanyos (Stir-Melter, Inc.) and P. Shafer (PNL) on August 12, 1994.
3. Fluor Daniel, Inc. August 1994. "Alternative Melter Systems Assessment 20 Metric Tons per Day HLW Glass Production." Prepared under contract #04-436304 with Westinghouse Hanford Company.
4. Letter from R.W. Powell (WHC) to J.M. Creer (PNL), "Double-Shell Tank/Single-Shell Tank Waste Blend Composition for High-Level Waste Vitrification Processes Testing." May 1994.
5. Fax from C.A. Cicero (WSRC) to M. Elliott (PNL) dated August 10, 1994.
6. Telephone conversation between D. Bennert (Clemson University Environmental Systems Engineering Department), M. Elliott (PNL), and P. Shafer (PNL) on August 11, 1994.
7. Fax from C.A. Cicero (WSRC) to P. Shafer (PNL) dated January 10, 1995.
8. Telephone conversation between D.S. Kim (PNL) and P. Shafer (PNL) on August 12, 1994.
9. Telephone conversation between D. Bennert (Clemson University), M. Elliott (PNL), and P. Shafer (PNL) on August 15, 1994.
10. Letter from K. Kormanyos (Stir-Melter, Inc.) to P. Shafer (PNL) dated August 1, 1994.
11. Memorandum from C.F. Jenkins, Equipment & Materials Technology, Materials Consulation Group, to D.F. Bickford, DWPT. April 28, 1994. *Stirred Melter Pot Failure, Clemson Research Melter (U).* SRT-MTS-945062.
12. Telephone conversation between D. Bennert (Clemson University) and P. Shafer (PNL) on January 4, 1995.

Data Package 3

Low-Frequency Induction Melter

Description of Technology

This melter technology uses a two-step process to convert the waste into glass. The waste slurry is first fed to a rotary calciner that converts the feed solution to a calcined mixture of oxides and nitrates (See Figure 3.1). The calcine is continuously mixed with frit and transferred to an inductively heated metal melter that converts the calcine to glass. This technology is currently used to vitrify reprocessing wastes at the R-7 and T-7 vitrification plants in La Hague, France, and at the Windscale Vitrification Plant in Sellafield, England.

The rotary calciner tube is 0.3 m in diameter by 3-m long and is constructed of Uranus 2520 alloy. Tube rotation is usually 20 rpm. The tube is slightly inclined from the horizontal (~3%) so that the feed slowly progresses to the melter. The calciner has an internal rabble bar (2.5 m long) to break up the calcine and keep it from sticking to the walls. The calciner has a holdup of 1-2 kg of solids. Heating is provided by a four-zone 94-kW resistance furnace (two 32-kW and two 15-kW zones). The calciner is operated at a reduced pressure (-1KPa), and air tightness is ensured by a graphite sealing ring in each of the end fittings (Beveridge 1990). The evaporative capacity of the calciner (Jouan, Hugony, and Maillet 1986) is 60 L/h. Glass frit is introduced through an air-lock system into the lower end-fitting of the calciner and falls into the melter with the calcine.

The melter is an oval pot, 1 m (major axis) x 0.35 m (minor axis) x 0.95 m high (see Figure 3.2), constructed from 10-mm-thick Inconel-601. A four-zone medium-frequency (4 kHz, 200 kW) induction coil heats the metal pot, which then heats the glass by thermal conduction. The pot contains internal fins to increase heat transfer to the glass. Because heating is supplied only to the outside of the melter, scale-up is limited to about 30 kg/h. The melter is equipped with a sparge tube to insure homogeneity of the glass.

Each melter includes a pouring nozzle and a draining nozzle. The nozzles are heated by separate induction coils and are normally plugged with solid glass. To initiate routine pouring, the pouring nozzle is heated to melt the glass plug. The pouring nozzle is equipped with a siphon to maintain a minimum level of glass in the melter during plant operation. The glass is cast over 30-min loads, leaving a heel of about 70 kg in the melter (Sombret 1987). When the melter must be removed for maintenance, the draining nozzle is used to empty it (ECA 1993).

The off gas from both the calciner and melter flows counter-currently through the system and out the top of the calciner. The off gases are treated in a dust scrubber, a condenser, an absorption column, and a washing column before final filtration across high-efficiency particulate air (HEPA) filters. The dust scrubber solution is recycled back to the calciner.

Basic parameters for this technology are presented in Table 3.1. This technology would require that 14 to 27 melter lines be constructed to meet the processing rate requirements. Mr. Antoine Jouan of CEA, France, notes that this may be "...too much for the low-frequency induction melter (LFIM)."[1] He suggested that starting the Hanford plant with this technology and retrofitting a newer, higher capacity melter into the plant at a later date would reduce the number of LFIMs required in the initial plant.

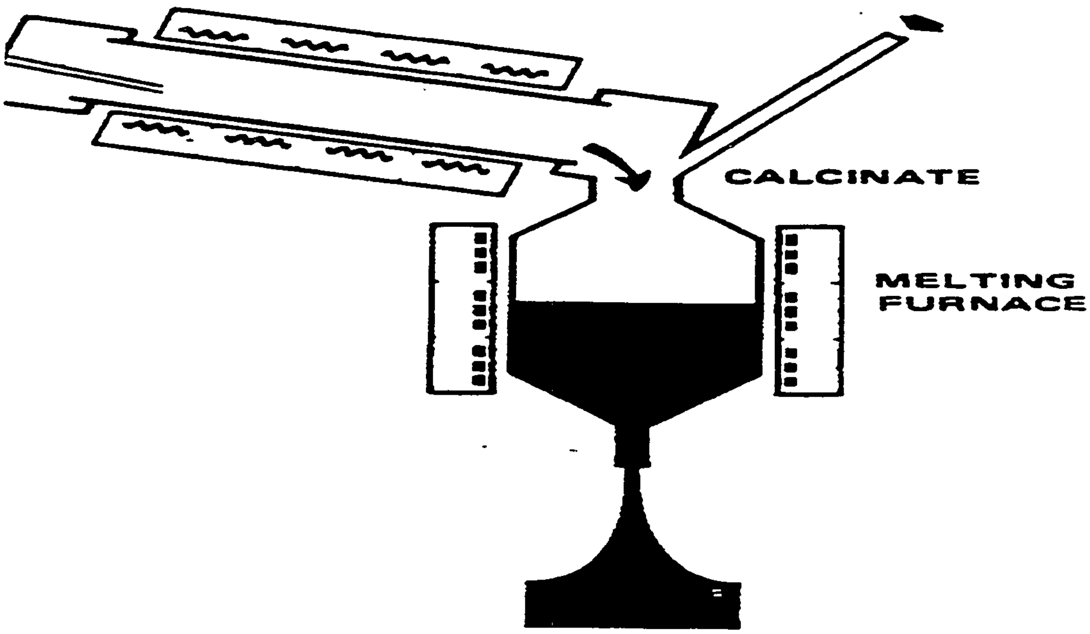

Figure 3.1. Low-Frequency Induction Melter

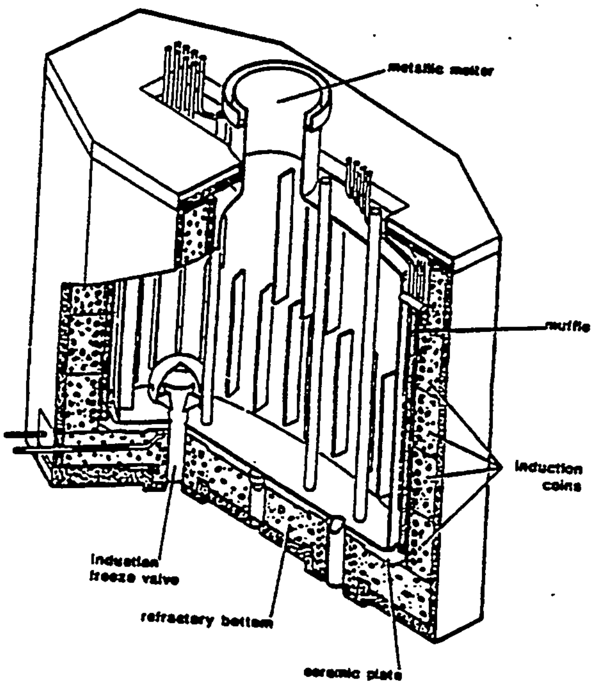

Figure 3.2. Melting Furnace

Table 3.1. Operating Parameters for Low-Frequency Induction Melter with Calciner

Nominal Glass Production Rate per Melter	25 kg/h	
Oxide Loading in Waste Slurry (w/o frit) to Calciner[a]	200 g/L	
Bulk Glass Temperature	1050-1100°C	
Melt Pool Dimensions (oval)	0.35 m x 1.0 m	
Glass Surface Area per Melter	0.27 m^2	
Glass Depth[b] (crucible depth = 1.2 m)	0.34 m	
Glass Residence Time	6 h	
Total Operating Efficiency	60%	
Glass Holdup per Melter[c] (MT)	0.23	
Waste Loading in Glass	25 wt%	50 wt%
Number of Melter/Calciner Lines Required	27	14
Slurry Feed Rate to Each Calciner	31 L/h	63 L/h[d]
Total Glass Production Rate (MT/day)	16.2	8.4
Glass Production Rate per melter (kg/h)	675	350
Waste Processing Rate (kg oxide/h)	169	175

(a) Assumption of slurry concentration based on WHC direction given to Fluor. This is probably the highest concentration of waste slurry that can still be pumped. Note that the melters that combine the glass formers with the waste slurry before addition to the melter have 125 g waste oxides/liter.

(b) Calculated based on 2500 kg/m^3 glass density.

(c) Estimated based on 200 kg glass poured per batch, plus estimated 30 to 70 kg heel remaining.

(d) If 50% waste loading is achieved, the current calciner (60 L/h max) will have to be slightly enlarged.

1. Process Range of Composition

For the LFIM, the waste form is assumed to be borosilicate glass at 25 wt% waste loading. The choice of borosilicate glass was explained in Data Package 1.

A. Temperature

The maximum operating temperature of these melters is 1050°C to 1100°C.

"Nominal operating temperature is today in La Hague R7T7 facility 1100°C. Lower operating temperature increases, of course, the life time of the pot; it's also a problem of glass composition choice; if a glass, reaching the quality requirements, could be made and poured at 1050°C or 1070°C, why not?"[2]

B. Range of Waste Handling Capabilities

Both parts of the LFIM system, the calciner and the induction melter, must be considered when determining the waste handling capabilities for the LFIM. This section first addresses the capability of the LFIM to vitrify Hanford Site wastes, the capability of the calciner to dry the waste before frit addition and vitrification.

The actual compositions of the Hanford Site wastes are yet to be determined. Initial scoping studies used various assumptions about the extent of blending that will be possible among the 177 Hanford Site tanks. The first study used an "All-Blend" composition that assumed perfect mixing of all 177 tanks and was calculated from tank inventory records that are only approximate. The Compositional Variability Study (CVS) model developed for the neutralized current acid waste (NCAW) predicted that this melter technology can produce glass with 45% to 50% waste loading at 1150°C. This remains to be confirmed with experimental results. It is also not clear how much reducing the melting temperature to between 1050 and 1100°C will affect waste loading or durability.

A more realistic tank blending scenario is that complete blending of all tank wastes will not be possible. The CVS model predicted maximum waste loadings for 15 different wastes if only the wastes in each tank farm were blended. The result was high waste loadings for some tank farms and low waste loadings for others, in a range of from 17 wt% to 65 wt%. This preliminary information cannot be used for final flowsheet development. Without knowing the mass of waste oxides in each tank farm it is not possible to know the average waste loading for this blending scenario. For conservative estimates, 25 wt% loading is assumed for sizing this melter technology. WHC is currently evaluating which waste composition(s) should be used for flowsheet development. (All information in the previous two paragraphs was provided by PNL.)

Environmental Corporation of America (ECA) provided the following regarding feed components (ECA 1993):

> "Phosphates — The reference plant process (T7 at La Hague) has limited experience with the higher levels of phosphates expected in the waste stream at the Hanford Site. As discussed in the DOE's background package, there are three approaches to the vitrification of phosphates:
>
> > One is to incorporate them in borosilicate glass. The experience of the reference plant is to limit phosphates in the glass to 3% so as not to impair characteristics such as viscosity, crystallization, and the like.
> >
> > A second approach is to formulate a phosphoborosilicate glass. A glass of this kind with 8.5% phosphate by weight is currently being studied in connection with the reference process. It is expected that a small amount of such glass will be produced in the R7 plant to eliminate a backlog of uranium molybdenum waste. The effect of phosphate on the operating life of the melter, however, remains a serious concern, and it may not be practical to process a large amount of this waste.
> >
> > Finally, the third approach is to eliminate phosphates by alkaline washing. This is a very attractive approach. Not only would such treatment eliminate the concern about phosphate, it would also remove aluminum and chromium and reduce the volume of high-level waste by 50% or more."

The rotary calciner has been suggested for use by the French, who use it at the R-7 and T-7 vitrification plants at La Hague; the British use it at the Windscale Vitrification Plant at Sellafield. These calciner designs have been thoroughly tested for acid wastes from nuclear fuel reprocessing plants. ECA (ECA 1993) provided the following comments about the compatibility of the rotary calciner with certain waste constituents.

> "Alkaline Metals — When alkaline metals including, Na, K, and Li — constitute 50% or more of the waste, they must be combined with aluminum in the feedstock in a ratio of aluminum to alkaline metals of about 0.3 (molar). This balance is required for both calcination and vitrification. For instance, Na can cause caking in the calciner unless balanced by Al, while Al, which is inert and highly refractory, will resist vitrification unless balanced by Na. A ratio of 0.3 (molar) ensures proper performance in both systems."

> "Organics — The presence of ferrocyanides requires special attention: when concentrated at high temperature with nitrates, ferrocyanides can react very forcefully...the calciner may be able to destroy ferrocyanides in limited quantities. If this alternative is preferred, it will be necessary to evaluate the ability of the calciner in this regard and, more generally, to evaluate the behavior of ferrocyanides throughout the whole reference process."

Mr. Jouan provided the following information concerning the range of waste handling capabilities:

> "LFIM must work with a predrying system, calciner for instance. The calciner can handle solid; the calcine is a solid, it comes from solution or insoluble products. All the solutions (even containing solids) cannot be calcined as they are, most of them can be, when there is mainly alkaline metals it is necessary to use additives to help the calcination, Al which is an usual component of the glass can be used: When alkaline metals (AM) constitute the major component of the waste (i.e., 1.1, around 50% or more, they must be in combination with Al in the feedstock at a ratio of Al/AM of about 0.3 (molar), where AM is any alkaline metal including Na, K, and Li."[1]

Table 3.2 presents feeds that have been successfully processed through the rotary calciner at the La Hague and Marcoule vitrification plants. Most of the French experience has been with calcining acidic wastes. It is unclear whether the baseline flowsheet for this technology requires that the waste be acidified before feeding to the system. This question was asked of Mr. Jouan, who replied as follows:

> "We have made short tests (less than one week) with alkaline feed to the calciner without special problems; but the acid way has certainly a lot of advantages in terms of transfer and metering of the solution and in terms of mean of work of the first scrubber in the solution of which the most part of the dust escaping the calciner must be dissolved. In the case of using an alkaline solution, this scrubber solution would contain precipitate and become a kind of sludge. In the case of acidification of the solution, the off-gas system will be similar to La Hague."[2]

Acceptable glass properties -

> "Viscosity must be lower than 200 poises at 1100°C for LFIM

> Electrical conductivity must not be taken into account for LFIM"[1]

Ability to handle slurry feeds -

> "The LFIM must work with a predrying system, calciner for instance."[1]

C. Incorporation of Semivolatiles

In the LFIM system, volatilization can occur in both the calciner and the melter. No information about calciner volatilities was received. Past information indicated that carryover of volatile species from a rotary calciner can be significant, but this is not a problem if a dust scrubber /recycle system is attached at the off-gas exit of the calciner. Decontamination factors reported for the rotary calciner and the rest of the primary off-gas equipment at the Windscale Vitrification Plant at Sellafield are shown in Table 3.3.[3] The secondary off-gas system at the Windscale plant removes any residuals of the elements shown.

Mr. Jouan addressed volatilization from the melter as follows:

> "This is made in the LFIM and can be made with the CCM due to the presence of the cold glass layer on the glass bath; but we must take care not to pour the glass at a too high temperature, because semivolatiles could escape during the pouring."[1]

D. Ability to Handle Insoluble and Conductive Compounds

Mr. Jouan suggests agitating the LFIM if there is a problem with solids accumulation:

> "LFIM (low-frequency induction melter) is able to handle them, much more than there is in Hanford wastes; this is made at La Hague; CCM is able also, using agitation like for LFIM."[1]

E. Waste Loading

The waste loading in the glass is defined as the weight percent of waste (as oxides) in the final glass. The waste loading of the glass is extremely important, because it determines both the required production rate of the melter and the quantity of glass that will be produced from the Hanford Site tank wastes. Data Package 1 discussed low-temperature glass formulations conducted with various Hanford Site tank blends.

2. Control Product Quality

The baseline description for this technology is a calciner coupled to the LFIM. The waste solution is calcined and then the frit/glass formers (dry) are added to the dried feed as it is transferred to the melter. This reduces the amount of water that must be evaporated in the calciner and melter, but it also complicates the qualification of the product glass. Glass quality depends on control of the equipment that meters the frit to the melter. The conventional U.S. method of qualifying the complete batch (glass formers and frit) in one tank is no longer possible. The DWPF in Savannah River and the

Table 3.2. Feeds Processed at La Hague and Marcoule

	R7 g/l					T7 (g/l)			Marcoule	NCAW	C 106
	1	2	3	4	5	6	7	8			
Al	2.8	2.8	3.5	2.7	2.9	2.8	2.5	4.6	25	6	17.15
Na	13	11.4	12.8	10.9	12.5	15.4	10.7	18	19	19.8	16.7
Cr	0.3	0.4	0.3	0.3	0.3	0.19	0.2	0.2	1.8	0.2	
Fe	2.1	2.23	1.75	1.6	6.4	2.8	5.4	6.3	5.9	25	16.24
Ni	0.7	0.6	0.6	0.5	0.6	0.3	0.3	0.6	1.2	2.2	---
P	0.8	0.8	0.1	0.5	---	0.3	0.2	0.5	---	0.5	1.06
Mg	0.3	0.4	0.08	0.2	0.1	0.02	0.1	0.04	20	---	1.06
U	1.2	1.1	1.16	1.7	0.9	0.22	0.4	0.4		5	
Pu	0.01	0.01	0.01	0.01	0.01	0.002	0.002	0.004			
Np	0.25	0.2	0.23	0.21	0.22	0.04	0.6	0.4			
Am	0.66	0.5	0.62	0.5	0.5	0.9	0.8	0.85			
Ca	---			0			9			2	2.04
Zn	---						7.2				
Sr	1.3	1	1.3	1.1	1.4	1.3	1.1	1.1	0.9	0.12	
Zr	5.6	4.6	0.5	3.4	5.2	5.75	3.3	6.2	1.8	13.9	
Mo	4.6	4.2	3	2.4	4	4.5	3.3	3.8	1.8	0.47	0.17
Ru	3.7	2.6	2.6	2.9	2.4	2.4	2.2	3.1	---	0.38	
Pd	1.1	0.9	1.6	1.3	1.3	1.7	1.7	2	---	0.13	
Cs	6.3	5	5.3	5	5	5	4	6.1	---	0.71	

Table 3.3. Decontamination Factors at the Windscale Vitrification Plant

Element(s)	Calciner	Dust Scrubber	Condenser	NO_x Absorber
Ru	20	2	100	25
Tc and Cs	2 ($CsTcO_4$ only)	2	100	25
I	1	1	2.5	1

West Valley Nuclear Services plant in New York propose to mix all of the feed constituents (waste, recycle, and frit) before acceptance of each batch. Although different from the current US paradigm, the method of product control proposed for the LFIM is clearly possible. The La Hague vitrification plants in France and the Windscale Vitrification Plant at Sellafield, England qualified this method of product control not only for domestic use but also with several foreign clients for the vitrification of reprocessing wastes.

A. Product Quality

"LFIM and CCM are able to make 'good' glasses, using generally mixing. This has been proved with the cold prototypes using R7-T7 glass."[1]

B. Waste Homogenization Capabilities

"In the melter, a good glass homogeneity can be obtained by the uniform heating of the melter walls and air bubbling, thanks to its small hold-up (100^{l})" (ECA 1993).

See also 2.D.

C. Analytical Requirements for Quality Acceptance

"Waste solution composition and glass additives must be analyzed very accurately; and if the acceptance requirements are not reached, the solution must be adjusted."[1]

"Before the waste stream is fed to the process, the fission product solutions and clarification fines, each contained in separate feed make-up tanks, are sampled. The fission product solutions are analyzed for free acid, dry extract, precipitate dissolution, plutonium and neptunium concentrations, activity content, heat release calculations, radionuclide concentrations, and chemical composition. The fines are rinsed, weighed and chemically dissolved, and are analyzed for plutonium, uranium, molybdenum, technetium and zirconium concentrations, activity content and for heat release calculations. Based on analytical results, the solutions and fines are adjusted as necessary to remain within the specified range for waste feed composition" (ECA 1993).

D. Minimum and Optimum Residence Time

"It's difficult to speak exactly of residence time because, with the air sparging, the vitrification pot looks like a completely stirred reactor; so the residence time (would) follow 'a gauss repartition' with a middle value of 6 h (if the flow rate is 25 kg/h and if 200 kg are poured every 8 h and taking into account the presence of a siphon giving 2 h more of residence time)."[2]

"Residence time is not an important criteria; what is more important is the temperature and duration of time at a given temperature; the time duration can decrease when the temperature increases."[1]

E. Unpredictable Evaporation (Segregation) of Glass Components

The only unsteady conditions that could occur in this melter would be unsteady flow of solids out of the calciner, which occurred during initial testing of the rotary calciner in England (Morris et al. 1988). This issue was resolved during subsequent testing of the rotary calciner.

3. Develop Technology on Schedule

This category deals mainly with the maturity of the technology. This technology is very mature and is currently used in three radioactive vitrification plants around the world. The La Hague plant alone has produced over 2400 canisters (964 MT) of glass by this technology. Because nearly all of the waste tested with this technology has been in nitric acid solutions, it was suggested that the Hanford Site waste be acidified before calcining.

A. Ability to Meet TPA Milestones[a]

This should be decided by the TAC.

B. Demonstrated Scale of Operation

"Designed for 40 kg of glass per hour the LFIM is used today in R7T7 (La Hague plants) at a flow rate of 20 kg/h due to the dilution of the fission product solution, and to the limited evaporation capacity of the calciner. The nominal R7T7 flowsheet flow rate is 25 kg/h; all the cold tests have been made at this flow rate; one 100 h cold test has been made at 30 kg/h without any problem; another 100 h cold test has been made at 30 kg/h with the cold English glass composition."[4]

"For LFIM: 25 kg/h is the nominal R7T7 running way, which is not reached because of the limited capacity of the calciner and of the solution dilution. 40 kg/h is the conceptual design value; 30 kg/h has been reached during 100 h tests without accumulation. The LFIM can only be used for a first step, followed by the use of CCM."[1]

"Air sparging has been initially tested to homogenize the glass bath...and successfully. In the LFIM (low-frequency induction melter) at first (used today in La Hague facilities R7 and T7); In CCM after and with the same success, even if it was perhaps less useful."[2]

C. Availability of Data or Access to Data to Allow Evaluation for Melter System Technology Assessment and Melter System Candidate Selection

Most of the data has come from Mr. Jouan of CEA, the ECA implementation plan, and published work by CEA and BNFL.

(a) Final melter selection by the end of 1998, plant startup by 2009, completion of campaigns by 2028.

D. Magnitude/Amount of Technical Development Required

Substantial work would be required to verify the capability to dissolve Hanford Site wastes in acid and then calcine those wastes in a rotary calciner. Glass formulations would have to be made for Hanford Site wastes at 1100°C (as would be true for any melter technology selected).

E. Additional Technical Development Required for Deployment

To be determined.

F. Probability of Technical Success Within Schedule and Resource Constraints

This should be decided by the TAC.

G. Processing Rate

"Yes, the scale up is limited and difficult to increase significantly. Is able, as built in La Hague today, to 70 l/h of fission product solution and 30 kg/h of glass. Such equipment is not compatible with the amount of liquid wastes stored in Hanford; it can be used only for a first demonstration period; and CCM equipment could be used in a second one, with their higher flow rate to treat, then, the total liquid waste volume."[4]

"25 kg/h of glass production rate, yes it's a safe value."[2]

H. Extent of Mock-Ups and Test Facilities Required

Existing testing facilities include, but are not limited to 60 L/h calciner(s) and 25 kg/h LFIMs at CEA in Marcoule, France.

I. Necessity for New Inventions

Not known at this time.

4. Integration with Process and Facility - *This section is provided by Fluor Daniel, Inc.*[5] *except for the following.*

A. Feed Preparation Requirements

"...acid feed is easier to manage."[1]

"We have made short tests (less than one week) with alkaline feed to the calciner without special problems; but the acid way has certainly a lot of advantages in terms of transfer and metering of the solution and in terms of mean of work of the first scrubber in the solution of which the most part of the dust escaping the calciner must be dissolved. In the case of using an alkaline solution, this scrubber solution would contain precipitate and become a kind of sludge. In the case of acidification of the solution, the off gas system will be similar to La Hague."[2]

"The reference plant process operates well with waste acidified to the level of free acidity ($[H^+] > 0.5N$) before it is fed to the calciner. Nitric acid added to the waste for this purpose - together with nitrates already present in the waste - will decompose in the calciner and be combined and captured in the off-gas system" (ECA 1993).

B. Offgas System Requirements

"...offgas system requirements, no specific one, see La Hague example."[1]

C. Number of Melters

"too much for the LFIM."[1] (Mr. Jouan suggested that starting the Hanford plant with this technology and then retrofitting a newer, higher capacity melter into the plant would reduce the number of LFIMs required in the initial Hanford vitrification plant)

D. Melter Dimensions and Weight

"The 25 kg per hour melter, for example, weighs only about 450 kg and may be removed by a small crane to a dismantling cell" (ECA 1993).

"LFIM size 350 x 1000 x 1200 mm < 500 kg for the melter."[1]

5. Control and Maintenance of Process and Facility

This section addresses the capability of the melter technology to allow safe and efficient operation of the vitrification facility.

A. Ease of Control

"For LFIM, wall temperature is the main parameter with the inside temperature to be controlled and adjusted; this is automatically made with the power variation. Amount of oxides coming from the solution and of glass frit are also continuously controlled, but this, which is the must balance, is made for all the processes."[1]

"The waste feed is mechanically stirred in the feed make-up tank at a specified rotation speed. If stirring is interrupted, the waste would not be homogeneous, and waste feed to the calciner is therefore stopped.

Waste is continuously fed to the calciner by a measuring wheel. Several direct parameters are monitored to ensure that the feed rate is within the specified range, including the rotation speed of the measuring wheel and the level of waste solutions in the seal pot and in the feed tube. Indirect parameters to determine waste feed rate are the heat supplied to the calciner and the expansion of the calciner tube.

The waste is evaporated and dried to a powder in a rotary calciner. The rotation speed of the calciner tube must fall within a given range to obtain the desired product quality and is monitored both directly and indirectly.

The feed rate of glass frit to the melter is a process parameter related to glass quality. A robot is used to feed the frit and to detect operating conditions outside the specified range. The frit feed rate is indirectly verified by hourly weighing of the frit.

For the three controlled parameters discussed above, non-conformity triggers a shut-down of the feed mechanism and switches waste feed to water feed of the calciner.

Temperatures at various areas in the melter are monitored directly with internal thermocouples, and glass pouring cannot be initiated at temperatures below 1040°C. Melter temperatures can be indirectly verified through electrical measurements of the inductors and by comparing temperature recordings at various times.

Glass mixing in the melter is an important factor in obtaining a homogeneous glass product. It is achieved by inert gas bubbling in the melter. Glass pouring is not initiated until a mixing rate of 150 to 200 L/h has been sustained for a minimum of ½ h.

Glass pouring is initiated when the nominal glass weight has been reached in the melter. Two glass pours are required to fill the canister. The canister is continuously weighed during pouring" (ECA 1993).

B. Remoteability

"The reference plant (T7 at La Hague) includes many other technical advantages, including 1) jumpers designed for fast and easy fitting of pipes with equipment during maintenance; 2) a saw and shearing machine in the dismantling cell to cut used melters and other equipment into pieces; 3) disposal of high-level technological waste in the same size canisters as vitrified waste; and 4) placement of all canisters in interim storage by a seamless transfer using a mobile, shielded transporter."[1]

"Seems to be easy using the La Hague concept with crane, master/slaves and special tools (electric screw-drivers etc...) for LFIM and CCM."[1]

C. Reliability

"Parts of calciner can fail and must be removed: graphite seals and rollers are the two main pieces to be removed; they are very little solid waste. Other calciner parts last usually more than five years."[1]

D. Maintainability

The following, provided by ECA, discusses maintenance in their reference T7 plant at La Hague. The general maintenance philosophy is as follows:

> Welded process equipment - All equipment that can be designed and constructed for the life of the plant is welded in place ("hard-piped" plant approach). This includes mainly chemical process equipment (tanks, pipes...). They are installed in segmented cells, according to their functions and activity level. This equipment requires no maintenance; however, if a problem

arises, redundant lines are implemented to guarantee plant availability. In addition, in exceptional failure conditions, direct access is still possible after decontamination, thanks to the segregation of contamination obtained with the segmented cells approach.

Other equipment - Other equipment is equipment whose size does not permit standardized replacement (calciner, melter, dust scrubber, metering wheels, condenser canister handling, and conditioning equipment). They are located in the so-called "mechanical cells," which are equipped with remote maintenance devices:

- in-cell cranes
- through-the-wall master/slave manipulators
- specific tools

Observations are made through shielded windows in the walls separating the cells from the working areas. Connection between removable equipment and welded pipes is performed by jumpers. Pipe ends are located very close to the equipment, so that jumpers are small and easily handled. The compliant design of the jumpers makes perfect alignment of the pipe end and the equipment end unnecessary. Exchange of jumpers is performed in less than 10 min. When removed, the equipment is transferred to the overhead dismantling cell, where it is cut into pieces to minimize active waste volume. As an example, the cut up melter can be inserted into 2 glass type canisters (about 300 liters). Each of the mechanical cells has an associated hoist park, whose functions are:

- garage and shielding for cranes when not in use
- decontamination and maintenance of the in-cell cranes
- reception of new equipment
- insertion of defective items into baskets

Maintenance options - Maintenance options are fully integrated in process operations, to minimize down time and to increase the operating availability to the facility. As an example, the replacement of the melter (which occurs on average every 2500 h of operation) requires only a 3 day down time.

Depending on the drying method used for the feed, maintenance requirements could increase for this melter technology. If a rotary calciner is used, the graphite seals will have to be replaced about every 6 months. The disassembly of the calciner increases the potential for contamination of the melter cell. It should not impact any other facilities.

"The combination of multiple production lines and compact isolated cells provides a twofold increase in plant availability. First, when any given line is down for maintenance, the two other lines and the common systems continue to operate at full capacity. Second, the isolated and compact nature of the cells means that maintenance is easier, faster, and safer in the line that is down" (ECA 1993).

E. Estimated Lifetime

Table 3.4 shows the maximum and average melter lifetimes experienced at the T7 plant in La Hague (ECA 1993).

Mr. Jouan of CEA noted the following regarding melter lifetimes:

> "Melter life: Reaches today 3000 to 4000 h in R7, T7 La Hague vitrification plant."[4]

> "LFIM life time melter is now more than 3000 h at La Hague; high-level solid wastes are lower than 3% of the glass container number."[1]

F. Ability to Confine Radioactive Materials

A significant source of radioactive materials is from maintenance of equipment. Frequent melter changeouts increase the likelihood for contamination of the melter cell, but this should not be a problem if the contamination is confined to this area.

G. Potential for Radioactive Source Buildup and Achievement of ALARA

The LFIM has very little glass holdup relative to the other melters being evaluated (roughly 0.34 metric tons). The calciner or evaporator will be much larger than the LFIM, so that the drying equipment will have the greatest potential for building up radioactive material. "The calciner contains only 1 to 2 kg of radioactive calcine at any moment" (ECA 1993). This should not affect ALARA if it is properly contained.

Off-gas treatment is discussed in the Fluor Daniel, Inc. document.

This melter has a bottom drain that can be used to drain the glass from the melt cavity at the end of the melter life. This may be optimistic. Melter failure could occur such that the glass could not be drained from the melter or the melter contents could be lost to the melter muffle.

Table 3.4. Maxium and Average Melter Lifetimes

Maximum Lifetimes	Hours
1991	2138
1992	2711
1993	3103
Objective for 1994	4000

Average Lifetimes	Hours
1991	1424
1992	1972
1993	2350
Objectives for 1994	2750

H. Sealing and Containment Relative to Melter and Drying Equipment

"The melter crucible is linked to the calciner by means of a lead glass seal between the crucible neck and the calciner lower end fitting" (Beveridge 1990). Graphite seals are used for sealing the moving parts on rotary calciners. Leakage around these seals will only cause an increase in in-leaking air as long as a proper vacuum can be maintained on the equipment.

I. Modular Design Concepts that Simplify Replacement or Repair

This melter design is modular, so that replacement of the LFIM or calciner should be possible without any changes to current facility plans. The Fluor Daniel, Inc. document evaluates melter disposal costs as a function of melter size.[5]

J. Refractory Life

See 5.C.

K. Electrode Life/Replacement

Not applicable.

L. Ability to Safely Handle Organics

Most of the organics should be destroyed in the calciner.

"Organics - The presence of ferrocyanides requires special attention: when concentrated at high temperature with nitrates, ferrocyanides can react very forcefully....the calciner may be able to destroy ferrocyanides in limited quantities. If this alternative is preferred, it will be necessary to evaluate the ability of the calciner in this regard and, more generally, to evaluate the behavior of ferrocyanides throughout the whole reference process" (ECA 1993).

M. Operational Simplicity

Depending on the CCM configuration chosen, this system may have several moving parts. The rotary calciner or wiped-film evaporator (WFE) is a dynamic system that will require attention. Agitation would increase the production rate, but it would also increase system complexity. Controllability of the CCM is discussed in Section 5.A.

N. Estimated Lifetime

See Section 5.E.

O. Estimated Downtime to Repair

"The time required to change a melter is only three days" (ECA 1993).

Additional information regarding downtime is not available.

6. Minimize Total Cost - *This section is provided by Fluor Daniel, Inc.*[5] *except for the following.*

   "The cost of the metallic melter of the LFIM process is between 100 and 150 Kilo dollars."[1]

7. Minimize Risk -

   C. Operational Safety

   "Using a precalcination step there will not be products accumulation and explosion problems: the residence time in a calciner is very low, the amount of the product is therefore very low and the decomposition of the product (organics or minerals) occurs continuously.

   LFIM is a safe process, even in case of failure; there is no particular safety risk. CCM is also a safe process, even if water is not far from the hot melted glass. Safety tests have been made in France to investigate the possible interaction between hot melted glass and water. The result is of course that an over pressure can occur in case of contact but there is no chemical reactions between the both."[1]

   "The molten glass may be cast from metal nozzles extending through the water-cooled metal hearth supporting the melt. This raises a potential safety hazard of water ingress into the molten glass in the extremely unlikely event of a breach in one of the metal sectors forming the crucible. In order to assess the danger of an interaction between the water and the melt, the CEA investigated pressurized water injections into molten glass: the water boiled, but not violent pressure rise occurred in the facility" (Moncouyoux et al. 1991).

   Because of the small size of the equipment, a limited amount of energy is accumulated in it at any given time during operation. Hazards such as explosions, therefore, are reduced or completely eliminated.

   Based on AVM and R7 experience, safety analyses have been performed on the effects of various hazards of all origins in T7. For each of these hazards, safety has been demonstrated and specific measures have been implemented when found necessary. The studied hazards can be divided into "not specific to vitrification " and "specific to vitrification."

   Hazards specific to vitrification - They are mostly related to containment. The use of high temperature generates the possibility of volatile products release. Specific measures taken to cope with this hazard include the use of sugar in the calciner and the off-gas treatment unit. Pouring also generates a gas release hazard, which is coped with by a specific local ventilation. The use of remotely dismountable equipment generates, in some cases, a hazard of loss of containment after earthquake. For such cases, the containment is ensured by the cell.

   D. Criticality

   "LFIM and CCM are very little furnaces easy to be controlled from time to time by emptying them."[1]

   E. Passive Shutdown

Endnotes

1. Fax from Mr. Jouan of CEA to P. Shafer of PNL dated August 11, 1994.
2. Fax from Mr. Jouan of CEA to P. Shafer of PNL dated August 5, 1994.
3. Presentation by Tony Maxted of BNFL, March 18, 1994.
4. Fax from Mr. Jouan of CEA to P. Shafer of PNL dated August 8, 1994.
5. Fluor Daniel, Inc. August 1994. "Alternative Melter Systems Assessment 20 Metric Tons per Day HLW Glass Production." Prepared under contract #04-436304 with Westinghouse Hanford Company.

Data Package 4

High-Temperature, Joule-Heated, Ceramic-Lined Melter

Description of Technology

The high-temperature, joule-heated, ceramic-lined melter (HTCM) has several variations. In this context, high-temperature is defined as ≥1200°C. The variations include the high-temperature melter (HTM) being developed at the Pacific Northwest Laboratory (PNL), the ceramic melter developed in Russia for vitrification of HLW, the Penberthy Electromelt design, the ceramic melter developed by Glassification Inc. for vitrification of hazardous wastes, a high-temperature stirred melter developed by Stir Melt, Inc., and a high-temperature melter design being developed by Duratek. Information was solicited for all of these melters, but was received only from PNL and Penberthy Electromelt. Kerforschungszentrum Karlsruhe GmbH (KfK) in Germany gathered information about the Russian melters. The body of this data package refers to the PNL HTM; the Penberthy and Russian designs are described in appendices to this package. Unless otherwise stated, information in this package was supplied by PNL.

Results of a life-cycle cost analysis of the management of defense high-level waste (HLW) across the U.S. Department of Energy complex (Merrill and Chapman 1993) led to development of this melter at PNL. This study was performed to identify areas where changes in the vitrification facility could bring about cost savings in the management of HLW. The system changes investigated are canister length, diameter, shape, wall thickness, and fill fraction and waste loading in the glass product. Implementing the changes results in the production of fewer canisters, shortens the required time to treat the waste inventory, or both. The single overriding factor in the total cost was the final disposal cost of the vitrified waste product, which is directly related to the volume of glass produced. Thus, increasing waste loading in the final product would reduce the life-cycle cost of HLW management. The economic evaluation revealed that increasing waste loading from the reference value (≈25%) to 45% could realize up to $2.2 billion in savings at the Hanford Site alone.

The HTM was originally envisioned (and development work on the technology was so targeted) as a replacement melter for the low-temperature, joule-heated, ceramic-lined melter in the Defense Waste Processing Facility (DWPF) in South Carolina and the Hanford Waste Vitrification Plant (HWVP) in Washington State. At the end of the life of the DWPF or HWVP melter, an HTM would be installed into the melt cell. Changes required to the vitrification facility to incorporate an HTM that could process waste at 4 times the reference rate of the HWVP were investigated in a 2-phased study, the Hanford Waste Vitrification Plant Increased Production Capacity Evaluation (Shah 1993 and Fluor Daniel, Inc. 1993). Information from this evaluation will be cited in this data package.

The HTM is an advancement of the lower temperature liquid-fed ceramic melter (LFCM). Although several modifications/ advancements over the LFCM have been fielded in the United States (e.g., bottom drain, replaceable electrodes), the primary difference between the HTM and the LFCM is the electrode material. The refractories are or could be the same as those used throughout the world in lower-temperature nuclear-waste melters. Thus, the HTM can just as easily be operated at the same temperatures as its lower temperature cousins. As is not the case with the LFCM, the HTM operator can increase temperature merely by increasing the power. The consequent flexibility allows the vitrification facility to more easily process a wider range of feed types with a single melter system.

Increasing the temperature allows the use of more refractory glass formulations and thereby improves the durability of the glass product. The capability to increase the operating temperature decreases the level of controls that have to be placed on the incoming feed, because a higher temperature provides a larger compositional envelope within which an acceptable glass product is produced.

The production-scale HTM could have several configurations, the choice of which will be based on the development work currently in progress at PNL. Two HTM test-bed systems are installed at PNL, the small-scale HTM (SSHTM) and the pilot-scale HTM (PSHTM). The SSHTM has a 46-cm by 46-cm processing area (0.21 m^2) with a nominal glass depth of 30 cm. Electrical power is supplied to the melter by one of two electrode systems, top-entering electrodes, and a proprietary electrode system. Glass product is removed from the SSHTM through either an inductively heated freeze valve bottom drain or a vacuum assisted overflow section. The melter can be fed slurry, solids, or a combination thereof. The PSHTM has a cylindrical geometry, 158-cm diameter, a nominal glass depth of 107 cm, and a processing area of approximately 2 m^2. The PSHTM is equipped with the same two electrode systems. Both melters have an upper operating temperature of 1550°C.

The configuration of the HTM assumed for the purposes of this data package is slightly different from that assumed for the increased production capacity study. Figure 4.1 shows the HTM design used in this study. In the Phase II HTM, non-feedable, top-entering molybdenum electrodes sheathed in cooled Inconel-690 firing to a bottom iron electrode were the primary electrode system. In this data package the primary electrode system is assumed to be a three-phase proprietary system with a secondary configuration of feedable, replaceable top-entering molybdenum (or other material) electrodes. In the Phase II HTM, an inductively heated bottom drain (which was off-center to fit in the HWVP melter envelope) provided final drainage of the melter before its removal from the cell. The configuration assumed for this data package moves the bottom drain to the center of the melter and is assumed to be used for routine glass product removal. In the Phase II HTM, the vacuum-assisted overflow section was radiantly heated by replaceable heaters. The primary source of overflow heating assumed in this data package is direct joule heating of the overflow, bypassing an electrical current directly through the overflow block in a fashion similar to that used by the Germans in their melters.

The configuration assumed in this data package is as follows:

- three-phase, three-electrode power system providing the joule heating
- primary electrodes: proprietary electrode system
- secondary electrodes: top entering molybdenum (or other material) electrodes
- both an inductively heated bottom drain and an overflow system for routine discharge of glass to a 2 ft x 15 ft canister
- plenum heaters for boosting and startup
- Monofrax K-3 fused cast refractory.(a)

(a) The Carborundum Company.

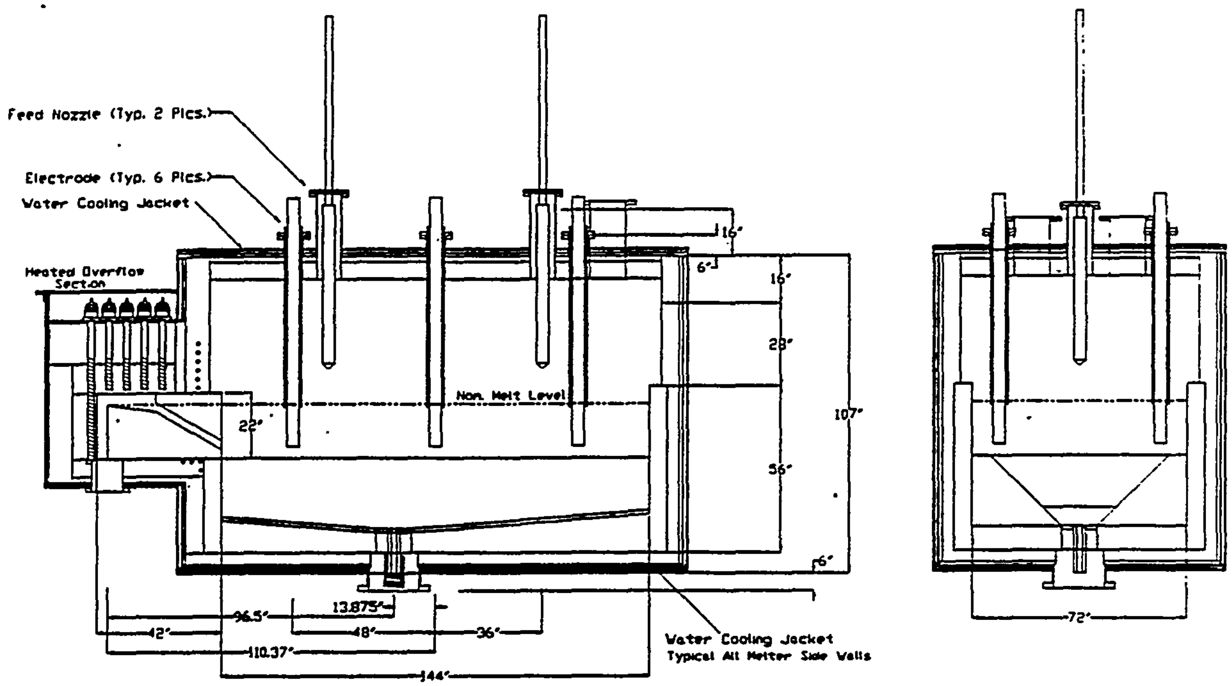

Figure 4.1. Conceptual Design of a Plant-Scale HTM

The three-phase power to the melter is provided by three-single phase power supplies. Each power supply consists of a multiple-tap transformer providing power to a silicon-controlled rectifier (SCR) power controller that provides current to the electrodes and, ultimately, the glass melt. Single-phase equipment is in a delta-delta arrangement; the SCRs are wired inside the delta. The apexes of the secondary delta feed the three melter electrodes. An estimated 825 kW would be required to meet the required daily glass production rate of about 8 tons.

The electrodes are arranged in a three-phase system with two side electrodes and one bottom electrode (see Figure 4.1). For larger melters, the number of electrodes may increase but the electrodes on each side will be fired from the same phase. The melter surface geometry will be set by two criteria: the surface area required to meet production requirements, and the depth required to provide an adequate glass residence time. The baseline melter will be slurry fed, similar to the way the previous HWVP melter was fed. Glass can be discharged by either an inductively heated bottom drain or a vacuum overflow. The bottom drain can be used for final draining of the melter as well as routine glass pouring. Production of 8 tons/day of glass with 50% waste loading at a 40 $kg/h{\bullet}m^2$ specific process rate (the assumptions presented in this data package) requires a total glass surface area of 8.5 m^2. This can be accomplished by either using one melter or multiple melter lines. For example, the glass pool geometry for a single, 8 ton/day melter would be 2 m x 4 m (assuming a 2:1 aspect ratio). If two melter lines are used, the glass surface would be 1.5 m x 3 m (4.3 m^2). Figure 4.1 is an elevation view schematic of a representative 6.7 m^2 HTCM. This melter design was completed as part of a previous effort at Westinghouse Hanford Company (WHC) that investigated retrofitting the former HWVP to increase its capacity by a factor of four. If only one or two melters are used, multiple feed nozzles will be required to ensure complete slurry coverage. Basic parameters for this melter technology are presented in Table 4.1. The basis for most of these numbers are explained later in this data package.

Table 4.1. Operating Parameters for High-Temperature, Joule-Heated, Ceramic-Lined Melter(s)

Method of Feeding	Slurry			
Specific Glass Production Rate	40 kg/h•m^2			
Waste Loading in Glass	50 wt%			
Oxide Loading in Slurry	400 g/L			
Bulk Glass Temperature	≤1450°C			
Plenum Temperature	650°C			
Glass Depth	2 m			
Glass Residence Time	120 h			
Total Operating Efficiency	60%			
Number of Melter Lines	1	2	3	4
Glass Surface Area (m^2)	8.5	4.3	2.8	2.1
Glass Production Rate (MT/day)	8.2	4.1	2.7	2.0
Glass Production Rate (kg/h)	340	170	113	85
Slurry Feed Rate (L/h)	850	425	280	210
Glass Holdup[(a)] (MT)	42	22	14	10

(a) Assumes a molten glass density of 2500 kg/m^3.

In late 1979 and early 1980, the bench-scale HTCM was operated at PNL (Barnes 1980). Three test runs produced about 270-kg of high-temperature borosilicate glass. The HTCM was 0.2-m by 0.61-m by 0.63-m deep and used air-cooled tin-oxide electrodes. The upper operating design temperature of the HTCM was 1500°C, although no tests were performed in excess of about 1300°C. The objective of the testing was to assess the impacts of elevated temperatures for waste vitrification, test air lift pouring, assess temperature effects on cesium volatility, and assess glass production rates at high temperatures.

1. Process Range of Composition

The assumption of a sodium-aluminum-silicate glass with an increased waste oxide loading (50%) is based on the results of glass formulation studies performed in support of the HTM. Glass formulations have been developed for two Hanford waste types, neutralized current acid waste (NCAW) and a blended single-shell/double-shell tank waste Table 4.5 Borosilicate glass was not chosen because preliminary work at PNL had shown that addition of boron does not benefit high temperature glasses at increased waste loadings; this technology can, however, produce borosilicate glass if necessary. The assumption of 50% waste loading is explained in Sections 1.B and 1.E.

A. Temperature

The maximum operating temperature of these melters is limited by the electrode materials, the glass formulation, and the capability to maintain a protective layer of cold glass against the refractory. The HTM at PNL was designed for a nominal operating temperature of 1450°C and a maximum temperature of 1550°C. The maximum operating temperature for the HLW melter will be determined by the capacity of the glass formulation to control volatilization from the glass, and the inherent ability of the melter to suppress volatilization (e.g., cold cap coverage).

B. Range of Waste Handling Capabilities

The actual compositions of the Hanford Site wastes remain uncertain. Initial scoping studies used various assumptions about the extent of blending that will be possible among the 177 Hanford tanks. The first study used an "All-Blend" composition, which assumed perfect mixing of all 177 tanks and was calculated from tank inventory records, which are only approximate. In 1993, several "All-Blend" glass formulations were tested at crucible scale at PNL as part of glass development for the HTM. A glass that had 62% waste loading and was formulated at 1350°C had acceptable properties (viscosity = 70 poise; electrical resistivity = 20.9 Ω-cm at 1350°C). In a similar development with NCAW simulant, a glass that had 50% waste loading and was developed at 1350°C had acceptable properties (viscosity = 70 poise; electrical resistivity = 2.5 Ω-cm at 1350°C) (Kim et al. 1994).

A more realistic tank blending scenario is that complete blending of all tank wastes will not be possible. The Composition Variability Study (CVS) model developed for theNCAW predicts maximum waste loadings for 15 different wastes. The assumption that the wastes within each tank farm were blended, results in high predicted waste loadings for some tank farms but not for others: 19 wt% to 84 wt% at 1350°C. The resulting 15 waste compositions are shown in Table 4.2 along with the "All-Blend" waste (referred to as Case C in the table) and the NCAW for reference. The row labeled "High-T" shows the predicted maximum waste loadings achievable at 1350°C, and the first row shows the limiting constituent in each glass formulation. Again, this preliminary information cannot be used for final flowsheet development. Without knowing the mass of waste oxides in each tank farm it is not possible to predict the average waste loading. A conservative 50 wt% waste loading is assumed for sizing this melter technology. WHC has evaluated what waste composition(s) should be used for flowsheet development (Lambert and Kim 1994).

Compounds or elements that require special treatment in the off-gas system:

Tritium, mercury, carbon-14, and iodine cannot be incorporated into glass at the temperatures of this melter technology, but must be captured in the off-gas system and sent out as a secondary waste stream. Carbon-14 will probably be released to the atmosphere if the Clean Air Act standards are met.

Chlorine, fluorine, tellurium, technetium, cesium, cadmium, and ruthenium, are partially soluble in the glass but require special considerations in the off-gas treatment system for recycle. These will be discussed later in Sections 1.D (incorporation of semi-volatiles) and 4.B (off-gas system requirements).

Noble Metals: As discussed in Data Package 1, noble metals (Rh, Pd, Ru) are virtually insoluble in the reference borosilicate glass and all other expected glasses made from Hanford Site blended wastes. It is not clear whether noble metals are a concern for the Hanford HLW melter. The "All Blend" composition[1] includes only 0.07 wt% total noble metals ($Rh_2O_3 + PdO + Ru_2O_3$). At 50% waste loading, the noble metals concentration will be 0.04 wt%. Even if the noble metals accumulate, they may not cause melter failure before other components fail. The melter-tank geometry of the HTM is designed to be compatible with noble metals. The bottom of the melter is flat (sloped-bottom designs are currently in progress), but the upper set of electrodes is arranged in such a way that 2/3 of the melter volume would be filled with noble metals before a short circuit would develop between the bottom and side-wall electrodes. The bottom drain permits routine pouring of glass and draining of noble metals.

Table 4.2. Tank Farm Waste Compositions

	Others Components			Zr-Phase		Spinel				Durability			Si	Al			
Oxide	TF-B (Wt%)	TF-T (Wt%)	TF-SX (Wt%)	TF-C (Wt%)	TF-DST (Wt%)	TF-A (Wt%)	TF-AX (Wt%)	TF-TY (Wt%)	TF-BY (Wt%)	TF-S (Wt%)	TF-DSSF (Wt%)	TF-U (Wt%)	TF-TX (Wt%)	TF-BX (Wt%)	Oxide	Case C (Wt%)	NCAW (Wt%)
SiO2	0.76	0.49	9.37	0.06	8.31	0.32	0.57	29.20	5.84	2.13	29.44	18.85	17.33	21.37	SiO2	10.00	4.03
B2O3					0.47		0.00				0.00				B2O3	0.00	0.01
Na2O	52.19	56.03	33.93	10.38	31.98	17.31	51.89	22.29	23.75	69.31	66.00	39.89	30.07	25.14	Na2O	25.30	21.42
Li2O					0.01		0.00								LiO2	0.00	0.00
CaO	0.03	0.00	1.24	9.39	0.79	0.03	2.79	0.00	5.66	0.00	0.62	0.00	0.01	0.12	CaO	2.06	0.79
MgO					0.27		0.00				0.00				MgO	0.08	0.20
Fe2O3	7.93	8.95	12.76	11.00	8.75	59.60	23.52	15.42	9.89	2.70	0.00	2.28	3.91	5.91	Fe2O3	11.00	28.21
Al2O3	1.20	0.66	22.74	7.55	2.65	1.48	1.46	10.06	12.33	13.20	2.00	16.73	15.83	22.98	Al2O3	13.00	9.04
ZrO2	0.22	0.42	0.01	25.85	35.20	0.04	0.05	2.52	0.22	2.93		0.30	0.40	0.33	ZrO2	7.08	15.11
Others	37.67	33.45	19.93	35.77	11.56	21.23	19.71	20.51	42.31	9.74	1.94	21.96	32.45	24.14	Others	31.41	21.19
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	Total	100.00	100.00
Bi2O3	6.43	8.83		0.05				0.33	0.03			0.04	0.05	0.04	Bi2O3	1.95	
CeO2	4.23	5.38	2.07	0.03	0.08	0.48	0.33	1.05	1.99	1.11		2.24	2.76	2.96	CeO2	2.73	0.60
Cr2O3	0.02	0.02	3.92	0.01	0.40	0.00	0.43	0.03	0.00	0.72	0.02	0.19	0.01	0.00	Cr2O3	0.45	0.26
F	0.72	0.50	0.04	1.56	1.43	0.00	0.01	0.04	0.52	0.12	0.07	00.07	0.12	0.17	F	0.56	0.10
La2O3	0.04	0.12			0.66										La2O3	0.43	0.65
MnO2	0.48	1.09	1.67	7.76	0.87	7.18	11.48	0.10	0.41	0.46	0.00	0.21	0.75	0.84	MnO2	1.82	2.14
NiO	0.23	0.03	0.30	5.69	0.47	0.22	0.66	0.00	11.64	0.17	0.00	0.01	0.25	1.25	NiO	2.27	2.30
P2O5	14.20	15.39	0.42	0.28	00.34	0.02	0.02	3.47	1.82	0.54	0.02	0.74	4.10	2.56	P2O5	4.71	0.87
SO3	0.18	0.03	0.22	0.16	0.43	0.41	0.02	0.59	0.23	0.28	0.07	0.06	0.51	0.54	SO3	0.34	0.65
SrO	0.00	0.00	0.01	0.00	0.02	0.02	0.00	0.00	3.45	0.00	0.00	0.00	0.00	0.05	SrO	0.41	0.12
U3O8	9.95	1.88	9.19	19.87	2.67	12.76	6.51	14.71	21.99	5.89	0.01	18.35	23.72	14.12	U3O8	14.30	4.74
Subtotal	36.47	33.27	17.84	35.40	7.37	21.09	19.45	20.32	42.08	9.29	0.19	21.90	32.27	22.53	Subtotal	29.97	12.43
Balance	1.20	0.18	2.09	0.37	4.19	0.14	0.26	0.19	0.23	0.44	1.75	0.00	0.18	1.62	Balance	1.44	8.76

Waste Loading (wt%)

Low-T	21	19	26	35	31	17	38	65	51	33	35	58	64	61	Low-T	45-50	33
High-T	21	19	26	46	40	25	43	84	64	39	41	60	73	61	High-T	62	50
Limit	P	P	Cr	Crystal	P?	Fe	Na	P	Others	Na	Na	Others	P	P	Limit	P	Crystal

Spinels: For several of the Hanford wastes, spinels (iron, chrome, nickel compounds) are the first crystals to form in the glass upon cooling. The Waste Acceptance Preliminary Specifications (WAPS) do not specify a limit for the amount of crystalline material allowable in the glass (Larson 1989). The concern regarding spinels (or any crystalline phase) is that the crystals will either reduce the durability of the waste form or affect the operation of the melter by filling the melt cavity with crystals. There are two ways to deal with spinel formation: 1) design a melter that is compatible with crystals and ensure that crystals do not affect the glass durability, or 2) formulate the glass to minimize crystal formation. Glass development for the HTM has centered around formulating glasses that will not devitrify in the melter. Conservative devitrification tests are conducted for each composition for 24 h at 100 °C below the expected bulk glass temperature. This melter design should be able to handle some crystal formation without adverse effects. Removal of crystalline materials that might settle to the bottom through the bottom drain will help prevent them from accumulating.

Acceptable glass properties: Waste form development efforts for the HTM have maintained the limits shown in Table 4.3. These are considered to be safe operating limits for the melter.

Ability to handle slurry feeds: This melter design can be either dry or slurry fed. All testing to date has used slurry feeding without problems. Depending on the size of the melter, more than one feed nozzle may be required to ensure adequate coverage of the melt surface. The 6.7 m^2 design completed for the Phase II evaluation had two feed nozzles equally spaced along the centerline of the melter. The SSHTM and PSHTM use a water-cooled feed nozzle similar to the DWPF design.

C. Incorporation of Semivolatiles

Volatile losses from a liquid-fed melter may be affected by certain parameters, for example cold cap coverage, plenum temperature, and feed/glass composition. Because the specific activity of cesium is high, its volatility is of particular interest. Cesium is believed to volatilize as many different species, depending on glass composition, including Cs metal, Cs_2O, CsOH, and other compounds (IAEA 1982 and Erlebach 1960). CsCl is assumed to be the primary volatile species in this case. The presence of chloride in the feed will substantially increase the volatility of cesium (Burkholder and Allen 1987). The addition of technetium increases volatility through formation of $CsTcO_4$. On addition of technetium to a feed, cesium losses increased to 18% from 2-to-5% (without Tc) (Baumgartner 1984).

Table 4.3. Acceptable Glass Property Ranges for HTM Glasses

Property	Lower Bound	Upper Bound
Redox: Fe^{+2}/Fe^{+3}	0	0.3
Processing Temperature (°C)	N/A	1450
Viscosity at Processing Temperature (Pa-s)	2	10
Liquidus Temperature (°C)	N/A	100 °C less than processing temperature
Electrical Conductivity at Processing Temperature °C (S/cm)	0.1 (ρ=10 Ω-cm)	0.5 (ρ=2 Ω-cm)

Little information is available on decontamination factors for cold crown melters at elevated temperatures. Three short-term tests were completed at PNL in 1979 to 1980 on the High-Temperature Ceramic Melter (HTCM) with a dry feed. The last of these tests examined cesium volatility from the melter at 1200°C to 1300°C. The following results were reported:

> "Cesium was the major feed percentage-loss element. The combined HEPA and scrub solution losses constituted 0.44% of the cesium present in the feed (DF = 230). This loss corresponds to a volatilization rate of 115 mg/cm^2-h, or approximately half of the volatilization rate reported by WJ Gray (Gray 1976) for a low-melting borosilicate waste glass at the 100-poise viscosity temperature (1050°C). The difference in volatilization is partially due to the presence of an unreacted-feed cold cap in the HTCM (Gray's experiments were conducted with bare molten glass surfaces), but other researchers report decreased cesium volatility with increased viscosity at constant temperature (Kupfer and Schultz 1973; Ross and Mendel 1980), indicating that cesium volatility is diffusion-limited. The comparable cesium volatilization rate at equal viscosities of the residual-liquid and low-temperature compositions is in agreement with these findings" (Barnes 1980).

The HTM design relies on the batch blanket (either solid or slurry) to control volatilization. During idling (nonfeeding) periods at elevated temperatures, the melter will be water-fed to control volatilization and maintain mixing in the melt pool, until the bulk glass temperature is reduced.

D. Ability to Handle Insoluble and Conductive Compounds

See Section 1.B.

E. Waste Loading

The waste loading in the glass is defined as the weight percent of waste (as oxides) in the final glass. Waste loading determines both the required production rate of the melter and the quantity of glass that will be produced. The quantity of glass produced from the Hanford tank wastes is important for two reasons: 1) The costs to place canisters in the federal repository are high; an estimated $2 billion or greater savings can be realized by increasing the waste loading of Hanford glass(es) from 25 wt% to 45 wt%, (Merrill and Chapman 1993), and 2) The first U.S. repository has a limited allocation for HLW canisters. DOE-RW is currently evaluating the impact of the increased number of canisters resulting from TPA changes.

In 1993, several "All-Blend" glass formulations were developed and tested on a crucible-scale at PNL as part of the glass development for the HTM. A glass that had 65% waste loading and was formulated at 1350°C had acceptable properties (viscosity = 118 poise and electrical resistivity = 1.8 Ω-cm at 1350°C). In a similar development for NCAW simulant, a glass with 50% waste loading at 1350°C had acceptable properties (viscosity = 70 poise and electrical resistivity = 2.5 Ω-cm at 1350°C) (Kim et al. 1994). Both formulations have been tested in the SSHTM at PNL. During one test, the melter produced 500 kg of the NCAW glass formulation. Although difficult to process, an acceptable glass was produced at 1350°C to 1400°C.

2. Control Product Quality

For reasons stated in Section 1, the waste form for the high-temperature melter is assumed to be sodium-aluminum-silicate glass with an increased waste oxide loading (50%).

A. Product Quality

Work was conducted in 1993 to develop durable glasses with increased waste loadings (>25 wt%) (Kim and Hrma 1994).[2] As discussed, a 50% waste loaded glass was developed for NCAW and a 62 wt% glass was developed for the Hanford blended waste. Both were produced in the laboratory and tested for durability with the Product Consistency Test (PCT). The NCAW glass released 0.46 g $Na/m^2/7$ days and 0.17 g $Si/m^2/7$ days. The glass from simulated blended waste released 0.43 g $Na/m^2/7$ days and 0.14 g $Si/m^2/7$ days. These release rates are more than an order of magnitude less than the HLW glass standard (EA glass)[(a)] for durability. The NCAW glass formulation with 50% waste loading has been processed through the SSHTM, but the durability of the glass from the test has not been measured.

B. Waste Homogenization Capabilities

The HTM has a residence time of 60 to 120 h. This long residence time assures proper dissolution and mixing of the waste and glass. In the new plant melter, this can be controlled by design of the melter depth. The presence of undissolved feed in the glass is unlikely, because the convection cells are slow and do not provide a path for unmelted feed.

C. Analytical Requirements for Quality Acceptance

The glass formers and waste will be combined and analyzed before released to the melter. The combined feed analysis will consist of anion analysis by ion chromatography, cation analysis by either fusion and ICP analysis or ICP/laser ablation, and total oxides analysis. It is assumed that limited samples of the radioactive product glass will also be required for acceptance of any glass to the Federal Repository.

D. Minimum and Optimum Residence Time

The 60 to 120 h long residence time ensures proper dissolution and mixing of the waste and glass. It also provides a dampening effect for any feed variations, so that fluctuations in feed composition are diluted by the large volume of glass in the melter. The drawbacks of providing a long residence time in the melter are that 1) insoluble particles have a longer time to settle to the melter floor; 2) glass holdup is larger, so that removing a failed melter full of glass would require larger handling equipment; and 3) the large glass holdup provides a larger radiation source term in the event of an accident. These competing mechanisms make it difficult to determine what the "optimum" residence time would be.

(a) EA glass release rates are 6.67 g $Na/m^2/7$ days and 1.96 g $Si/m^2/7$ days.

At a constant production rate per melter surface area, residence time is a function of the melter depth. Without a sloped bottom, this melter technology has no significant requirements for the melter depth. The only requirement is sufficient depth that the electrodes' current density limit (see Section 5.K) is not exceeded. Current density limits will be a problem only if the glass is highly conductive or the electrodes are very close together.

E. Unpredictable Evaporation (Segregation) of Glass Components

This melter operates continuously under steady conditions, so that process upsets are rare. Increased feed volatility would be a problem only during startup after a feed outage, that is, when slurry is fed onto an open, hot glass surface. This is usually not done, and when it is, water is first fed to the melter to cool the upper glass surface to minimize feed volatilization during restart.

3. Develop Technology on Schedule

This category deals mainly with the maturity of the technology.

A. Ability to Meet TPA Milestones[a]

The HTM is part of the current Hanford HLW baseline. The schedule and resources required to implement this technology in the Hanford HLW vitrification plant have been detailed and fit within DOE constraints.

B. Demonstrated Scale of Operation

This technology has been used extensively for commercial glass production. The main difference between the HTM design and commercial glass melters is that the waste/glass composition is expected to cause increased electrode wear. Electrode design modifications are described in Section 5.K. Another unique design feature of the HTM is the use of a bottom drain to routinely discharge the glass. Glass flow is controlled by a water cooled induction coil operating at 3 to 10 kHz, as has been demonstrated radioactively on the PAMELA melter. The only modification to the HTM design is the materials of construction. The SSHTM and PSHTM both have molybdenum bottom drains with platinum liners; molybdenum is used for structural support of the platinum tube. A nitrogen blanket is maintained over the bottom drain section to protect the molybdenum surface from oxidation. This high-temperature bottom drain has been successfully demonstrated on the SSHTM. More than 1300 kg of glass was discharged through the bottom drain during recent tests (800 kg of LLW simulant and 500 kg of HLW simulant). One modification to this bottom drain for use in a HLW plant would be to use a heavier gage platinum tube, so that the molybdenum pipe and nitrogen blanketing of the bottom drain section would not be needed.

The HTM technology has been demonstrated nonradioactively at PNL, including:

- SSHTM (0.22 m^2) using top-entering, Inconel electrodes at low temperatures (up to 1150°C) and an alternative electrode design at high temperatures (up to 1450°C). This melter operated at an average feed rate of 15 L/h (650 grams oxide/liter, 10 kg/h, 42 $kg/h \cdot m^2$, 1350°C) with

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[a] Final melter selection by the end of 1998, plant startup by 2009, completion of campaigns by 2028.

LLW simulant during a recent 4-day test. It operated at an average feed rate of 16.5 L/h (440 g oxide/lr, 50% waste loading, 7.3 kg/h, 33 kg/h•m^2, 1350°C-1400°C) with NCAW HLW simulant during a recent 3-day test. The maximum sustainable rate was 10.5 kg/h (48 kg/h•m^2) during the HLW test.

- HTCM (0.12 m^2) with tin-oxide electrodes up to 1325°C (Barnes and Hanson 1979). This melter was dry-fed during three short tests in 1979 to 1980 at PNL. The maximum reported production rate was 18 kg/h (160 kg/h•m^2). An average production rate was not reported.

This melter technology has also been demonstrated by Penberthy Electromelt and at the Mayak Vitrification Plant in Russia (see appendices to this data package).

C. Availability of Data or Access to Data to Allow Evaluation for Melter System Technology Assessment and Melter System Candidate Selection

Data are readily available.

D. Magnitude/Amount of Technical Development Required

Technical development is still needed. The current materials of construction (electrodes) are adequate, but their improvement is an on-going effort at PNL. Experience with high-temperature electrodes is discussed in Section 5.K. PNL initiated corrosion rate experiments for various materials in early 1994; however, results were not available at the time of completion of this data package.

Because of the large increase in production rate over the previous HLW melter designs, use of only one or two melters in the plant would require substantial scale-up work, including design of a bottom drain that can control glass pouring at rates up to 680 kg/h (assuming that maximum pour rates will be two times the average production rate).

E. Additional Technical Development Required for Deployment

To be determined.

F. Probability of Technical Success Within Schedule and Resource Constraints

The HTM is part of the current Hanford Site HLW baseline. The schedule and resources required to implement this technology in the Hanford Site HLW vitrification plant have been detailed and fit DOE constraints.

G. Processing Rate

The SSHTM (0.22 m^2) has processed LLW simulant at 15 L/h (650 g oxide/ltr, 10 kg/h, 42 kg/h•m^2, 1350°C) and HLW simulant at an average of 16.5 L/h (440 grams oxide/liter, 50% waste loading, 7.3 kg/h, 33 kg/h•m^2, 1350°C-1400°C). The maximum sustainable rate was 10.5 kg/h (48 kg/h•m^2) during the HLW test.

The HTCM (0.12 m^2) was tested with tin-oxide electrodes up to 1325°C. The melter was dry-fed during three short tests in 1979-1980 at PNL. The maximum reported production rate was 18 kg/h (160 kg/h•m^2); an average production rate was not reported.

Melter Performance Comparison

Numerous bench-scale and pilot-scale tests have been conducted to support HLW vitrification projects in DOE. These projects include the HWVP, the DWPF, and the WVDP. To attempt characterization of melter performance, operating information was obtained for a number of PNL slurry-fed vitrification tests performed in recent years. The melter test data used for the tests included the high-bay ceramic melter (HBCM),(a) the PSCM,(b)(c)(d)(e)(f)(g)(h)(i) the LFCM (Bjorklund and Brouns 1982), and the SSHTM. Data were accumulated for power, feed rate, melter surface area, and slurry oxide concentration versus run time. This information was taken only for steady operation (steady feed rate) periods during each test.

To compare melter performances, the data for each melter test was plotted as the feed rate of the slurry material, normalized to the melter glass surface area, versus transferred melter power, also normalized to the melter glass surface area. The transferred melter power was determined by subtracting the total melter power losses through cooling jackets or penetration through the cold-cap into the melter plenum space, for example. Simply measuring the idling (no slurry feeding) power of a melter would not account for the insulative contributions of a transitional feed layer on top of the glass pool or other processing effects. Therefore, the power losses were determined by first plotting the feed rate against total input power from the melter electrodes and plenum heaters (if any were present) for the various steady operating segments. Next, the x-axis intercept of this plot was determined, which indeed yields the effective total power losses. The resulting plot of the melter performance data is shown in Figure 4.2.

(a) Buchmiller, W.C. et al. "High Bay Ceramic Melter Experiment Summary Report: HWVP-13/HBCM-86-2," 7H35-86-12/HLV1B, Pacific Northwest Laboratory, June 1986.

(b) Sevigny, G.J. et al. "PSCM-3 Summary Report," Pacific Northwest Laboratory, October 1981.

(c) Dierks, R.D. et al. "PSCM-5 Summary Report," Pacific Northwest Laboratory, March 1982.

(d) Sevigny, G.J. et al. "PSCM-6 Summary Report," Pacific Northwest Laboratory, October 1982.

(e) Perez, J.M. et al. "PSCM-11, HWVP-5 Test Report," Pacific Northwest Laboratory, January 1983.

(f) Perez, J.M. et al. "West Valley Waste Vitrification Experiment: PSCM-15 Summary," Pacific Northwest Laboratory, September 1983.

(g) Peterson, M.E. et al. "Hanford Waste Vitrification Program: PSCM-17 Summary," Pacific Northwest Laboratory, November 1984.

(h) Perez, J.M. et al. "West Valley Pilot-Scale Melter Experiment: PSCM-19/19E Run Summary," Pacific Northwest Laboratory, January 1985.

(i) Peterson, M.E. et al. "Pilot-Scale Ceramic Melter, Nonradioactive Experiment No. 20 (PSCM-20) Summary Report," Pacific Northwest Laboratory, June 1985.

Figure 4.2 shows a tight linear dependence on the data from all of the melters studied. The slope of a linear regression through any one data set is inversely proportional to the melting enthalpy of the feed material. For slurried melter feeds, this enthalpy is mostly a function of the water in the slurry. As a result, the melting enthalpies of most of the different melter feeds are nearly equal.

Other than size, the only difference between the systems is that the LFCM used plenum heaters and the SSHTM ran at higher temperatures. In the LFCM, processing rates were high as 75 l/h•m^2 due to plenum power boosting. However, the SSHTM data shows a 30% increase over any other system because of higher processing temperatures.

As described, the melter power losses were determined to generate the Figure 4.2 data. Table 4.4 shows these values for each melter and feed material. The melter power loss estimates for each PSCM data set are within the error ranges of one another, approximately 9 kW. This consistency is expected because no system changes were made between the different tests. The LFCM appears to be the most inefficient system; although much larger than the others, it was also the only system equipped with plenum heaters, which greatly increased the power losses. The difference between the LFCMs, HWVP, and DWPF melter efficiency numbers is due a rebuild in the intermittent. The SSHTM performed at the elevated processing rates while still yielding relatively low power losses, which were due to the inherently direct heat transfer in the system configuration.

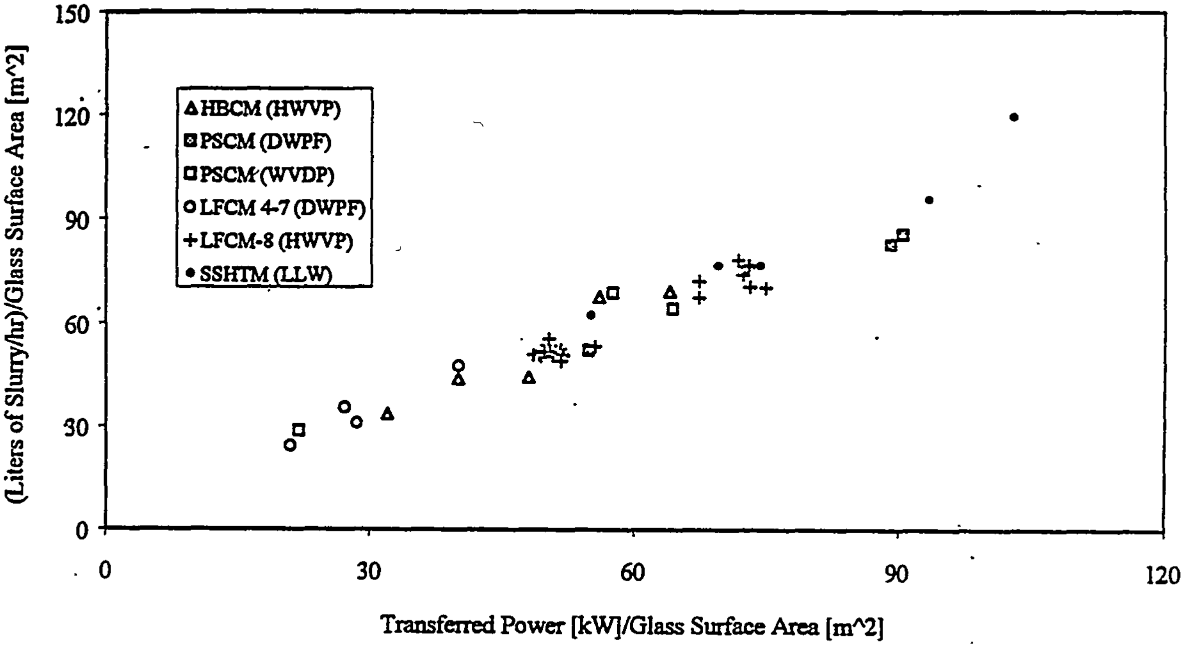

Figure 4.2. Performances of Previously Tested PNL Slurry-Fed Glass Melters

Table 4.4. Tabulated PNL Slurry-Fed Melter Performance Data

PNL Melter System	Waste Slurry Type	Test ID Number(s) in Data Set	Melter Surface Area (m^2)	r Squared of Linear Regression	Melter Power Loss Calculated from X-Intercept (kW)
HBCM	HWVP	1, 2	0.25	0.91	5 ± 4
PSCM	DWPF	3, 4, 6	0.73	1.00	9 ± 0
PSCM	WVDP	9, 11, 15, 16, 19, 20	0.73	0.75	21 ± 22
PSCM	HWVP	17, 22	0.73	0.99	6 ± 7
LFCM	DWPF	4, 5, 6, 7	1.05	0.92	125 ± 50
LFCM	HWVP	8	1.05	0.94	83 ± 2
SSHTM	LLW	0	0.21	0.95	19

H. Extent of Mock-Ups and Test Facilities Required

Existing testing facilities include

- the SSHTM (0.22 m^2) at PNL
- the PSHTM (2 m^2) at 1550°C at PNL
- Penberthy Electromelt melter(s) (available facilities unclear at this time)
- Duratek is currently designing an HTM for mixed waste vitrification.

I. Necessity for New Inventions

New inventions would be required for items not previously considered for HLW vitrification. This is partially a result of the increased melter size (depending on how many parallel lines of melters would be used in the plant). Use of only one line would require new feed distribution systems, melter moving equipment, bottom drain, and plenum heaters. The bottom drain for a single melter would have to be designed to control glass pouring at rates up to 680 kg/h (assuming that maximum pour rates will be two times the average production rate).

Contrary to statements made at the June TAC meeting, inventions are not required for the electrode materials in the HTM. This issue is described in Section 5.K.

4. Integration with Process and Facility - *This section is provided by Fluor Daniel, Inc.*[3]

5. Control and Maintenance of Process and Facility

This section includes a discussion about safe and efficient operation of the vitrification facility.

A. Ease of Control

Operation of this melter should be similar to the LTCM with the following exceptions. If consumable electrodes are used, electrode feeding and level will have to be controlled. Electrode consumption is measured by monitoring the load resistance. Control of the bottom drain temperature is accomplished by an optical pyrometer until the proper induction power levels are determined for pouring, after which only the power and frequency are controlled. Glass temperature measurement is accomplished with a platinum thermowell and Type B thermocouples (Pt/Rh).

B. Remoteability

The HTM uses most of the remote features of the LTCM with the following exceptions. If consumable electrodes are used, an electrode feeding mechanism will be needed. Automatic electrode feeders are currently available from the electric arc furnace industry and would be incorporated into the electrode design shown in Section 5.K. If a molybdenum bottom drain is used, an automatic airlock system would be required to isolate the bottom drain during canister changeout. This was done on the SSHTM with a simple knife-gate valve and purge system.

C. Reliability

The reliability is measured by the total operating efficiency (TOE), defined as the total number of hours that the melter operates divided by the total number of h that the melter is in place, including the time required for melter changeout. The assumed TOE for the HWVP was 60%. This was arrived at by assuming that the melter was on-line 70% of the time and that it required a six month changeout every three years. Few data are available to support the assumption of a 60% TOE for the HTM; on-line efficiency during the SSHTM test with LLW simulant was 88%.

D. Maintainability

This should be the same as that of the LTCM melter except for the additional maintenance of possible electrode feeding, supplying inert gases to the electrode sheaths, and additional cooling water for the top-entering electrodes (if used).

E. Estimated Lifetime

As stated in Data Package 1, noble metals accumulation can be a threat to melter life. It is unclear at this time if noble metals accumulation will be a problem with the new blended feed. The melter could be designed with a sloped bottom to channel noble metals or crystal accumulations to the bottom drain. Testing will be required to determine whether noble metals are a problem for the blended feed, and, if so, whether the sloped bottom design can prevent accumulations.

F. Ability to Confine Radioactive Materials

A vacuum is kept on the melter plenum and overflow (glass discharge) section so that airborne release of radionuclides to the vitrification cell is unlikely. One problem that can occur with LFCMs is the accumulation of deposits (e.g., cesium) in the off-gas line. This can be controlled by using a film cooler to quench and dilute the hot off gas or by regularly cleaning the off-gas line with either a reamer or an air "blaster."

The melter is equipped with an emergency off-gas line to provide backup vacuum to the melter during shutdown of the primary off-gas system.

A significant source of radioactive materials is from maintenance of equipment. This does not appear to be directly related to the melter technology.

G. Potential for Radioactive Source Buildup and Achievement of ALARA

Off-gas treatment is discussed in the Fluor Daniel, Inc.[3] data package.

This melter has a bottom drain that can be used to drain the glass from the melt cavity at the end of the melter life. This may be optimistic. Melter failure could occur such that the glass could not be drained from the melter. This is an unresolved problem for most of the melters being considered in this evaluation. Because of the required size of this melter (if only one or two melter lines are used), the glass/radiation source remaining in the melter after its failure could be substantial.

H. Sealing and Containment Relative to Melter

Measures to seal the melter to prevent inleakage to the off-gas system and prevent out-leakage to the melter cell have always been a significant challenge for designing remote melters. Metal bellows are provided for sealing the canister to the melter during glass pouring. Packing materials are used to seal all flanged connections such as the melter lid, off-gas pipes, and lid penetrations.

I. Modular Design Concepts that Simplify Replacement or Repair

This melter design is not modular except for the supporting systems (canister handling, etc.). The Fluor Daniel, Inc. data package evaluates melter disposal costs as a function of melter size.[3]

J. Refractory Life

This melter design uses a combination of Carborundum Monofrax K-3(a) and Monofrax-E(b) fused cast refractories in contact with the glass. These refractories are used in high-wear areas of commercial glass melters. The current HTM design uses 6 in. of each fused cast refractory for all glass contacting surfaces, but this thickness is by no means a limit. As shown in Data Package 1, K-3 has very good corrosion resistance for HLW glasses at lower temperatures (1150°C). No data currently exist for K-3 refractory corrosion at 1450°C with a glass like the HLW glass. Corrosion rate experiments for K-3 and E refractories are underway at PNL for these and other refractory materials. Refractory corrosion is not expected to limit the melter life. Laboratory corrosion tests for Monofrax-E suggest an estimated life in excess of 4 years, predicated on the most conservative corrosion results, i.e., metal line corrosion.

The melter plenum refractory is castable Carborundum Alfrax-66,(c) supported by either ceramic or Inconel hangers. Past failures of the plenum refractory have mainly been associated with improper hangers and allocation for thermal expansion (Larson 1989).

(a) Carborundum Monofrax K-3: 60% Al_2O_3, 27% Cr_2O_3, 6% MgO, 4% Fe_2O_3, 2% SiO_2.

(b) Carborundum Monofrax E: 6.5% Al_2O_3, 77.5% Cr_2O_3, 7.4% MgO, 5.9% Fe_2O_3, 1.7% SiO_2.

(c) Carborundum Alfrax-66: 96% Al_2O_3, 4% CaO.

K. Electrode Life/Replacement

Extensive electrode investigation work has been performed. PNL evaluated a wide variety of materials including molybdenum, coated molybdenum, precious metals, and other electrode materials. The most extensive work has been targeted at the assessment of electrode material life (corrosion rate measurement) in Hanford Site HLW glass.

Except for a few early experiments, all of the corrosion investigations have been performed at 1350°C. Most have used the N508 glass formulation, a 50 wt% NCAW waste glass. Early experiments were performed with a 25 wt%, 1150°C borosilicate formulation. The experimental setup used for the corrosion test is as follows. Two 5-mm molybdenum rods sheathed in sealed alumina tubes were inserted into a platinum crucible containing the molten glass sample. (The electrodes were sheathed to protect them from the oxidizing environment in the 1150°C or 1350°C furnace.) During most of the experiments a potential was placed across the two electrodes sufficient to allow current flow at a density of 1 A/cm^2.

The first few corrosion rate experiments used a low-temperature (1150°C), LLW loaded (25 wt%) borosilicate glass formulation with no current flowing through the test electrodes. Corrosion rates in these runs were low, about 5 x 10^{-4} cm/day based on the results of the 48-h experiment and

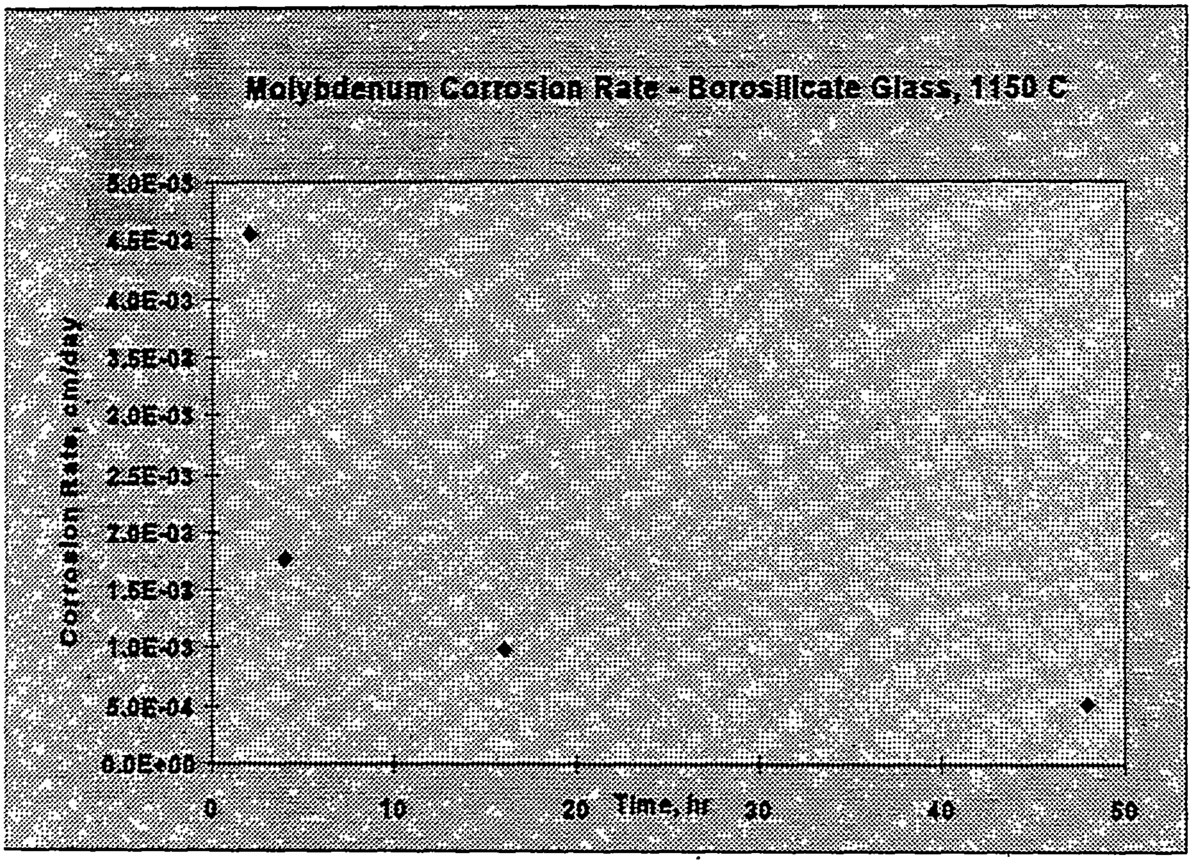

Figure 4.3. Molybdenum Corrosion in 1150°C Borosilicate Glass

decreased with time. The results of these experiments are presented in Figure 4.3; the data points are based on the average of 1 or 2 diameter measurements along the exposed molybdenum rod at the end of the test. No potential was applied during these tests.

The next series of corrosion rate tests used molybdenum in the N508 glass composition at a temperature of 1350°C. In the following synopsis of the conditions and observations of these experiments, letter designations correspond to the data points presented in Figure 4.4. The presented data represent the average of 4 to 6 diameter measurements along the exposed length of the molybdenum rod.

A. Current density: 1 A/cm^2

B. Current density: 1 A/cm^2; the power supply was not equipped with a D.C. filter which resulted in approximately 0.2V D.C. potential in addition to the A.C. potential

C. Current density: none

D. Current density: 1 A/cm^2; removing the test electrodes from the crucible while the temperature was still 1350°C allowed the glass to run off the electrodes, so that oxidation of the furnace plenum may have increased the observed corrosion rate. In all previous and subsequent experiments, the furnace was allowed to cool to about 1000°C before electrodes were pulled from the crucible.

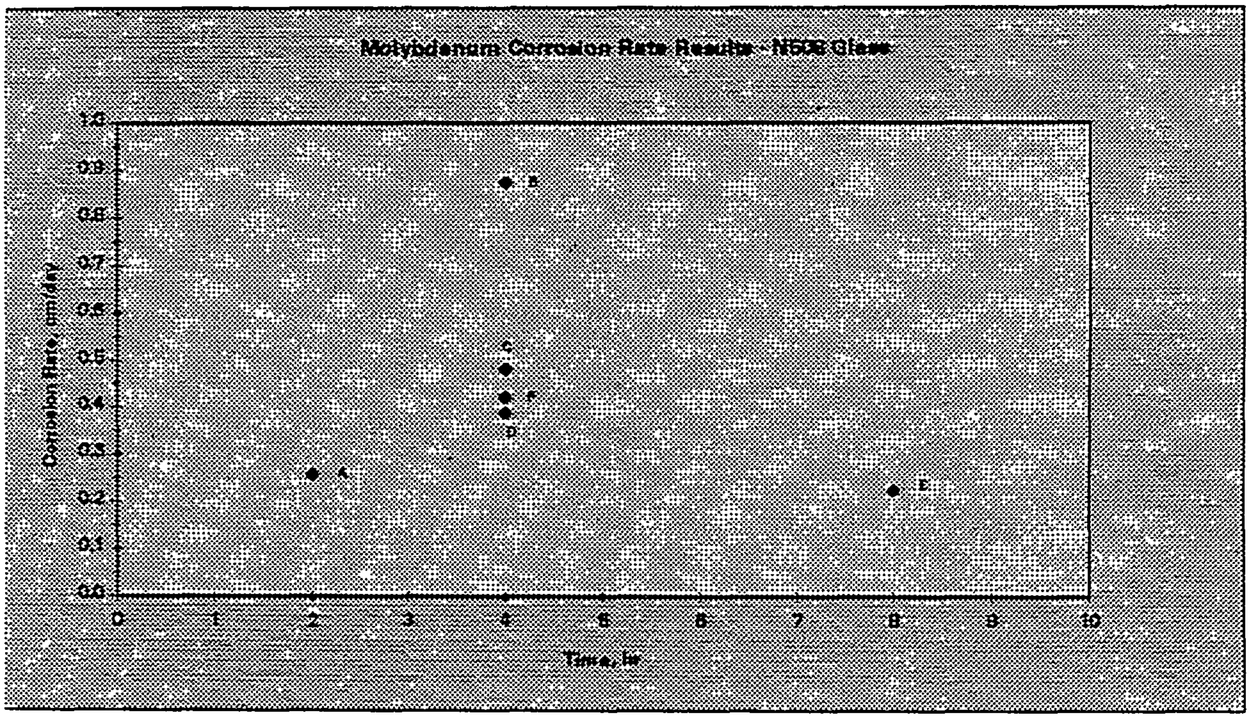

Figure 4.4. Molybdenum Corrosion in N508 Glass at 1350°C

E. Current density: 1 A/cm^2; during this test a D.C. passivation current was applied through a platinum wire to one of the two electrodes. electrode. The data presented in Figure 4.4 represent an average of the corrosion rate of both electrodes. The rates for each electrode are as follows: unprotected electrode, 0.22 cm/day; protected electrode, 0.23 cm/day. Therefore, cathodic protection is not conclusive; further work is planned.

F. Current density: 1 A/cm^2; This molybdenum used in this test was a TZM stabilized molybdenum.

The data presented in Figures 4.3 and 4.4 are the same as those presented by Dr. Pavel Hrma during the June TAC meeting.

In all of the corrosion reaction layers, increased concentrations of nickel and copper were observed. Several additional experiments were performed to determine if these transition-group elements were the causal agents. First, iron was removed from the melt with no observable effects on the corrosion rate. Next, removal of all the transition group materials, with the exception of iron, significantly diminished the corrosion rate by approximately a factor of 6. When only nickel and copper were removed from the N508 glass, corrosion was about a factor of 2 lower than that observed with the unchanged N508 glass. Thus, although nickel and copper had a large effect on the rate, other constituents are involved in the corrosion of the molybdenum.

If it is assumed that the molybdenum is replaced, i.e., fed to the melter, at a rate equivalent to the corrosion rates reported above, then the replacement rate ranges from 82-cm/year to 320-cm/year based on test conditions E and B, respectively. Feeding electrodes into the melter at these rates would not be complicated, even in a remote environment, because all motion required to feed electrodes is vertical. Technology is readily available from the arc furnace industry for electrode feeding. Commercial arc furnaces operate in an essentially remote environment because temperatures are too high for routine personnel access to the top of the furnaces. The new taper-threaded electrode sticks are added to the existing electrodes with a crane. In addition to feeding electrode material, the entire electrode assembly could be replaced as required, further extending the life of the melter.

Additional corrosion tests have been performed and are continuing with various coatings on molybdenum and other materials. All of the coatings tested extended the time before molybdenum corrosion began. The time lag resulted from the time required for constituents to diffuse through the coatings or for the coating to be degraded or removed from the surface. Coating tests were performed for 4, 69, and 168 h. The 4 and 69-h tests resulted in little or no observable degradation of the molybdenum. Corrosion was observed in the 168-h test, where the chromium protective layer was porous through the entire surface.

Other potential electrode materials evaluated include tantalum, iron, graphite, and a chromium /alumina cermet. The results of these tests are summarized:

Tantalum: The corrosion rate was approximately equivalent to that of molybdenum in a test of similar length. One primary difference was in the corrosion reaction layer, where only tantalum oxide was present; increased concentrations of transition group metals were present in the molybdenum reaction layer. Thus, the tantalum corrosion might result from a simpler mechanism and might be more conducive to cathodic protection. A current density of 1 A/cm^2 was applied.

Iron:	In direct contact with the glass, the iron did not survive a 4-h test at a 1 A/cm^2 current density.
Graphite:	In direct contact with the glass, the graphite did not survive a 4-h test with a 1 A/cm^2 current density.
Cermet:	Results from the testing of the chromium/alumina cermet have been very promising. Corrosion tests have been completed with test times of 4 h, 24 h, 49 h, and 72 h. Although the structure of the material was significantly modified during the tests, corrosion was essentially the same in the 24-h and 49-h tests, approximately 0.06 cm/day. The first three tests (4 h - 49 h) were performed with no current applied; the 72-h test was performed at a 1 A/cm^2 current density. The structure of the material was changed throughout its entire width, but the thickness of the material was essentially unchanged between the 24-h and 72-h tests. The results to date for this material are very promising, and further tests are planned.

L. Ability to Safely Handle Organics

It is planned that all organics will be destroyed in the plenum space of the melter. The current design of this melter does not have plenum boosting for two reasons: it was not considered necessary, and the expected temperatures were above the normal use limit for most resistance heaters. After the first two tests of the SSHTM, it appeared that plenum heaters would survive in the plenum. Even during idling at 1400°C, the plenum temperature never rose above 1150°C. Therefore; plenum heating with resistance heaters sheathed in Inconel-690 is an option. It is not clear at this time if it is a needed option. During the first two SSHTM runs, the average plenum temperature was 450°C to 550°C. It is not clear if the plenum gases come to equilibrium temperature before they leave the melter. Because of this uncertainty, DREs are usually demonstrated for organic materials expected in the feed. The DREs for the HTM will have to be measured. If the destruction is incomplete, either plenum heaters or a post heater may be required.

M. Operational Simplicity

Except for the variability of the cold cap, this melter technology does not operate dynamically. There are very few moving parts, and process dynamics are very slow because of the large time constant of the glass pool.

N. Estimated Lifetime

See Section 5.E.

O. Estimated Downtime to Repair

Replacement of the HWVP melter was estimated to take six months. Replacement times or various melter-related items were estimated for the West Valley melter (Westsik et al. 1987), which are shown in Table 4.5. The WVNS plant is canyon remote with limited manipulator access, and although the melter operates at lower temperatures, the replacement times should be similar to those of the HTM.

6. Minimize Total Cost - *This section is provided by Fluor Daniel, Inc.*[3]

Table 4.5. Replacement Times for Melter Components

Item	Repair Time
Thermowell replacement	1 day
TV camera replacement	8 h
Dip tube (level measurement) replacement	1 day
Overflow heater replacement	2 days
Overflow heater connection replacement	3 days
Film cooler replacement	2 days
Feed nozzle replacement	1 day
Electrode failure	high
Inner refractory cooling system failure	high
Canister load cell replacement	2 days

7. Others: Issues Raised at June TAC Meeting

High Temperature Glass Impacts on Canister Filling

The impacts of elevated glass temperature on canister filling were assessed by modeling the temperatures throughout the waste glass canister during fill-up and cool-down. TEMPEST, a numerical heat transfer analysis code developed at PNL, was used for this modeling. To simplify the modeling, no preset fill rate was assumed; instead the canister was assumed to be at room temperature then instantaneously filled with the glass at the processing temperature. The transient heat-up and cool-down of the canister and glass were then modeled by the TEMPEST code. This modeling assumption differs from actual filling because only a layer of glass poured in the canister is typically molten at any one time; however, an instantaneous canister fill assumption is a conservative scenario in attempts to identify maximum canister temperatures.

The following parameters and assumptions were used in the modeling:

Canister geometry = Cylindrical
Outer diameter of canister = 0.61 m (2 ft)
Height of canister = 2.29 m (7.9 ft)
Ambient (room) temperature = 40°C
Canister construction material = 304L stainless steel
Canister wall thickness = 1 cm
Heat generation due to radioactive species in glass =1400 Watts

Additionally, the assumed physical properties of the glass and canister material are shown in Table 4.6.

Table 4.6. Glass and Canister Physical Properties Used in TEMPEST Modeling

Glass Thermal Conductivity (vs. temperature)		Surf. Heat Transfer Coeff. (vs. temperature)		Emmisivities	
Temp. °C	K (W/m K)	Temp. °C	hc (W/m^2 K)	Can Emmisivity	Sink Emmisivity
0	0.3	600	8.3	0.30	1.00
650	0.7	500	8.0	0.40	0.55
1000	2.0	400	7.6	0.50	0.43
1200	7.0	300	7.1	0.60	0.38
1400	12.0	200	6.4	0.70	0.34
2000	31.0	100	5.1	0.80	0.32
		50	3.5	0.90	0.31
				1.00	0.30

The glass thermal conductivity data were from extrapolated HLW glass data, and the canister heat transfer coefficient and emmisivities were obtained from fits with canister cool-down data measured at SRL[1] during several different 1150°C glass pours. The aggregate used for the model fit was a 35-h maximum surface temperature cool-down to 100°C and a 17-h maximum canister centerline temperature cool-down to 500°C. After adjustment of the heat transfer coefficients and the emmisivities in the TEMPEST model, both of these actual data sets fit the values in Table 4.6. Representation of the emmisivity values as a list rather than one source and one sink emmisivity was chosen so that all the pairs shown will produce the same result in the radiant heat transfer equations.

The final results of the TEMPEST modeling for both 1150°C and 1500°C glass fill cases are shown in Figure 4.5, which provides maximum canister centerline and surface temperatures for both of these starting temperatures. Both sets seem to nearly superimpose by around 5 h of cool-down time, despite the initial differences in temperature. The convergence is due to the higher glass thermal conductivities and heat transfer rates at the elevated temperatures. These data suggest that little difference in canister cool-down performance would exist between 1500°C glass and actual 1150°C glass-pouring experience after 5 h cool-down time.

The maximum canister surface temperatures obtained for both simulations were 620°C after 16 min., for the 1150°C simulation, and 865°C after 10 min., for the 1500°C simulation. The maximum surface temperature observed during the SRL testing was approximately 500°C, which shows the conservatism in the 'full canister' scenario. Nevertheless, both maximum surface temperature curves show cooling to below 500°C within 2.5 h.

The canister material, 304 L stainless steel, has a melting temperature above 1000°C. The creep properties of this material are between 1x10^5 to 2x10^5 lb/in^2 at around 600°C and 800 to 1500 lb/in^2 at 840°C, all for a 0.1%/1000 h creep rate.[2] Even though a two order of magnitude decrease in required pressure for a given creep rate exists for the given temperature increase, detectable deformations in the

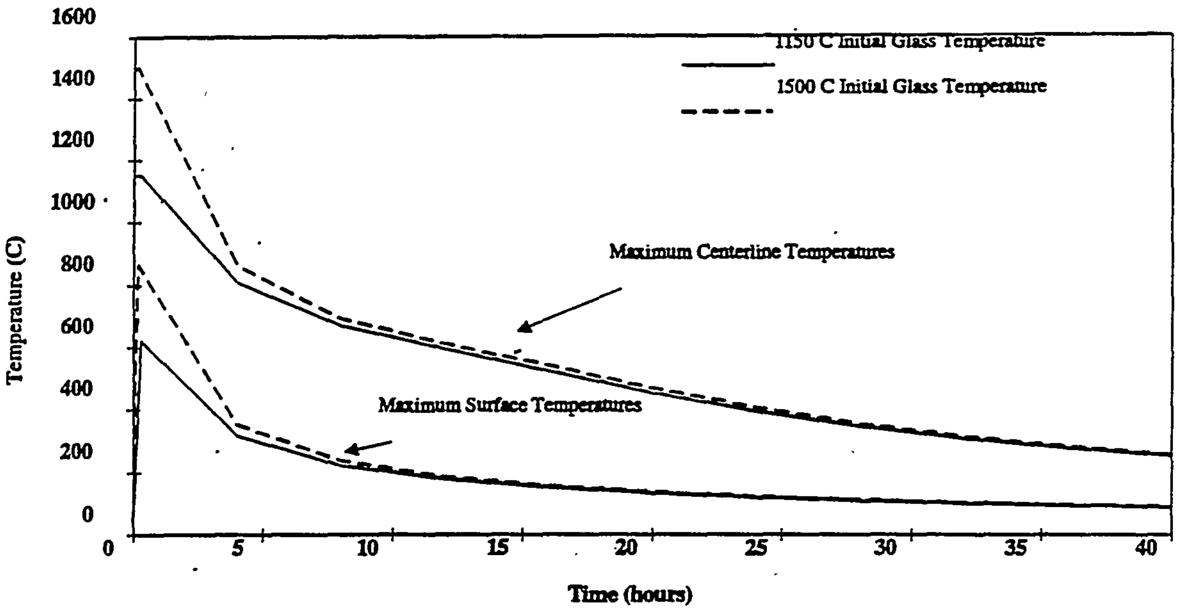

Figure 4.5. Predicted Canister Cool Down Curves for 1150°C and 1500°C Glasses

higher temperature scenario are not certain. Because the canister temperatures are only expected to remain at these higher temperatures for a relatively short time and the predicted maximum surface temperature for the 1500°C fill is expected to be conservatively high due to the 'full canister' assumption in the model, appreciable canister deformation is not expected with the higher temperature glass..

Supporting evidence of little or no expected increase canister deformation was observed during SSHTM pouring with acceptance testing glass. Pours of glass at temperatures in excess of 1400°C were made into 35-gal carbon steel drums. The drum walls were much thinner than those of a waste glass canister. No noticeable deformations were observed in the 3 to 4 drums poured during this testing.

Endnotes

1. Letter from R.W. Powell of WHC to J.M. Creer of PNL, "Double-Shell Tank/Single-Shell Tank Waste Blend Composition for High-Level Waste Vitrification Process Testing." May 1994.

2. Chemical durability testing results HTB625P from M. Schweiger, PNL dated August 2, 1994.

3. Fluor Daniel, Inc. August 1994. "Alternative Melter Systems Assessment 20 Metric Tons per Day HLW Glass Production." Prepared under contract #04-436304 with Westinghouse Hanford Company.

Data Package 4, Appendix A

High-Temperature, Joule-Heated, Ceramic-Lined Melter: Penberthy Design

This appendix to the data package for the HTCM contains information received from Mr. Larry Penberthy about his design for the Hanford HLW vitrification plant. This information was received at WHC/PNL on August 23. This did not allow sufficient time for a thorough review and follow up before the August meeting. The information received was complete, and it follows the order of the other data package, so that we have attached the letters from Mr. Penberthy in full.

Further information was received from Mr. Penberthy during a phone conversation with Mr. George Janicek of WHC:[a]

> "(Mr. Penberthy) didn't respond to PNL's letter with HLW melter questions because he believed that subject was well into the future and there wasn't any urgency to his giving it any attention, and so, had set it aside. I explained to him our timetable and need to determine which two melter technologies to fund for development and testing in FY 1995.
>
> - His company is a vendor of glass melters and currently has 10 employees. He's been in this business since 1948 and built approximately 80 melters, the largest being 110 tons/day.
> - His melters require 5 sq. ft/daily ton. A 10 ton/day melter would be 6 ft wide x 8 ft long. A 20 ton/day one would be 6 ft wide x 16 ft long. Either would be about 7 ft high.
> - The melter is refractory lined. Normal refractory life is 4 years, actual is 10 years (assumed to be based on his service conditions).
> - Electrodes are Molybdenum (moly) and are apparently sidewall mounted. They are also consumed by the glass and thus have a mechanism for feeding them into the melt. Electrode consumption is small, however. Believe he stated it was like 2 in./month (this is also assumed to be based on his service conditions). He claimed that he was the inventor of moly electrodes.
> - Molten glass is discharged from the melter via a sidewall channel located near the bottom of the glass melt pool. Glass pour control is accomplished electrically with heating elements (no additional clarification).

(a) Conversation between Mr. Larry Penberthy of Penberthy Electromelt International and Mr. George Janicek of WHC, August 5, 1994.

- Normal operating temperature of his melters is 1320°C.

- He proposes a soda-lime-alumina-silicate glass for HLW vitrification instead of borosilicate. Claims this glass has a much higher retention of Cs. Claims the volatility of Cs from borosilicate glass at 1150°C is 5 times as great as from his proposed glass at 1350°C."

Glass Melting Processes for the Glass and Waste Industry

Penberthy Electromelt International, Inc.

631 South 96th Street

Seattle, Washington 98108, U.S.A.

Telephone
(206 762-4244
Fax
(206 763-9[illegible]

August 19, 1994

Phyllis Shafer, Research Engr, ETC
MS P7-41
Battelle - PNL
POB 999
Richland, WA 99352

Re: **Revised HLW Vitrification Program**

Dear Ms. Shafer:

I received both your letters, April 21 and July 13, 1994, enlisting our interest in the above program. When I realized the target date for action is 2009, I put them in the Dormant file. There was no discernible reason for putting any unfunded today-time into such a delayed program.

George Janicek, WHC, called to try to get some information. He revived my interest in the project by saying that there will be funding (for us) in FY95. Therefore, I have prepared a detailed reply to your detailed questions.

<u>Other Factors</u>
In addition to your questions, there are other important factors to be considered:

A. Battelle is mesmerized, even enthralled, by the concept "borosilicate glass." But this is a false concept for a glass requiring longevity against water attack. See Doremus: Glass Science (1973), p. 44. "The separation of borosilicate glasses into two liquid phases has long been recognized." The essence of the flaw is that the boric oxide separates as alkali borate, which is fully soluble. The alkali will include cesium if present. Thus, Battelle's inclusion of boric oxide solubilizes an important radionuclide which Penberthy makes very insoluble as vitreous cesium/alumino/silicate. The crystalline form of that compound is pollucite, which is the ore, stable for geologic time.

B. Sodium-cesium borate has a high vapor pressure at molten glass temperatures. Buehlt showed me the alkali-borate smoke coming from the downstream of his melter, some 12 years ago. Battelle had an accident in B cell with a cesium-137 borate loaded filter 6-10 years ago. The whole cell became contaminated. The cleanup was expensive.

The attached Pyro 111-C shows that the 5x vaporization loss of borosilicate glass at its melting temperature, 1150°C (2100°F), compared with alumino-silicate at its melting temperature, 1290°C (2350°F).

The Big Question

The big question for you is whether you are going to open up HLW vitrification to mainstream American glass science, technology and engineering practice. Restated, do you want to get the job done in finite time at affordable cost? If so, a different approach is required, compared to the approach used in the past.

What to Do

1. Open up your panel to people who are strong in modern glass practice.

2. Shorten the timetable.

3. Open up the pathways under consideration to, for example:

   slurry up the entire contents of the tanks, and nozzle-mix the slurry with Hanford soil to make an excellent glass.

   We demonstrated sodium nitrate plus soil vitrification for Battelle PNL in 1974. We are ready to demonstrate that again, with a surrogate including the sludge.

4. Order a 10-ton per day furnace for (3) now and have it on site by July 1995.

5. Allow us to debate the time and cost advantages of <u>not</u> separating any radionuclides, and of <u>not</u> washing the sludge. Good glass needs the alumina and soda.

We are keenly interested in getting Hanford's work done. Do you want me to participate in your panel?

Sincerely,

PENBERTHY ELECTROMELT INT'L, INC.

Larry Penberthy

Larry Penberthy
LP/nc
Enc: Pyro 111-C

We are sending background papers by express mail.

cc: George Janicek

FOUNDATION FOR
NUCLEAR WASTE DISPOSAL
631 So. 96th St.
Seattle, Washington 98108
206-762-4244
Telex 329473

VAPORIZATION OF GLASSES INTENDED FOR NUCLEAR WASTE

In 1958, Atomic Energy of Canada Ltd. made and published glasses containing radioactive fission products. They are in the alumino-silicate family, characterized by high alumina (6-10%), low soda (8-12%), medium lime (8-12%), balance silica. Alumina plus silica exceeded 75%. Melting was in refractory ceramic at 1400°C (2550°F).

The AECL glass is very durable indeed. It is similar to glasses used for sight gages for observing water level in steam boilers. Field testing of actual radioactive glass over 24 years has been outstandingly successful.

Other workers on radwaste glass wanted to melt in stainless steel canisters. This is called in-can melting. Unfortunately, the top service limit for stainless steel is about 1150°C (2100°F). They could not melt the AECL glass.

These other workers added excess soda-lithia and boric oxide to the composition to lower the melting point. Again unfortunately, the excess soda-lithia destroys the three-dimensional silica network, and the boric oxide raises the vapor pressure much more than it lowers the melting point.

Specifically, the vaporization loss of Savannah River Laboratory borosilicate glass held at 1150°C (2100°F) for 90 minutes is five times as great as the vaporization loss from P-19 alumino-silicate at 1290°C (2350°F) for the same time.

P-19 glass has 15% soda, no lithia, no boric oxide. This composition is intended for West Valley, glassify-all process.

P-3 glass has 11% soda, no lithia, no boric oxide. It is intended for Savannah River and West Valley sludges without supernate. P-3 has an even lower vaporization rate.

Test Method

A platinum crucible 50 mm square x 20 mm deep was suspended in a glow bar heated furnace by a platinum wire connected to a digital laboratory balance above the furnace. 50 g of glass had been preplaced and warmed before the crucible was introduced into the heated furnace.

Readings of weight remaining were taken every 5 minutes, and the results plotted as grams loss per sq meter against time.

Furnace temperature for the SRL borosilicate glass was 1150°C (2100°F) and for P-19 alumino-silicate, 1290°C (2350°).

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safely,
effectively,
promptly,
Affordably!

From other work, the material lost from borosilicate glass is alkali borate, including cesium if present.

\- - - - - - - - - - - -

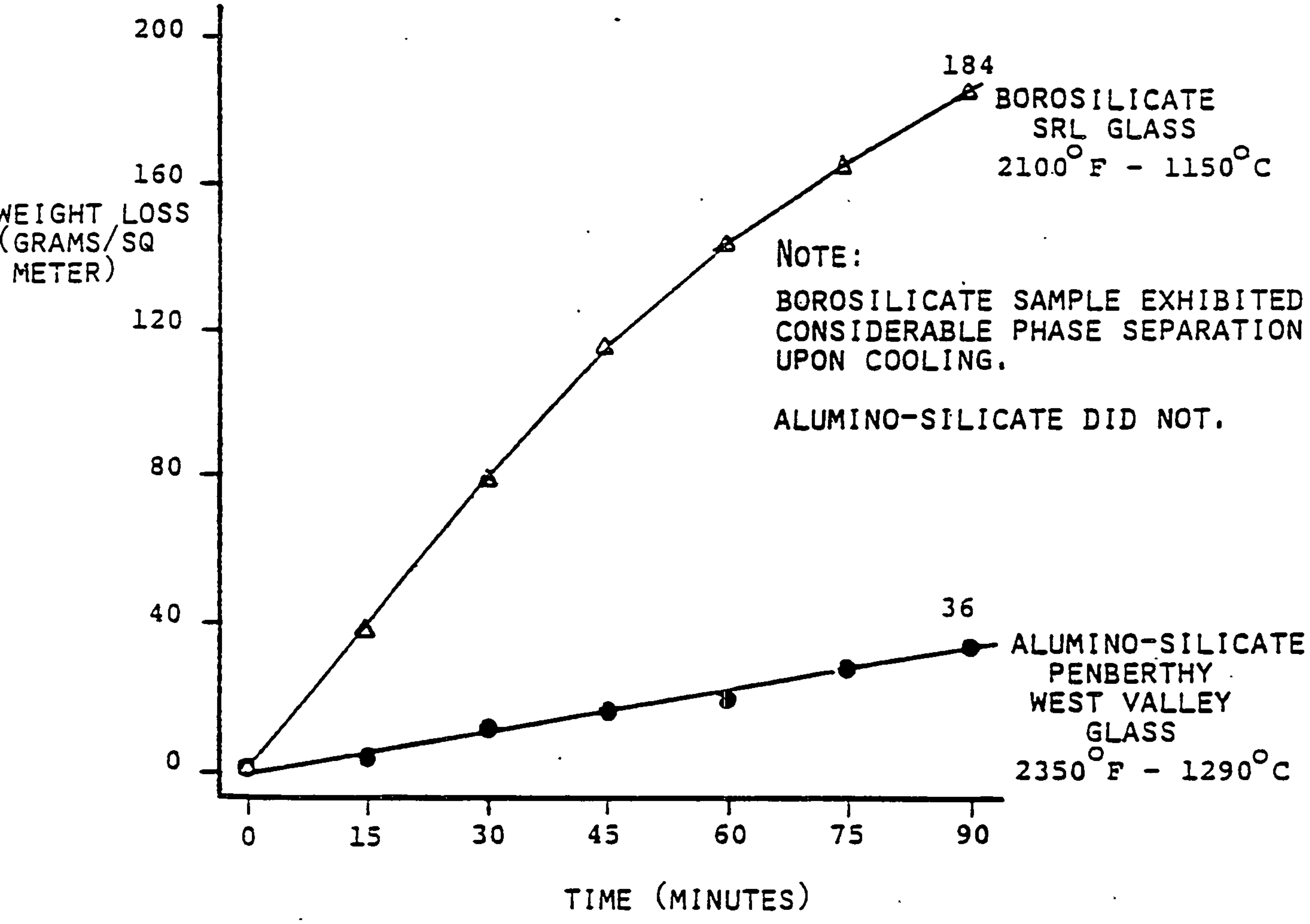
The Foundation for Nuclear Waste Disposal has as one of its purposes the correction of incorrect statements regarding nuclear waste. Please help by communicating this report to anyone who has been misinformed.

Larry Penberthy

See also: Structure of Glass as a Host for Radwaste or
Why We Need a Glass Better Than Borosilicate

VAPORIZATION
FROM
ALUMINO-SILICATE AND BOROSILICATE GLASSES AT MELTING TEMPERATURES

by Larry Penberthy Feb. 1983
Dennis Hotaling



NOTE:

BOROSILICATE SAMPLE EXHIBITED CONSIDERABLE PHASE SEPARATION UPON COOLING.

ALUMINO-SILICATE DID NOT.

50 GRAM SAMPLES IN 25 SQ CM PLATINUM CRUCIBLE SUSPENDED IN STILL AIR IN ELECTRICALLY HEATED FURNACE

Penberthy Electromelt International, Inc.
631 South 96th Street Phone 206/762-4244
Seattle, Washington 98108, U.S.A. Fax 206/763-9331

ANSWERS TO THE QUESTIONS RELATING TO THE ALTERNATIVE MELTER SYSTEM ASSESSMENT FOR MELTER SELECTION WORKING GROUP FOR HIGH LEVEL WASTE

The following comments are following the checklist provided by Phyllis Shafer of Battelle PNL in her letter of July 13, 1994.

1. Process Range of Composition

Flexibility to Process Expected Glass Composition Within Melter Parameters

__Attributes__

a. **Temperature - flexibility to process glass compositions within the 1100°C to 1450° temperature range.**

The Penberthy Melter system is readily able to operate within the temperature range, although we would comment that 1450° is a rather high temperature for commercial melting which is a lot closer to 1320° to top of 1400°. Therefore, the Penberthy furnace should be categorized as being able to handle both low temperature and high temperature, ceramic, Joule heated melter.

Word of caution here is that qualitative words should not be used. Low temperature is not that much lower than normal temperature of glassmelting and high temperature is well above the temperature used commercially for glassmelting. It is better to use numbers, for example: The low temperature is given as 1150°C, compared to commercial glassmelting at 1320°C, and the high temperature melting at 1500°C for melting hard glass, such as Pyrex baking ware.

b. The range of waste handling capabilities with the Penberthy Melter System is very wide. Attached is a list of glasses which have been melted commercially in Penberthy furnaces.

Special treatment of volatile components is automatically taken care of by the batch blanket, whereby the volatile materials are captured in the batch blanket and carried back into the melt.

The acceptable processable glass property range is quite broad.

Viscosity is not a limiting factor.

Electrical conductivity vs. temperature is easily handled. If the resistance of the glass is higher, the voltage is higher and the amperage is lower, and reverse. There are certain classes of glass which require special electrode arrangements. These arrangements are well proven in industrial practice using Penberthy's furnaces.

Precipitates are commonly avoided by melting at a temperature above where there is any precipitation. Certain materials, such as the noble metals, lead, or copper, are handled by a proprietary method.

The ability to handle slurry feeds is excellent. The solid feed materials are fed in through a screw auger and the liquid or slurry portion is added fairly close to the discharge into the furnace. This is called nozzle mixing. PEI demonstrated it years go, including for the West Valley furnace in 1981.

The limits on feed viscosity are very broad, all the way from ½" mesh down to powders and liquids. The glassformers are the common ones, based on soda-lime-alumino-silicate system.

Melter feed system clogging is avoided by the methods of pumping. The soda which is to be used in the melt is applied partly as hydroxide, which is lubricious. Pre-fired glass frit is definitely to be avoided because the glass frit has sharp angles and is susceptible to packing and plugging at bends, flanges, and valves of the pump system. This is a problem that was encountered with disastrous consequences at Savannah River Laboratory fairly recently. In a Penberthy furnace the slurry is added to the solid particles. The solid particles are partly diatomaceous earth which soaks up the excess liquid. The final product going into the furnace is granular.

There are no special or unique features to prepare the feed.

c. **Incorporation of Semivolatiles.**

The Penberthy System uses the Cornelius batch blanket system which is to have a floating layer of 6" of batch on top of the melt. This batch blanket captures the volatiles, such as fluoride and lead oxide and boric oxide, if any, and selenium, and other materials. Cesium is included in this capture.

Batch blanket system feeds the volatile materials back down into the melt. Problem chemical components would be the chlorides above 1% expressed as sodium chloride. Sulfur compounds are also a problem, requiring reduction with an off-gas of sulfur dioxide.

Nitrate is not a problem because the nitrate batch is reduced using sugar.

What is the meaning of recycle ratio? The offgas system load depends on what is fed in. Water vapor will go through the fiberglass filter in the flue and can be condensed out on the other side of the HEPA filters before exhausted to the atmosphere.

d. Please give some examples of insoluble and conductive compounds. I am not aware of any, except actual metals, which we prefer not to have.

e. Waste loading is generally controlled by the desire to have a good insoluble glass. This requires a silica content in the range of 57% or more and alumina and iron in the range of 6%. Soda can be from 15 to 20% and provide good melting at reasonable melter operating temperatures.

2. Control Product Quality

Penberthy furnaces have a considerable glass dead weight and therefore the variations in feed are averaged out. The tolerance for changes in composition are broad. Certainly changes can be detected and alterations in the feed can be adjusted so that none of the product need be out of composition.

Attributes

a. Product quality

Melter operation effects on durability depend on the glass composition and adequate melting temperature. Phase separation is a matter of having compatible batch components. Boric oxide is the worst offender in this respect in a silicate melt. Both silica and boric oxide make glasses, but not together.

Crystallinity can be avoided by having a sufficient amount of glass to absorb all the sludge components. This question is rather broad and should be made more clear with a better target as to what it meant. Homogeneity is no problem for a Penberthy furnace because there is thermal convection current mixing. If additional mixing is desired or required, Penberthy furnaces can be equipped with spargers or with mechanical stirrers.

b. Waste Homogenization Capabilities.

The Penberthy Melter is automatically a homogenizer, assuming there is adequate mixing of the incoming feed. The potential for undissolved feed is nil, because the batch floats and the glass exits through the sidewall two feet below the batch.

The glass residence time is not given in a single discrete number. This time of residence has been studied considerably in large melters using strontium and silver as tracers.

c. Analytical requirements for quality acceptance are not a problem. The operator knows what material is going in, and the averaging capability of the Penberthy furnace is very good. Quality is one of the characteristics of Penberthy furnaces.

d. The minimum and optimum residence time is again related to a curve. The tracer is introduced into the batch, and the initial appearance of the tiniest amount is usually about 3 or 4 hours. A peak is reached after about 6 or 8 hours and from then on the taper-off of tracer in the glass product can run to two weeks.

e. Unpredictable evaporation, segregation of glass components is not to be expected unless mistakes are made in a selection of glass composition. Or in the failure to maintain a batch blanket.

3. Develop Technology on Schedule

The ability of the Penberthy technology to provide furnaces that meet the needs of this program has already been well established over the last 40 years. The range of furnace capacities is very broad, such as 1 to 160 tons per day. The schedule could be met in the following way.

Design, build and deliver to Hanford a 10 ton per day furnace on trailer by July of 1995.

Design, build and put into operation a 40 ton per day melter at Hanford: end of 1996. Provide 5 more furnaces of the same size by the end of 1997.

There are no features of the technology which carry a high degree of risk. All of the components have been tested in commercial practice for a very long time. If the panel thinks there is some technical risk that has not been addressed, please bring it to our attention.

Attributes

a. The ability to meet the Tri-Party Agreement milestones is very good. See the time table proposals above. Unfortunately, the TPA milestone is often the never-never land. It would save a great deal of money to speed up the schedule to be in accordance with the ability of industry to provide the equipment and technology.

b. Demonstrated scale of operation is up to 4,000 kg of glass per hour. This has been demonstrated in commercial operation in a dozen furnaces. The feed types are the same as would be planned for the high level waste. Namely, the soda-lime-alumino-silicate system, in which a number of substitutions of similar materials can be accommodated. See Pyro 107 for a description of this capability.

c. This paragraph is quite complicated and should be amplified for clarity. There is considerable availability of data in the production furnaces which can be readily transferred to the melter system technology assessment for the high level waste. Additional factors required for high level waste are those related to remote operation. These are simple engineering matters, such as advancing electrodes. For the purposes of this program, however, it would be good practice to operate a 10 ton per day furnace for a period of time at Hanford, working first on non-rad materials and then later on rad materials. As noted above such a furnace can be provided by July of 1995.

d. The magnitude/amount of technical development is rather small. Standard variations would be made in furnace design, such as using higher grade refractories (AZCS) and thicker, such as 2 feet thick instead of 1 foot thick.

e. Technical development required for deployment will already have been worked out on the low-level waste program for high soda, which is already being addressed. At first, there was thought in the high-soda program to clean the waste sufficiently so that operation would be remote and contact maintained, such as pushing the electrodes in. There is a changing attitude whereby the thought is to make the maintenance also remote.

f. The probability of success within schedule is high if the program is advanced to reasonable times, such as within a year and 18 months. The furnaces can be built and the whole job done long before the start-up date of 2009. This assumes that there will not be major bottlenecks in some other part of the system. For example, there is no need to wash the sludge to remove from it soda or alumina. Both are required in making a good glass, and if there is a 25% waste loading, the existing content of alumina and iron and soda do not need to be removed.

h. The extent of mock-ups is nil. Penberthy Electromelt knows so much about these furnaces that a demonstration facility should be built at once. The suggested size for this furnace is 10 tons per day, mounted on a trailer. It can be built and in operation by summer of 1995.

i. There are no really new inventions required for this furnace. the development of remote electrode advancement is only mechanical engineering.

4. INTEGRATE WITH PROCESS AND FACILITY

Not enough detail has been given in this set of questions as to what the rest of the process and facility are that need to be integrated with.

Attributes

a. Feed preparation requirements are generous for the Penberthy Melter. If soil is used, then the largest size should be a ½" mesh.

Hydrochloric acid in feed is a problem if too high, since sodium chloride is soluble in glass only to the extent of about 1%. Nitrate is broken down by sugar to nitrogen. This is soon to be demonstrated in the high-soda facility. High sulfur is not expected, but sulfates are broken down to sulfur dioxide by using a carbon reductant, such as sugar.

b. Offgas requirement has already been demonstrated in Penberthy's RCRA hazardous waste destruction facility. This is shown in the accompanying 8172 diagram.

c. The number of melter trains: question not understood.

d. **Plant Service Requirements.**

There is no need for steam. Water is used for cooling of the electrodes, and is recirculated. Water is likely to be needed for the cooling of the walls of the room or cooling of the walls of the furnace itself. Energy required is about 1,000 KWH per ton of feed. Combustion gases are related to the amount of water in the slurry feed. This water goes through the in-line fiberglass filter in the flue as a vapor and then can be condensed and treated as liquid water or can be discharged as vapor to the atmosphere after further filtering.

e. The outside melter dimension for 20 tons per day is 10 feet wide by 20 feet long. In the present context, the furnace would be located in a pit adjacent the tank farm, and would not be replaced when spent. Instead, the pit would be filled in and capped.

f. There would be no other packaging of failed melter system components, at least not the furnace. Smaller items would be stored right in the pit and covered later when the whole pit is filled.

g. There is no particular environmental remediation requirement. The only possible significant waste stream would be a sludge in the scrubber which would be based on precipitating sulfur oxide with soda and calcium oxide. The filters themselves would be put back in the furnace.

h. There are no special safety requirements other than those that are expected in radioactive operations.

i. There is no special maintenance or support system or related facility.

j. A calculation will be made as to the mass and volume of the liquid waste per unit time. The melter is rated by the ton, rather than whether the material is solid or liquid.

k. The composition of liquid waste stream would be from the scrubber for sulfur gases as described above.

l. Process flow sheet and mitigation method for problem waste streams is not clear. Please provide additional explanation.

m. Container considerations are no different for the Penberthy furnace than for any other type of furnace.

n. The impact of this furnace for high-level waste on the LLW processing facility is the same as for any other high-level facility.

o. Impact on internal recycle system is not clear. There isn't expected to be any internal recycle such as would be given by off-specification glass. If there is, the off-spec glass is simply introduced into the auger and goes back into the furnace as if it were glassmaking material.

5. CONTROL AND MAINTAIN PROCESS AND FACILITY

Attributes

a. **Ease of Control.**

The required controls are quite simple, being mostly the rate of feed and the power input as related to resulting melter temperature.

b. Remotability is high, because the operation of the furnace is so simple.

c. Reliability

Normal glass furnaces operate 363 days a year, shutting down only twice a year for the maintenance of the machines which require lubrication.

d. Maintainability.

The normal maintenance requirements are low. A system is being worked out for using the experience of one-year life of electrodes for use in the high soda program.

e. The melter sidewalls by use of AZCS material 2 feet thick is six years. The estimated lifetime of the augers for the batch feeding is easily one year. Provision is made for removing a worn auger and replacing with a new one by running clean batch material through the auger for an hour or so. In any event, the main length of the barrel of the auger is not contaminated with radioactive material.

The ability of the Penberthy furnace to confine volatile materials is very high, operating under the Cornelius batch blanket system, combined with Penberthy electrodes, since 1951. That particular furnace is still operating. It is melting 30 tons of glass a day.

g. Potential for radioactive source build-up is small. Some cesium will build up in a layer inside the batch blanket just above the fusing soda layer. An unknown is the accumulation of radioactive materials in the bottom of the furnace. This refers only to gamma emitters, since alpha and beta emitters are not important when made into a glass.

h. Sealing and containment are easy, since the furnace is in a sealed metal casing.

i. The design concepts are modular to simplify replacement or repair.

j. Refractory life is noted above.

k. Electrode life and replacement are discussed above.

l. The furnace can safely burn off organics; however, there is no description of how much organic. Small amounts of organics are simply pyrolyzed in the melter and provide carbon in place of the sugar for use as a reductant. If there is a large amount of organic, this needs to be made known.

m. Operational simplicity of the Penberthy Furnace System is very good. Furnaces in commercial operation have been operated remotely in production, such as 80 tons a day.

Television monitors are used from an operator's control booth.

n. Estimated lifetime is six years.

o. The thought to repair this furnace is dubious because the only part saved would be the casing. This is too low in cost to justify dismantling by remote operation. It is better to bury the whole furnace when it is spent.

6. MINIMIZE TOTAL COST.

Attributes

a. The development costs for this furnace are relatively modest because so many similar furnaces have been built already in production. As noted above, a ten ton per day furnace on trailer can be built by summer of 1995 and delivered to Hanford for immediate operation after about two weeks of installation.

b. Deployment costs are normal for a furnace in the glass industry, because many of the features will have been worked out prior to building the furnace. Engineering development of this furnace should not be overplayed, because already there have been 40 years of experience with this system.

c. Replace and repair costs for the Penberthy furnace are relatively moderate. The repair costs are not expected to occur, as discussed above.

d. Solid waste disposal costs have been discussed above. There isn't any solid waste disposal from the melter change out.

e. Product disposal costs are related to the waste loading in the glass. However, a caution should be observed in loading the glass so highly that the thermal loading in a canister exceeds about 20 KW. In such a condition, the glass will not cool for a very long time, which will lead to devitrification.

f. Operating costs are no more than for any other melter system.

7. MINIMIZE SAFETY AND ENVIRONMENT RISKS

a. As discussed above, the Penberthy furnace can be operated in a remote environment, and the probability or consequences of an unsafe or costly upset event are low. The safety would not apply to the workers, since all operations would be observed through lead glass windows in the parapet rim of the pit.

b. The ability to remediate the offgas so that it can meet the requirements of the Clean Air Act are excellent, by methods that are already well known in the nuclear industry.

c. There is no potential for high energy events, such as over-pressure or explosion. Penberthy demonstrated to Savannah River Lab people in 1979 the ability of a glass furnace to accept a cup of water just thrown in on the melt surface. They were apprehensive, thinking that there might be a problem such as does happen with salt. However, glass is quite different from salt in its chilling and viscosity relationship.

d. Criticality
Accumulation of fissionable materials in the melter system is not expected to happen if there is an adequate amount of glass being made. The particular composition shows an appreciable amount of uranium. This is given as 14 wt % of uranium, which when blended down with inert glassformers will be about 3 to 4% uranium oxide. That much uranium is no problem. We have made glasses with 8% uranium oxide, with no sign of any separation or accumulation.

e. Passive shut-down occurs if you turn off the power.

8. OTHER RISKS/LIMITATIONS

a. There is no risk to the schedule if there is a will and a plan to get the job done. The present schedule of 2009 is far too long for minimizing the costs.

Institutional barriers, and/or unusual considerations need to be clarified before an answer can be given.

Enc: List of Glasses melted by Larry Penberthy
Pyro 28
Pyro 29-B
4164-1
8172
Pyro 107, 111-C, 21-A, 111-E, 36, 36-WV

GLASSES MELTED BY LARRY PENBERTHY:

Lab, Pilot and Production, 100 grams to 140 tons/day

Soda-lime-alumino-silicate for containers:
Clear, reduced iron sulfide amber, oxidized chromium green, cadmium-selenium red, copper blue, high-chromium copper frit

Soda-lime-alumino-silicate for frit:
High nickel, high chromium, high cobalt, high copper, high iron, high selenium

Soda-lime-alumino-silicate for filters and welding eye-protection.
High iron-nickel, neodymium

Alumina-phosphate with molybdenum-copper for eye protection

Silver-doped phosphate glass for radiation dosimeters

Uranium and thorium containing glasses

Cerium and lanthanide containing glasses

Lime-alumino-silicate (E glass fiber), very low alkali

Lead oxide silicate, 30% for tableware, 56 and 81% for radiation shielding windows. Also gadolinium content for neutron absorption

Borosilicate, hard, 80% silica for baking and laboratory ware

Borosilicate, very soft, 41% silica for PNL nuclear waste glass

Borosilicate neutral, for ampule tubing.

Soda-lime-fluoride-silicate glass, opal, for cosmetic jars and tiles

Borosilicate, soft, 54% silica, for glass fiber insulation.

Basalt + 15 lime, for rockwool insulation

Basalt and ash for TRU waste

PENBERTHY ELECTROMELT INTERNATIONAL, INC.
Seattle, Washington

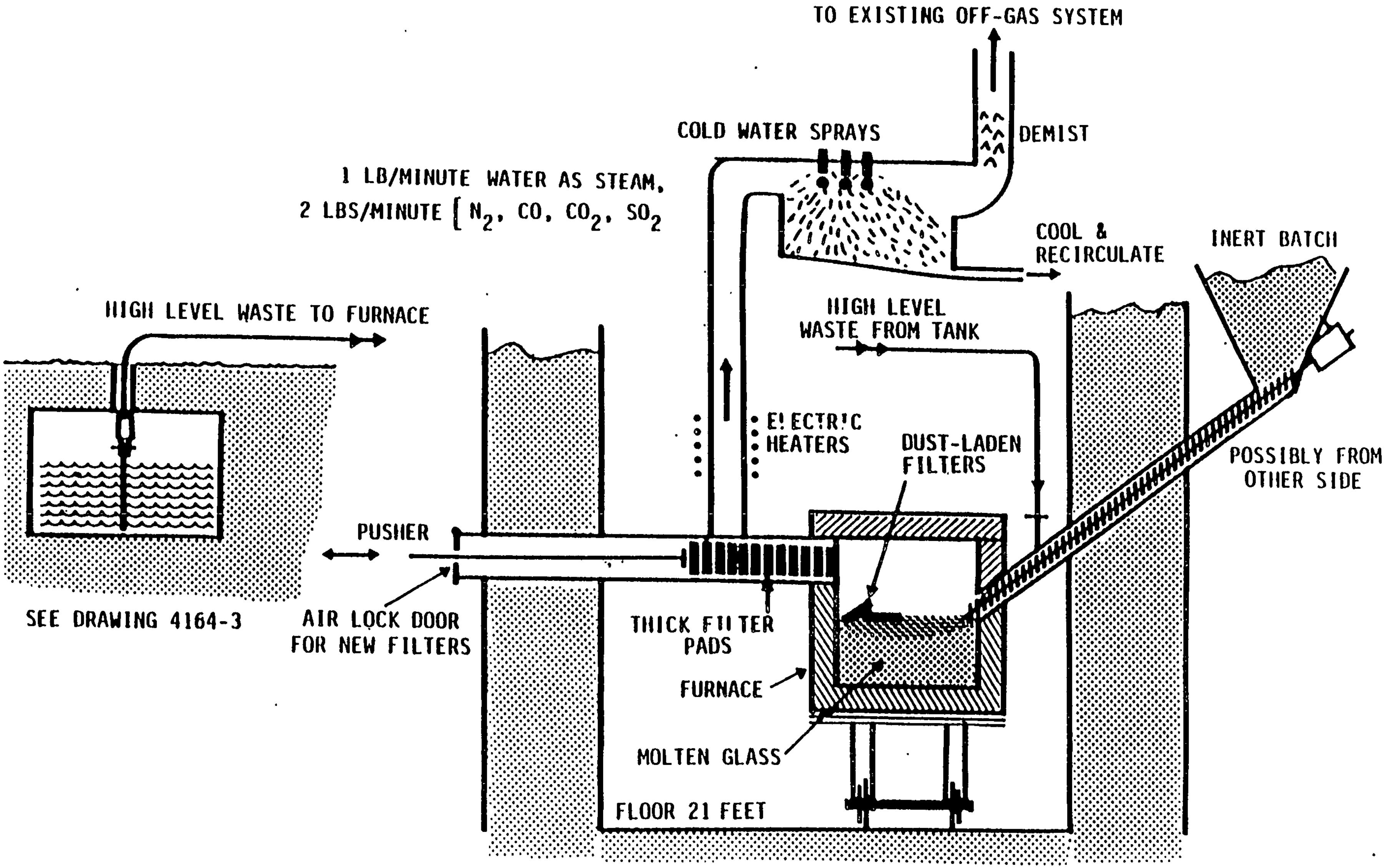
DESIGN & CONSTRUCTION EXPERIENCE
GLASS ELECTRIC-FURNACE PROJECTS

DATE	GLASS CAPACITY (TONS/DAY)	GLASS TYPE	LOCATION
1988 (designed)	10	hazardous waste	Washington
1985	62	insulator glass	Mexico
1981	6	nuclear waste	Washington
1981	1.2	plutonium lab.	Ohio
1980	4	hazardous waste	Washington
1976	35	container glass	Canada
1974	100	container glass	South Africa
1974	15	lead glass	Italy
1974	10	lighting glass	Italy
1974	6	tubing glass	Italy
1974	20	opal glass	Italy
1974	7	container glass	Israel
1974	6	press glass	Germany
1974	2.4	fiber glass	Oregon
1973	100	container glass	South Africa
1973	8	lighting glass	Italy
1973	18	container glass	Spain
1973	10	lead glass	Mexico
1973	3.5	specialty glass	France
1973	18	press glass	Canada
1972	60	container glass	South Africa
1972	22	container glass	Spain
1972	14	lead glass	Belgium
1972	4	lead glass	Ireland
1972	17	lead glass	Italy
1972	10	lead glass	Germany
1971	35	container glass	Sudan
1971	22	container glass	Spain
1971	23	lead glass	France
1971	50	table glass	Ohio
1971	75	container glass	Tennessee
1971	75	container glass	Tennessee
1970	22	container glass	Spain
1970	120	container glass	South Africa
1970	10	lighting glass	Italy
1970	40	opal boro glass	Ohio
1969	90	container glass	Germany
1969	1	hand glass	United Kingdom
1969	6	tubing glass	Italy
1968	77	container glass	Italy
1968	3	optical glass	Italy
1968	14	hand glass	Germany
1967	60	container glass	Indiana
1967	110	container glass	New Jersey
1967	9	container glass	Israel

(over)

DATE	GLASS CAPACITY (tons/DAY)	GLASS TYPE	LOCATION
1967	22	lead glass	France
1967	38	table glass	France
1967	2	technical glass	Washington
1967	100	container glass	Tennessee
1967	135	roll plate glass	Tennessee
1967	0.8	colorant	Canada
1966	0.6	experimental glass	New York
1966	110	container glass	Texas
1966	2.5	enamel	New York
1966	110	container glass	Tennessee
1966	100	container glass	Czechoslovakia
1966	1	soda lime glass	Finland
1966	80	container glass	Holland
1966	18	opal boro glass	France
1966	8	press glass	Italy
1966	6	press glass	Canada
1966	0.8	colorant	Alabama
1965	100	container glass	Czechoslovakia
1965	90	container glass	California
1965	60	container glass	India
1965	7	container glass	Italy
1965	2	hand glass	England
1965	55	container glass	Pennsylvania
1965	0.8	colorant	Pennsylvania
1965	7	hand glass	West Virginia
1964	135	container glass	Ohio
1961	60	container glass	Tennessee
1958	12	table glass	England
1958	30	container glass, electrodes	Norway
1958	30	table glass	South Africa
1957	12	opal glass	England
1957	60	container glass	South Africa
1956	12	soft glass	England
1956	40	container glass	South Africa
1955	40	container glass, electrodes	Norway
1955	7	soda lime glass	Finland
1953	30	electrodes, amber	Washington
1952	30	electrodes, amber	Washington
1949	1	optical glass	Washington
1949	0.5	amber experimental	Washington

IN ADDITION, WE HAVE MADE OVER 600 INSTALLATIONS OF OUR ELECTRODE GLASSMELTING SYSTEM IN FUEL-FIRED FURNACES TO INCREASE PRODUCTION. THE TOTAL PRODUCTION OF GLASS FROM PENBERTHY ELECTRODES IS 40,000 TONS/DAY.



VERTICAL SECTION VIEW FROM DOOR

BATCH FEEDER, OFF-GAS, HIGH LEVEL WASTE PIPES

ELECTRIC FURNACE IN CHEMICAL PROCESSING CELL, NFS, WEST VALLEY, N.Y. LARRY PENBERTHY 31, MARCH 1979 DRAWING 4164-1	PENBERTHY ELECTROMELT INTERNATIONAL, INC 631 SOUTH 96TH STREET SEATTLE, WASHINGTON 98108

Why Glass Is a Good Host for Hazardous Waste

A look at the structural factors that make it useful for containing heavy metal oxides

By Larry Penberthy
Penberthy Electromelt International
Seattle, Wash.

GLASS is an excellent host for permanent sequestering of heavy metal oxides found, for example, in ashes from hazardous waste incineration, contaminated soils, arc furnace dust, and electroplating wastes. The heavy metals of concern here are arsenic, barium, cadmium, chromium, lead, selenium and silver. (Mercury is also on the list, but is not retained in a glass melt.)

These metals in oxide form are compatible with the oxide matrix of silica and are bound therein, protected from attack (dissolving) by water and common acids. This property of insolubility allows glass to be so useful in materials of daily living, such as containers and windows.

A solid is said to be in the vitreous state when it has retained the general atomic structure, including free volume, that it had when it was liquid. Glass is a subdivision of the vitreous state, defined for this paper as follows:

> *Glass is an amorphous inorganic substance typically formed by fusion of sand (silica) with a flux (soda) and a stabilizer (lime, alumina) so that a mass is produced that cools to a rigid condition without crystallization. The free volume is commonly about 15 percent.*

Quartz (crystalline silica) can be made into vitreous silica just by heating it to about 1670°C (3200°F). There is a pronounced volume expansion in the course of the conversion, but no corresponding shrinkage on cooling. The new solid, vitreous silica, has the open atomic structure that it had when it was a liquid.

Vitreous silica could be used as a host for the heavy metal oxides but has the disadvantage of high melting point and high viscosity. The viscosity and working temperature can both be lowered markedly by adding fluxes, soda (Na_2O) and lime (CaO). Soda especially breaks the strong silicon-oxygen-silicon bonds in the continuous four valent (four-way) sponge-like silica matrix. (See Fig. 1.)

There are now two free-swinging monovalent endings in place of the original bridging oxygen, thus lowering the viscosity.

Calcia can also break the bridging oxygen bonds. Calcium doesn't fully let go, however, because it is divalent. (See Fig. 2.)

In industrial glass practice, soda and calcia are used in combination for breaking bonds. Standard container and window glasses have the following composition:

	wt. %	Glass Melting Temp.
Silica	73.5	
Soda	14.5	2500°F
Calcia	10.5	1315°C
Alumina	1.5	

Note particularly that the total of the fluxes, soda and calcia, is about 25 percent. This retains three valence bonds for each silicon. The resulting glass has excellent resistance to attack by both water and acids.

When a soda-lime-silica glass is exposed to groundwater, the atoms of sodium in the surface layer are dissolved and replaced by hydrogen atoms.

Groundwater usually contains dissolved calcia, magnesia, and ferrous oxide, which immediately displace the hydrogen in pairs to supply a healing effect, protecting against further attack by water. (See Fig. 3.)

Alumina very markedly improves the resistance of glass to water attack. Alumina forms a viscous hydroxide gel a few molecules thick that impedes diffusion of soda outward and water inward.

Alumina also inhibits the crystallization of silica-calcia (devitrification) because it does not fit in the crystalline lattice and stops the growth of such crystals.

When present in larger ratio, alumina binds to calcia/ferrous oxide to form another compatible vitreous system.

Glassmaking ingredients can be considered in four classes, spoken of as RO_2, R_2O, RO, and R_2O_3 and presented in Table 1. Substitutions of ingredients within each class can be made without upsetting the vitreous state.

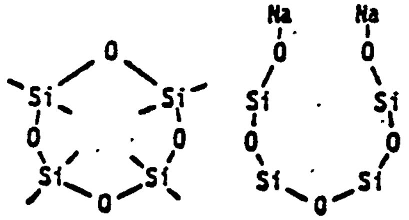


Fig. 1—Silicon-oxygen bond broken by soda.

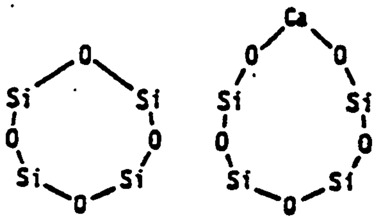


Fig. 2—Silicon-oxygen bond broken by calcia.

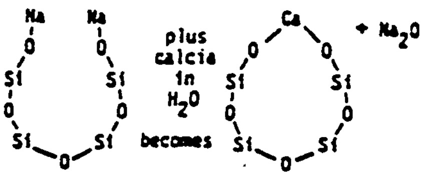


Fig. 3—Healing effect of calcia, magnesia, and iron oxide.

TABLE 1

RO_2 Network Formers	R_2O Fluxes Bond Breakers	RO Stabilizers Healers	R_2O_3 Crystallization Inhibitors
SiO_2	Na_2O	CaO ZnO	Al_2O_3
TiO_2	K_2O	MgO MnO	Fe_2O_3
ZrO_2	Cs_2O	BaO AgO	As_2O_3
	Li_2O	CdO CoO	B_2O_3 (limited)
		FeO PbO	Cr_2O_3 (limited)

TABLE 2—Sample TCLP Test

	As	Ba	Cd	Cr (ppm)	Pb	Hg	Se	Ag
Allowable max. conc. in leachate	5	100	1	5	5	0.2	1	5
Sample TCLP test	ND	0.002	0.005	0.01	ND	ND	0.3	0.01

ND = None Detected

Some glassmaking ingredients do not participate in forming the vitreous matrix, but instead precipitate out in microcrystalline or colloidal form where they act as light diffusers, when above a certain percentage and slowly cooled or reheated. The common ones are calcium phosphate, calcium fluoride, tin oxide, colloidal gold, colloidal copper, cadmium/selenium sulfide, iron sulfide, titanium dioxide, chromium silicate.

The presence of opalizing components does not interfere with the sequestering action of the glass as long as there is enough glass to surround and isolate each crystallite.

Various of the glassmaking ingredients cause the glass to be colored. They are: cobalt oxide, dark blue; copper oxide, bright blue; chromium oxide, green; manganese oxide, purple; iron sulfide, amber; iron oxide, green; cadmium sulfide, yellow; cadmium-selenium sulfide, red; copper, colloidal, red; silver oxide, weak yellow; uranium, yellow-green fluorescent.

Sulfate above 1 percent is immiscible with silica glass and separates out on the surface as molten sodium sulfate. Addition of a reducing agent (charcoal) converts the sulfate to sodium oxide, which enters the glass, and sulfur dioxide, which exits as a gas.

Chloride is immiscible with glass above 1 percent and floats on the surface as a molten salt.

Glass structure is like a sponge, having about 15 percent free volume throughout. When heavy metal oxides are added while molten, the glass matrix has no difficulty bending locally on an atomic scale to accommodate the added material. Within limits, the added materials stay within the vitreous structure, surrounded and protected by the silica and alumina/calcia.

Investigators at Atomic Energy of Canada Ltd. in 1955 moved to use this property to sequester radioactive fission products into a glass matrix and published in 1955-1960 excellent papers on their work.[1] They used a batch containing 85 percent nepheline syenite and 15 percent lime (CaO) as their host glass composition. The final glass was: SiO_2, 51%; Al_2O_3, 20.4%; CaO, 15%; Na_2O, 8.5%; K_2O, 4.3%; other, 0.8%.

This is an excellent composition, proven by 20 years of exposure of their radioactive glass blocks to groundwater, being buried five feet deep in wet soil.

Interest in the glass method of sequestering radioactive fission products has spread and is being used in production routinely in France.

In the EPA-RCRA hazardous waste management program, vitrification is a matter of some urgency. Vitrification has been chosen as the best demonstrated available technology for various waste streams, accentuated by the landfill disposal ban taking effect May 8, 1992.

The purpose of vitrification is to make the heavy metals so leach resistant that they are no longer in the EPA regulatory sphere. The situation is dynamic in that the Court of Appeals struck down the derived-from rule that EPA was using to keep in the EPA net produced glass that had been associated with hazardous waste destruction furnaces, such as in the Molten Glass Furnace Process.[2] EPA reinstated the rule on an interim basis until April, 1993, intending in the meantime to relax the rule.

The foregoing problem applies to hazardous wastes which have been processed commercially. However, individual plants can process their own secondary materials, making the mineral portions into glass, without EPA jurisdiction.[3]

EPA for a long time used the Extraction Procedure Test (EP Tox) for determining the leachability of heavy metals from a substrate. The leaching solution was weak acetic acid. Glass is perfect as a host for heavy metal oxides by this test.

Recently, the test was changed to Toxic Characteristic Leaching Procedure (TCLP), which additionally looks for organic materials. There are no organic materials in glass, so that portion of TCLP can be skipped.

The defect in the TCLP is that its authors included an 18-hour tumbling step in contact with the solution, which artificially abrades the few-molecules-deep healed surface of the glass, exposing fresh glass continuously. When the glass is properly compounded and melted, even this does not cause the glass to test out of limits. But the tumbling also makes microchips, which should be centrifuged out of the filtrate before testing by a flame method (AA and ICP).

A typical TCLP result for a production glass is given in Table 2. ☆

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2. U.S. Patent 4,299,611, L. Penberthy, 1981. Method for Converting Hazardous Material to a Relatively Harmless Condition.

3. The Impact of the 1987 Court Decision Regarding EPA's Secondary Materials Regulatory Claim. L. Penberthy, Aug. 1991.

FOUNDATION FOR
NUCLEAR WASTE DISPOSAL
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Seattle, Washington 98108
206-762-4244
Telex 329473

VAPORIZATION OF GLASSES INTENDED FOR NUCLEAR WASTE

In 1958, Atomic Energy of Canada Ltd. made and published glasses containing radioactive fission products. They are in the alumino-silicate family, characterized by high alumina (6-10%), low soda (8-12%), medium lime (8-12%), balance silica. Alumina plus silica exceeded 75%. Melting was in refractory ceramic at 1400°C (2550°F).

The AECL glass is very durable indeed. It is similar to glasses used for sight gages for observing water level in steam boilers. Field testing of actual radioactive glass over 24 years has been outstandingly successful.

Other workers on radwaste glass wanted to melt in stainless steel canisters. This is called in-can melting. Unfortunately, the top service limit for stainless steel is about 1150°C (2100°F). They could not melt the AECL glass.

These other workers added excess soda-lithia and boric oxide to the composition to lower the melting point. Again unfortunately, the excess soda-lithia destroys the three-dimensional silica network, and the boric oxide raises the vapor pressure much more than it lowers the melting point.

Specifically, the vaporization loss of Savannah River Laboratory borosilicate glass held at 1150°C (2100°F) for 90 minutes is five times as great as the vaporization loss from P-19 alumino-silicate at 1290°C (2350°F) for the same time.

P-19 glass has 15% soda, no lithia, no boric oxide. This composition is intended for West Valley, glassify-all process.

P-3 glass has 11% soda, no lithia, no boric oxide. It is intended for Savannah River and West Valley sludges without supernate. P-3 has an even lower vaporization rate.

Test Method

A platinum crucible 50 mm square x 20 mm deep was suspended in a glow bar heated furnace by a platinum wire connected to a digital laboratory balance above the furnace. 50 g of glass had been preplaced and warmed before the crucible was introduced into the heated furnace.

Readings of weight remaining were taken every 5 minutes, and the results plotted as grams loss per sq meter against time.

Furnace temperature for the SRL borosilicate glass was 1150°C (2100°F) and for P-19 alumino-silicate, 1290°C (2350°).

From other work, the material lost from borosilicate glass is alkali borate, including cesium if present.

* * *

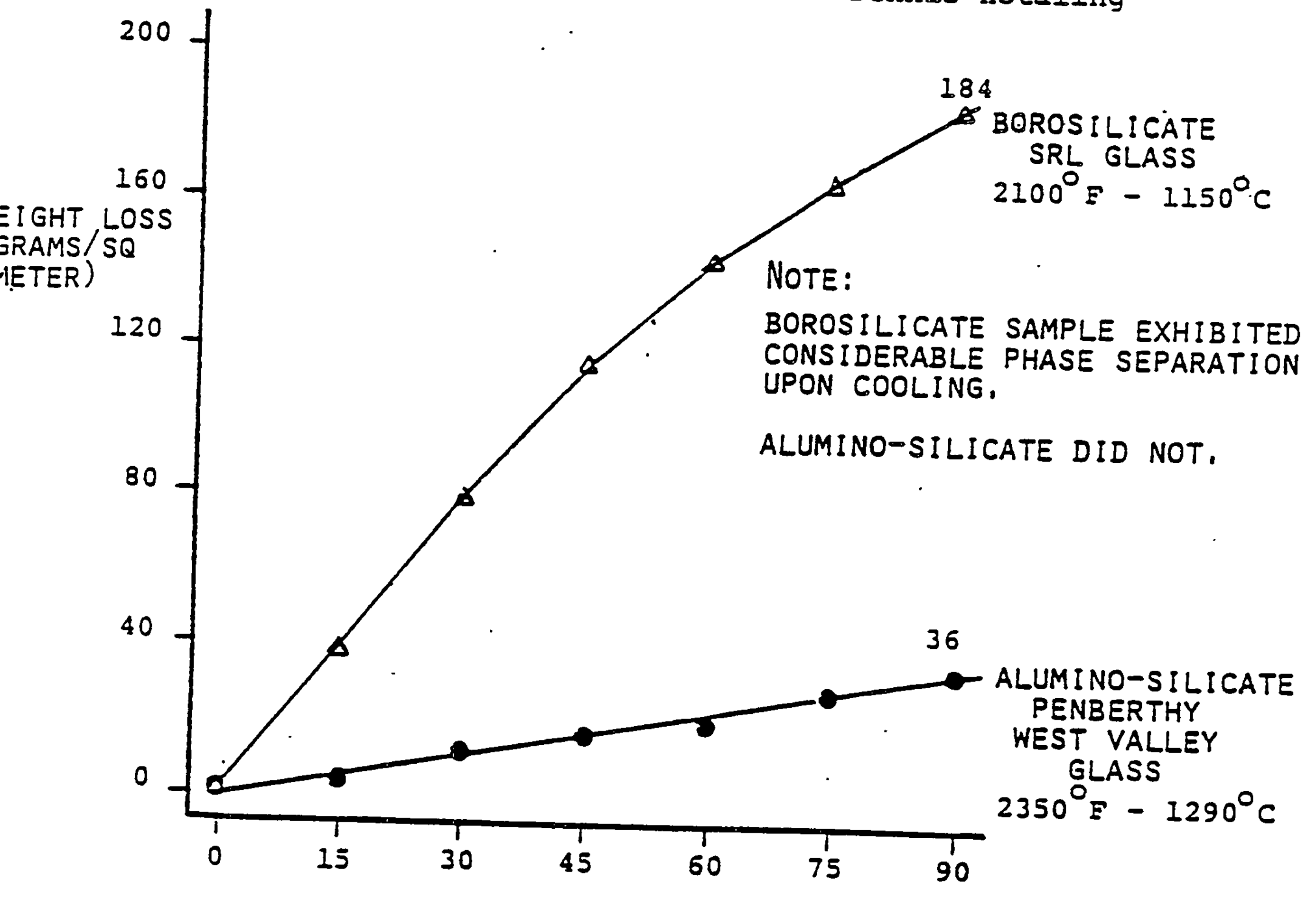
The Foundation for Nuclear Waste Disposal has as one of its purposes the correction of incorrect statements regarding nuclear waste. Please help by communicating this report to anyone who has been misinformed.

Larry Penberthy

See also: Structure of Glass as a Host for Radwaste or
Why We Need a Glass Better Than Borosilicate

VAPORIZATION
FROM
ALUMINO-SILICATE AND BOROSILICATE GLASSES AT MELTING TEMPERATURES

by Larry Penberthy
Dennis Hotaling
Feb. 1983



NOTE:

BOROSILICATE SAMPLE EXHIBITED CONSIDERABLE PHASE SEPARATION UPON COOLING.

ALUMINO-SILICATE DID NOT.

) GRAM SAMPLES IN 25 SQ CM PLATINUM CRUCIBLE SUSPENDED IN STILL AIR IN
ECTRICALLY HEATED FURNACE

Pyro 21-A

United States Patent [19]

Penberthy

[11] 4,299,611

[45] Nov. 10, 1981

[54] METHOD AND APPARATUS FOR CONVERTING HAZARDOUS MATERIAL TO A RELATIVELY HARMLESS CONDITION

[76] Inventor: H. Larry Penberthy, 631 S. 96th St., Seattle, Wash. 98108

[21] Appl. No.: 113,346
[22] Filed: Jan. 18, 1980
[51] Int. Cl.^{3} C03B 5/02; C03B 5/16
[52] U.S. Cl. 65/27; 65/134; 65/135; 65/136
[58] Field of Search 65/27, 134, 135, 136, 65/336

[56] **References Cited**

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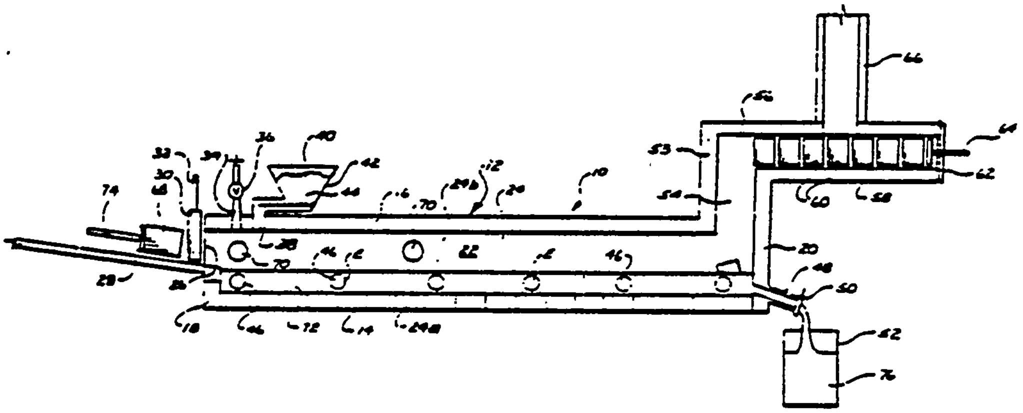
Primary Examiner—Ronald Serwin
Attorney, Agent, or Firm—Hughes, Barnard & Cassidy

[57] **ABSTRACT**

A glass material is directed into an elongate enclosed conversion chamber, where it is either converted to or maintained in a molten state by heating through the Joule effect. Waste material is directed onto the glass material at the inlet end of the conversion chamber, and sufficient oxygen is directed into the chamber to cause combustion of the waste material which is capable of being burned. A portion of the ashes created by combustion fall on the glass material and become a part thereof. The gaseous combustion products proceed horizontally through the elongate conversion chamber, and additional ash material suspended in the gaseous combustion products settles onto the glass material and also becomes a part thereof. The gaseous exhaust is directed through a plurality of ceramic fiber filter components which capture the small particulate material that remains suspended in the gaseous exhaust. These filter components are periodically discharged into the molten glass material to become a part thereof and/or to become oxidized. The glass material, with the other material added thereto, is periodically discharged to a cooling area to form a solidified product incorporating the ash product of the waste material.

20 Claims, 2 Drawing Figures



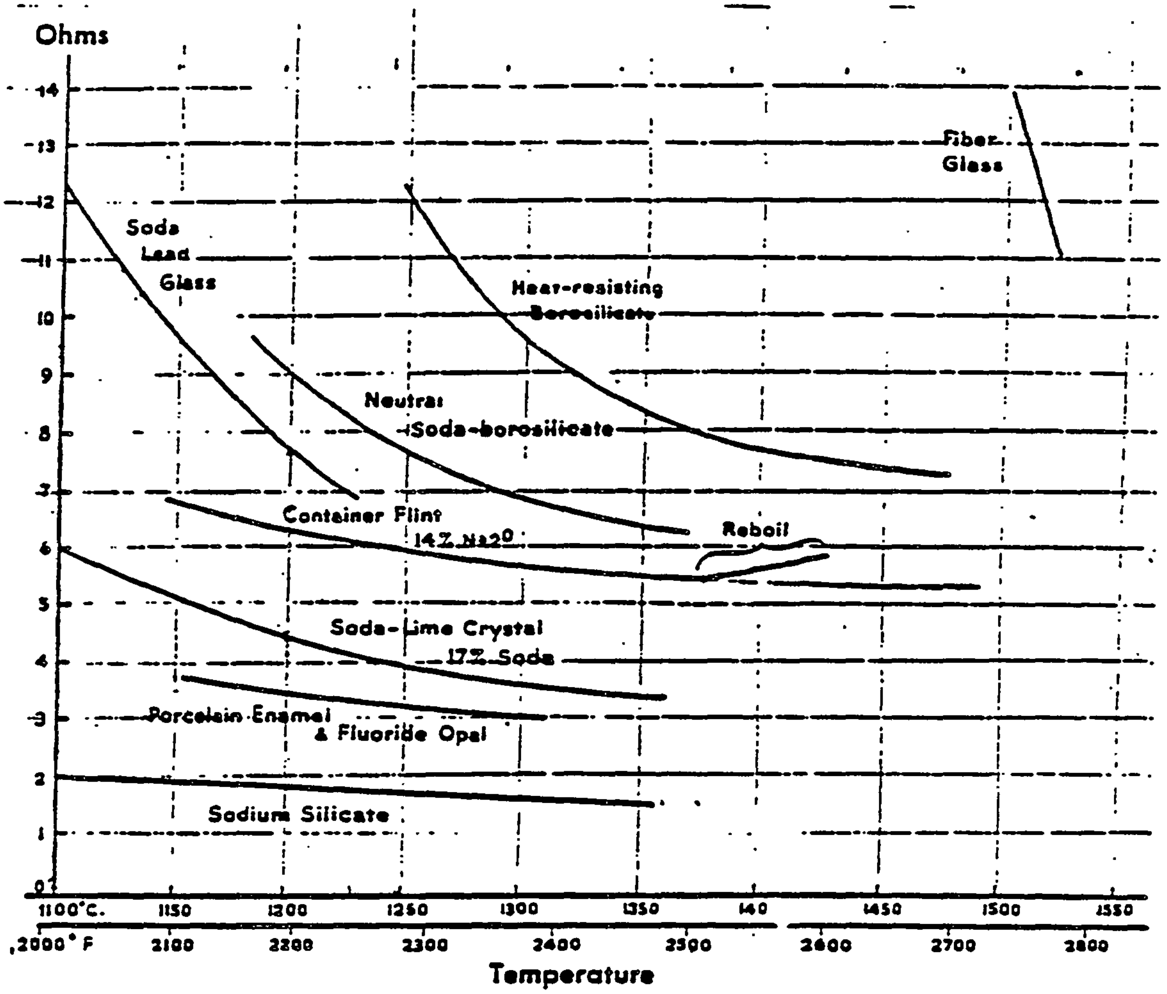


Figure 1. Resistance-temperature curves for various glasses. Resistance (60 cycles ac) in ohms measured between parallel platinum electrodes 1 cm x 1 cm spaced 1 cm apart. Variable voltage, constant 0.4 amperes. Data by the author.

Larry Penberthy, Handbook of Glass Manufacture 1960, 1974.

Pyro 29-B

About Penberthy Electromelt . . .

Founded in 1952 by Larry Penberthy, Penberthy Electromelt pioneered to the glassmaking world the technology of electric melting of glass using rod molybdenum electrodes, Patent 2,693,498. This method found immediate acceptance, and is now being used in over 1,000 furnaces, producing over 40,000 tons of glass per day. PEI for years had 150–170 employees in glass furnace engineering.

In 1981, he was granted Patent 4,299,611 extending the original glass furnace concepts to the thermal destruction/detoxification of hazardous materials. This invention was ahead of its time. The engineering prototype furnace was used only as a demonstrator until April, 1989, when the landfill disposal bans created the market for this technology.

That furnace has now processed over 1,000 tons of hazardous wastes, and is industrially proven, ready for national use.

Larry Penberthy has a BS degree in physics and chemistry, and has since added mechanical, electrical, furnace and chemical engineering, plus glass technology. He has been granted 42 US patents, and is applying for several more.

He started his career as an assayer at a hardrock copper mine in the mountains of Washington state. Mountain climbing became his major sport. He has climbed Mt. Rainier 29 times.

Before and during WWII he was a military optics production engineer at Eastman Kodak, Rochester, NY. He then moved back west and started his own company in Spokane, making optical glass. He invented, and was for years, the only manufacturer of extra high density (6.2) lead glass used for nuclear radiation shielding windows. He sold that business in 1962, continuing the furnace engineering.

In 1968, as a result of his mountaineering sport, he founded Mountain Safety Research which became a manufacturer of high integrity and performance ice axes and stoves. He sold that business in 1982 to concentrate on glass furnace engineering for radioactive and hazardous waste.

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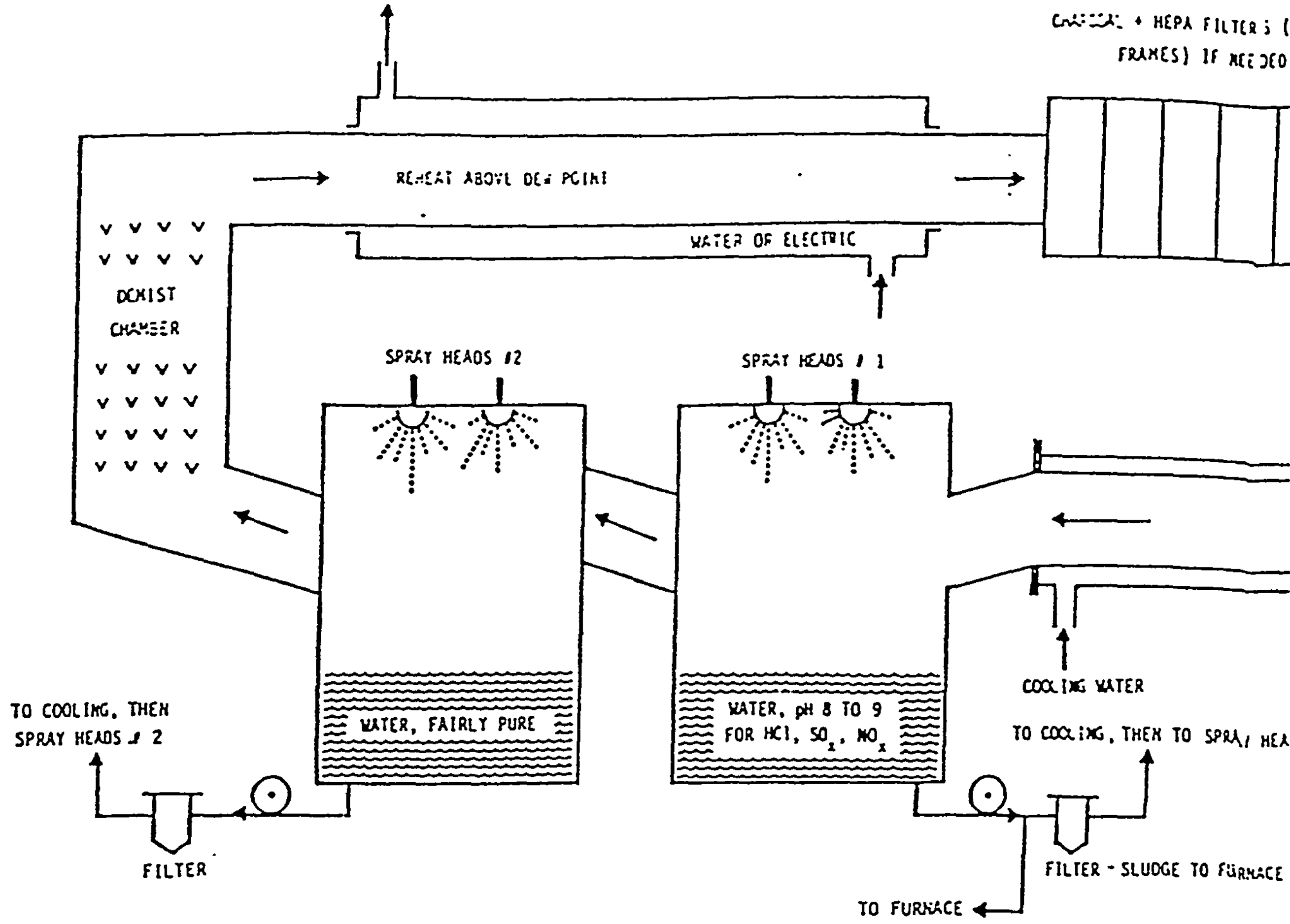

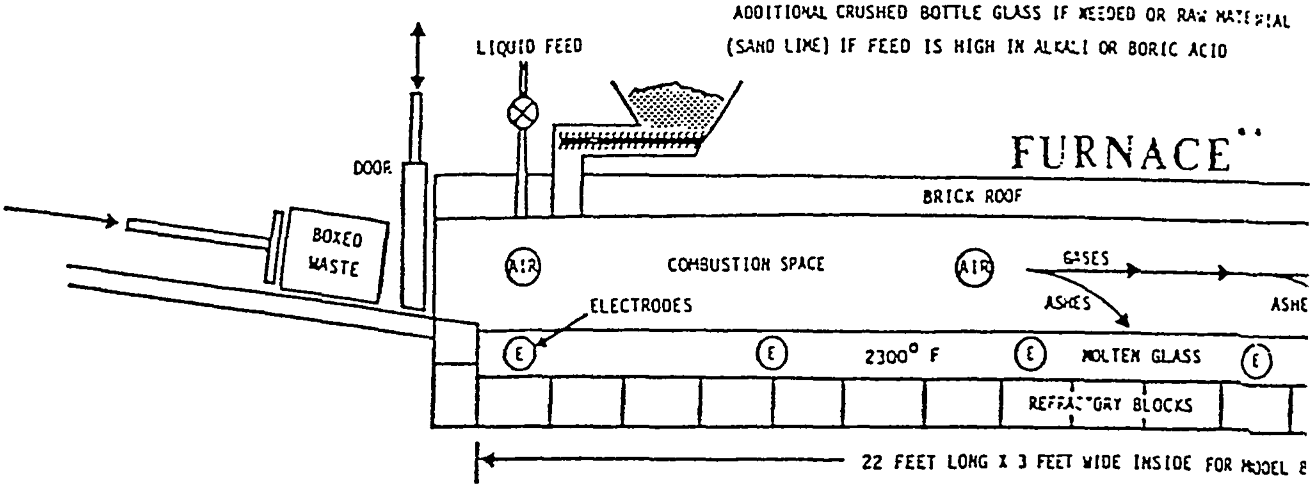

FEED, EXOTHERMIC	VOLUME REDUCTION*
RUBBER, PLASTICS	PRACTICALLY NO ASH
RAGS, WOOD, PAPER (COMPACTED OR LOOSE)	30 TO · 1
ION-X RESINS, DETERGENTS	P N A
CHARCOAL FILTERS	0 TO 1
UREA-FORMALDEHYDE, WET OR DRY	P N A
BITUMEN, ASPHALT	100 TO 1
ARSENICALS (ORGANIC)	40 TO 1
PCB's, PESTICIDES, HERBICIDES	10 TO 1
TOLUENE, ORGANICS IN GENERAL	P N A
EPOXY	P N A
OIL	P N A

* DEPENDS ON ASH CONTENT

FEED, ENDOTHERMIC	VOLUME REDUCTION
BORIC ACID (12% SOLUTION)	6 TO 1
CONTAMINATED WATER ELECTROPLATING SOLUTIONS	DEPENDS ON INORGANIC SOLIDS CONTENT
DIRT, GRAVEL, CONCRETE	1 TO 1
CAUSTIC SODA (15% SOLUTION)	2 TO 1
OXIDES OF IRON, CHROMIUM, BARIUM, LEAD, COBALT, MOLYBDENUM, ARSENIC, COPPER, ANTIMONY, ET AL.	0.1 TO 1
FILTER & ELECTROPOLISHING SLUDGES	1 TO 1
FILTER SAND, HEPA FILTERS (EXCEPT METAL PARTS)	1 TO 1
FISSION PRODUCTS, RADIOACTIVE, DRY OR WET	0.3 TO 1
ANIMAL CARCASSES	10 TO 1
GLASS	1 TO 1
VERMICULITE, DIATOMITE	20 TO 1

CAPACITY 3
WOOD, PAPER
OR
TOLUENE
AND
CAUSTIC SODA
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AND
BORIC ACID (S

POWER REQUIRE
DORMANT
EXOTHERMIC FE
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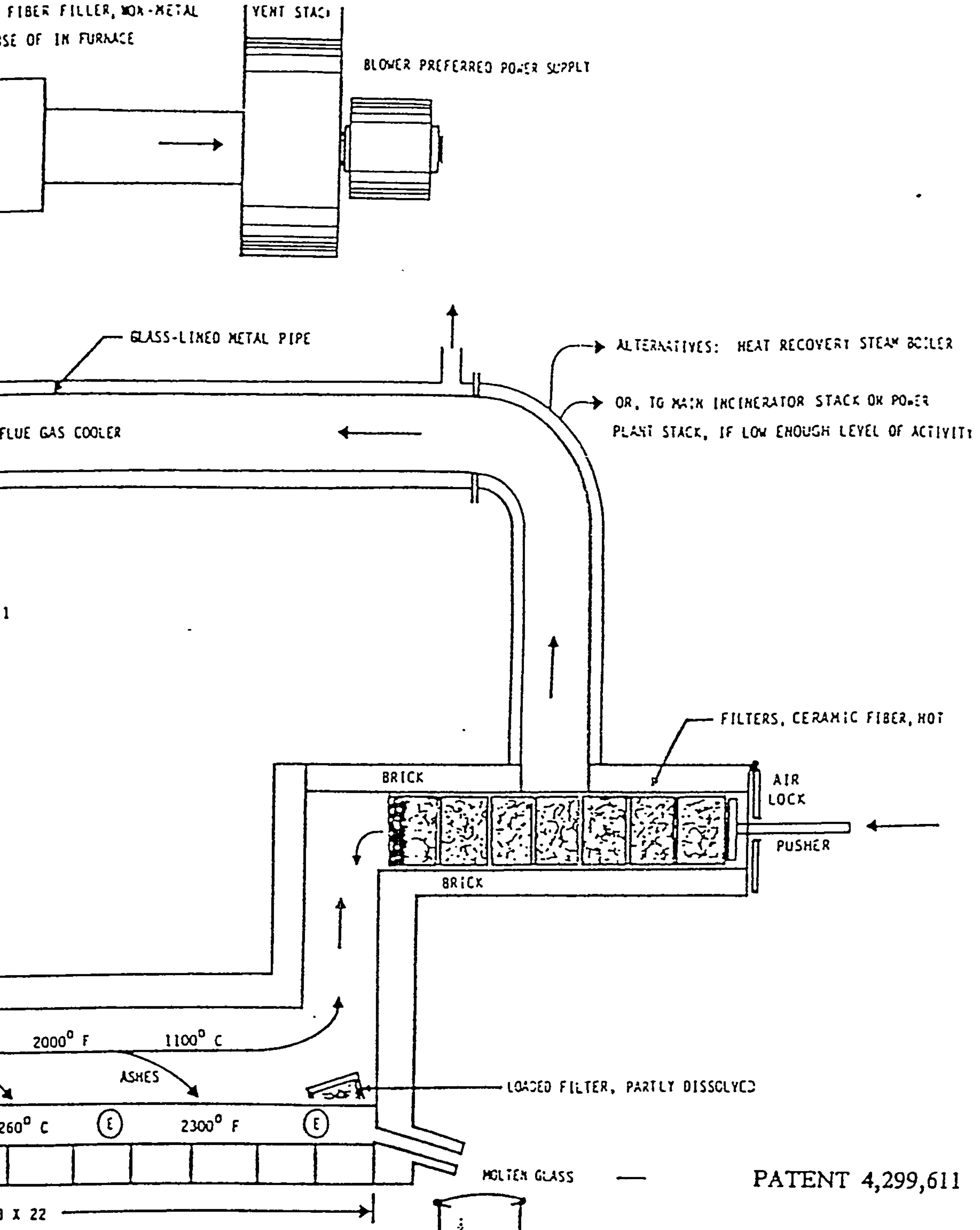
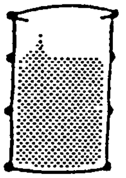


PATENT 4,299,611



SIZE	UNITS
	1000 LBS/HR
	130 LITERS/HR = 250 LBS/HR
	220 LBS/HR
AY	
	220 LBS/HR

	UNITS
	200 KW STEADY
	50 KW STEADY
	400 KW STEADY
	200 KW STEADY + 0.5 KWH/LB

** FURNACE SIZE DEPENDS ON APPLICATION LARGE OR SMALLER SIZES AVAILABLE

NOTE: SULFATES AND METAL OBJECTS ARE SPECIAL CASES. PLEASE INQUIRE

LOW AND MEDIUM LEVEL RADWASTE DIRECT-TO-GLASS INCINERATOR

PROPRIETARY

PENBERTHY ELECTROMELT INTERNATIONAL, INC.
631 SOUTH 96TH STREET
SEATTLE WASHINGTON 98108

Larry Penberthy 9 OCTOBER 1979

DRAWING NUMBER 8172

Data Package 4, Appendix B

High-Temperature, Joule-Heated, Ceramic-Lined Melter: Russian Design

This is an appendix to the data package for the high-temperature, joule-heated, ceramic-lined melter (HTCM) contains information gathered about the Russian melter design for vitrification of HLW. Most of this information was provided by KfK of Germany. It was questionable whether this melter technology should be included as a high-temperature or low-temperature melter (it operates at 1200°C); it is included with the HTMs because it incorporates molybdenum electrodes.

Description of Technology

The Russian melter design for HLW is based on designs used for glass-tube manufacturing (Bradley 1991). The first facility, EP-100, was developed to demonstrate the suitability of the ceramic melter process. Work has been done with both phosphate and borosilicate glasses, but most of the radioactive operations have been with phosphate glasses. The EP-100 melter was successfully operated for six years to evaluate electrode materials, refractories, etc. A radioactive production plant at Mayak contains two 500 L/h melters (EP-500). Operation of the first melter was halted after failure of the electrode holders. Improvements were made to the second melter; it was started in 1991 and apparently is still operating. A complete description of both the EP-100 and EP-500 melters is attached (Roth, Tobie, and Grünewald 1994).

A radioactive pilot facility with a 30 kg/h production capacity was operated at the Radon Institute. Information on the configuration of this melter is sketchy. It operated for five years, producing about 10 tons of different vitrified intermediate level liquid wastes from both pressurized water reactors and boiling water reactors (Lifanov 1993). Information was received on two wastes that were incorporated into borosilicate glass and is shown in Table B.4.1.

Table B.4.1. Power Reactor Waste Vitrified at the Radon Institute

Item	Kyrskaya Station (Kg/m^3)	Kalininskaya Station (Kg/m^3)
$NaNO_3$	281.1	123.5
KNO_3	7.4	18.1
Na_2CO_3	13.1	82.5
NaCl	8.2	2.6
Na_2SO_4	7.7	0.7
NaOH	-	56.5
$NaBO_2$	-	100.5
$CaCO_3$	-	1.5
$Ca_3(PO_4)_2$	1.9	-
$MgCO_3$	1.0	-
$Fe(OH)_3$	5.5	-
Residue	22.1	0.5
Capacity for LRW, L/h	30	50
glass, kg/h	22	30
Specific Capacity, kg/h•m^2	40	50
Specific power for glass, kW-h/kg	3.2	3.4
Melting Temperature, °C	1150	1150
Mixture moisture, mass%	20-25	20-25
Volume reduction	4.2	4.5
Solid matter carryover from melter, mass%	0.7	1.0
Radionuclides (^{137}Cs) carrying over from the melter, mass%	2.9	3.5

Melter concepts for vitrification of high level waste in Europe and Japan

\- Summary -

Dr. Roth
W. Tobie
W. Grünewald

KfK/PNL - contract No. 125818-A-I1
Supplement 3

~~**Test data:**~~

~~Total operation time: 1200 h~~
~~Vitrified solution: 42.5 m^3~~
~~Glass production: 5685 kg~~
~~Number of crucibles: 33~~

~~Effectiveness off-gas line: 10^7 - 10^9~~

~~**Problems:**~~

~~Seal problems with the device joining crucible and filter. Metal filters not sufficiently mechanically resistant (crack formation). Some concrete crucible broke under pressure.~~

~~**Consequences:**~~

~~Work never completed, abandoned~~

B) <u>CERAMIC MELTER (ONE-STAGE)</u>

Best-studied process in USSR, for phosphate and borosilicate vitreous materials. Process worked out in pilot-scale facilities with feeding capacities up to 100 l/h.

<u>EP-100 Facility (see fig.1)</u>

Facility for demonstration of operational suitability of ceramic melter process.

Melter structure:

Rectangular chamber with refractory block cladding and a stainless steel casing. Two separated zones: (1) melting zone and (2) accumulation zone, between which a bottom overflow is disposed. Cylindrical electrodes through the bottom serve for heating the melt. Start-up is accomplished by external heaters.

Melter refractory: high-silica zirconium „Bakor“

Electrodes material: Molybdenum (various alloys, tin dioxide)

Gas purification system:

bubble condenser, coarse and fine filters, columns for collecting RuO_4 and NO_x gases.

Design data:

Throughput (model sol.):	100 l/h
Glass production rate:	25 kg/h
Power requirements:	150 ± 7 kW
Glass melting temp.:	950 - 1150°C ± 50

Model solution (salt content up to 370 g/l)

Na_2O	22 - 26 wt%
Al_2O_3	21 - 25 wt%
P_2O_5	47 - 53 wt%
Fe_2O_3	≤ 1.5 wt%

Total production data:

Melter test time:	6 years
Melter operating time:	2 years
Volume of model solution:	1116 m^3
Volume of glass produced:	134 m^3

Operational results:

Max. melter losses:	Ru-106	5%
	Cs-137	0.6%
	Sr-90	0.2 - 0.4%
	Rare earth elements:	0.2 - 0.4%

Off-gas cleaning factor: 10^9

General result of testing: recommendation for trials with red wastes

Corrosion tests:

Studying of the electrode corrosion on the contents of sulphate-ion, iron and nickel oxides. Corrosion rates were estimated by the content of Mo in the glass. Direct relation of corrosion to the contents of Ni, Fe and $SO_3^{=}$-ions. Average corrosion rate 5 mm/year. Height of the electrodes decreased during the test time to 60% in the melting zone and to

40% in the accumulation zone. Electrodes shape after 6 years: like sharpened pencils, greatest current density obviously at the top of the electrodes. The results of testing of the corrosion resistance of refractory materials in form of corrosion rates are given in table 1.

Table 1:
Corrosion of the refractory materials in glass melt

Material	Corrosion rate, mm/a.	
	Melting zone	Overflow
Chamotte	44	12
Bacor ($SiO_2 + Al_2O_3 + Zr_2O$)	18	6
Tin dioxide	2	< 1
($Cr_2O_3 + Al_2O_3 + Zr_2O$) refractory	< 1	< 1

C) PROTOTYPE INDUSTRIAL PLANT EP-500

Intented for industrial waste solidification by phosphate glass. The plant comprises a solution preparation and metering system, an electrical large-scale furnace, off-gas treatment and a transporting system for containers delivery.

Melter description:

Rectangular melter shape. Melter brickwork surrounded by a stainless steel case with strengthening channels. The lower part of the case and the walls of the lower glass tank are equipped with tubular water coolers for avoiding loss of glass through the refractory brickwork.

The melter is divided into two zones, a melting and an accumulation zone. Molybdenum electrodes serve for power supply in both zones. They are fastened in water-cooled tubular current leads. The main characteristics of the melter are given in table 2.

The system of preparation and metering the solution comprises preliminary evaporation and concentration of the solutions, their mixing with the glass forming flux (phosphoric acid) and with the reductant (melasses), as well as the metering feeding into the melter. For uniform distribution of the melter feeding solution over the melting zone surface three

Table 2:
Main technical data of the EP-500 furnace

Maximum power requirement, kW	1520
Maximum temperature, °C	1200
Output of solution, l/h	400 ± 100
Single batch of glass melt, m^3	0.2
Electrode material	molybdenum
Specific electricity consumption, kW·h/l	2.0
Area of melting zone, m^2	10.7
Area of storage zone, m^2	1.8
Level of glass melt in furnace, m	0.35 - 0.45
Outside dimensions of furnace, mm	9480 x 4200 x 3200
Number of electrodes	56

independently working feeding devices are installed.

The gas treatment system subsequently contains a bubbler-condenser, in series connected rough and fine filters and columns for trapping ruthenium tetraoxide and nitrogen oxides. Steam-gas mixture from the melter enters the first stage along the gas duct being cooled, which is disposed in the side wall of the melting zone. The gas duct is provided with the device for intermittent washing off solid deposits. The gas treatment system allows to produce steam-gas flow decontamination factors not less than 10^9.

Glass draining is carried out through two drain devices (an operating and a spare one), disposed in the side wall of the accumulation zone. The device represents a water-cooled metal plug equipped with a mixing mechanism, and a water-cooled through. A multi-position mobile conveyer is arranged under the drain device normally to the melter longitudinal axis. An empty container is transferred under the drain device along it and filled with glass. This process is controlled with the help of a weighing device, built into the mobile conveyer. The filled container is transported to the end position and then with the help of a lift it is pushed into the complectation chamber. Per three filled with glass mass containers are loaded into a box. The filled boxes are sent to a temporary storage for vitrified wastes.

In 1986 in PU 'Majak' the erection of a pilot-industrial shop for high-level radioactive waste vitrification (HLW) was finished. There were two electric melters EP-500, systems for solution preparation and gas treatment, transporting units and solidified wastes storage in the shop.

While mastering the process of actual production solutions treatment a number of difficulties were met. They were connected with the heterogeneity of the solution chemical composition and their significant difference from imitators. Under the conditions of nonstable technological progress the melter has worked for nearly 8 months on actual production solutions. In the course of operation 998 m^3 of solutions were processed and 162 t of glass were produced, into which 3 864 000 Cu of radioactivity were fixed. In February 1988 the melter was stopped because of the depressurization of the water-cooled electrode units and outflow of radioactive glass mass into the melter canyon.

As a result of the analysis of the causes for electrode failures a decision was adopted to make a thorough inspection of all former principles on electrode units, to carry out necessary calculations and experimental investigations and on their basis to develop a reconstruction plan for the second electric melter in the vitrification shop with the elimination of all possible drawbacks in technological and design principles.

The investigation results and new design principles found their reflection in the plan of reconstruction and improvement of the second electric melter EP-500. Unlike the former design principles the elements of electrode fastening and the running part of current leads are changed. A more large deepening of the current leads into the furnace hearth and their more perfect insulation from the penetrating glass mass with the help of special bakor plates are also realized in the plan. Additionally to the existing side thermocouples there were introduced thermocouples for temperature measurement inside the electrodes, according to which glass melt temperature is determined.

The overflow and melting zones of the furnace were also changed.
The plan of reconstruction and improvement required practically full disassembly of the second melter, manufacture of a number of units anew.

In the fourth quarter of 1990 mounting works were finished and after inspection and testing of all systems in January 1991 the issued electrodes were switched on. At the end of June of the same year after optimizing the process operating conditions on imitators the melter was commissioned on actual production solutions. It should be noted that treatment of the first batches of solutions was rather hard because of thr search for opimum operating conditions to lower the temperature of glass mass melting and to increase its viscosity while draining. All these was achieved. Till December 1993 more than 6200 m^3 actual industrial radioactive solutions were processed and 1200 t of glass with the total radioactivity of 150 mln Cu were obtained. The glass was packed in 2860 canisters, that were placed in 920 boxes. As in January 1994 the design service life of the melter was over, an expert commission studied the equipment condition and made an conclusion concerning the prolongation of the melter operation for one more year.

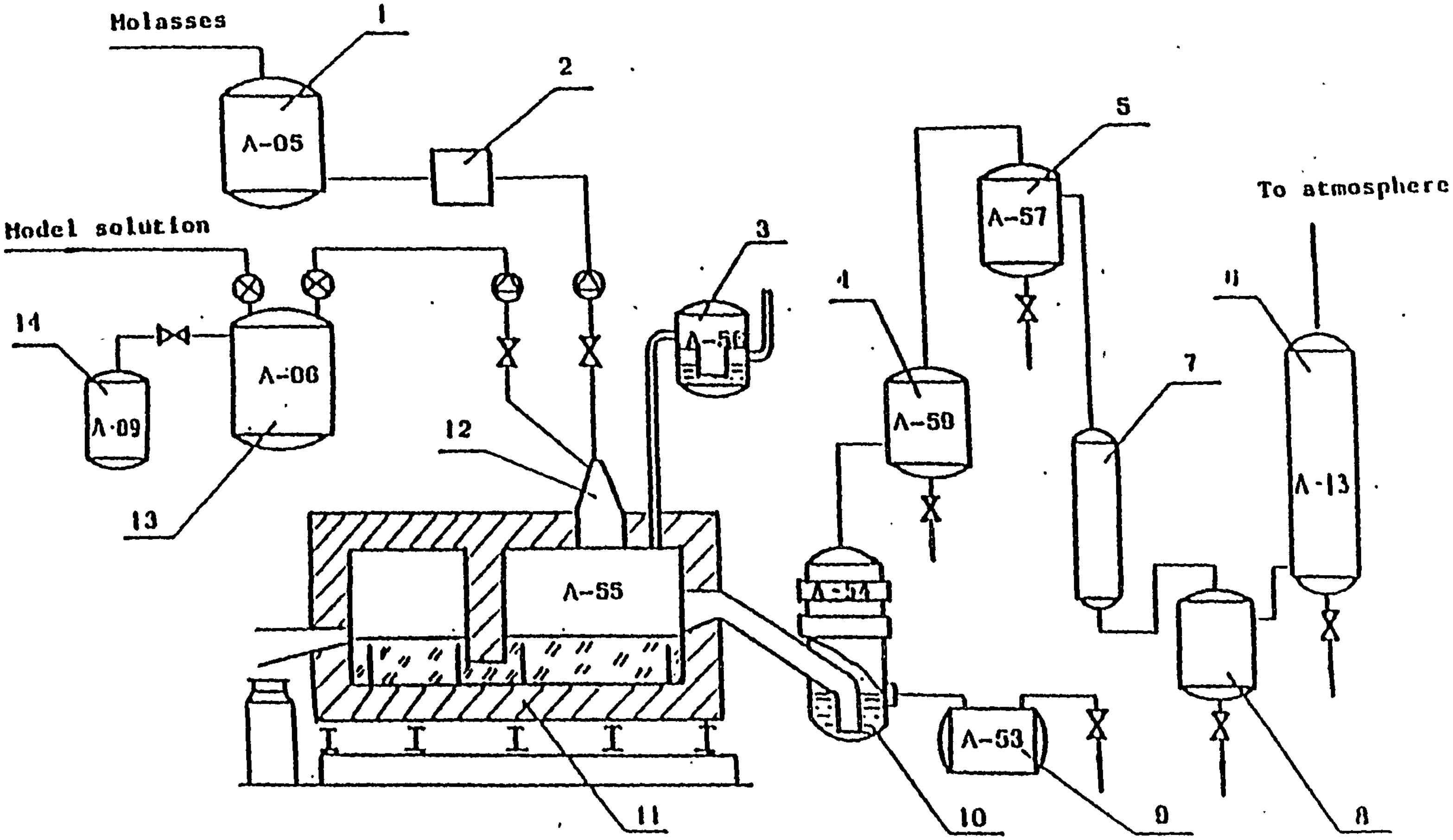


Fig. 1 Diagram of the vitrification plant

1, 13, 14: Montejus-type tanks; 2: Proportioning pump; 3: Hydroseal; 4: Coarse filter; 5, 8: Fine filters (FARTOS); 6: Absorption column; 7: Pyrolusite column; 9: Condensate storage tank; 10: Bubble refrigerator; 11: Electric furnace; 12: Feed system.

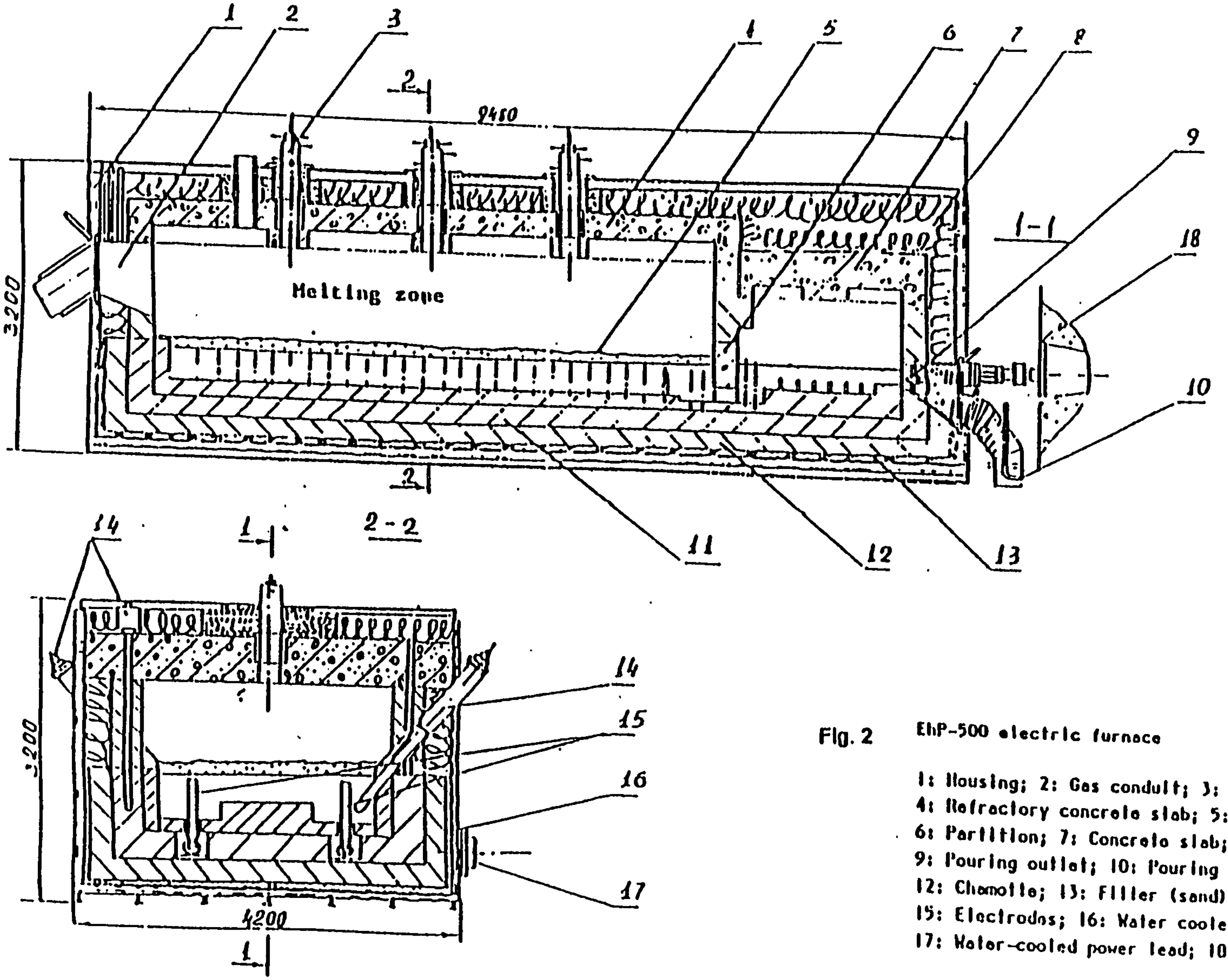


Fig. 2 EhP-500 electric furnace

1: Housing; 2: Gas conduit; 3: Feed systems;
4: Refractory concrete slab; 5: Glass melt level;
6: Partition; 7: Concrete slab; 8: Mineral wool;
9: Pouring outlet; 10: Pouring hose; 11: Bakor lining;
12: Chamotte; 13: Filler (sand); 14: Thermocouples;
15: Electrodes; 16: Water cooled tubes;
17: Water-cooled power lead; 18: Biological shielding.

Data Package 5

High-Temperature, Joule-Heated, Cold Wall Melter

Description of Technology

This melter technology is a hybrid of the high-temperature, joule-heated melter ceramic-lined (HTCM), and the cold-crucible melter (CCM). The only examples of cold wall, joule-heated melters that could be found for this data-gathering effort are variations of the Pochet melter (see Figure 5.1) which has been traditionally used to produce E-glass (low-alkali glass used to make fiberglass, for example). This melter has either top-, side-, or bottom-entering electrodes, which create a hot spot in the center of the melter. The outer sides of the melter are protected by castable refractory and a water-cooled shell. Glass is removed through a metal tube in the hot spot, and glass flow is controlled by a top-entering control rod. The electrodes are traditionally made out of molybdenum, and the drain tube is made of molybdenum or a precious-metal alloy. The usual practice of dry-feeding these melters appears to be a convenience, rather than a requirement. As described later, several improvements and variations to this design have been made.

Three sources of information were found for the Pochet melter: Cataphote Inc., GAF, and Ferro Corporation. Cataphote is a small company that makes such materials as glass frit and spheres; they currently have the contract for supplying frit to the SRS. Cataphote uses a water-jacketed Pochet melter that has a 30-in. diameter glass surface (0.5 m^2), an 8-in. castable refractory lining, and a maximum operating temperature of 1500°C. They do not run it in a cold wall mode; consequently, they rebuild the refractory after each run (approximately every two months). The melter has three top-entering and four bottom-entering molybdenum electrodes. The top-entering electrodes are water-cooled and sheathed in the plenum region; they are fired in a three-phase delta arrangement. The bottom-entering electrodes are fired from a three-phase Y configuration. The center (neutral) electrode is a molybdenum plate with four holes in a line for pouring glass. The holes have rhenium inserts for erosion/corrosion control. The other three electrodes are arranged in a triangle around the neutral electrode. Cataphote did not have any information on molybdenum corrosion control, but they said it is secondary to refractory corrosion.

Ferro Corporation has two types of high-temperature electric melters: hot-wall and cold-wall. One produces 1 ton/h of glass. They use a design similar to the Pochet melters: three molybdenum electrodes, a molybdenum tube in the bottom to drain glass, and a top-entering needle to control the flow. The glass flowing through the bottom drain tube is kept hot by a surrounding molybdenum resistance-heater coil. Ferro Corporation did not wish to divulge detailed information for this evaluation. They are primarily interested in formulating and making glass, not designing melters.

GAF uses modified Pochet melters to produce E-glass that is used to make glass tissue or mat for asphalt shingle reinforcements. GAF makes the bulk glass, which another company remelts and forms into glass tissue. They have built Pochet units ranging in diameter from 0.5 m to 3 m. They are currently running a 2.5-m-diameter (4.9 m^2) melter that produces 500 to 600 kg glass/h (12 to 14.4 MT/day; 100 to 122 kg/h•m^2). The melters have water-cooled shells and castable refractories. When the power to the melter is controlled properly, a thin layer of glass protects the refractory. The three or four top-entering molybdenum electrodes consist of a vertical molybdenum cylinder with a horizontal cylinder attached to

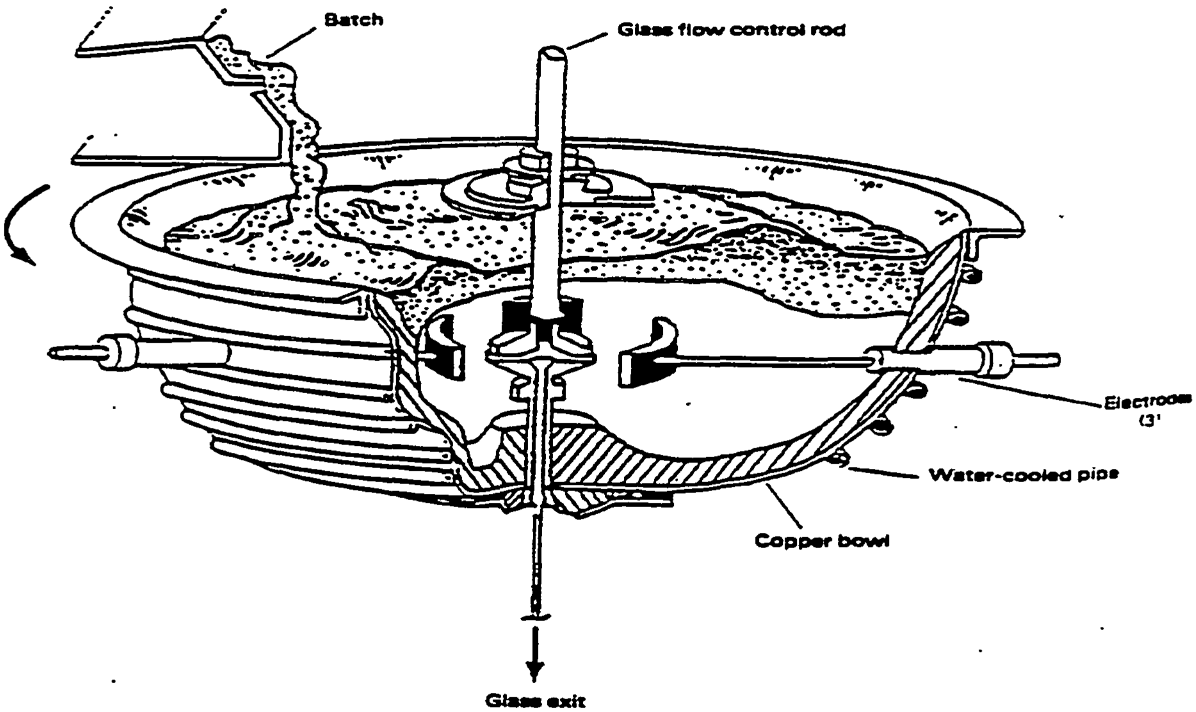


Figure 5.1. Pochet Melter

the bottom, to form a "shoe"-type electrode. The level and angle of the electrodes can be adjusted to control the size of the hot spot. They usually replace the electrodes (while running) when they see a 35% loss, usually after 180 to 200 days. GAF has modified the original Pochet bottom-drain design. A molybdenum bottom-drain tube still penetrates into the melter, but the flow is now controlled by an electrically heated Pt/Rh bushing/funnel, so that the bottom drain apparently operates like a freeze valve. The contact at GAF agreed to send more information on their melters. This information was not available in time for completion of this data package.

As stated, Pochet melters are always dry fed, but this is not a requirement. Dry feeding is a convenience of the commercial glass industry, where the feed materials are either dry-cullet or dry-batch chemicals. There is no apparent reason why this melter technology could not be slurry fed. Therefore, both dry- and slurry-fed cases will be discussed in this data package.

Because little detailed information was received on this technology, several sections of this appendix remain blank. When this technology resembles the HTCM or the CCM, the reader will be referred to Data Package 4.

Tables 5.1 and 5.2 present the requirements of a dry-fed melter system and a slurry-fed melter system, respectively. The bases for most of these numbers are explained later in this data package.

Table 5.1. Operating Parameters for High-Temperature, Joule-Heated, Cold Wall Melter (Dry Fed)

Method of Feeding	Dry			
Specific Production Rate	110 kg/h•m^2			
Oxide Loading in Waste Slurry (without frit) to Dryer/Calciner(a)	200 g/L			
Bulk Glass Temperature	1150°C - 1500°C			
Total Operating Efficiency	60%			
Waste Loading in Glass	25 wt%		50 wt%	
Number of Melter/Calciner Lines	1	2	1	2
Glass Production Rate per Melter	680 kg/h	340 kg/h	340 kg/h	170 kg/h
Glass Surface Area per Melter	6.2 m^2	3.1 m^2	3.1 m^2	1.5 m^2
Melt Pool Diameter of Each Melter	2.8 m	2 m	2 m	1.4 m
Slurry Feed Rate to Each Calciner(b)	850 L/h	425 L/h	850 L/h	425 L/h
Total Glass Production Rate(MT/day)	16.3	16.3	8.2	8.2
Total Glass Production Rate (kg/h)	680	680	340	340
Waste Processing Rate (kg oxide/h)	170	170	170	170

(a) Assumption of slurry concentration based on WHC direction given to Fluor Daniel, Inc. This is probably the highest concentration of waste slurry that can still be pumped. Note that the melters that combine the glass formers with the waste slurry before its addition to the melter have 125 g waste oxides/liter. If an evaporator is used instead of a calciner, the glass formers would probably be combined with the waste before evaporation and the lower waste oxide concentration would be used.

(b) If an evaporator is used instead of a calciner, the glass formers would probably be combined with the waste before evaporation and the incoming slurry to the evaporator would have 125 g waste oxide. In this case, the slurry flow to the evaporator would be a factor of 1.6 higher than for a calciner.

1. Process Range of Composition

For this melter technology, the waste form is assumed to be sodium silicate glass with an increased waste oxide loading (50%). Borosilicate glass was not chosen because preliminary work at PNL has shown that addition of boron is not beneficial at increased waste loadings for high-temperature glasses. This technology can produce borosilicate glass if necessary. The assumption of 50% waste loading will be explained in Sections 1.B and 1.E.

A. Temperature

The maximum operating temperature of these melters is limited by the electrode materials, the glass formulation, and the capability to maintain a protective layer of cold glass against the refractory. Temperatures as high as 1500°C have been reported for Pochet melters, and this is probably not the limit. The maximum operating temperature for the HLW melter will be determined by the capacity of the glass formulation to control volatilization from the glass, and the inherent capability of the melter to suppress volatilization (e.g., cold-cap coverage).

Table 5.2. Operating Parameters for High-Temperature, Joule-Headed, Cold Wall Melter (Slurry Fed)

Method of Feeding	Slurry			
Specific Production Rate	44 kg/h•m^2			
Bulk Glass Temperature	1150°C - 1500°C			
Total Operating Efficiency	60%			
Waste Loading in Glass	25 wt%		50 wt%	
Oxide Loading in Slurry Feed to Melter	125 g waste oxides/L; 500 g total oxides/L		200 g waste oxides/L; 400 g total oxides/L	
Number of Melter/Calciner Lines	1	2	1	2
Glass Production Rate per Melter	680 kg/h	340 kg/h	340 kg/h	170 kg/h
Glass Surface Area per Melter	15 m^2	7.7 m^2	7.7 m^2	3.9 m^2
Melt Pool Diameter of Each Melter	4.4 m	3.1 m	3.1 m	2.2 m
Slurry Feed Rate to Each Melter	1400 L/h	680 L/h	850 L/h	425 L/h
Total Glass Production Rate (MT/day)	16.3	16.3	8.2	8.2
Total Glass Production Rate (kg/h)	680 kg/h	680 kg/h	340 kg/h	340 kg/h
Waste Processing Rate (kg oxide/h)	170	170	170	170

B. Range of Waste Handling Capabilities

This type of melter has not been used for waste vitrification. The only glass compositions that have been confirmed for this melter are E-glass (Volf 1990) and Savannah River Frit-202 (Hutson 1991) (see Table 5.3). Because of its geometry and range of operating temperatures, waste-handling capabilities of this melter should be similar to those of the cold-crucible and ceramic-lined, high-temperature melters. If this melter is dry fed, determinations of waste-handling capabilities must take into account both parts of the system, the dryer and the melter. Refer to Data Package 6 (cold crucible melter) for waste handling capabilities of a rotary calciner and the expected waste loadings for various Hanford Site wastes in HTMs.

C. Incorporation of Semivolatile

Refer to Data Packages 6 (the cold-crucible melter) and 4 (the high-temperature, joule-heated, ceramic-lined melter).

D. Ability to Handle Insoluble and Conductive Compound

Because the bottom drain tube is inserted into the hot spot of this melter, it appears that this technology could be designed to be compatible with sludges of conductive compounds (noble metals). Instead of draining the settled layer, a "sump" would be provided for collecting the compounds. This sump would have to be large enough to last the lifetime of the melter, and bottom-entering electrodes should be partially sheathed to avoid short-circuits through a settled layer.. As stated in Data Package 1, it remains to be established whether concentrations of noble metals in the blended Hanford Site waste will be high enough to cause settling problems.

Table 5.3. Compositions of Glasses Melted by the Pochet Melter

Component	E-Glass (wt%)	Frit-202 (wt%)
SiO_2	50-55	77
B_2O_3	7-15	8
Al_2O_3	13-16	-
MgO	3-5	2
Na_2O	0.3-1	6
K_2O	0-0.5	-
Li_2O	-	7

E. Waste Loading

Refer to Data Packages 6 (cold-crucible melter) and 4 (high-temperature, joule-heated, ceramic lined melter).

2. Control Product Quality

Composition control should not be a problem for this melter if the composition of the feed stream is constant. This is stated because Cataphote uses the Pochet melter produce Frit-202 for vitrification testing at Savannah River. The composition specifications of Frit-202 are ±1% for SiO_2, ±0.5% for Na_2O, B_2O_3, Li_2O, and ±0.25% for MgO (Hutson et al. 1991).

Coupling a calciner to this melter causes additional quality control issues. The frit would be added to the waste after it leaves the calciner. Precise metering equipment would be required to ensure that the waste and frit were added in proper proportions. This issue is discussed in Data Package 6 (cold-crucible melter) and will not be repeated here. This aspect of quality control would not be a problem if an evaporator were used instead of a calciner. The frit would be compatible with the evaporator and could be added to the waste slurry before evaporation.

A. Product Quality

In cold-wall melters, a frozen glass layer protects the cooled walls. This layer will contain glass that is below its liquidus temperature and therefore will be crystalline to some extent. If the glass level of the melter or the heat balance to the walls changes, part of the frozen layer could drain into a canister. That will not be a problem if the composition and durability of the final product can still be guaranteed; that is, if the devitrified layer has acceptable properties, it should not affect the quality of the bulk glass.

B. Waste Homogenization Capabilities

See section 2.D.

C. Analytical Requirements for Quality Acceptance

All waste solutions and solids should be analyzed for cations, anions, percent solids, wt% oxides, etc. before acceptance of a feed batch. Acceptance of any glass by the Federal Repository will require a limited number of samples of the radioactive product glass.

D. Minimum and Optimum Residence Time

The residence time of typical Pochet melters is not known. It is assumed that residence time can be increased by increasing melter depth.

E. Unpredictable Evaporation (Segregation) of Glass Components

Unpredictable volatility of glass components is not expected as long as this melter is operated with a cold-cap (either solid or slurry).

3. Develop Technology on Schedule

This category deals mainly with the maturity of the technology. As mentioned, this technology is mature in the commercial glass industry but immature in waste vitrification.

A. Ability to Meet TPA Milestones(a)

This may be difficult because of the limited use of this technology. Most of the companies that use these melters make glass, not melters. Of the companies contacted, only GAF showed interest in designing and selling this type of melter for waste vitrification.

B. Demonstrated Scale of Operation

All of the following are dry-fed, cold-crown melters used for commercial glass production.

- 30-in. (0.5 m^2) diameter glass surface for frit production (Cataphote)
- 1 ton/h frit production (Ferro Corporation)
- 0.5 m to 3 m diameter for E-glass (GAF)
- 2.5-m-diameter (4.9 m^2) ; produces 500 to 600 kg/h of E-glass (GAF)

C. Availability of Data or Access to Data to Allow Evaluation for Melter System Technology Assessment and Melter System Candidate Selection

As discussed, information on joule-heated, cold-wall melters was very limited. Data gathering consisted of conversations with glass companies and literature searches. Further information is expected from GAF. Of the six technologies being evaluated, this is the only one not tested for waste vitrification.

(a) Final melter selection by the end of 1998, plant startup by 2009, completion of campaigns by 2028.

D. Magnitude/Amount of Technical Development Required

This remains to be determined. Although these melters have a proved background in the commercial glass industry, they have not been used for waste vitrification. Evaluating the applicability of this melter technology to HLW vitrification may require significant technical development.

E. Additional Technical Development Required for Deployment

To be determined.

F. Probability of Technical Success Within Schedule and Resource Constraints

To be determined by the Technical Advisory Committee (TAC).

G. Processing Rate

The process rate reported by GAF was 100 to 122 kg/h•m^2 for dry feeding a 2.5 m Pochet melter.

Estimating a processing rate for slurry feeding this melter brings up a difficult question that has appeared before: what production rate increase should be expected for slurry feeding? This is thoroughly discussed in Appendix A to Data Package 1 and is briefly summarized here. The dry-feeding rule-of-thumb for production rates in the commercial glass industry is 3 to 5 ft^2 day/ton, which converts to 17 to 28 lb/h•ft^2 (82 to 135 kg/h•m^2) or an average of 21 lb/h•ft^2 (102 kg/h•m^2). The nominal production rate assumed for the slurry-fed HWVP melter was 40 kg/h•m^2, or a factor of 2.5 less than commercial glass melters, an obviously crude approximation because the melters process different glasses at different temperatures. Ceramic-lined, joule-heated melters for HLW vitrification have been tested with dry feeding. A search of PNL reports was carried out to identify work that would allow a reasonable comparison of melter processing rates in slurry-fed and calcine-fed ceramic melters. This search is thoroughly discussed in Appendix A to Data Package 1 and summarized here. Briefly, the effect of dry-feeding versus slurry-feeding a joule-heated melter can range from no increase in melt rate to a 5-fold increase in melt rate. However, because the many other factors known to influence the melt rate were not carefully controlled, the increased melt rate should be viewed with caution. Experienced melter personnel agree, however, that dry feeding is likely to cause some measurable increase in the melt rate if all other factors are accounted for. Therefore, a 2.5-fold increase in production rate will be assumed for dry feeding versus slurry feeding. The average production rate for the GAF melter is 111 kg/h•m^2, so that the predicted production rate for slurry feeding is 44 kg/h•m^2, close to the nominal value of 40 kg/h•m^2 used for the former HWVP melter.

H. Extent of Mock-Ups and Test Facilities Required

To be determined.

I. Necessity for New Inventions

To be determined.

4. Integration with Process and Facility - *This section is provided by Fluor Daniel, Inc.*[1] *except for the following.*

   C. Number of melters

   This is dependent on the assumed waste loading in the glass, the method of feeding (slurry or dry), and size limit for a single melter. The only apparent difficulties with scale-up are the increase in mass and the limited flexibility of the facility if only one melter is used. The optimum number of melters can be determined only by a systems engineering study to evaluate the capital costs, operating costs, and D&D costs. The disposal costs for this melter were not evaluated in the Fluor study. Because of the expected processing rate, the disposal costs should be similar to the HTCM. Without knowing the expected lifetime of this melter, it is difficult to evaluate the number of melters that will have to be disposed.

   As shown earlier in Tables 5.1 and 5.2, a single dry-fed Pochet melter would be 2 m in diameter and a single slurry-fed Pochet melter would be 3.1 m in diameter (for 50% waste loading). As noted in the introduction, the largest Pochet melter used by GAF is 3 m in diameter. A single slurry-fed melter would be just slightly larger than the GAF melter. This may be a significant extrapolation if slurry feeding complicates the operation of a Pochet melter.

   E. Melter Dimensions and Weight

   The melter dimensions and weight should be slightly smaller than the HTCM for slurry feeding. The refractory layer is only 8 in. thick for this type of melter. The cooling jacket would be about 2 in. thick. Therefore approximately 0.5 m is added to the melt pool diameters shown in Tables 5.1 and 5.2 to get the outside diameter. This assumes that the frozen layer of glass next to the refractory is negligible. It is not clear at this time how deep a Pochet melter would have to be for this application.

5. Control and Maintenance of Process and Facility -

   This section includes a discussion about the ability of the melter technology to allow safe and efficient operation of the vitrification facility.

   A. Ease of Control

   This may be an issue for the Pochet melter. As noted in the introduction, some of the Pochet melters are operated with a hot wall and some are operated with a cold wall. It was indicated by GAF that maintaining a frozen glass layer can be difficult. The electrode spacing, power input, and cooling must be properly balanced to maintain a protective layer. This may be difficult in a remote environment with a variable feed stock.

   B. Remoteability

   Top-entering electrodes would probably be required for this system if they are to be remotely replaced. This requirement will be dependent on the expected lifetime of the electrodes.

C. Reliability

Unknown at this time.

D. Maintainability

If a dryer or calciner is coupled to this melter, maintenance requirements could increase for this melter technology. If a rotary calciner is used, the graphite seals will have to be replaced about every 6 months. The disassembly of the calciner increases the potential for contamination of the melter cell. It should not impact any facilities outside of the melter cell.

Wiped film evaporators also have moving parts that require maintenance. This usually involves adjusting or replacing the wiper blades and greasing the bearings. Blade maintenance is required about every 6 months and regular greasing of the bearings is required.[2]

An other maintenance issue is the replacement of electrodes. A shoe-type electrode cannot be continuously fed so that it must be removed and replaced upon failure. As noted in the June TAC meeting, molybdenum has a limited lifetime in the HLW glass; electrode replacement may be required for this melter if molybdenum is used. This adds to the complexity of the remote design. Other electrode materials are currently being evaluated for the HTM at PNL that have better durabilities than molybdenum in HLW simulant. Use of these materials may reduce the need to replace electrodes in the Pochet melter. Data Package 4 discusses this further.

E. Estimated Lifetime

Unknown at this time.

F. Ability to Confine Radioactive Materials

A significant source of radioactive materials is from maintenance of equipment. Depending on the drying method used for the feed, maintenance requirements could increase, and thus, contamination of the melter cell could increase. The maintenance requirements of the proposed dryers and calciners are discussed in Section 5.D, above.

G. Potential for Radioactive Source Buildup and Achievement of ALARA

Off-gas treatment is discussed in the Fluor Daniel, Inc. data package.[1]

This melter has a bottom drain that can be used to drain the glass from the melt cavity at the end of the melter life. This may be optimistic. It is conceivable that the melter failure could occur so that the glass could not be drained from the melter. This is an unresolved problem for most of the melters being considered in this evaluation.

H. Sealing and Containment Relative to Melter and Drying Equipment

Refer to Data Packages 4 and 6.

I. Modular Design Concepts that Simplify Replacement or Repair

This melter design is modular such that replacement of the melter or calciner/evaporator should be possible without any changes to current facility plans. The Fluor Daniel, Inc. report evaluates melter disposal costs as a function of melter size.

J. Refractory Life

This should not be a problem as long as a protective layer of glass can be maintained on the refractory surface. Control of this layer is discussed in Section 5.A, above.

K. Electrode Life/Replacement

As stated earlier, a shoe-type electrode is used for these melters. This type of electrode cannot be continuously fed such that it must be removed and replaced upon failure. As noted in the June TAC meeting, molybdenum has a limited lifetime in the HLW glass so that electrode replacement may be required for this melter if molybdenum is used. This adds to the complexity of the remote design. Other electrode materials are currently being evaluated for the HTM at PNL that have better durabilities than molybdenum in HLW simulant. Use of these materials may reduce the need to replace electrodes in the Pochet melter. Data Package 4 discusses this further.

L. Ability to Safely Handle Organics

Most of the organics should be destroyed in the calciner if one is used. If an evaporator is used, the plenum temperature of the melter will have to be kept hot enough to destroy organics. It is not clear if this is possible because of the extensive cooling on the outside of this melter. This will have to be proven during testing.

M. Operational Simplicity

See 5.A above.

N. Estimated Lifetime

Unknown at this time.

O. Estimated Downtime to Repair

Information currently not available.

6. Minimize Total Cost - *This section is provided by Fluor Daniel, Inc.*[1]

Endnotes

1. Fluor Daniel, Inc. August 1994. "Alternative Melter Systems Assessment 20 Metric Tons per Day HLW Glass Production." Prepared under contact #04-436304 with Westinghouse Hanford Company.

2. Phone conversation between B. Glover of LCI and M. Elliott of PNL.

Data Package 6

High-Frequency Induction Melter (Cold Crucible Melter)

Description of Technology

As early as 1905, it was suggested that metals could be fused in a solid shell of the same material[1] (Aleksandrov et al. 1978). Work was begun in the middle 1960s on direct high-frequency fusion of high-temperature materials at the Lebedev Physical Institute of the Union of Soviet Socialist Republic (Former Soviet Union), (USSR) Academy of Sciences (Aleksandrov et al. 1978). A process was developed for fusing materials that were non-conducting at room temperature. Work initially concentrated on producing crystalline materials but later progressed to high-temperature glasses. The method uses a high-frequency induction field to heat material contained in a cooled crucible. A thin layer or frozen material ("garnissage") protects the crucible from corrosion. Because the energy source is outside of the crucible, the crucible must be invisible to the energy. This was initially done by making the crucible out of a dielectric material, such as quartz. The crucible can also be made out of metal that has been broken up into isolated vertical sectors to prevent the formation of induction currents in the metal. The melting processes were 1) operated in a batch mode, or 2) the material was withdrawn through the top of the crucible by a seeding method, or 3) the material was continuously removed through the bottom of the container to form a solid ingot. The third method is commonly used to melt, refine, and continuously cast metal alloys into ingots. An auxiliary heating source must be used to start this process because the refractory materials being produced cannot be inductively heated at low temperatures. This has been done using microwave heating, radiant heating, flames, electric arcs, or thermite reactions.

The cold-crucible melter (also referred to as the Cold Wall Melter and the Two-Stage Vitrification System) uses the concept described above to continuously vitrify glass. In the 1970s, development of a CCM for glass production was started in France at the Commissariat A L'Énergie Atomique (CEA). The original design used direct induction heating of the glass inside a refractory chamber; development was halted and later resumed in 1981. The design was changed, and the refractory crucible was replaced by a water-cooled, sectorized, stainless steel crucible. Because of the inefficiency of direct induction heating, CCMs are usually coupled to an evaporator or calciner, so that the melter can be dry fed. The French have suggested using a rotary calciner to dry and decompose the waste before adding the frit and vitrifying the mixture in the CCM. A schematic of the French CCM without its calciner is shown in Figure 6.1. Corrosion of the crucible is reduced or eliminated because keeping the metal wall below 200°C produces a frozen layer of glass that protects the metal. The bottom of the melter is also water cooled to prevent corrosion/melting of the crucible. The principles of the CCM are explained in the paper in Attachment 1. The important parameters to be controlled are the frequency of the induction signal, the electrical resistivity of the material to be heated (glass in this case), and the penetration depth of the induced currents. The smaller the CCM, the higher the required induction frequency. The parameters impose size limits on the CCM. Small CCMs (< 15 cm) are difficult to heat because the required induction frequency is high and an appropriate signal generator is required. Large CCMs are difficult to heat because the induction frequency is so low that it will not couple to the glass.

The French CCM contains two bottom drains controlled by freeze valves. One, the casting nozzle, extends into the melt so that a glass heel is maintained to allow continued induction heating after casting a batch. Glass flow through the casting nozzle is controlled either by a medium-frequency, inductively-

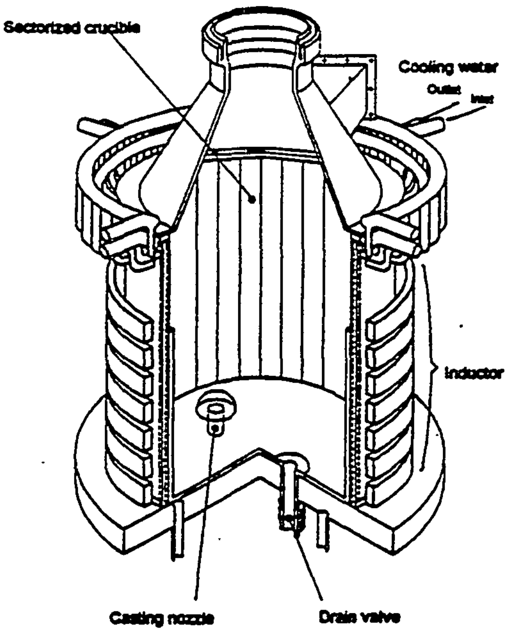


Figure 6.1. French Cold Crucible Melter without Calciner

heated freeze valve or by a separate mechanical shutter. The CCM can pour glass in large batches, as described, or it can continuously pour glass to maintain a constant level in the melter.[2] The drain nozzle is flush with the melter bottom to allow draining of the glass heel at the end of a run. The flow of glass through the drain nozzle is controlled by an inductively-heated freeze valve. Air or argon can be extended into the melt by stirring if needed to ensure thermal and chemical homogeneity. Materials of construction for the bottom drains and agitators are proprietary.

Microwave heating is used to start the French CCMs. Minute quantities of a suitable additive are added to the glass so that the glass can absorb microwaves. Microwave power is supplied by a 25-kW generator at 915 MHZ, which is connected to the furnace bead by a stainless steel waveguide through a gas-tight quartz window that is transparent to microwaves.

Several thousand hours have been logged on the French CCMs. The CCM can be operated at high temperatures because it is a skull-type melter; the French melter has been used to melt refractories up to 2500°C. The maximum glass production capacity has been 25 kg/h (260 kg/h•m^2) for the 35-cm diameter CCM and 50 kg/h (210 kg/h•m^2) for the 55-cm diameter CCM. The 55-cm CCM is operated at 150 to 500 kHz and holds 300 kg of glass (200 kg/pour with a 100 kg heel). The French CCMs have been agitated with gas sparging or mechanical agitators, which increased the production rate by 50%. The La Hague vitrification plant (R-7) glass formulation has been processed at temperatures of 1150°C to 1380°C. (The information in the previous four paragraphs was obtained through published literature [CEA 1991; Sombret 1993; Moncouyoux et al. 1991].)

The Russians have developed a CCM in parallel with the French. The Russian system is usually referred to as a two-stage vitrification process. For consistency, the term CCM will be used for the Russian two-stage vitrification process in this document. The Russian literature on the CCM was sparse, and no response was received from our letters requesting information. The best sources of information were a 1991 PNL report by Don Bradley reviewing radioactive waste management in the USSR

(Bradley 1991) and information provided by KfK of Germany. The Russians began CCM development in the 1970s. The operating principle of the Russian CCM is similar to the French CCM, but the approach is different. The Russian CCM is rectangular in cross section instead of round (see Figure 6.2). It has a main melting chamber and a separate overflow section separated by a throat. The melter appears to have a constant overflow glass discharge. It is not clear how the glass flow is interrupted to change canisters; probably by halting feed or varying the vacuum on the discharge section. The Russian design originally used a spray calciner in series with the CCM. Recent information indicates that evaporators, spray calciners, uniflow evaporators, and rotary calciners have been tested (Lifanov et al. 1993).[3] The most complete information is on a 5 to 10 kg/h Russian CCM with a 0.056 m^2 melt pool at the Radon Institute. This unit operates at 1.76 MHZ, 160 kW, and has a temperature range of 900°C to 2300°C. The feed is dried to 20% moisture content with a rotary evaporator. The Russians have tested their CCMs with several different minerals, including glass. They have processed radioactive simulants of the Kyrskaya Station and Chrnobilskaya Station liquid wastes through this CCM system.

Further information on the Russian CCM capabilities was gathered by Ben Johnson of PNL during a recent trip to Russia.[4] The Russians are still pursuing the CCM technology. They have several units, ranging from 1 to 2 kg/h to "industrial scale." They operate their nonradioactive units at the All-Union Design-Construction Scientific-Research and Technological Conglomerate in St. Petersburg. They recently constructed a radioactive system consisting of three 25 to 30 kg/h CCMs that are fed by a single vertical wiped-film evaporator, which dries the feed to 20% moisture. It is not clear if this system is at the Radon Institute or at Chelyabinsk. It is also not clear if the radioactive system has gone into active operation yet. A thorough description of the proposed vitrification system was given in a 1993 paper (Lifanov et al. 1993), which is included as Attachment 2. Agitation for waste vitrification was not mentioned; however, agitation with gas sparging and or mechanical agitators is used in the production of commercial glasses with Russian CCMs (Nezhentsev et al. 1987). Vectra (Richland, Washington) has designed a CCM but has not finished construction.

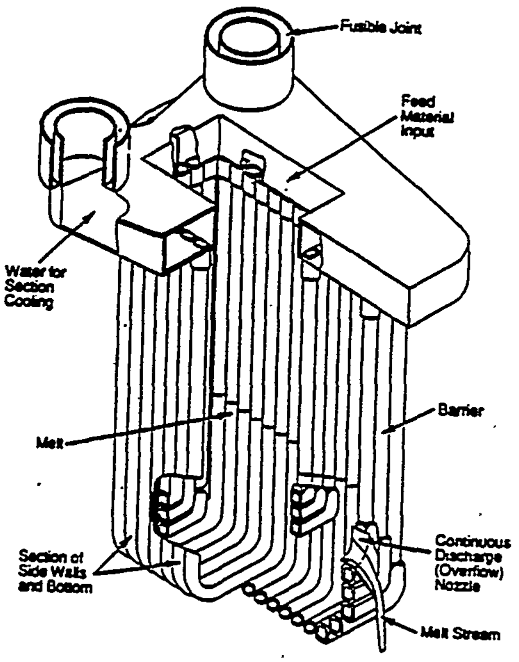


Figure 6.2. Russian Cold Crucible Melter without Calciner

Basic parameters for this technology are presented in Table 6.1. The bases for most of these numbers are explained later in this data package.

1. Process Range of Composition

For the CCM, the waste form is assumed to be sodium silicate glass with an increased waste oxide loading (50%). Borosilicate glass was not chosen because preliminary work at PNL has shown that addition of boron is not beneficial at increased waste loadings for high-temperature glasses. This technology can produce borosilicate glass if necessary. The assumption of 50% waste loading is explained in Sections 1.B and 1.E.

A. Temperature

The maximum operating temperature of these melters is nearly limitless. Temperatures as high as 2300 °C have been reported by the Russians (Bradley 1991) and 2800 °C by the French,[5] much higher than will be necessary for an HLW melter with alkaline waste. The maximum operating temperature for the HLW melter will be determined by glass formulating capabilities to control volatilization from the glass and the inherent capability of the melter to suppress volatilization (e.g., cold-cap coverage).

Table 6.1. Operating Parameters for High-Frequency Induction Melter with Calciner (Cold Crucible Melter)

Maximum Glass Production Rate per Melter	200 kg/h	
Oxide Loading in Waste Slurry (w/o frit) to Calciner[(a)]	200 g/L	
Bulk Glass Temperature	1350 °C	
Melt Pool Diameter	1-1.2 m	
Glass Surface Area per Melter	0.8-1.1 m^2	
Glass Depth[(b)]	0.8m	
Glass Residence Time	9 h	
Total Operating Efficiency	60%	
Glass Holdup per Melter[(c)] (MT)	1.6-2.2	
Waste Loading in Glass	25 wt%	50 wt%
Number of Melter/Calciner Lines	4	2
Slurry Feed Rate to Each Calciner	250 L/h	500 L/h
Total Glass Production Rate (MT/day)	19.2	9.6
Total Glass Production Rate (kg/h)	800	400
Waste Processing Rate (kg oxide/h)	200	200

(a) Assumption of slurry concentration based on WHC direction given to Fluor Daniel Inc.. This is probably the highest concentration of waste slurry that can still be pumped. Note that the melters that combine the glass formers with the waste slurry before addition to the melter have 125 g waste oxides/liter.

(b) Assumed based on WHC Phase I study.

(c) Assumes a molten glass density of 2500 kg/m^3.

B. Range of Waste Handling Capabilities

Both parts of the CCM system, the calciner or evaporator, and the induction melter must be considered when determining the waste handling capabilities of the CCM. The capability of the CCM to vitrify Hanford Site wastes will be discussed first, followed by the capability of the proposed systems to dry or calcine the waste before frit addition and vitrification.

The actual compositions of the Hanford Site wastes are uncertain at this time. Initial scoping studies used various assumptions about the extent of blending that will be possible among the 177 Hanford Site tanks. The "All-Blend" composition, which assumed perfect mixing of all 177 tanks, was calculated from tank inventory records that are only approximate. Several "All-Blend" glass formulations were developed and tested on a crucible-scale at PNL in 1993 as part of the glass development for the High-Temperature Melter. A glass with 62% waste loading and formulated at 1350°C had acceptable properties (viscosity = 70 poise and electrical resistivity = 20.9 Ω-cm at 1350°C), as did a similar glass made from NCAW simulant, 50% waste loading developed at 1350°C (viscosity = 70 poise and electrical resistivity = 2.5 Ω-cm at 1350°C) (Kim et al. 1994). Either of these glasses could be processed in the CCM.

A more realistic scenario is that complete blending of all tank wastes will not be possible. Using the Composition Variability Study (CVS) model developed for the NCAW, maximum waste loadings were predicted for 15 different wastes assuming that only the wastes within each tank farm were blended. This results in high waste loadings for some tank farms and low waste loadings for others. The predicted waste loadings vary from 19 wt% to 84 wt% at 1350°C. The resulting 15 waste compositions are shown in Table 6.2 along with the "All-Blend" waste (referred to as Case C in the table) and the NCAW for reference. The row labeled "High-T" is the predicted maximum waste loadings achievable at 1350°C. The first row of the table shows the limiting constituent in each glass formulation (zirconia phase, spinel formation, etc.). Again, this preliminary information cannot be used for final flowsheet development. Without knowing the mass of waste oxides in each tank farm it is not possible to predict the average waste loading for this blending scenario. For conservative estimates, a 50 wt% waste loading is assumed for sizing this melter technology. WHC is currently evaluating what waste composition(s) should be used for flowsheet development. (All information in the previous two paragraphs was provided by PNL.)

The French have suggested use of the rotary calciner, which they use at the R-7 and T-7 vitrification plants at La Hague and the British use at the Windscale Vitrification Plant at Sellafield. These calciner designs have been thoroughly tested for acid wastes from nuclear fuel reprocessing plants. The following comments were provided by Environmental Corporation of America (ECA 1993) about the compatibility of the rotary calciner with certain waste constituents (refer to Table 6.2 for the expected range of waste compositions at Hanford). The word "vitrification" in the following quotes refers to the low-frequency induction melter, not the CCM.

> "Alkaline Metals - When alkaline metals — including, Na, K, and Li — constitute 50% or more of the waste, they must be combined with aluminum in the feedstock in a ratio of aluminum to alkaline metals of about 0.3 (molar). This balance is required for both calcination and vitrification. For instance, Na can cause caking in the calciner unless balanced by Al, while Al, which is inert and highly refractory, will resist vitrification unless balanced by Na. A ratio of 0.3 (molar) ensures proper performance in both systems."

Table 6.2. Tank Farm Waste Compositions

	Others components			Zr-phase		Spinel				Durability			Si	Al			
Oxide	TF-B (Wt%)	TF-T (Wt%)	TF-SX (Wt%)	TF-C (Wt%)	TF-DST (Wt%)	TF-A (Wt%)	TF-AX (Wt%)	TF-TY (Wt%)	TF-BY (Wt%)	TF-S (Wt%)	TF-DSSF (Wt%)	TF-U (Wt%)	TF-TX (Wt%)	TF-BX (Wt%)	Oxide	Case C (Wt%)	NCAW (Wt%)
SiO2	0.76	0.49	9.37	0.06	8.31	0.32	0.57	29.20	5.84	2.13	29.44	18.85	17.33	21.37	SiO2	10.00	4.03
B2O3					0.47		0.00				0.00				B2O3	0.00	0.01
Na2O	52.19	56.03	33.93	10.38	31.98	17.31	51.89	22.29	23.75	69.31	66.00	39.89	30.07	25.14	Na2O	25.30	21.42
Li2O					0.01		0.00								LiO2	0.00	0.00
CaO	0.03	0.00	1.24	9.39	0.79	0.03	2.79	0.00	5.66	0.00	0.62	0.00	0.01	0.12	CaO	2.06	0.79
MgO					0.27		0.00				0.00				MgO	0.08	0.20
Fe2O3	7.93	8.95	12.76	11.00	8.75	59.60	23.52	15.42	9.89	2.70	0.00	2.28	3.91	5.91	Fe2O3	11.00	28.21
Al2O3	1.20	0.66	22.74	7.55	2.65	1.48	1.46	10.06	12.33	13.20	2.00	16.73	15.83	22.98	Al2O3	13.00	9.04
ZrO2	0.22	0.42	0.01	25.85	35.20	0.04	0.05	2.52	0.22	2.93		0.30	0.40	0.33	ZrO2	7.08	15.11
Others	37.67	33.45	19.93	35.77	11.56	21.23	19.71	20.51	42.31	9.74	1.94	21.96	32.45	24.14	Others	31.41	21.19
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	Total	100.00	100.00
Bi2O3	6.43	8.83		0.05				0.33	0.03			0.04	0.05	0.04	Bi2O3	1.95	
CeO2	4.23	5.38	2.07	0.03	0.08	0.48	0.33	1.05	1.99	1.11		2.24	2.76	2.96	CeO2	2.73	0.60
Cr2O3	0.02	0.02	3.92	0.01	0.40	0.00	0.43	0.03	0.00	0.72	0.02	0.19	0.01	0.00	Cr2O3	0.45	0.26
F	0.72	0.50	0.04	1.56	1.43	0.00	0.01	0.04	0.52	0.12	0.07	00.07	0.12	0.17	F	0.56	0.10
La2O3	0.04	0.12			0.66										La2O3	0.43	0.65
MnO2	0.48	1.09	1.67	7.76	0.87	7.18	11.48	0.10	0.41	0.46	0.00	0.21	0.75	0.84	MnO2	1.82	2.14
NiO	0.23	0.03	0.30	5.69	0.47	0.22	0.66	0.00	11.64	0.17	0.00	0.01	0.25	1.25	NiO	2.27	2.30
P2O5	14.20	15.39	0.42	0.28	00.34	0.02	0.02	3.47	1.82	0.54	0.02	0.74	4.10	2.56	P2O5	4.71	0.87
SO3	0.18	0.03	0.22	0.16	0.43	0.41	0.02	0.59	0.23	0.28	0.07	0.06	0.51	0.54	SO3	0.34	0.65
SrO	0.00	0.00	0.01	0.00	0.02	0.02	0.00	0.00	3.45	0.00	0.00	0.00	0.00	0.05	SrO	0.41	0.12
U3O8	9.95	1.88	9.19	19.87	2.67	12.76	6.51	14.71	21.99	5.89	0.01	18.35	23.72	14.12	U3O8	14.30	4.74
Subtotal	36.47	33.27	17.84	35.40	7.37	21.09	19.45	20.32	42.08	9.29	0.19	21.90	32.27	22.53	Subtotal	29.97	12.43
Balance	1.20	0.18	2.09	0.37	4.19	0.14	0.26	0.19	0.23	0.44	1.75	0.00	0.18	1.62	Balance	1.44	8.76

Waste Loading (wt%)

Low-T	21	19	26	35	31	17	38	65	51	33	35	58	64	61	Low-T	45-50	33
High-T	21	19	26	46	40	25	43	84	64	39	41	60	73	61	High-T	62	50
Limit	P	P	Cr	Crystal	P?	Fe	Na	P	Others	Na	Na	Others	P	P	Limit	P	Crystal

"Organics - The presence of ferrocyanides requires special attention: when concentrated at high temperature with nitrates, ferrocyanides can react very forcefully...the calciner may be able to destroy ferrocyanides in limited quantities. If this alternative is preferred, it will be necessary to evaluate the ability of the calciner in this regard and, more generally, to evaluate the behavior of ferrocyanides throughout the whole reference process."

The following information was received from Mr. Jouan concerning the range of waste-handling capabilities:

> "CCM must work with a predrying system, calciner for instance. The calciner can handle solid; the calcine is a solid, it comes from solution or insoluble products. All the solutions (even containing solids) cannot be calcined as they are, most of them can be, when there is mainly alkaline metals it is necessary to use additives to help the calcination, Al which is an usual component of the glass can be used: When alkaline metals (AM) constitute the major component of the waste (i.e., 1.1, around 50% or more, they must be in combination with Al in the feedstock at a ratio of Al/AM of about 0.3 (molar), where AM is any alkaline metal including Na, K, and Li."[6]

Table 6.3 presents feeds that have been successfully processed through the rotary calciner at the La Hague and Marcoule vitrification plants. Most of the French experience has been with calcining acidic wastes. It is unclear whether the baseline flowsheet for this technology requires that the waste be acidified before feeding to the system. This question was asked of Mr. A. Jouan of CEA and the following response was received:

> "We have made short tests (less than one week) with alkaline feed to the calciner without special problems; but the acid way has certainly a lot of advantages in terms of transfer and metering of the solution and in terms of mean of work of the first scrubber in the solution of which the most part of the dust escaping the calciner must be dissolved. In the case of using an alkaline solution, this scrubber solution would contain precipitate and become a kind of sludge. In the case of acidification of the solution, the off gas system will be similar to La Hague."[7]

The following Information was received from Russia:

> "Elements introduced into waste composition, loading 15-25 mass%. CeO_2 5%, Cs_2O 5%, SrO 3%, Fe_2O_3 2%.
>
> High Reliability and effectiveness of melt process, obtaining glass crystal and mineral-like materials"[8]

Information on two compositions vitrified in the CCM pilot facility at the Radon Institute is shown in Tables 6.4 and 6.5. The resulting glass composition is further described in Section 3 of this data package as well as in Attachment 2.

Acceptable glass properties -

> "The (viscosity) limit is greatly higher (than 200 poise) for the CCM."
>
> "For the CCM it would be better not to be higher than 10 Ω-cm (for electrical resistivity)"[6]

Table 6.3. Feeds Processed at La Hague and Marcoule

	R7 g/l					T7 (g/l)			Marcoule	NCAW	C 106
	1	2	3	4	5	6	7	8			
Al	2.8	2.8	3.5	2.7	2.9	2.8	2.5	4.6	25	6	17.15
Na	13	11.4	12.8	10.9	12.5	15.4	10.7	18	19	19.8	16.7
Cr	0.3	0.4	0.3	0.3	0.3	0.19	0.2	0.2	1.8	0.2	
Fe	2.1	2.23	1.75	1.6	6.4	2.8	5.4	6.3	5.9	25	16.24
Ni	0.7	0.6	0.6	0.5	0.6	0.3	0.3	0.6	1.2	2.2	---
P	0.8	0.8	0.1	0.5	---	0.3	0.2	0.5	---	0.5	1.06
Mg	0.3	0.4	0.08	0.2	0.1	0.02	0.1	0.04	20	---	1.06
U	1.2	1.1	1.16	1.7	0.9	0.22	0.4	0.4		5	
Pu	0.01	0.01	0.01	0.01	0.01	0.002	0.002	0.004			
Np	0.25	0.2	0.23	0.21	0.22	0.04	0.6	0.4			
Am	0.66	0.5	0.62	0.5	0.5	0.9	0.8	0.85			
Ca	---			0			9			2	2.04
Zn	---						7.2				
Sr	1.3	1	1.3	1.1	1.4	1.3	1.1	1.1	0.9	0.12	
Zr	5.6	4.6	0.5	3.4	5.2	5.75	3.3	6.2	1.8	13.9	
Mo	4.6	4.2	3	2.4	4	4.5	3.3	3.8	1.8	0.47	0.17
Ru	3.7	2.6	2.6	2.9	2.4	2.4	2.2	3.1	---	0.38	
Pd	1.1	0.9	1.6	1.3	1.3	1.7	1.7	2	---	0.13	
Cs	6.3	5	5.3	5	5	5	4	6.1	---	0.71	

Table 6.4. Characteristics of Kyrskaya Station Waste Vitrified at Radon Institute

Item	Concentration (Kg/m^3)
$NaNO_3$	281.1
KNO_3	7.4
Na_2CO_3	13.1
NaCl	8.2
Na_2SO_4	7.7
$Ca_3(PO_4)_2$	1.9
$MgCO_3$	1.0
$Fe(OH)_3$	5.5
Residue	22.1
Isotope	Specific Activity (Bq/m^3)
^{137}Cs	$4.1x10^9$
^{134}Cs	$8.5x10^8$
^{60}Co	$5.3x10^7$
^{239}Pu	$5.0x10^6$
^{90}Sr	$1.5x10^9$

Ability to handle slurry feeds -

"The CCM must work with a predrying system, calciner for instance."[6]

C. Incorporation of Semivolatiles

Volatilization can occur in both the calciner and melter in the CCM system. No information was received for calciner volatilities; past information indicates that carryover of volatile species from a rotary calciner can be significant, but this is not a problem if a dust scrubber/recycle system is attached at the off-gas exit of the calciner. Decontamination factors reported for the rotary calciner and the rest of the primary off-gas equipment at the Windscale Vitrification Plant at Sellafield are shown in Table 6.6.[9] The secondary off-gas system at the Windscale plant removes any residuals of the elements shown.

Table 6.5. Composition of Chernobilskaya Station Waste Simulant Vitrified at Radon Institute

Type of Waste	Quantity Produced, m^3/day	Composition, g/l
Spent alkali desorbing solutions	2	50 $NaNO_3$, 5 $KMnO_4$, 5-10 $Fe(OH)_3$
Spent sour desorbing solutions	2	100 HNO_3, 2 $H_2C_2O_4$, 2 NaF, 5-10 $Fe(OH)_3$
Spent etching solutions	2	100 HNO_3, 4 N_2H_4, 2 NaF
Pulps from abrasion	0.5	150 SiO_2
Pulps of spent non-organic materials	0.7	100 (for solid phase)

Table 6.6. Decontamination Factors at the Windscale Vitrification Plant

Element(s)	Calciner	Dust Scrubber	Condenser	NO_x Absorber
Ru	20	2	100	25
Tc and Cs	2 ($CsTcO_4$ only)	2	100	25
I	1	1	2.5	1

^{137}Cs carryovers of 3.0-to-3.9 wt% (DF = 26-33) were noted for the pilot CCM facility operating at 1250°C at the Radon Institute (Lifanov et al. 1993).

Volatilization from the melter was addressed by Mr. Jouan:

> "This is made in the LFIM and can be made with the CCM due to the presence of the cold glass layer on the glass bath; but we must take care not to pour the glass at a too high temperature, because semivolatiles could escape during the pouring."[6]

Little information on decontamination factors for cold crown melters at elevated temperatures is available. Three short-term tests were completed at PNL in 1979 to 1980 on the High-Temperature Ceramic Melter (HTCM) with a dry feed. The last of these tests examined the cesium volatility from the melter at 1200°C to 1300°C. The following results were reported:

> "Cesium was the major feed percentage-loss element. The combined HEPA and scrub solution losses constituted 0.44% of the cesium present in the feed (DF = 230). This loss corresponds to a volatilization rate of 115 mg/cm^2-h, or approximately half of the volatilization rate reported by W.J. Gray (Gray 1976) for a low-melting borosilicate waste glass at the 100-poise viscosity temperature (1050°C). The difference in volatilization is partially due to the presence of an unreacted-feed cold cap in the HTCM (Gray's experiments were conducted with bare molten glass surfaces), but other researchers report decreased cesium volatility with increased viscosity at constant temperature (Kupfer and Schultz 1973; Ross and Mendel 1980), indicating that cesium volatility is diffusion-limited. The comparable cesium volatilization rate at equal viscosities of the residual-liquid and low-temperature compositions is in agreement with these findings" (Barnes 1980).

D. Ability to Handle Insoluble and Conductive Compounds

Mr. Jouan of CEA suggests agitating the cold crucible melter if there is a problem with solids accumulation:

> "LFIM (low-frequency induction melter) is able to handle them, much more than there is in Hanford wastes; this is made at La Hague; CCM is able also, using agitation like for LFIM."[6]

Also,

> "...there could not be a sludge buildup in an air spraying or mechanical stirred glass melter. If it's a "mixture" difficult to melt, it's possible to add a special glass composition to dissolve it and pour the final composition. A second way is to stop the melter, to clean it with the telemanipulation equipment if this possibility has been taken into account during the initial design (this is possible because the glass layer when cold, doesn't stick to the melter wall)."[7]

Agitation in the Russian CCMs for waste vitrification was not mentioned; however, agitation with gas sparging or water-cooled mechanical agitators is used in the production of commercial glasses using Russian CCMs (Nezhentsev et al. 1987).

E. Waste Loading

Waste loading in glass is defined as the weight percent of waste (as oxides) in the final glass. Waste loading of the glass is extremely important because it determines both the required production rate of the melter and the quantity of glass that will be produced from the Hanford Site tank wastes. The costs to place canisters in the federal repository are high; estimated savings in excess of $2 billion can be realized by increasing the waste loading of Hanford glass(es) from 25 wt% to 45 wt% (Merrill and Chapman 1993). Furthermore, the first United States repository has a limited allocation for HLW canisters. DOE-RW is currently evaluating the impact of the increased number of canisters resulting from TPA changes. Section 1.B discussed high-temperature glass formulations conducted with various Hanford Site tank blends.

> "CCM is more flexible than LFIM (low-frequency induction melter) due to the possibility to reach higher temperature, but it is mainly a glass composition problem and it depends, of course, on the solution composition."[6]
>
> "About the waste loading increasing with temperature; yes, possibly, but there is a lot of parameters to take into account, glass, leaching, volatility during making and pouring etc...and I'm not sure that a very high temperature glass is the best choice; but OK higher temperature melters give more flexibility in the glass composition choice."[7]
>
> "Elements introduced into waste composition, loading 15-25 mass%. CeO_2 5%, Cs_2O 5%, SrO 3%, Fe_2O_3 2%."[8]

2. Control Product Quality

The baseline description for this technology is a calciner or evaporator coupled to the CCM. The waste solution is dried or calcined, and then the frit/glass formers (dry) are added to the dried feed as it is transferred to the melter. This reduces the amount of water that must be evaporated in the calciner and melter, but it also complicates the qualification of the product glass. Glass quality is dependent on control of the equipment that meters the frit to the melter. The conventional U.S. method of qualifying the complete batch (glass formers and frit) in one tank is no longer possible. The DWPF in Savannah River and the West Valley Nuclear Services plant in New York propose to mix all of the feed constituents (waste, recycle, and frit) before acceptance of each batch. Although different from the current U.S. paradigm, the method of product control proposed for the CCM is clearly possible. It has been used at the La Hague vitrification plants in France and the Windscale Vitrification Plant at Sellafield, England. These plants have qualified this method of product control not only for domestic use but also with several foreign clients for the vitrification of reprocessing wastes.

A. Product Quality

"LFIM and CCM are able to make 'good' glasses, using generally mixing. This has been proved with the cold prototypes using R7-T7 glass."[6]

"A lot of glass composition have been melted in the CCM from R7T7 glass to basaltic glasses, sodacalcic, phosphate glasses, but the durability of these glasses has not often been checked; it was not the purpose of the tests. It has been made only for the R7T7 and the results were good.

But I would like to add a comment: I think that the glass durability is, at first, a problem of composition choice; of course it's necessary to find the operating conditions to make glass and these operating conditions are to be delimited in a range of value in which the quality requirements are included and this operating criteria are difficult to find. But I think their ranges are large enough and probably, the most important one is the high temperature, which is very easy to reach in the CCM."[7]

"Testing of product by heating up to 650°C, radiation with doses up to 10^{10} rad. Determination of chemical resistance with distilled water at 60°C for 1 h, dealing (release) rate 2 to 3 times lower than borosilicate glass."[8]

B. Waste Homogenization Capabilities

See 2.D.

C. Analytical Requirements for Quality Acceptance

"Waste solution composition and glass additives must be analyzed very accurately; and if the acceptance requirements are not reached, the solution must be adjusted."[6]

D. Minimum and Optimum Residence Time

"Residence time is not an important criteria; what is more important is the temperature and duration of time at a given temperature; the time duration can decrease when the temperature increases."[6]

Because the specific production rate of the CCM is high, residence time is relatively short. For example, the specific glass production rates reported by CEA are 284 $kg/h{\bullet}m^2$ with agitation and 182 $kg/h{\bullet}m^2$ without agitation,[7] which would result a 9-h and 14-h residence times, respectively, for a melter that is 1 meter deep and is operated at a constant level.

E. Unpredictable Evaporation (Segregation) of Glass Components

The only unsteady condition that could occur in this melter is unsteady flow of solids out of the calciner, as was observed during initial testing of the rotary calciner in England (Morris et al. 1988). This issue was resolved during subsequent testing of the rotary calciner.

3. Develop Technology on Schedule

This category deals mainly with the maturity of the technology. As mentioned, this technology has been in development since the 1970s. It has been used on a limited scale for waste vitrification pilot tests and extensively for metal melting, crystal growing, and melting of refractory compounds.

A. Ability to Meet TPA Milestones[a]

"I think, yes, the CCM process is able to meet tri-party agreement milestones; predrying step, which can be calcination step must be checked."[6]

B. Demonstrated Scale of Operation

"The CEA has built and tested a simplified cold-crucible furnace 1 m in diameter containing over 500 kg of molten glass. In this design, the inductor itself constitutes the cold crucible, and this is supplied with a 10 kHz current by a high-frequency generator. The tests have demonstrated the feasibility of 10 kHz direct-induction glass melting in a large diameter crucible" (Monocouyoux et al. 1991).

This unit was operated as a proof-of-principle (scale up). Production rate data has not been obtained.

Mr. Jouan confirmed that the following production rates have been attained:
"ϕ 60 cm 50 kg/h with raw materials
ϕ 55 cm 25 kg/h with calcine + frit (was not the upper limit) all that without agitation! 200 kg/h is a possible capacity for the CCM but predrying system must be checked."[6]

"Air sparging has been initially tested to homogenize the glass bath...and successfully. In the LFIM (low-frequency induction melter) at first (used today in La Hague facilities R7 and T7); in CCM after and with the same success, even if it was perhaps less useful.

Mechanical stirring has been tested to measure the increasing of capacity. Tests have shown that when feeding the CCM 50 cm diameter with raw materials, the flow rate of glass formation was increased from 36 to 56 kg/h and 56 was not the upper limit. This test made at 1350°C shows that mechanical stirring can increase glass making flow rate by 1.5 (minimum value) and probably more.

I cannot give today for commercial reasons, information about the materials of construction (of the agitator), the basic design and the operating conditions of the mechanical stirrer. It's a new concept and its life time is excellent.

(a) Final melter selection by the end of 1998, plant startup by 2009, completion of campaigns by 2028.

Tests are necessary to choose the best diameter and we must be careful in our answer. If I take the example 36 kg/h in the 50 cm diameter CCM and I take the hypothesis that the flow rate increases with the surface area (ϕ^2) (see information in Table 6.7); we see that even with a 1 m diameter and with a mechanical stirrer we can reach more than 200 kg/h; that at 1350°C.

The (selection of melter size) must be made taking into account the wished working temperature which depends from the glass, from the possible difficulties to melt the Hanford waste from which you say that is very very difficult...

To feed a 200 kg/h CCM, making a 25% waste loading glass, a calciner able to deliver 50 kg/h of oxides from the solution is necessary.

The La Hague type calciner ϕ 30 cm L=3 m is working at 50 l/h (FP solution) and capable of 70 l/h. This 50 l/h flow rate gives 25 kg/h of glass; with a preconcentration step (factor 2) it would deliver 50 kg/h of glass and would be able of 70 kg/h; increasing the diameter from 30 cm to 40 cm will increase the capacity of 4/3 giving the possibility to about 90 kg/h...and its always possible to use two. But we have today in French nuclear field no larger calciner, even if it could be possible to design and make one. But it's perhaps not the best apparatus choice for a 400 to 500 l/h evaporation step?"[7]

The Russians have tested boiling bed evaporators, spray calciners and uniflow evaporators:

> "Boiling bed: extremely sensitive to waste composition, esp. when containing $NaNO_3$, large volume of air required (5 to 6 m^3/l waste). Abandoned.
>
> Spray Calciner: Less sensitive to composition, reliable, simple to operate. Effectiveness practically independent on salt concentration (100 to 600 g/l) even with a solid phase of 150 g/l. Air volume consumption 0.3 m^3/l. Loss to off-gas: Ru-106 2%, Cs-137 0.5 %, others 0.1%.
>
> Uniflow evaporator: Experimental verification up to 100 l/h (up to 350 g/l salt)

Table 6.7. Scale up Information Provided by Mr. Jouan

	CCM Diameter	Production Rate (without agitation) (kg/h)	Production Rate (with agitation) (kg/h)
demonstrated	50 cm	36	56
extrapolated	1 m	144	224
extrapolated	1.2 m	207	322

Cold crucible testing: Experimental temperature range 1200 to 2300°C. Laboratory tests with spray dryer, drum. High reliability and effectiveness of melt process, obtaining glass crystal and mineral-like materials.

Melter data:	
Melt surface:	0.05 to 0.12 m^2
Power supply:	160 kW (oscillator)
Frequency:	1.76 MHz
Melt temperature:	1500°C (average)
Output:	12 to 18 kg/h

Information for the Radon Institute:

- "Pilot facility, intermediate-level waste - crucible surface 5.63 dm^2 (0.056 m^2), rotary evaporator.

  Testing: Sulphate-containing radwaste into borosilicate glass (simulated and real waste). Result will allow start of development of full-scale pilot industrial facility with 300 to 400 l/h capacity (3 melter lines), continuous process, possible automation of process in the active zone, possible remote replacement of units."[8]

Further information on the pilot CCM (0.056 m^2) with a rotary film evaporator at the Radon Institute was found in the literature (see Table 6.8) (Lifanov et al. 1993).

The rotary evaporator is used to dry the waste slurry to 20% moisture prior to transfer to the CCM. This moisture content was determined to allow sufficient spreading of the charge on the surface of the glass melt and maintain low radionuclide release of off gases. The properties of the glass from the Kyrskaya Station waste is presented in Table 6.9.

Table 6.8. Operating Data from CCM Pilot Facility at the Radon Institute

Item	Kyrskaya Station Waste	Chrnobilskaya Station Waste
Capacity for Glass, kg/h	6.8-9.0	7.9-10.0
Specific Capacity for Glass, kg/h•m^2	120-160	140-180
Specific power supply, kW-h/kg	5.0-6.0	4.5-6.0
Average temperature of glass, °C	1250	1250
Solid matters carrying-over from the melter, mass%	1.0-1.2	-
Radionuclide carrying-over (^{137}Cs), %	3.0-3.9	-

Table 6.9. Glass Properties from Kyrskaya Station Waste

Item	Value
Component content in glass, mass%	
Na_2O	16.1
K_2O	0.5
CaO	15.5
Al_2O_3	2.5
Fe_2O_3	1.7
B_2O_3	7.5
SiO2	48.2
Na_2SO_4	1.1
NaCl	1.2
Other Components	5.7
Specific Activity of Glass, Bq/kg	$7.0 \cdot 10^6$
Viscosity of glass, Pa-s	
900°C	33.5
1000°C	16.3
1100°C	6.6
1150°C	4.3
1200°C	3.9
Specific electrical resistance, Ω-m	
900°C	0.065
1000°C	0.041
1100°C	0.032
1150°C	0.029
1200°C	0.028

C. Availability of Data or Access to Data to Allow Evaluation for Melter System Technology Assessment and Melter System Candidate Selection

Most of the data has come from Mr. Jouan of CEA except for a few papers from Russia and information gathered by KfK during a visit to Russia. We received no response to our letters that were sent to Russia.

D. Magnitude/Amount of Technical Development Required

It appears that development of a complete flowsheet is still required for this system. Mr. Jouan pointed out that some type of predrying system is required, and a lot of discussion is given to use of a rotary calciner. He feels that if a calciner is used it, may be easier to acidify the waste, but this is not a strict requirement. It is also realized that some calciner development may be required for a 200 kg/h CCM. Depending on the waste loading in the glass, this would require a 250 to

500 l/h calciner, which would be a 5 to 10X increase over the current design used at La Hague. This appears to be the reason for his statement about using one or more calciners to feed each large CCM, "But it's perhaps not the best apparatus choice for a 400 to 500 l/h evaporation step?"[7] It is possible to use an evaporator instead of a calciner. It appears that the Russians have selected a wiped-film evaporator with steam heating for use in their radioactive CCM facility.

Figure 6.3 shows the flowsheet proposed for vitrification of radioactive waste in Russia (Lifanov et al. 1993). This flowsheet has one wiped film evaporator supplying three 25 kg/h CCMs. It is not clear from reading the paper whether the facility is on-line yet. The paper is included as Attachment 2. The characteristics of the vitrification facility are presented in Table 6.10 and the individual melter characteristics are presented in Table 6.11. The wiped film evaporator is also discussed in the appendix to Data Package 1, which discusses dry feeding a low-temperature, joule-heated melter.

E. Additional Technical Development Required for Deployment

To be determined

F. Probability of Technical Success Within Schedule and Resource Constraints

This should be decided by the TAC.

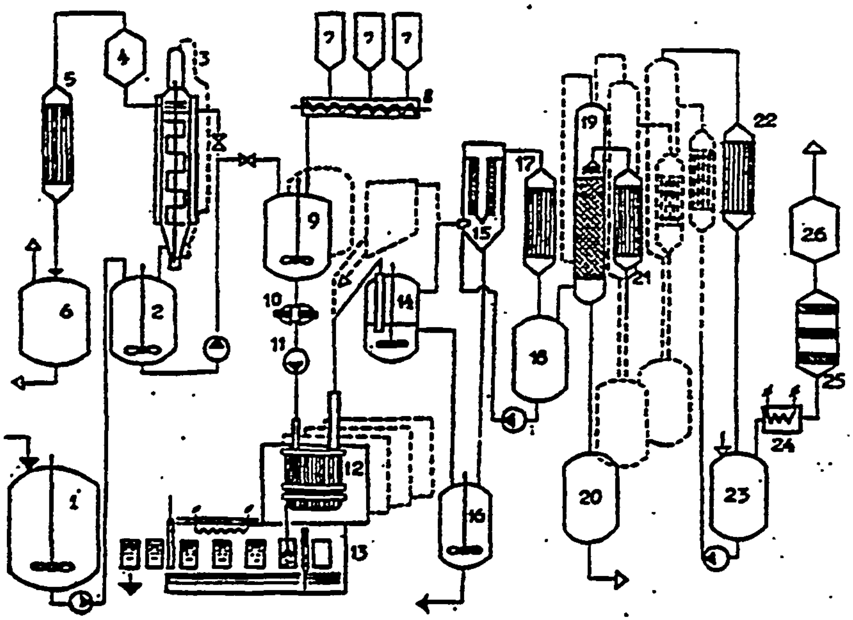


Fig 1. SHEME OF THE PLANT FOR VITRIFICATION OF RADWASTE.
1- repository; 2-concentrator; 3-rotary evaperator; 4,26-filters; 5,17,21,22-heat exchanger; 6,16,20-collector; 7-glass forming additives; 8-mixing screw; 9-mixer; 10-grinder; 11-feeder; 12-unit of melters; 13-furnace; 14-coarse filter; 15-fine filter; 18,23-canister; 19-column; 24-heater; 25-reactor.

Figure 6.3. Flowsheet for Russian Vitrification Plant with Cold Crucible Melter

Table 6.10. Characteristics of the Russian CCM Vitrification Facility

Operation	continuous
Process	two-staged, LRW concentration in advance
Control	remote control, operation in automatic regime
Capacity for glass, kg/h	up to 75
for LRW, m^3/h	up to 330 (salt content 200 kg/m^3)
Specific activity of initial LRW, Bq/l	up to $3.7 \bullet 10^7$
of glass blocks, Bq/kg	$5.5 \bullet 10^7$
Dimension of glass block, mm	250x250x350
Glass mass in container, kg	50

G. Processing Rate

The 50 cm diameter CCM in France operated at 36 kg/h (183 $kg/h \bullet m^2$) without agitation and 56 kg/h (285 $kg/h \bullet m^2$) with agitation. This run was conducted by direct dry feeding without a calciner. These numbers are the basis for the extrapolation provided by Mr. Jouan in Section 3.B. The 0.18 m^2 CCM at the Radon institute has processed 30 kg/h (170 $kg/h \bullet m^2$). The feed composition at which the above processing rates were recorded is unknown. As discussed, the 0.056 m^2 CCM at the Radon Institute has processed 120-180 $kg/h \bullet m^2$ (120 to 160 $kg/h \bullet m^2$ for the glass shown in Table 6.9).

H. Extent of Mock-ups and Test Facilities Required

Existing testing facilities include, but are not limited to:

- 55 cm diameter (0.24 m^2) CCM at CEA (nonradioactive)
- 60 cm diameter (0.24 m^2) CCM at CEA (nonradioactive)

Table 6.11. Characteristics of the Russian CCM Melters

Capacity for glass, kg/h	up to 25
Operating frequency, MHz	1.76
Power of generator, kW	160
Mass of melter with the glass, kg	130
Minimal volume of glass in the melter, m^3	0.034
Dimensions of melter, mm	250x800x700
Area of surface melting, m^2	0.16
Operating temperature of the process, °C	1250
Specific power supply, kW per kg of glass	4.5-5.5
Supply of cooling water, m^3	1.5

- Approximately 50 to 60 L/h rotary calciner at CEA (nonradioactive)
- Wiped film evaporator with three 25 kg/h CCMs in Russia (radioactive)
- 0.056 m^2 CCM at Radon Institute in Russia (radioactive)

I. Necessity for New Inventions

Not known at this time.

4. Integration with Process and Facility - *This section is provided by Fluor Daniel, Inc.*[10] *except for the following.*

A. Feed Preparation Requirements

"...acid feed is easier to manage."[6]

"We have made short tests (less than one week) with alkaline feed to the calciner without special problems; but the acid way has certainly a lot of advantages in terms of transfer and metering of the solution and in terms of mean of work of the first scrubber in the solution of which the most part of the dust escaping the calciner must be dissolved. In the case of using an alkaline solution, this scrubber solution would contain precipitate and become a kind of sludge. In the case of acidification of the solution, the off gas system will be similar to La Hague."[7]

B. Offgas system requirements

"...offgas system requirements, no specific one, see La Hague example."[6]

C. Number of melters

"4 for the CCM."[6] It should be noted that Mr. Jouan's estimate of four CCMs was assuming that the waste loading was 25%. Only two 200 kg/h CCMs would be needed if 50% waste loading is achieved.

D. Plant Service Requirements

"electric energy: 2.5 to 3 kW-h per kg of glass to be produced must be installed (about 2 would be used). Cold water for cooling the melters to evacuate the equivalent of the electric power."[6]

The Russians have reported 4.5 to 6 kW-hr/kg glass for the 0.056 m^2 CCM at the Radon Institute (Lifanov et al. 1993).

E. Melter Dimensions and Weight

"Size 1 m to 1.2 m diameter, weight 500 kg (a first estimation!)"[6]

"It should have a long service life and, on dismantling, would form a compact and easily conditioned waste mass of about 500 kg (i.e. 62 liters) of stainless steel, probably with a very low contamination level" (Moncouyoux et al. 1991).

F. Disposal System Requirements

See 4.E above.

5. Control and Maintenance of Process and Facility

This section includes a discussion about the capability of the melter technology to allow safe and efficient operation of the vitrification facility.

A. Ease of Control

"For CCM, electric intensity (Amps) and voltage are two very important parameters which are the picture of the inside CCM content, the glass in which induction occurs; glass level and temperature are also very important."[6]

It appears that the CCM is sensitive to perturbations in operating conditions. This may be an issue if the CCM is operated in an unsteady mode (batch pours) or if the batch level is unsteady. A Russian paper noted the difficulty in controlling the temperature in the CCM by balancing the voltage and frequency of the high-frequency oscillator and presented the mathematics of a CCM control system.

> "Cold crucible glass founding is a multiparameter process characterized by a large number of control and perturbing actions. Prime among them are disruptions of the heat balance as a result of changes in melt heat losses or the power released in the molten glass. The stability of operating conditions depends on the choice of working coil and crucible dimensions and on glass chemical composition and melt temperature....Modern units for melting oxides and glass in cold crucibles have systems for stabilizing the oscillator tube plate voltage and the oscillator frequency, but this is not sufficient to maintain proper temperature conditions and stabilize the working frequency during founding" (Nezhentsev 1991).

Control information about evaporation is currently not available. Calciners supporting 25 kg/h are currently in operation at the La Hague plants and at the Windscale Vitrification Plant. These calciner designs have been thoroughly tested on acid wastes from nuclear fuel reprocessing plants; experience with alkaline wastes is limited.

B. Remoteability

Remote CCM vitrification units have been operated in Russia, although on a limited scale (0.056 m^2). Remote calciners (25 kg/h) have been operated in France and England.

"Seems to be easy using the La Hague concept with crane; master slaves and special tools (electric screw-drivers etc...) for LFIM and CCM."[6]

C. Reliability

"Parts of calciner can fail and must be removed: graphite seals and rollers are the two main pieces to be removed; they are very little solid waste. Other calciner parts last usually more than five years.

CCM melter lifetime will probably be years; it can be made in separated pieces: coil, main cooled segments, bottom and upper part; and repairing time would be in the same order of magnitude than for the LFIM and in case of failure this part could be medium or low level wastes"[6]

D. Maintainability

Depending on the drying method used for the feed, maintenance requirements could increase for this melter technology. If a rotary calciner is used, the graphite seals will have to be replaced about every 6 months. The disassembly of the calciner increases the potential for contamination of the melter cell. It should not impact any facilities outside of the melter cell.

The Russians operated spray calciners in their original CCM pilot facility, KS-KT-100; they noted problems with cracking of the ceramic metal filters on this calciner (Romanovski 1990). It is not clear if that was why they switched to an evaporator for their next pilot CCM.

Wiped film evaporators also have moving parts that require maintenance, which usually involves adjusting the wiper blades to maintain the proper gap between the blades and the steam tube.

E. Estimated Lifetime

See Section 5.C.

F. Ability to Confine Radioactive Materials

Maintenance of equipment is a significant source of radioactive materials. Depending on the drying method used for the feed, maintenance requirements and consequent contamination of the melter cell could increase. The maintenance requirements of the proposed dryers and calciners are discussed in Section 5.D.

G. Potential for Radioactive Source Buildup and Achievement of ALARA

The CCM has very little glass holdup relative to the other melters being evaluated (roughly 2 metric tons). The calciner or evaporator will be much larger than the CCM, so that the drying equipment will have the greatest potential for building up radioactive material. This should not affect ALARA if properly contained.

Off-gas treatment is discussed in the Fluor Daniel, Inc.[10] data package.

This melter has a bottom drain, which can be used to drain the glass from the melt cavity at the end of the melter life. This may be optimistic. Melter failure could occur in such a way that the glass could not be drained from the melter. This is an unresolved problem for most of the melters being considered in this evaluation. However, Mr. Jouan pointed out that if the glass solidified in a failed melter, it would not stick to the cold stainless steel wall and could possibly be removed and placed into a new melter.[11]

H. Sealing and Containment Relative to Melter and Drying Equipment

Measures are taken to seal the melter to prevent inleakage to the off-gas system and prevent outleakage to the melter cell. This has always been a significant challenge for designing remote melters. Metal bellows are provided for sealing the canister to the melter during glass pouring. This was noted to be a significant problem during operation of the first Russian CCM pilot plant. This CCM was different from current designs; rather than pouring from the crucible, the full crucible was removed and replaced with an empty crucible. Graphite seals are used for sealing the moving parts on rotary calciners. Leakage around these seals will increase inleakage of air only as long as a proper vacuum can be maintained on the equipment.

I. Modular Design Concepts that Simplify Replacement or Repair

This melter design is modular, so that replacement of the CCM or calciner/evaporator should be possible without any changes to current facility plans. The Fluor Daniel, Inc.[10] report evaluates melter disposal costs as a function of melter size.

J. Refractory Life

See Section 5.C.

K. Electrode Life/Replacement

Not applicable.

L. Ability to Safely Handle Organics

Most of the organics should be destroyed in the calciner if one is used. If an evaporator is used, water-cooling of the plenum might limit destruction of organics.

M. Operational Simplicity

Depending on the CCM configuration that is chosen, this system may have several moving parts. The rotary calciner or wiped-film evaporator is a dynamic system that will require attention. Agitation would increase the production rate, but it would also increase the system complexity. Controllability of the CCM is discussed in Section 5.A.

N. Estimated Lifetime

See Section 5.E.

O. Estimated Downtime to Repair

Information currently not available.

6. Minimize Total Cost - *This section is provided by Fluor Daniel, Inc.*[10] *except for the following.*

"The cost of a CCM melter (for the part inside the hot cell) could be about 200 Kilo dollars - it's my appreciation."[6]

7. Minimize Risk -

C. Operational Safety

"Using a precalcination step there will not be products accumulation and explosion problems; the residence time in a calciner is very low; the amount of the product is therefore very low and the decomposition of the product (organics or minerals) occurs continuously.

LFIM is a safe process, even in case of failure; there is no particular safety risk. CCM is also a safe process, even if water is not far from the hot melted glass. Safety tests were made in France to investigate the possible interaction between hot melted glass and water. The result is of course that an over pressure can occur in case of contact but there is no chemical reactions between the two [sic]."[6]

"The molten glass may be cast from metal nozzles extending through the water-cooled metal hearth supporting the melt. This raises a potential safety hazard of water ingress into the molten glass in the extremely unlikely event of a breach in one of the metal sectors forming the crucible. In order to assess the danger of an interaction between the water and the melt, the CEA investigated pressurized water injections into molten glass: the water boiled, but no violent pressure rise occurred in the facility" (Moncouyoux et al. 1991).

D. Criticality

"LFIM and CCM are very little furnaces easy to be controlled from time to time by emptying them."[6]

E. Passive Shutdown

"Safety analysis is to be made and passive means are probable to be designed and installed (to maintain water cooling)."[6]

Endnotes

1. Bolton, W.V. and Z Elektrochem., 11:45 (1905).
2. Statement made by Mr. A. Jouan at the June TAC Meeting.
3. Boiling bed, spray calciner, and uniflow evaporator information provided by KfK of Germany.
4. Trip report will be published by April 8, 1994.
5. Presentation by Mr. Jouan.
6. Fax from Mr. Jouan of CEA to P. Shafer of PNL dated August 11, 1994.
7. Fax from Mr. Jouan of CEA to P. Shafer of PNL dated August 5, 1994.
8. Information gathered by KfK for Russian melters.
9. Presentation by Tony Maxted of BNFL, March 18, 1994.
10. Fluor Daniel, Inc. 1994. "Alternative Melter Systems Assessment 20 Metric Tons per Day HLW Glass Production." Prepared under contract #04-436304 with Westinghouse Hanford Company.
11. Fax from Mr. Jouan of CEA to P. Shafer of PNL dated January 16, 1995.

ATTACHMENT 1 TO DATA PACKAGE 6

DESCRIPTION OF THE CCM

The Cold-Crucible Glass Melter

Claude G. Sombret

Commissariat à l'Energie Atomique
France

Savannah River Center
May 10–11, 1993

ATT 1.3

INTRODUCTION

The vitrification process currently implemented in France to solidfy concentrated fission product solutions uses melters in which the heat source is an induction-heated metal chamber. This process meets the requirements of the French and English reprocessing plants, but does not allow melting at temperatures above 1200°C.

In the 1970s, advantages were perceived in developing a facility with a larger throughput capacity, capable of achieving higher melting temperatures. A heating process was developed implementing direct induction in the glass inside a refractory chamber. The development of this process was interrupted in the late 1970s to meet the workload arising from commissioning of the Marcoule Vitrification Facility (AVM) and from the UP3 and UP2/800 reprocessing plant projects with their two vitrification units, R7 and T7.

A direct induction process using a water-cooled metal crucible was developed in 1980 to melt metal waste. The experience acquired made it possible to consider renewed development of the direct induction glass melting process beginning in 1981, but with a water-cooled sectorized metal crucible instead of the initial hot refractory crucible. The new process not only allows fabrication of high-silica glass and eliminates crucible corrosion problems, but also considerably increases the melter capacity without increasing the overall dimensions of the facility.

OPERATING PRINCIPLE

The glass is fabricated and melted in a generally cylindrical, water-cooled metal crucible. The glass in contact with the cooled wall solidifies to a depth of a few millimeters, as the wall temperature does not exceed 200°C. The bottom of the crucible is also a water-cooled metal plate, so the glass is fully contained in a solid glass "crust", hence the term "skull melting".

The crucible is surrounded by the coils of an inductor supplied with a high-frequency alternating current, which induces currents in the molten glass that dissipate heat by Joule effect (the resistivity of molten glass is a few Ω·cm). In order to ensure suitable electrical efficiency when transferring power from the inductor to the melt, the frequency must be determined so the penetration depth of the induced currents in the glass is less than the crucible radius. The penetration is given by the following relation:

$$p = \sqrt{\frac{\rho}{\pi\mu_0\mu_r F}}$$

where p is the penetration depth in meters, ρ the glass resistivity in Ω·m, μ_0 the magnetic permeability of empty space ($4\pi \times 10^{-7}$ H·m^{-1}), μ_r the relative magnetic permeability of the glass and F the inductor frequency in Hz. The following simplified formula is generally used:

$$p = 503\sqrt{\frac{\rho}{F}}$$

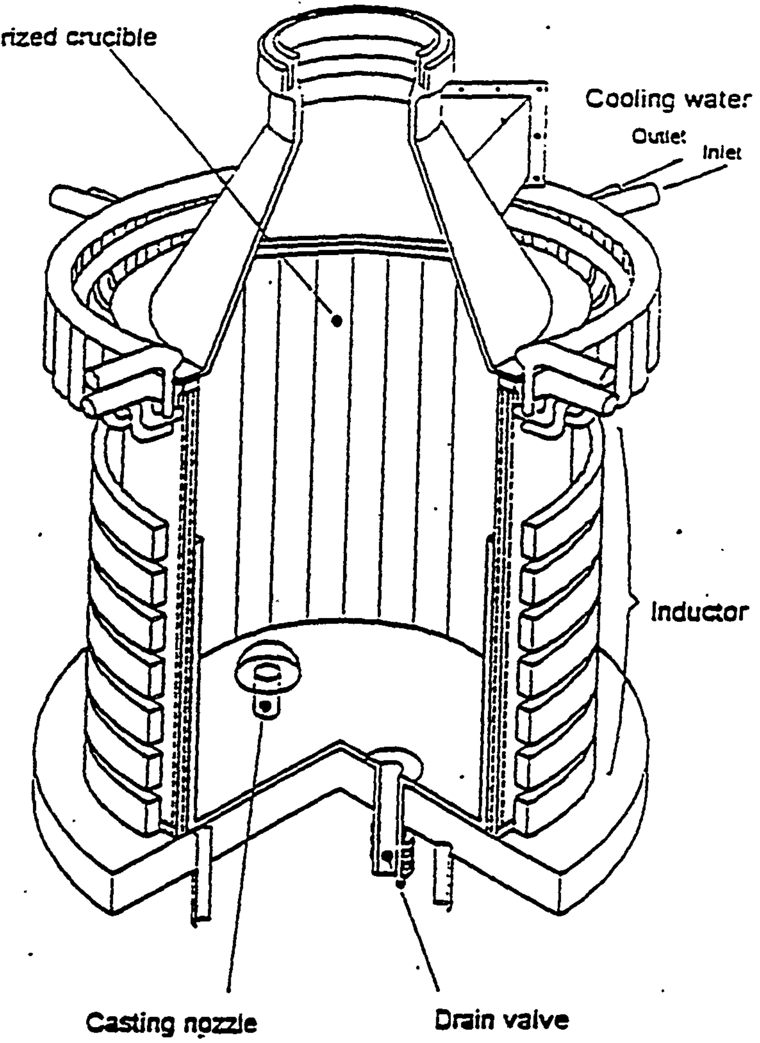


Figure 1. French Cold-Crucible Melter

High-Frequency Generator

A vacuum tube generator with three shunted triodes supplies 240 kW at 12 000 V at a frequency of 335 kHz for a crucible 0.55 m in diameter. A high-frequency line consisting of two water-cooled copper sections connects the generator to a multiple-winding inductor placed around the cold crucible. The geometry of the oscillating circuit and the distribution of the trimming capacitors ensure a null potential between the cold crucible – containing the molten glass – and earth, making additional insulation unnecessary between the crucible and its supporting structure.

Preheating System

Various methods were considered, including expendable or recoverable susceptors, a heated arch, gas burner, plasma torch, graphite additive, etc. Finally, a microwave system was adopt

The metal crucible containing the glass must be sectorized to ensure relative transparency to the electromagnetic field generated by the inductor: otherwise, it would constitute a Faraday cage, preventing the formation of induction currents to heat the glass. The power density transmitted to the glass decreases to zero from the wall to the center of the melt. This gradient provides for convective stirring within the molten glass. The glass level rises along the wall and diminishes in the center of the crucible. There is no electromagnetic stirring effect, since the electromagnetic forces are one or two orders of magnitude lower than those generated by the thermal gradient.

DESCRIPTION

A direct-induction glass melting facility comprises four subsystems:

- a water-cooled sectorized cold crucible;
- a crucible bottom structure supporting the glass casting nozzle;
- a high-frequency generator, inductor and trimming capacitors;
- a glass preheating system required on startup, since cold glass is a poor conductor and must be preheated until the energy transmitted by induction exceeds the thermal losses.

Cold Crucible

The crucible (Figure 1) is an assembly of stainless steel sectors forming a cylindrical structure. Typical crucibles are 0.55 m in diameter and 0.70 m high, although the actual dimensions may be smaller or larger (e.g. 1.50 m diameter). A three-dimensional computer model is used to optimize the dimensions and ensure better than 80% electrical efficiency. Each sector has a rectangular-cross section, and includes water ports mating with the inlet and outlet manifolds. The sectors are separated from one another by electrically insulating material. The structure is maintained externally by strapping with refractory fabric.

Crucible Bottom Structure

The cold crucible is supported by a bottom structure comprising a water-cooled stainless steel center plate and a refractory cement outer ring. The refractory assembly is molded to allow handling. Water cooling of the center plate and crucible walls is sufficient to solidify the glass in contact with the refractory ring, forming a continuous layer around the melt. The center plate supports the following elements:

- a casting nozzle extending into the melt, designed to retain a sufficient glass heel to allow continued induction after casting; it comprises either a glass freeze valve controlled by a medium-frequency inductor, or a separate mechanical shutter;
- a drain nozzle with an induction-heated freeze valve at the bottom of the crucible to empty the glass heel;
- air or argon injectors extending into the melt to ensure thermal and chemical homogeneity by stirring if necessary.

because it allows energy to be transmitted to the cold glass without contact and without requiring placement of the generator in the shielded cell containing the melter: no mechanical or electronic components of unproven reliability are therefore located inside the cell.

Most of the cold crucibles implemented to date have used a 25 kW microwave generator operating at a frequency of 915 MHz, transmitting energy to the melter via a rectangular waveguide with inside dimensions of 124 × 248 mm. The waveguide is connected to the tapered upper junction between the melter and the calciner; a quartz window on the melter end ensures a leaktight seal.

ADVANTAGES

The process avoids any contact between molten glass and the cold metal wall, thereby preventing crucible wear regardless of the glass temperature or the melt composition. This type of crucible has successfully been used to melt UO_2 at 2500°C.

Not only is corrosion eliminated, but the energy input to the glass is unlimited, allowing high production rates. The glass melting temperature may easily be raised above 1200°C if necessary.

PERFORMANCE

Several thousand hours of tests have been conducted to date with melters 0.35, 0.55 and 1.20 m in diameter, supplied with ground glass, or with glass and calcinate (either premixed or with the melter coupled to a calciner of the same type used in the R7 vitrification facility), and at temperatures ranging from 1150 to 1380°C. The maximum capacity has been about 25 $kg \cdot h^{-1}$ for the 0.35 m diameter melter, and 50 $kg \cdot h^{-1}$ for the 0.55 m diameter melter. The actual throughput depends not only on the melter diameter, but also on the temperature. At 1300°C, a melter 1 meter in diameter can produce 200 kg of glass per hour when supplied with dry material. Testing with liquid feed resulted in a lower capacity, and raised some technological problems.

APPLICATIONS

In addition to melting metal waste, the high capacity and high temperature capability of the cold crucible melter are compatible with many applications in the area of radioactive waste vitrification: concentrated fission product solutions, low- and intermediate-level solutions with vitrifiable compositions, and solid inorganic waste that is either unfit for incineration or for which incineration would produce a heterogeneous ash/oxide mixture and a low volume reduction ratio (e.g. restoration of contaminated soils).

Among other projects, the French are now building a vitrification facility for low-level radioactive liquid waste from the Temelin power station in the Czech Republic. A full-scale prototype unit with a cold crucible 0.60 m in diameter will begin operating at the site in 1994.

Coulée de verre haute température par induction directe en creuset froid

APPLICATIONS

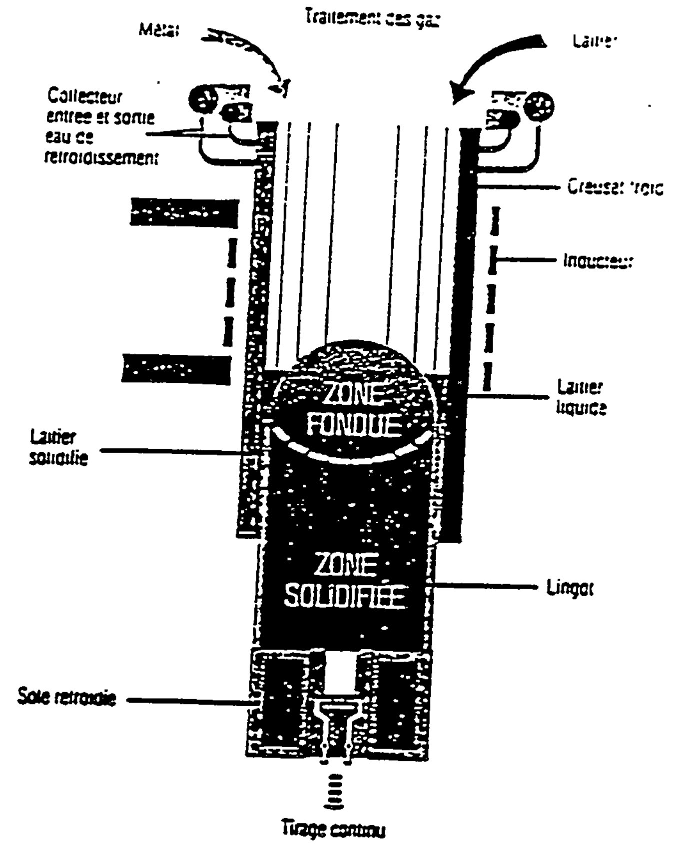
La fusion inductive en structure froide se développe et révolutionne les techniques d'élaboration de nouveaux matériaux :

- verres et céramiques quelle que soit leur agressivité ou leur température de fusion, avec un haut degré de pureté.
- métaux avec un haut degré de pureté (titane, zirconium, hafnium, super-alliage),
- confinement par vitrification de déchets minéraux toxiques.

OFFRE TECHNOLOGIQUE

Le CEA sur le centre de Marcoule met à la disposition des industriels une plate-forme d'essais équipée :

- d'un four à creuset froid de 500 mm de diametre pour l'élaboration en continu des verres et céramiques.
- d'un four à creuset froid de 150 mm de diametre pour la fusion des métaux avec



Principe de la fusion des métaux

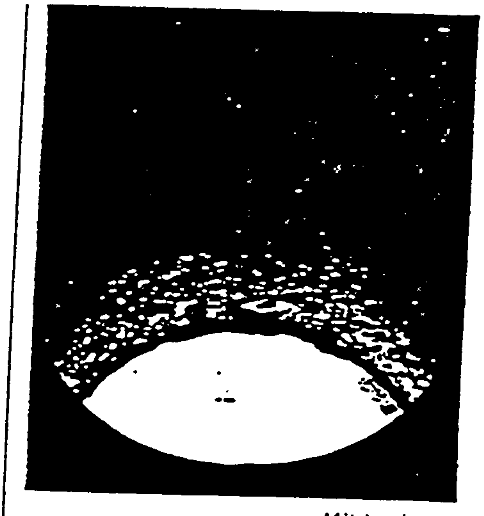
EDF, la Compagnie Française d'Electrothermie Industrielle (C.F.E.I.), et le laboratoire MADYLAM de l'Institut National Polytechnique (I.N.P.) de Grenoble peuvent apporter leur concours à la réalisation de projets industriels.

CADRE DE TRAVAIL DU CEA

Après signature d'un accord de confidentialité, le CEA peut effectuer :

- des essais de démonstration,
- des essais de faisabilité,
- une adaptation du procédé au produit proposé par le client.

La collaboration peut se poursuivre par l'étude, la réalisation et la mise en service d'une installation industrielle par la société C.F.E.I. avec l'assistance technique du CEA.



Métal en fusion

cea
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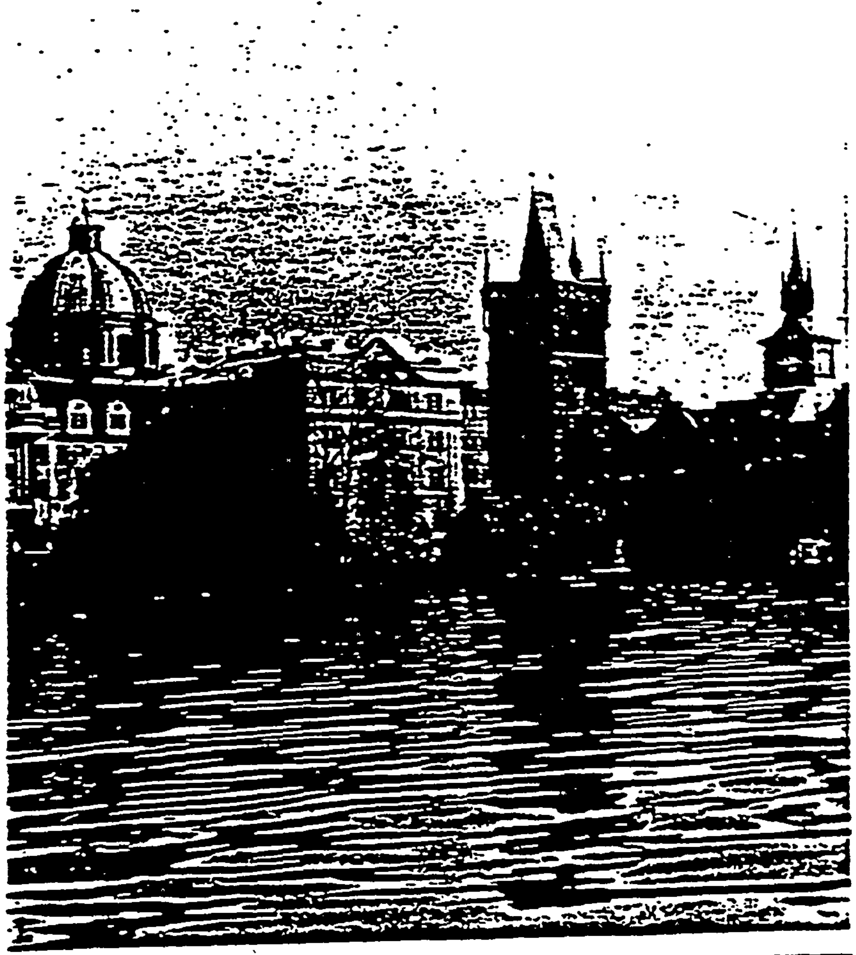
ATTACHMENT 2 TO DATA PACKAGE 6

DESCRIPTION OF THE RUSSIAN CCM DEVELOPMENT

LLW

VOL. 3

~~ENVIRONMENTAL REMEDIATION AND ENVIRONMENTAL MANAGEMENT ISSUES~~



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ATT 2.3

VITRIFICATION OF INTERMEDIATE LEVEL LIQUID RADIOACTIVE WASTE

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According to modern safety requirements concerning the management with intermediate level liquid radioactive waste, this waste must be transformed into solid inert form. The cementation and bitumenization methods, which were developed and are being used for this purpose do not provide the essential reduction of initial waste volume and obtaining the final product of high stability (1). But it is well known that glasslike materials are the best materials for radwaste localization among all the matrix materials, which can be used for this purpose. Application of glasslike materials means good volume reduction of initial liquid radwaste, high chemical resistance and fire resistance in the process of management with final product.

The results of preliminary technology-economic comparisons of vitrification and bitumenization methods (represented in table 1), showed that method of vitrification is a quite competitive one. Annual affect for the Moscow scientific industrial association "Radon" in prices of 1989 can make more then 100 000 rubles. The large part of economic-expenses saving gives the reduction of expenditures for maintaining the repository, due to reduced volume of final product.

The effect will be the most appreciable when using the alternative of centralized regional repositories for the purpose of transport expenditure reduction. Taking into accountall this circumstances we consider the vitrification of the intermediate level liquid radwaste.

At present the Moscow scientific industrial association "Radon" is developing the facility for vitrification of such waste.

In the process of vitrification method elaboration the following work was carried out choosing the best glass composition for immobilization of waste, choosing glass forming additives, studying the radwaste and glassforming additives behaviour in the process of vitrification, studying the final product properties, improving the technological process and the system for its realization.

Table 1. Initial indices of technology-economic comparison for methods for LRW treatment.

Item	Vitrification	Bitumenization
Annual reprocessing volume, m^3	2000	2000
Salt content in initial LWR, kg/m^3	200	200
Salt content of initial LRW in final product mass, %	30	50
Final product volume, m^3	240	700
Final product mass, t	600	800

Experimental testing of chosen decisions and technological designs were carried out on experimental stands developed at the Moscow scientific industrial association "Radon". On the first stage the works were carried out with ceramic melter on the base of direct joule heating (3,4). Now the Moscow scientific industrial association "Radon" has a pilot facility on the base of such a melter, the capacity for glass is up to 30 kg/h.

During 5 years of operation this facility gave about 10 ton of glassblocks and vitrified different types of intermediate level liquid radwaste, and among them waste of atomic power station with PWR, and BWR reactors (5).

Characteristics of liquid radwaste from Kurskaya and Kalininskaya atomic power stations are given in table 2. The waste from Kurskaya power station can be effectively vitrified by adding the borosilicate glass forming materials. In the process of Kalininskaya power station waste vitrification, which have boron compounds in their composition, borosilicate glass forming materials adding is not necessary that reduces greatly the expenditure for the process realization.

The main technological parameters of Kurskaya and Kalininskaya power station waste vitrification are represented in table 3, composition and properties of glass melt and vitrified wasted wastes are given in table 4.

Table 2 Characteristics of atomic power station waste.

Item	Kyrskaya station	Kalininskaya station
Component content according to analysis, kg/m^3		
$NaNO_3$	281.1	123.5
KNO_3	7.4	18.1
Na_2CO_3	13.1	82.5
NaCl	8.2	2.6
Na_2SO_4	7.7	0.7
NaOH	-	56.5
$NaBO_2$	-	100.5
$CaCO_3$	-	1.5
$Ca_3(PO_4)_2$	1.9	-
$MgCO_3$	1.0	-
$Fe(OH)_3$	5.5	-
Indefinite residue	22.1	0.5
specific activity, Bq/m^3		
^{137}Cs	$4.1 \cdot 10^9$	$1.8 \cdot 10^9$
^{134}Cs	$8.5 \cdot 10^8$	$1.0 \cdot 10^9$
^{60}CO	$5.3 \cdot 10^7$	$4.5 \cdot 10^7$
^{239}Pu	$5.0 \cdot 10^6$	$1.5 \cdot 10^6$
^{90}Sr	$1.5 \cdot 10^9$	$4.4 \cdot 10^9$

In terms of pilot plant testing, it was found out that the most important unit, which is responsible for the operation of the hole system - is the melter. Such features of ceramic melter as its complex configuration, large dimensions and mass, limited period of operation and problems with repairing and replacement in case of decommissioning restrict its application. Recently the alternative of small dimensioned waste cooled garnissage melter on the base of high-frequency induction heating (the melter "cold crucible") is under development. The melter of such type allows to remove some drawbacks of direct heating furnace.

The absence of melt direct contact with melter material greatly reduces the problems concerning melter corrosion while possible heating of the hole volume of glassforming material provides the melting process intensification.

The Moscow scientific industrial association "Radon" has developed the experimental stands with the induction melter "cold crucible" with power supply from high-frequency lamp generators of 160 kW and 60 kW and working frequency of 1.76 MHz.

On these stands a number of works on LWR simulators vitrification, in particular on LWR simulators from Kurskaya and Chemobilskaya power stations were carried out.

Table 3. Parameters of atomic power station liquid radwaste vitrification in ceramic melter of direct heating.

Item	Kyrskaya station	Kalininskaya station
Capacity for LRW, l/hr glass, kg/hr	 30 22	 50 30
Specific capacity for glass, kg/hr*m^2	40	50
Specific power supply for glass kW*hr/kg	3.2	3.4
Melting temperature °C	1150	1150
Mixture moisture, mass %	20-25	20-25
Volume reduction factor	4.2	4.5
Solid matter carrying over from the melter, mass %	0.7	1.0
Radnuclides(^{137}Cs) carrying over from the melter, mass %	2.9	3.5

The characteristics of Chemobilskaya atomic power station waste, the composition of which is the mixture of spent solution pulps and silts from decontamination service, are represented in table 5.

Taking into consideration the necessity of joint treatment for all the volume of waste, delivered during day-period, the composition of glassforming materials, including inorganic sorbent, clinoptilolite, as glassforming component was optained.

The main technological parameters of the process for the atomic power station simulated waste vitrifying, which was carried out on experimental stand are given in table 6. The stand comprises high-frequency generator of serial production with the power of 60 kW and frequency 1.76

MHz, melter "cold crucible" with working surface of 5.63 dm^2, rotary evaporator, batchers and auxiliary equipment. The charging on the base of liquid radwaste concentrate and glass forming additives as paste of about 20 mass % humidity, was fed into the melter.

Table 4. Composition of glass and vitrified waste.

Item	Kyrskaya station	Kalininskaya station
Component content in glass, mass %		
Na_2O	16.1	24.0
K_2O	0.5	1.9
CaO	15.5	6.2
Al_2O_3	2.5	4.3
Fe_2O_3	1.7	1.8
B_2O_3	7.5	9.0
SiO_2	48.2	46.8
Na_2SO_4	1.1	0.8
NaCl	1.2	0.9
	5.7	4.3
Another components specific activity of glass, Bq/kg	$7.0 \cdot 10^6$	$2.7 \cdot 10^6$
Viscosity of glass, Pa·s		
at temperature 900°C	33.5	20.8
1000°C	16.3	7.9
1100°C	6.6	2.9
1150°C	4.3	2.0
1200°C	3.9	1.6
Specific electrical resistance, ohm·m		
at temperature 900°C	0.065	0.052
1000°C	0.041	0.035
1100°C	0.032	0.032
1150°C	0.029	0.028
1200°C	0.028	0.027
Leaching rate of ^{137}Cs, $g/cm^2 \cdot day$ during the continuous contact with water		
1 day	$1.4 \cdot 10^{-5}$	$3.2 \cdot 10^{-5}$
28 days	$1.4 \cdot 10^{-5}$	$4.4 \cdot 10^{-6}$
112 days	$1.1 \cdot 10^{-5}$	$3.0 \cdot 10^{-6}$

We continue the work on experimental stand in order to improve the melter construction and process organization. The melter cold crucible allows to obtain glass and minerallike materials of different composition, and also glass composition on the base of waste, including components incompatible or of limited compatibility with glass matrix. E.G. sulphate radioactive waste, from atomic power station activity.

In the process of glass obtaining, the sulphates float on glass surface, forming the insoluble film, which can't be immobilized in glass, so called "yellow phase". Nuclide concentration in "yellow phase" is about 10 times greater, then nuclide concentration in glass.

Table 5. Composition of desorbing solutions and pulps from decontamination service of the Chernobilskaya power station

Type of wastes	Quantity, m^3/day	Composition, g/l
Spent alkali desorbing solutions	2	50 $NaNO_3$, 5 $KMnO_4$, 5-10 $Fe(OH)_3$
Spent sour desorbing solutions	2	100 HNO_3, 2 $H_2C_2O_4$, 2 NaF, 5-10 $Fe(OH)_3$
Spent etching solutions	2	100 HNO_3, 4 N_2H_4, 2 NaF
Pulps form abrasion	0.5	150 SiO_2
Pulps of spent non-organic materials	0.7	100 (for solid phase)

*Specific activity of desorbing solutions and pulps- $3.7 \cdot 10^5$ Bq/l.

Table 6. The parameters of the process for the atomic power station simulated waste vitrifying in the induction melter "cold crucible".

Item	Kyrskaya station	Chrnobilskaya station
Capacity for glass, kg/hr	6.8-9.0	7.9-10.0
Specific capacity for glass, $kg/m^2/hr$	120-160	140-180
Specific power supply, kW·hr/kg	5.0-6.0	4.5-6.0
Average temperature of glass, °C	1250	1250
Solid matters carrying-over from the melter, mass %	1.0-1.2	-
Radionuclides carrying-over(^{137}Cs), %	3.0-3.9	-

The final product of treatment can't be buried, due to low water resistance of "yellow phase". There are another waste of low compatibility with glass matrix, e.g. chlorides and molybdates. The technological process for treatment of liquid radwaste with such components, provides their immobilization in glass matrix, obtaining glass composites (8,9).The waste sulphates, molybdates, chlorides ets. distributes homogeneously in the glass matrix in the form

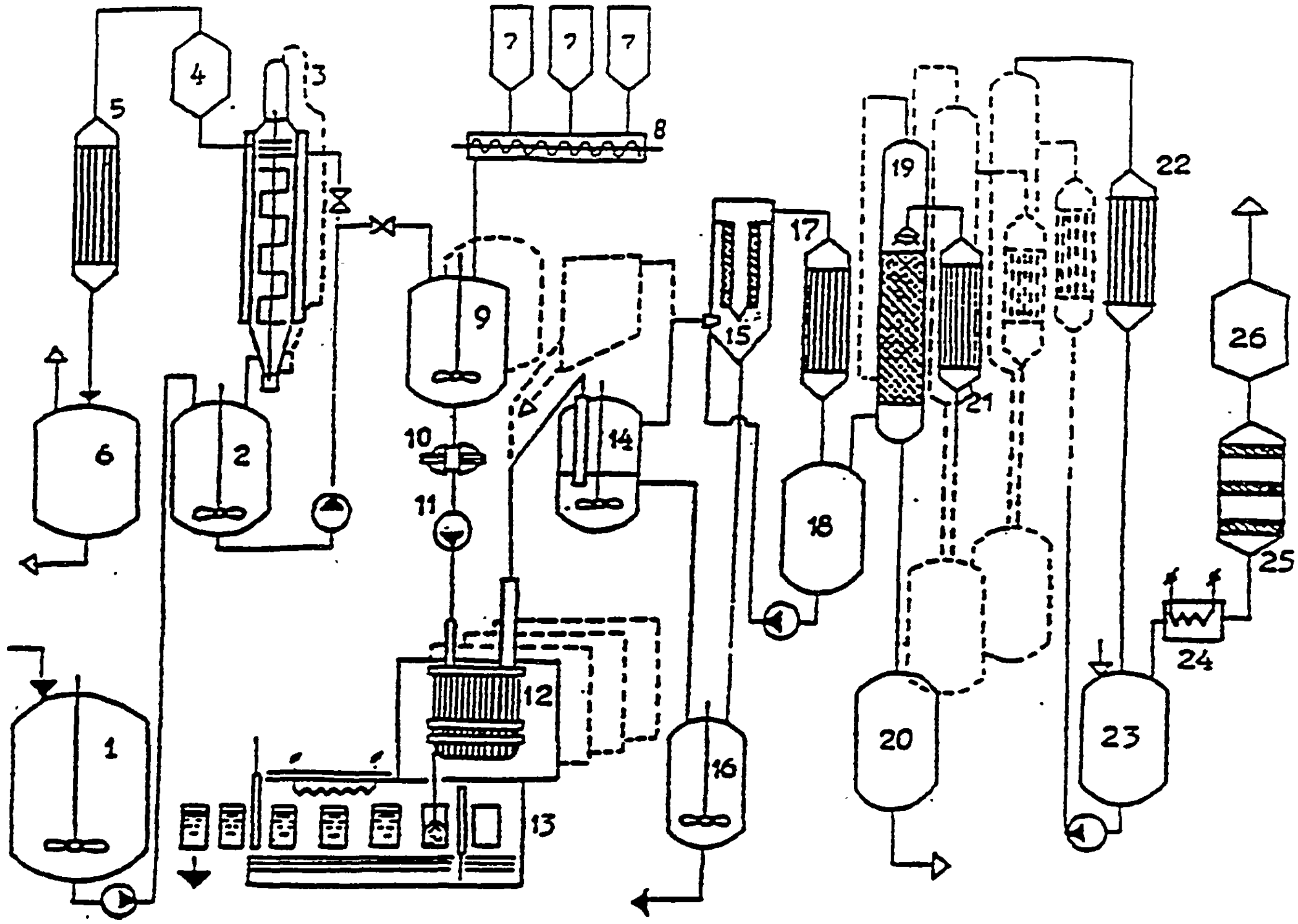

Fig 1. SHEME OF THE PLANT FOR VITRIFICATION OF RADWASTE.
1- repository; 2-concentrator; 3-rotary evaporator; 4,26-filters; 5,17,21,22-heat exchanger; 6,16,20-collector; 7-glass forming additives; 8-mixing screw; 9-mixer; 10-grinder; 11-feeder; 12-unit of melters; 13-furnace; 14-coarse filter; 15-fine filter; 18,23-canister; 19-column; 24-heater; 25-reactor.

of dispersed phase the of dispersed phase in 100-200 μ. This method allows variation of glass forming materials and waste compositions in sufficiently wide range.

The main results of work are the following

- the process for glass composites obtaining by including of sulphate radwaste into borosilicate glass melt is developed,
- glass composites, containing up to 30 % of sulphate phase, both on the simulated waste and on the base of real radwaste are optained. It was found out that leach rate of ^{137}Cs form borosilicate matrix is within $5.0 \cdot 10^{-6}$-$5.0 \cdot 10^{-5}$ g/cm^2/day and by using of different additives it is possible to obtain composites with water resistance within 10^{-7} - 10^{-6} g/(cm^2•day),
- laboratory and experimental pilot stand for optaining glass composites is developed. Pilot stand is assembled on the base of induction melter "cold crucible" and has capacity of about 10 kg/hr,
- pilot plant designing on the base of induction melter with high-frequency generator BCHG-8-160/1,76 and mixer with capacity up to 25 kg/hr is on the way of accomplishment.

The obtained results allows to start the development of full-scale pilot industrial facility for radwaste vitrifying. The facility must meet the following requirements:

1. Sufficiently high capacity in comparison with capacity of real faculties for bitumenization (up to 100 kg/hr for glass, or 300-400 l/hr for LRW.
2. Possible automation of technological process in active zone.
3. Continuity of the process.
4. Possible replacement of the units with limited life time, and in particular the melter.
5. High safety due to rigit joints between all the main units of the facility and synchronizing of their work.

6. Providing of off-gasses and secondary waste purification from radionuclides and dangerous chemical compounds.

7. Maximal application of units, produced in Russia.

The full-scale facility, which meets all the mentioned requirements is shown in +. 1. The system includes the following units: unit for receive of LRW (receiver), unit of LWR concentrating, unit for preparation of glass forming additives, unit for preparation materials, making composition, required for glass obtaining (charging), unit for feeding the charging into the melter, furnace for glassblock production with discharging system, gas purification system. There are also auxiliary systems for power supplying, sampling, radiation monitoring and so on The given system uses the principle of two staged process organization, which is as follows: the liquid radwaste are concentrated and the mixture of charging in the form of suspension of 22-25 mass % humidity and glass forming additives are fed into the melter. The humidity % is determined by sufficient spreading of charging on the surface of glass melt and sufficient low radionuclide releases of off gases.

The shot characteristic of main units:

- the unit of concentration is appointed for evaporation of initial pump to optain concentrate with salt content 1000-1100 kg/m^3 and feeding the concentrate to the unit for charge preparation. The unit is made on the base of rotary film evaporator 3, heated with steam. This unit allows to treat the waste of wide initial salt content and does not require heating steam pressure for stabilisation and container for evaporated pulp. The concentrate, collected in the collector 6 is fed for purification and besides another evaporation units can be used in this system.
- the unit for charging preparation is appointed for pastelike charging of 22025 mass % humidity and consists of apparatus for glass forming additives preparation 7, mixing screw 8 and two mixers 9. As glass forming additives quarts sand, mild clay and datolite concentrate are used.

The system is equipped 3 high-frequency melters "cold crucible". Every crucible is placed in separate box and supplies energy from separate generator. Simultaneously, different number of melters can work, this depends either on required capacity or on work regime.

The charging is fed into the melters by the chargers in automatic regime 10.

The joule furnace serves to control cooling of glass block. It is designed as a tunnel kiln annealing furnace with 4 zones of heating-cooling.

The next unit - is gas purification unit. The main task of this unit is to trap the nuclides, macroelements of LRW and charging and the products of their thermal decomposition, released with off-gases, the main of which are nitric oxides. There are 2 alternatives of gas purification. The first way is the following. The off-gases are cleaned from nuclides and macroelements releases, then the nitric oxides are removed and nitric acid is regenerated and at last auxiliary removal of nitric oxides is carried out.

The second alternative the particle denitration (about 90 %) is carried out directly in the melter by adding organic compounds into the charging, them the off-gases are cleaned from aerosols, and auxiliary removal of nitric oxides is carried out.

By choosing of trapping method (method of aerosol removing from the melter) it was taken into consideration, that "wet" methods of purification produce a great volume of secondary waste. Among the "dry" methods gas filtering is preferable, because it provides high-efficient cleaning of thin dispersed aerosols (about 1 micron) arising in the process of vitrification.

Aerosol removing are carried out in 2 steps. On the first step a coarse filter is used 14, the spent filter is included into glass melt.

On the second step the fine filter from thin fibber glass, that is easily included into glass melt, is used.

The apparatus for nitric oxides trapping must have low hydraulic resistance, hence we used packed column for this purpose.

The catalyst method of nitric oxides regeneration by ammonia on aluminium-vanadium catalyst in reactor was chosen for final cleaning: This process is realised in the range of temperatures 250-400 °C, i.e. the ammonia serves only for nitric oxides regeneration. One should not use such gases as CH_4 and H_2 for catalyst regeneration, because during the regeneration by CH_4 the limiting concentration of O_2 in gases must not exceed 4 mass % and limiting concentration of H_2 in gases must not exceed 3 mass %, due to high -exothermic oxidation reactions. The spent catalyst material, as Al and V oxides mixture, can be easily included in glass.

The effectiveness of system in both variants was tested on experimental stands in the process of vitrification in the melter "cold crucible". The test was carried out on real liquid radioactive waste, the dry residue of which has the following composition, mass % : Na^+ 20, Ca^{+2} 8.5, NO_3^- 55, SO_4^{-2} + Cl^- 1-4. The total specific activity is about $1*10^{-6}$ Bq/l.

Table 7 represents the results of off-gas purification from aerosols.

Table 8 represents the results of off-gas purification from nitric oxides.

The obtained nitric acid, the characteristic of which are given in table 9, can be used for ion-exchange column regeneration. The final choice of off-gas purification has not made yet. Effectiveness for off-gases purification from nitric oxides.

Vitrification facility is equipped with automatic control system, providing the control of all units processing all the data and transmitting them to the operator. The possible realization of the total process in automatic regime is foreseen.

Table 7. Effectiveness for off-gases purification from radioactive aerosols.

Version of off-gas purification	Specific activity, Bq/m^3		
	at the entry to the system	at the exit from the system	effectiveness for off-gas purification
1	100	$1.0*10^{-3}$	>99:9
2	100	$1.0*10^{-4}$	>99.9

Table 8 Effectiveness for off-gases purification from nitric oxides.

Version of off-gas purification	Nitric oxides concentration, mg/m^3			
	at the entry to the system	after absorbtion	at the exit from the system	effectiveness for off-gas purification
1	$(0.2-2.0)*10^5$	$2.0*10^4$	20	>99.9
2	$(2-5)*10^3$	-	20	990

Table 9. Characteristics of nitric acid.

Specific activity,	HNO_3 concentration,	Admixture concentration		
Bq/l	g/l	Na^+	Cl^-	SO_4^{2-}
100	100-250	<0.03	<0.1	<0.02

Table 10 represents the basic characteristics of the vitrification facility and the melter "cold.crucible". Testing of separate units is scheduled for 1992.

Table 10. The basic technological characteristics of vitrification facility and the melter "cold crucible".

Operation	continuous
Process	two-staged, LRW concentration in advance
Control	remote control, operation in automatic regime
Capacity for glass, kg/hr for LRW, m^3/hr	up to75 up to 330(salt content 200 kg/m^3
Specific activity of initial LRW, Bq/l of glass blocks, Bq/kg	 up to $3.7*10^7$ $5.5*10^7$
Dimension of glass block (container), mm	250*250*350
Glass mass in container, kg	50

Melter characteristics	
Capacity for glass kg/hr	up to 25
Operating frequency, MHz	1.76
Power of generator, kW	160
Mass of melter with the glass, kg	130
Minimal volume of glass in the melter, m^3	0.034
Dimensions of melter, mm	250*800*700
Area of surface melting, m^2	0.16
Operating temperature of the process, ^{o}C	1250
Specific power supply, kW per kg of glass	4.5-5.5
Supply of cooling water, m^3/hr	1.5

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Supplemental

Vectra Technologies, Inc.

The following information was provided by Vectra Technologies, Inc. immediately prior to the August meeting. Due to time constraints, it was not reviewed or included in any of the previous data packages. The information they provided is applicable to three different vitrification technologies, i.e., Data Packages 3, 5, and 6. Rather than disseminating the information, it was decided to include it as a supplement to the final report.

VECTRA

QA Plan ETC-001
Task 1.2.2.04.01
File Cat. T/C.2.4
Page 1 of 10
PShafer 10-19-94

TRANSMITTED TO RECORD CENTER

August 26, 1994
R94-0099.JBM

Ms. Phyllis J. Shafer, Research Engineer
Battelle Pacific Northwest Laboratory
Engineering Technology Center, MSIN: P7-41
Battelle Blvd.
Richland, WA 99352

Subject: High Level Waste (HLW) Melter
Technical Information

Dear Ms. Shafer:

We have received your inquiry dated July 13, 1994 for additional information on VECTRA's melter technologies for possible application in vitrification of HLW. This letter will provide available design information for your review.

I. Status of Technology

VECTRA has designed three types of melters for use in vitrifying a wide variety of low level radioactive and mixed wastes (LLRW) such as paper, plastic, resins, debris and metal objects. In order to successfully vitrify such a wide variety of LLRW's, a range of glass formulations is being developed. In developing our commercial EnviroGlass™ vitrification system, we reviewed existing melter technology and developed design criteria that would provide maximum flexibility in varying glass formulation and glass temperature - specifically to vary viscosity and conductivity and to melt metal objects that are introduced into the melter with the waste feed. As a result, our melters are all designed with bottom drains to allow removal of both molten glass and metals. A side tap could also be utilized but is not currently incorporated in our commercial LLRW melter systems. A novel top glass tap has been designed which could be an attractive option in the HLW application - as it could be remotely exchanged with relative ease.

It should be noted that most aspects of the three VECTRA melters have been successfully used in test or production installations in the metal melting or glass industry. The unique integrated VECTRA melter designs have not yet been tested in glass/waste vitrification applications.

The current development status of each melter is discussed below.

Cold-Wall Induction Melter (High frequency)

Our specialty melter vendor has completed detailed design of the melter and is ready to begin fabrication and testing of the commercial scale LLRW melter. The high frequency and low frequency induction power supplies have been built and tested. To fully demonstrate this melter - only the cold-wall, segmented, crucible assembly remains to be fabricated. The fabrication effort will require no more than 2 months with startup and testing to follow.

We have called this melter the Inducto-Skull™ melter as it is induction heated and utilizes a thin solidified glass layer (skull) to protect the cold wall crucible and reduce heat losses.

Design calculations indicate that this melter could be fabricated and operated with single melter throughput capacities of up to 25 metric tons of glass per day. This melter requires substantially more power to make up for relatively high heat losses to the cold-wall. Electrical efficiency is 70-80 percent with 20-40 percent energy losses to the cold-wall. The principal advantages of this melter are that there are no electrodes or refractory that need periodic replacement and the unlimited operating temperature range and ease of changing glass formulations.

A color isometric drawing of the melter is attached for your reference. The Inducto-Skull™ melter is pending patent application.

Cold-Wall Induction Melter (Low frequency)

VECTRA has initiated the design of a unique cold-wall, low frequency, induction heated melter for use in our Modular EnviroGlass™ system.

This Melter has an effective 4-12" thick layer of glass skull that protects the cold-wall and induction coils from the molten glass. Susceptor materials are placed inside the melter with the susceptor being directly heated by the low frequency induction coils. The hot susceptor materials then heat the surrounding glass to maintain melt temperatures. This melter is ideal for our EnviroGlass™ system as it can directly melt metal objects in the melter as well as provide internal heat for self-startup; i.e., allows cold startup without any external heat source.

The detailed design of this melter is proceeding with completion of final design by late September, 1994. We do not expect to fabricate this melter at this time as it will only be a back-up for the Inducto-Skull™ melter or if high metal content waste (>25% metal) is to be processed. This melter is pending patent application.

Design Calculations indicate that this melter could be fabricated and operated with single melter throughput capacities of up to 30 metric tons of glass per day.

<u>Cold-wall, Joule-heated Melter</u> (Vertical Electrode)

VECTRA has designed a cold-wall, joule-heated, vertical electrode melter specifically to handle high throughput vitrification of LLRW and HLW. We have applied for a patent on this design which we call VE-SKULL™, for Vertical Electrode - SKULL lined (cold-wall) melter. We have attached a color isometric drawing of the melter for your reference.

Design calculations indicate that the VE-SKULL™ melter could be readily built and efficiently operated in radioactive service with single melter throughput capacities of up to 100 metric tons of glass per day.

The melter housing detailed design is complete. This melter can be integrated into our Modular EnviroGlass™ system. The power supply and electrode designs are in progress. We expect the commercial scale VE-SKULL™ melter (2 TPD glass) to be in operation for testing by January 5, 1995.

VECTRA has been advised by Westinghouse Hanford Company (WHC) that a contract award will be forthcoming for preliminary testing of the VE-SKULL™ melter as part of the Hanford High Sodium Waste Vitrification Demonstration Program. Melter testing for this anticipated contract is scheduled to begin in January, 1995.

The VE-SKULL™ melter has numerous positive features that could facilitate vitrification of LLRW and HLW and provide significant maintenance and life cycle cost advantages over typical ceramic lined joule-heated melters, as discussed below. Many of these same features and advantages are also common to the Inducto-Skull™ (high frequency cold-wall, induction heated) melters.

- Upon Completion of a melt campaign it is possible to dramatically decrease radiation levels inside the melter by reducing waste loading in the molten glass pool and increasing glass temperature to 1500°C or higher which will melt a portion of the inner glass skull. The molten glass is then drained from the melter leaving a layer of clean, non-radioactive skull in place.

- No refractory is in contact with the molten glass inside the melter. Refractory requires high personnel exposure, expense and downtime to maintain or replace. If desired, a thin layer (1" to 4") of startup refractory may be installed. During initial heat up, 1% by weight of iron or other suitable infrared absorber will be added to the melt to preclude radiative heat transport from the bulk glass to the Inner Vessel wall. This then limits heat transfer to principally conduction through the Skull.

- Greatly reduced heat loss over other cold-wall designs because of insulative property of thick, solidified glass skull between melter inner vessel wall and molten glass pool.

- Outer cooling jacket generates usable low-pressure steam with energy losses from radiative cooling of inner vessel wall. The projected savings of 600 kw of electrical energy per 20 TPD melter should save over $ 200,000 in operating costs per year for a single 20 TPD vitrification facility (assumes 5 cents per kwhr).

- Vertical Electrodes are remotely removable (retractable) at any time - even during hot operation with melter full of glass.

- Low capital costs for melter since no expensive refractory is used. The VE-SKULL™ melter vessels should cost less than half the cost of an equivalent ceramic lined, joule heated melter.

- Melter has no moving parts, except retractable electrodes. Stirred melters and plasma centrifugal furnaces will require frequent maintenance and downtime. Gas sparge mixing as well as mechanical stirring can be utilized with VE-SKULL™ melters if testing shows significant throughput increases are warranted.

- Extensive, large scale operational experience exists on melter "powertrain", i.e., electrodes, power supplies, start-up and operating procedures, etc. based on ISV (Battelle and Geo-Safe), Roger Ek & Associates, and Corning experience.

- Vertical electrode design eliminates potential loss of containment where horizontal side entry or bottom entry electrodes could fail and allow glass to drain from melter to floor.

- High capacity melters to over 100 TPD glass are possible. Single, large ISV melters have demonstrated capacities of 170 to 200 TPD in-situ. The identical electrode design (by Roger Ek & Associates) is currently in commercial operation at a 30 TPD glass melter located in Portland, Oregon.

- All maintenance is from shielded top access area, except for Bottom Pour Valve assembly which will be remotely removable for maintenance.

- Integral, double wall, water cooled jacket provides total dry containment of glass in the extremely unlikely event of inner vessel wall failure. For similar failure mode, all other melters would expose molten glass directly to the circulating water in the cooling jacket which could cause an explosive steam release. The annulus between the double wall jacket and inner vessel wall can be pressurized with an inert gas. Alarms will indicate that a leak path has developed.

- Melter startup from cold shutdown can be accomplished WITHOUT need for auxiliary burner or high maintenance, electrical resistance, plenum heater (i.e., SiC). The startup method has been proven many times on large ISV process runs.

- Melter is designed specifically for highly radioactive service by eliminating refractory and all direct manual maintenance on melter and ancillary equipment.

- Melter can be easily shielded. Integral shielding can be built-into the melter vessel walls to facilitate ultimate disposal and periodic inspections. Integral shielding can be provided by use of heavier cooling jacket walls.

- Glass formulations can be changed at any time without affecting melter life. Typical melters require refractory which must be carefully selected for resistance to specified glass formulations and temperatures. If glass formulations are changed, already installed refractory may be subjected to accelerated corrosion, dissolution, and possible failure. The VE-SKULL™ melter uses no refractory in contact with glass.

- Vertical electrodes can be remotely positioned to vary electrode penetration into the melt and to VARY ELECTRODE SPACING ON-LINE. The ability to remotely change electrode spacing (**adjust approach angle and tip clearance**), even during operation, this <u>allows</u> optimal performance over an extremely wide range of glass formulations, to adjust for significant changes in operating melt temperature, glass viscosity and conductivity.

- Glass residence time of 12 hours or more is projected for 20 TPD VE-SKULL™ melter. This should assure excellent glass homogeneity. Testing indicates that four hours residence time is considered the minimum allowable to produce homogeneous glass. Longer residence times may be required if glass formers are not powdered or waste and glass formers are not thoroughly mixed.

- Melter vessel is of fully welded pressure vessel construction. There will be no leak paths to or from environment. This will prevent "puffs" of radioactively contaminated gases and dust in the event of pressure cycles inside melter.

- Vertical electrode diameter far exceeds size of typical horizontal electrodes. The use of smaller horizontal electrodes in other melters means more failure prone penetrations below glass level and much shorter electrode life. Gradual dissolution of molybdenum electrodes, especially by corrosive high Na_2O glass, together with small electrode diameter means that horizontal electrodes must be changed frequently compared to vertical electrodes. Such shutdowns require significant time for draining, cooldown, mechanical removal of corroded electrodes and restarting process. There should be no need for any shutdown for electrode replacement with VE-SKULL™ melters.

- Alternate electrode materials, i.e., chrome oxide, graphite, etc., could be readily tested and used to replace initial molybdenum electrodes, because vertical electrodes can be remotely retracted and replaced in the low radiation access area above the melter, even during hot operation. This allows flexibility in use of electrodes and changing electrode materials.

- Cylindrical pressure vessel construction provides strong structural containment that can be easily designed and simply fabricated while allowing full analytical analysis of structural, seismic and thermal stresses as well as cyclical fatigue and creep.

- Melter can be operated with cold-cap which serves to filter and hold volatized metals and radionuclides for re-incorporation into the melt.

- Melter can be easily idled in hot standby with no detrimental affects. Radiatively cooled melter plenum will reduce volatility from hot, idled melt pool by removing heat from top of melt to lower upper glass surface temperature, thereby reducing volatile metal losses.

- Eliminating refractory minimizes or eliminates risk of spilled refractory blockage of bottom pour nozzle.

Glass Tap Assembly

In addition to the three cold-wall high temperature melters described above, VECTRA has developed a cold-wall, induction heated, bottom mounted glass tap (Cold-Tap™) that could greatly extend the useful life of bottom glass tap assemblies. The cold-wall tap is shown on the bottom of the Inducto-Skull™ and VE-SKULL™ melters on the drawings that are attached. VECTRA is applying for patent protection for this design.

The unique features of the Cold-Tap™ include; 1) the central, hollow, tap pipe that can be easily replaced without disassembly of the melter bottom; 2) there is no melt-down failure mode as the cold-wall removes sufficient heat from the tap pipe that the glass is always contained within a full water cooled assembly at all times (for example, on typical induction heated bottom drains, if the metal drain pipe is overheated and melts, the glass inventory in the melter can be lost); and 3) the cold-wall quickly removes heat from the tap pipe and flowing glass to provide improved flow stoppage.

The Cold-Tap™ design is complete and a full scale test unit has been built. Testing of the Cold-Tap™ should begin by December 15, 1994. The Cold-Tap™ will be first utilized on VECTRA's Modular EnviroGlass™ system. A copy of the Module EnviroGlass™ system description is enclosed for your information.

II. Inquiry Response

In your letter (page 2), you listed a number of concerns related to VECTRA's melter technologies. Most of these concerns we cannot address because our melters are not yet operational. From our detailed analyses and design work, as briefly described in this letter, we believe VECTRA's cold-wall melter designs have substantial merit and could provide unparalleled performance in processing HLW.

In the balance of this letter, we will address the main areas of concern by means of engineering analysis and comparison; however, in all cases only actual future performance testing can verify the designs.

There are many other important considerations related to maintainability, life cycle costs, facility interface requirements, support requirements, etc. that cannot be ascertained until the melters are fully tested and detailed engineering analyses completed.

We hope the above information will be adequate for your current needs until testing is performed. We look forward to working with your on the continued HLW program development.

Very truly yours,

J. Bradley Mason, P.E.
Chief Engineer

JBM/ram

Enclosures - Modular EnviroGlass™ System Description
- VE-SKULL™ Drawing
- Inducto-Skull™ Drawing

Design and Operating Criteria	VE-SKULL™ Vertical Electrode-Skull Lined	Low Frequency Induction Heated Melter	INDUCTO-SKULL™ Induction-Heated High Frequency Cold Wall Melter
Operating Temperature	1050 - 1600°C	1050 - 1500°C	1050 - 2000°C
Glass Viscosity	Not critical, except for glass drain operation	Not critical, except for glass drain operation	Not critical, except for glass drain operation
Glass Conductivity	Must be within acceptable range	No impact, not joule heated	Must be within acceptable range
Liquidus Temperature	Must be within allowables at operating temperature	Must be within allowables at operating temperature	Must be within allowables at operating temperature
Precipitates/Insolubles	No impact, as long as precipitate size is less than 25% of bottom drain tap I.D.	No impact, as long as precipitate size is less than 25% of bottom drain tap I.D.	No impact, as long as precipitate size is less than 25% of bottom drain tap I.D.
Dry Calcined Feed	Yes, requires protective sleeve around vertical electrodes above glass	Yes	Yes
Slurry Feed	Yes, requires protective sleeve around vertical electrodes above glass	Yes	Yes
Feed System	Can use variety of feed systems	Can use variety of feed systems	Can use variety of feed systems
Glass Composition	Minimal impact, as melter has no refractory in contact with glass. Electrode corrosion and glass tap are only concerns.	Minimal impact, as melter has no refractory in contact with glass. Glass tap corrosion is only concern.	Minimal impact, as melter has no refractory in contact with glass. Glass tap corrosion is only concern.
Incorporate Semi Volatiles	Unknown	Unknown	Unknown
Waste Loading	Unknown	Unknown	Unknown

Design and Operating Criteria	VE-SKULL™ Vertical Electrode-Skull Lined	Low Frequency Induction Heated Melter	INDUCTO-SKULL™ Induction-Heated High Frequency Cold Wall Melter
Glass Homogeneity	Can achieve long residence times at high throughput due to large scale up range, good thermal gradient mixing around vertical electrodes	Convective currents due to thermal gradients	Strong convective currents due to induction field
Salt Phase Separation	Unknown	Unknown	Unknown
Metal Rich-Highly Conductive Bottom Layer	No impact, bottom drain eliminates buildup of metal rich (Ru) glass strata	No impact, bottom drain eliminates buildup of metal rich (Ru) glass strata	No impact, bottom drain eliminates buildup of metal rich (Ru) glass strata
Glass Residence Time	Best, long residence times possible at high throughput due to ease of fabrication of large melter	Good scale up capability	Good scale up capability
Optimum Residence Time	Unknown	Unknown	Unknown
Minimum Residence Time	Unknown	Unknown	Unknown
Unpredictable Segregation of Glass Components	Unknown	Unknown	Unknown

Design and Operating Criteria	VE-SKULL™ Vertical Electrode-Skull Lined	Low Frequency Induction Heated Melter	INDUCTO-SKULL™ Induction-Heated High Frequency Cold Wall Melter
Demonstrated Scale of Operation	Vertical electrode and power supplies have been proven in single unit operation to over 100 TPD - commercially and in test programs (Roger Ek & Associates and Geo-Safe). Cold-wall melter housing has not yet been demonstrated. Testing should begin on 2 TPD VE-SKULL™ in January, 1995 as part of WHC High Sodium Waste Vitrification Demonstration	Not commercially demonstrated.	Moderate size 0.5 - 1.0 TPD Glass units tested by French (Cogema) and Russians (Radon)
Availability of Data	Vertical Electrodes and <u>Power Supplies,</u> Data available from: Roger Ek & Associates, Geo-Safe, Battelle, Corning <u>Cold-Wall Housing:</u> Ansys and Tempest code design analyses are available on commercial scale (2 TPD) melter	Design information will be available in late September, 1994.	VECTRA detailed design information and analysis are currently available. Testing data is available from others - French and Russians. First Inducto-Skull™, melter will be operational in January, 1995 with operational data available by March, 1995.

Design and Operating Criteria	VE-SKULL™ Vertical Electrode-Skull Lined	Low Frequency Induction Heated Melter	INDUCTO-SKULL™ Induction-Heated High Frequency Cold Wall Melter
Remote Maintenance Features	VECTRA has designed melter to fit into Modular EnviroGlass™ System. Remote maintenance, shielding and support hardware and systems are being developed at this time for handling glass with contact dose levels of 2,000 to 5,000 REM/hr	VECTRA has designed melter to fit into Modular EnviroGlass™ System. Remote maintenance, shielding and support hardware and systems are being developed at this time for handling glass with contact dose levels of 2,000 to 5,000 REM/hr	VECTRA has designed melter to fit into Modular EnviroGlass™ System. Remote maintenance, shielding and support hardware and systems are being developed at this time for handling glass with contact dose levels of 2,000 to 5,000 REM/hr
Development Required	VECTRA test program can be extended to provide substantial information by mid-1995. One step scale up will be required to process up to 20 TPD glass	Fabrication of test melter is required. Test program can be extended to provide substantial information by mid-1995. One step scale up will be required to process up to 20 TPD glass	Crucible is ready to be fabricated and test program performed to provide substantial information by Feb.-1995. One step scale up will be required to process up to 5 TPD glass and a second scale up for 20 TPD

Design and Operating Criteria	**VE-SKULL™** **Vertical Electrode-Skull Lined**	**Low Frequency Induction Heated Melter**	**INDUCTO-SKULL™** **Induction-Heated High Frequency Cold Wall Melter**
Processing Rate (Calculated)	**Single Unit Expected Diameter and Melter Operating Weight**	**Single Unit Expected Diameter and Melter Operating Weight**	**Single Unit Expected Diameter and Melter Operating Weight**
Dry Calcined Feed (75 lb solids/hr per ft^2 glass)			
• 5 TPD Glass	5'-0" ID 27,000 lbs	5'-0" ID 27,000 lbs	3'-0" ID 12,300 lbs
• 10 TPD Glass	6'-6" ID 49,000 lbs	6'-6" ID 49,000 lbs	4'-0" ID 22,000 lbs
• 20 TPD Glass	8'-0" ID 84,000 lbs	8'-0" ID 84,000 lbs (maximum diameter)	6'-10" ID 65,000 lbs
Slurry Feed (20 lb solids/hr per ft^2 glass)			
• 5 TPD Glass	8'-0" ID 84,000 lbs	8'-0" ID 84,000 lbs	6'-0" ID 58,000 lbs
• 10 TPD Glass	10'-0" ID 119,000 lbs	5 TPD Limit 2 melters required	8'-0" ID 82,000 lbs (maximum diameter)
• 20 TPD Glass	13'-0" ID 178,000 lbs	5 TPD Limit 4 melters required	10 TPD Limit 2 melters required
New Inventions Required	No	No	No

Design and Operating Criteria	VE-SKULL™ Vertical Electrode-Skull Lined	Low Frequency Induction Heated Melter	INDUCTO-SKULL™ Induction-Heated High Frequency Cold Wall Melter
Test Facilities Required	Yes	Yes	Yes
Feed Preparation Requirements	Unknown, calculations required	Unknown, calculations required	Unknown, calculations required
Off-gas System Requirements	Unknown, calculations required	Unknown, calculations required	Unknown, calculations required
Minimum Number of Melter Trains:			
• Slurry Feed (20 TPD Glass)	One	Four	Two
• Dry Calcined Feed (20 TPD Glass)	One	One	One
Plant Service Requirement			
• Electrical	Calculations Required	Calculations Required	Calculations Required
• Off Gas	Calculations Required	Calculations Required	Calculations Required