Feed Process Studies - Research-Scale Melter

K. F. Whittington
D. K. Seiler
J. Luey
J. D. Vienna
W. A. Sliger

OCT 30 1996
OSTI

September 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
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Summary

The U. S. Department of Energy (DOE) Richland Operations Office has initiated a two-phased approach to privatizing the processing of hazardous and radioactive waste at Hanford. In support of this effort, Pacific Northwest National Laboratories (PNNL) was directed to conduct Research-Scale Melter (RSM) experiments to determine feed processing characteristics of two potential privatization Phase 1 high-level waste (HLW) glass formulations and to determine if increased amounts of silver, tellurium, and noble metals would have adverse effects on waste processing.

Feed processing characteristics were evaluated by examining the effects of feed compositions and process conditions on processing rate, cold cap behavior, off-gas characteristics, and glass properties. Two glass formulations developed by PNNL were used for the study: 1) NOM-2 was formulated so that the adjusted waste loading (defined as the waste loading of all components except silica and soda) was 25 wt % and 2) NOM-3 was a maximum waste loaded glass that had an adjusted waste loading of 30 wt %. The 25 wt % adjusted waste loading is the minimum requirement in the privatization Request For Proposal (RFP).

The RSM operated for 19 days divided into five run segments. A total of 1010 kg of feed was processed, producing 362 kg of glass. Test segment 1 provided a shakedown test and confirmed operations of the melter and feed systems. Test segments 2 and 3 established nominal conditions to provide a baseline for NOM-2 and NOM-3 respectively. Portions of test segment 2 and 3 were run at 10 to 30°C above the nominal temperature of 1150°C. Processing rates were significantly increased with the effect most pronounced in test segment 3.

Processing observations lead to the choice of NOM-3 for noble metal testing in segments 4 and 5. During noble metal testing, processing rates fell 50% from the baseline rates measured in segment 3. After completion of the noble metal test segments, destructive analysis of the melter showed that a layer of noble metals and noble metal oxides settled on the floor of the melter. This layer lead to current "channeling" which allowed the top section of the melter to cool reducing production rates.

Acknowledgments

The following Pacific Northwest National Laboratory staff contributed to the successful completion of the research-scale melter testing.

- Project Guidance/Review
 - Mike Elliott, technical guidance
 - Langdon Holton, project manager
- Test Conduction
 - Jim Davis, Janelle Demiter, Bill Buchmiller, and Pat Lowery for their support in operating the melter during all hours of the day and night.
 - Chuck Hymas and Mike Powell for the collection of off-gas samples and on-line off-gas analysis.
- Analytical Support
 - Bob Barbera and Meiling Gong sample preparation and analysis using inductively coupled plasma-atomic emission spectrometer (ICP-AES) and ion chromatography (IC); Karl Pool for ICP-AES model IRIS/AP and Eric Wyse for inductively coupled plasma-mass spectrometer (ICP-MS) support.
 - Jim Young for scanning electron microscopy (SEM) support.
 - Janelle Demiter for SEM sample preparation.
 - Dave McCready for x-ray diffraction support.
- Data Reduction
 - Janelle Demiter for file conversion and data reduction support.

Abbreviations and Acronyms

AA	Atomic Adsorption Spectroscopy
DACS	Data Acquisition and Control System
DOE	U.S. Department of Energy
DWPF	Defense Waste Processing Facility
EA	Environmental Assessment
EDL	Engineering Development Laboratory
EDX	Energy Dispersive X-ray
FY	Fiscal Year
HEME	High Efficiency Mist Eliminator
HEPA	High Efficiency Particulate Air
HLW	High-Level Waste
ICP	Inductively Coupled Plasma Spectroscopy
LAW	Low-Activity Waste
MPA	Melter Performance Assessment
NOM-2	Pacific Northwest National Laboratory glass designation
NOM-3	Pacific Northwest National Laboratory glass designation
PCT	Product Consistency Test
PHTD	PNNL HWVP Technology Development
PNNL	Pacific Northwest National Laboratory
RFP	Request for Proposal
RSM	Research-Scale Melter
SCR	Silicon Controlled Rectifier
SEM	Scanning Electron Microscopy
TWRS	Tank Waste Remediation System
WHC	Westinghouse Hanford Company
XRD	X-ray Diffraction

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1.0 Introduction

1.1 Background

The U.S. Department of Energy (DOE) determined that it is feasible to privatize portions of the Hanford Tank Waste Remediation System (TWRS) and issued a Request for Proposal (RFP) in February 1996. Plans call for privatizing the tank waste pretreatment and low-activity waste (LAW) vitrification functions with an option to treat high-level waste (HLW) with a phased approach. Phase 1 privatization will demonstrate that a viable private market exists for tank waste remediation and will also demonstrate processing of various Hanford tank wastes at a production scale. The Phase I plants will be about 1/5th scale of the current TWRS baseline.

1.2 Needs/Issues

In support of the privatization effort and to minimize risk to DOE, Pacific Northwest National Laboratories (PNNL) performed a number of studies on the Phase 1 privatization HLW stream. Studies at PNNL include: development of HLW glass compositions, determination of waste slurry properties, characterization of process chemistry and evaluation of melter feed processing behavior. This report documents vitrification studies to assess melter feed's processing behavior and determine if RFP Phase 1 privatization requirements are achievable.

Recent analyses of Phase 1 feed compositions show that the silver and noble metals concentrations are likely to be higher than the concentrations measured in the initial samples. Silver is known to alloy with noble metals and precipitate from the glass melt during processing (Cooper et al. 1994). The effects of increased amounts of silver and the possibility that increased silver concentrations could enhance precipitation of noble metals is a concern. Since many of the noble metal oxides and alloys are conductive, settling of these particles in the glass tank could lead to electrical shorting in a joule-heated melter. The noble metal accumulation would need to be removed or the glass tank replaced.

Pacific Northwest National Laboratories was directed to conduct Research-Scale Melter (RSM) experiments to determine feed processing characteristics of proposed Phase 1 glass formulations and to determine if the increased amounts of silver, tellurium and noble metals would have adverse effects on processing¹.

¹Washenfelter, D.J., letter # 9556446 to G.H. Beeman dated December 8, 1995, "Pacific Northwest National Laboratory Letter of Instructions for FY 1996 Tank Waste Remediation System High-Level Waste Addback Program Activities."

Feed processing characteristics were evaluated by examining the effects of feed compositions and process conditions on processing rate, cold cap behavior, off-gas characteristics, and glass properties for several glass compositions developed for the nominal Phase 1 HLW feed.

Relevant slurry and process variables were varied through the ranges of the RSM operating limits. The following variables were investigated:

- waste oxide loading in the glass
- glass process temperature
- noble metal concentrations in the feed.

Process data was used to determine the influence on melter operations of the different variables. To determine the effects on product quality and on secondary waste streams, analytical data were obtained for slurry, glass, and off-gas samples. In addition, post-test destructive examination of the melter was completed and melter glass/sediment samples collected and analyzed.

1.3 Test Objectives

The primary objectives of the fiscal year (FY) 1996 RSM feed processing studies were to evaluate the effects of feed compositions and process conditions on processing rate, cold cap behavior, off-gas characteristics, and glass properties for two glass compositions formulated for the nominal Phase 1 HLW feed. After establishing the reference melter conditions for each glass compositions, the test objectives were met by performance of five test segments implementing the following melter operating conditions and/or parameter measurements.

Evaluate the effects of temperature on melter performance by increasing the melter operating temperature up to 50°C above the nominal glass melting temperature.

The effects of temperature on processing rate, melter performance characteristics, glass quality and off-gas composition were investigated. After achieving a steady state temperature and operating conditions, the temperature of the melter was increased up to 50°C above the nominal operating temperature. The feed rate was adjusted to maintain steady state operations (i.e., 95% cold cap coverage). The maximum processing rate was obtained from this data. Off-gas composition and generation rate were monitored at a location between the RSM and the primary off-gas scrubber. To evaluate the quality of the produced glass, samples were subjected to glass characterization testing and compared to those produced at lower temperatures.

Assess the effect of processing maximum waste loaded glasses on melter performance.

The processing characteristics of a maximum (48 wt %) waste loaded glass were compared to a nominal (40 wt %) waste loaded glass with respect to spinel formation, melter operations, and glass pouring characteristics. Grab samples of the glass product were obtained of the product glass and were analyzed for spinel content. Samples of the glass on the bottom of the melter were obtained during post-test destructive analysis and also analyzed for spinel content and other separable phases.

Assess the effect of increased amounts of silver and noble metals in the Phase 1 feed composition on melter operations.

Recent analyses of Phase 1 feed compositions show that the silver and noble metals concentrations are likely to be higher than initially indicated. Silver is known to alloy with noble metals and precipitate from the glass melt during processing. The possibility that increased silver concentrations could enhance precipitation of noble metals is a concern and was evaluated during the RSM test segments 4 and 5.

Compare the results obtained in the RSM testing with previous PNNL RSM process tests.

The results obtained in the FY 1996 RSM testing were compared to the FY 1992 RSM testing in which noble metal testing was also performed at similar concentrations.

1.4 Test Matrix

The test matrix shown in Table 1.1 was used to examine the proposed privatization Phase 1 melter feed processing behavior. The two glass formulations investigated were developed by PNNL². The first glass composition was formulated so that the adjusted waste loading (defined as the waste loading of all components except silica and soda) was 25 wt %. This is the minimum waste loading requirement in the privatization RFP. The actual waste loading of this glass including silica and soda was 40 wt % on an oxide basis. This glass is referred to as the NOM-2 glass composition. The second glass formulation or NOM-3 had an adjusted waste loading of 30 wt % and an actual waste loading of 48 wt %.

Test segment 1 provided shakedown testing and confirmed operations of the melter and feed systems. Test segments 2 and 3 established baseline conditions for the NOM-2 and NOM-3 glass formulations respectively. Test segments 2 and 3 also had elevated

² Vienna, J.D., M.J. Schweiger, D.E. Smith, H. Li, and P. Hrma. 1996. DRAFT: Phase I Privatization High-Level Waste Glass Data Support Interim Data Package, Pacific Northwest National Laboratory, Richland, Washington.

temperature portions to analyze the effect of temperature excursions on processing rate, off-gas composition and glass quality.

Based on operational data obtained after test segment 3, the NOM-3 glass formulation was selected for the silver/tellurium/noble metal investigation conducted during test segments 4 and 5.

During test segment 4 and 5, noble metals were added to the feed to evaluate the effect on processing and product quality of higher silver and noble metals concentrations. Since many of the noble metal oxides and alloys are conductive, settling of these particles in the glass tank could lead to electrical shorting of the electrodes if corrective actions are not taken.

Table 1.1. RSM Test Matrix

Test Segment	Waste/glass type	Glass Temperature	Operational Parameter
1	Nominal waste loading 40 wt % (NOM-2)	1150°C	Shakedown testing of equipment
2	Nominal waste loading 40 wt % (NOM-2)	<1200°C	Slurry feed - nominal conditions
3	Maximum waste loading 48 wt % (NOM-3)	<1200°C	Slurry feed - nominal conditions
4	Maximum waste loading 48 wt % (NOM-3)	1150°C	Silver and noble metals
5	Maximum waste loading 48 wt % (NOM-3)	1150°C	Silver and noble metals

2.0 Conclusions and Recommendations

The RSM feed processing studies on Phase 1 HLW simulant was completed in September of 1996. Analysis and evaluation of the data provided the following conclusions (Section 2.1) and recommendations (Section 2.2).

2.1 Conclusions

- Processing the NOM-2 glass formulation was more difficult than processing the NOM-3 glass formulation. Operational difficulties were encountered in processing the 40 wt % waste loaded glass, NOM-2. The conductivity of the glass formulation caused over-current conditions, shutting down the system. Excessive feed nozzle plugging and cold cap mounding were frequent occurrences during processing. The 48 wt % waste loaded glass, NOM-3, processed with fewer difficulties. The slurried waste spread out over the molten surface and feed nozzle plugs were infrequent.
- Spinel crystals were not found by x-ray diffraction (XRD) in glass samples taken from the melter pour stream in NOM-2 or NOM-3 test segments. X-ray diffraction analysis of melter bottom sludge samples indicated the presence of very small amounts (<0.8 vol %) of spinel-type crystals composed primarily of copper, magnesium, and manganese oxide. Since melter sludge samples were not taken after the NOM-2 test segment, it is not known when the spinel crystals formed.
- Elevated processing temperatures increased the processing rate of the NOM-3 glass but had no significant effect on the NOM-2 production rate. An increase in the NOM-3 glass production rate of more than 10% was realized for a processing temperature increase from 1150°C to 1160°C. The NOM-3 glass production rate was over 30% higher for a temperature increase from 1150°C to 1170°C. The elevated processing temperatures had no significant effect on the NOM-2 and NOM-3 glass quality and off-gas composition.
- A layer of noble metals and noble metal oxides settled between the electrodes. This lead to a drop in the system resistance from 0.4 Ω to less than 0.2 Ω . This layer lead to current "channeling" which allowed the top section of the melter to cool while the 1150°C temperature was maintained by localized heating. The overall cooling of the melt reduced glass production rates in the final run segment to 50 % of the production rate observed for the baseline NOM-3 glass processed in test segment 3.
- The design of the RSM contributed to its inability to process noble metal spiked feed for an extended length of time. The RSM has a small melt pool 15 cm in

diameter with the electrodes placed directly on the K-3 crucible floor. As conductive species accumulate in the RSM, a region of enhanced conductivity is formed on the floor in the limited space between the electrodes. Since the RSM utilizes an overflow as the method of glass removal, the conductive layer builds undisturbed until the melter electrically shorts.

2.2 Recommendations

- Wastes containing noble metal species should be processed in a melter equipped with a bottom drain or similar mechanism to prevent the accumulation of these species in the melter.

3.0 Equipment and Operations

This section describes PNNL's Research Scale Melter system (RSM). The RSM system consists of a joule-heated melter surrounded by a firebrick kiln, feed system, off-gas equipment, and glass discharge system. A system diagram is shown in Figure 3.1. The equipment was originally designed to determine the impact of noble metals on the operational life of the reference HWVP melter in FY 1992 (Cooper et al. 1994). In FY 1996, the RSM was reassembled to evaluate the processing characteristics of proposed Phase 1 privatization HLW glass compositions.

A detailed drawing of the RSM is provided in Figure 3.2 and a list of features and important dimensions is supplied in Table 3.1. The RSM consisted of a 26 cm (10-1/4 in.) outside diameter x 44.45 cm (17-1/2 in.) high Inconel 601 shell, lined with ceramic paper and Alfrax 66. A crucible of K-3 provided a melt cavity that measures 15.24 cm (6 in.) in diameter. The operating glass height of the RSM was nominally 7.6 cm (3 in.) resulting in a glass volume of 1.4 L. The maximum operating temperature was approximately 1200°C with a nominal operating temperature of 1150°C. Additional external heating to overcome heat losses to the surroundings was provided by a kiln operated at a nominal temperature of 900°C.

Table 3.1. RSM Dimensions and Operational Features

Melt Cavity Diameter	15.24 cm (6 in.)
Glass Pool Surface Area	182 cm ² (28.3 in. ²)
Nominal Glass Height	7.6 cm (3 in.)
Glass Volume	1.39 Liters
Glass Weight	3.6 kg
Maximum Operating Temperature	1200°C
Nominal Operating Temperature	1150°C
Electrode Paddle Dimensions	7.6 cm x 7.6 cm (3 in. x 3 in.)
Current Limit for Electrode Paddles	120 Amps

The melter lid was equipped with a quartz covered viewport. The viewport allowed for visual observations of the melt surface and cold cap region. The viewport location is shown in Figure 3.3, which details the RSM lid.

Power to the RSM was provided by two, top-entering paddle electrodes. The electrode paddles were made from 0.64 cm (1/4-in.) Inconel 690 plate. The face of the electrode paddles measured 7.6 cm x 7.6 cm (3-in. x 3-in.) and extended to the bottom of the melter through the melter lid. Half of an Inconel tube was welded to the backside of each electrode providing a thermowell for a type K thermocouple in an inconel sheath. The thermowell was attached to the backside of the electrode to prevent upsets in the

processing behavior of a melter. Alfrax 66 was used to stabilize the electrodes in the melter lid and electrically isolate the electrodes from the melter shell. A detailed drawing of the RSM electrodes is provided in Figure 3.4.

During RSM operations a vacuum of 5.0 to 6.4 cm (2.0 to 2.5 in.) water column was maintained on the melter. This range was established during run segment 1 and is discussed in section 5.0. A 5.0 cm (2 in.) stainless steel pipe served as the off-gas line. A film cooler injected air along the walls of the first few inches of off-gas pipe to cool the off-gas and to discourage particles from adhering to the wall of the off-gas pipe. The off-gas was routed through a venturi scrubber where the off-gas was cooled and condensables removed. The scrubber solution pressure at the venturi nozzle was maintained at approximately 410 kPa (60 psi). The scrub solution loop was equipped with a heat exchanger, sample port, and solution transfer line. From the scrubber, the off-gas passed through a High Efficiency Mist Eliminator (HEME) to remove condensed phase aerosols. The off-gas was finally exhausted through the building ventilation system via the auxiliary off-gas blower. Collection of off-gas data was accommodated by sample ports located between the film cooler and the venturi scrubber. Type K thermocouples located at various locations throughout the off-gas and scrub lines provided temperature monitoring. Figure 3.5 provides a flow diagram of the off-gas, scrub system, and cooling water.

An Inconel discharge pipe out the side of the melter provided a gravity-controlled overflow for glass removal from the RSM. The discharge tube was surrounded by a clamshell heater to prevent glass from freezing before discharging. This heater was toggled on and off based on the temperature of the discharge area. Discharged glass was collected in a 4-liter stainless steel canister. A Pyrex pipe allowed for viewing of the glass discharge stream as it flowed from the discharge pipe to the discharge canister. The glass discharge canister was heated by a clamshell heater surrounding the canister and kept at approximately 700°C. This allowed the glass to slump into the canister before solidifying. The canister and clamshell were located on a platform scale for weighing the discharged glass.

The melter feed container, pictured in Figures 3.1 and 3.5, was located on the second floor above the RSM. The container rested on a platform scale which measured the mass of feed material. Slurry agitation was maintained with two variable speed agitators. A peristaltic pump located next to the feed container was used to motivate and regulate the feed rate to the melter. The feed slurry traveled from the pump through tubing to the feed nozzle.

A 0-340 kPa (0-50 psi) pressure transducer was located in the feed line and used to detect feed nozzle plugs. Feed line and nozzle plugs are a common occurrence during a RSM run because of the relatively low feed rates. Therefore, the feed line included a series of valves which allowed for water flushing of both the feed line and the nozzle. The feed nozzle was also equipped with a port for more aggressive means of line obstruction removal if the water flush system proved inadequate. Water cooling was used to prevent

drying of the feed slurry while still in the nozzle. The feed nozzle extended into the RSM plenum space where it discharged the feed at an approximate height of 11.43 cm (4.5 inches) above the melt surface. Figures 3.1 and 3.5 show a flow diagram of the feed system.

Operation of nearly all melter functions was under the control of a computer Data Acquisition and Control System (DACS). The voltage supplied to the electrodes, kiln, and discharge clamshell were controlled by silicon controlled rectifiers (SCRs). The SCRs controlled the voltage going to the load and are capable of adjusting it anywhere from zero to full line voltage based on a 4-20 mA signal supplied by the DACS.

The DACS had an automatic and manual modes of operation. In the automatic mode of operation the DACS compared the operational set point chosen by operating personnel with the actual temperature of the component. Any resulting difference results in a change to the SCR control signal. The manual mode of operation eliminated the temperature feedback. Control was based on an operator entered mA value that was sent to the SCR. The DACS maintained a discharge tube temperature by toggling the supply power to the discharge clamshell with the aid of a relay. The control of the peristaltic feed pump was also maintained by the DACS. Operating personnel adjusted the feed rate based on plenum temperature and cold-cap observations by entering a 4-20 mA value that the DACS sent to the peristaltic pump control box.

The DACS continually compared operating data to a set of alarm conditions specified by operating personnel. When an alarm condition was detected, the DACS performed the specified events for that alarm condition. For example, a high electrode current alarm triggered the following events; control set to manual mode, SCR output set to 4 mA (zero power), feed pump output set to 4 mA (off), the alarm set on, and a message was printed for operating personnel alerting them of the alarm condition. By turning the alarm on, the DACS activated an autodialer that dialed the phone number of a pager carried by the on-duty engineer or technician, alerting him/her that attention was required.

Figure 3.1. RSM System Layout

Scale: 2.54 cm = 7.62 cm (1 in. = 3 in.)

Figure 3.2. RSM Cross Section

Scale: 2.54 cm = 7.62 cm (1 in. = 3 in.)

Figure 3.3. RSM Top View and Lid Details

Scale: 2.54 cm = 7.62 cm (1 in. = 3 in.)

Figure 3.4. RSM Electrode Paddle

Figure 3.5. RSM Service Pipe Diagram

4.0 Feed Preparation

The Phase 1 simulant procedure was obtained from TWRS FY 1996 Activity H22A51³. This procedure described a method for preparing a waste simulant which represents the blended wastes from tanks AZ101, AZ102, C106, and AY102 that have been through water washing. The baseline feed composition used for this study was provided by WHC through the WHC letter 9650440, "Revised Estimates of Pretreated HLW Sludge Composition for Incorporation in Pacific Northwest National Laboratories Feed Process Studies," written to M. L. Elliott from D. J. Washenfelter on January 29, 1996.

The waste simulant preparation procedure is similar to the "all-blend" procedure (Tracy et al. 1995). The procedure tries to mimic the history of the actual tank waste. A stock simulant is prepared by first coprecipitating a hydroxide slurry from a nitrate/nitric acid solution containing major waste oxide elements (Fe, Ni, Nd, Zr, and Mn). The excess nitrate and sodium are removed from the major hydroxide slurry by washing with a basic nitrite solution. The soluble/slightly soluble salts (halides, hydroxides, nitrates, nitrites, sulfates, borates, phosphates, oxides, and oxalates) are then added to the slurry. Two other slurries are added to the mixture: 1) minor components as an insoluble compound slurry (oxides, fluorides) and 2) a mineral slurry to simulate the effects of aging on tank solids (formation of boehmite and cancrinite). A coprecipitated noble metal slurry was added separately to the waste simulant used in two of the five test segments. The noble metal slurry contained ruthenium, palladium, tellurium, and silver but did not contain rhodium. The decision to eliminate rhodium from the waste was based on the high cost of the material and the minimal impact associated with not including rhodium.

PNNL issued a purchase requisition to Optima Chemicals directing them to prepare 300 kg of waste oxide with a target waste loading of 100 g oxide/liter. Hold points were identified at various steps in the simulant preparation for PNNL to verify the composition of the simulated waste. Repeated analyses showed that Optima lost a portion of the components in the major and minor hydroxide slurry in the centrifuge/wash process. Optima ordered the shim chemicals and shipped the chemicals and slurry to PNNL "as is." PNNL personnel added shim chemicals to adjust the component levels to an acceptable range. The shimmed waste simulant was analyzed by with inductively-coupled plasma (ICP) - atomic emission spectroscopy (AES). A comparison of the results of the final analysis to the target composition is shown in Table 4.1. Note that the analyzed composition differs slightly from the target but the major oxides are within the 10 wt % requirement of the simulant preparation procedure.

³Smith, H.D. and R.L. Russell. 1996. DRAFT: Simulant Specification for the Blended Privatization Tank Waste for the HLW Vitrification Process Specified in the RFP, Pacific Northwest National Laboratory, Richland, Washington.

Table 4.1. Phase 1 Waste Simulant Analysis Results

Oxide	Target Oxide wt %	Analyzed* Oxide wt %
Ag ₂ O	0.06	0.02
Ag ₂ O***	0.56	0.19
Al ₂ O ₃	17.87	18.16
B ₂ O ₃	0.14	0.47
BaO	0.61	0.31
Bi ₂ O ₃	0.06	0.14
CaO	2.00	2.16
CdO	1.29	1.22
CeO ₂	0.12	0.09
Cr ₂ O ₃	0.33	0.12
CuO	0.07	0.08
Fe ₂ O ₃	24.63	26.09
K ₂ O	0.43	1.20
La ₂ O ₃	0.51	0.26
MgO	1.19	1.16
MnO	0.77	0.80
MoO ₃	0.01	0.02
Na ₂ O	23.82	22.19
Nd ₂ O ₃	1.02	0.89
NiO	1.03	0.73
P ₂ O ₅	1.04	1.41
PbO	0.34	0.15
PdO***	0.10	0.08
ReO ₂	0.57	**
RuO ₂ ***	0.35	0.33
SO ₃	0.47	0.69
SiO ₂	16.12	17.65
SrO	0.08	0.10
TeO ₂	0.14	0.07
TeO ₂ ***	0.20	0.13
TiO ₂	0.06	0.10
ZnO	0.04	0.06
ZrO ₂	3.91	3.66
Total	98.72	100.00

* normalized

** not analyzed

*** segments 4 and 5

The shimmed slurry was partially concentrated in a 500 gallon tank to 230 g oxide/liter. For each test segment, batches of simulated waste were transferred to a 55 gallon drum for additional feed makeup. Enough melter feed was prepared at one time to complete one test segment. The insulated 55 gallon drum rested on a drum heater so that the slurry could be further concentrated to 300-330 g oxide/liter. The rheology of the mixture made it necessary to add nitric acid (the mixture was quite thick and would not agitate or pump). Nitric acid was added until the pH of the mixture was below 7 and until the

slurry thinned and began to flow. Next, the appropriate chemical additions specified for the test segment were made to the slurry. The mixture was allowed to agitate for the next 48 hours while a sample was dried, fired, and analyzed to verify composition. The oxide concentration was adjusted at the beginning of each test segment to the reference value of ~500 g oxide/liter by adding deionized water.

5.0 Vitrification Process Results

Research-Scale Melter testing consisted of 19 days of melter operations, divided into five run segments. The test was divided into five segments for the purpose of evaluating two different glass formulations and the effect of noble metals on the melter operations. Test segment 1 provided a shakedown test and confirmed operations of the melter and feed systems. During test segments 2 and 3, nominal conditions were established to provide a baseline for the two glass formulations that were tested. During test segment 4 and 5, noble metals were added to the selected glass formulation to evaluate the effect on processing and product quality of higher silver and noble metals concentrations. An operational summary of the run segments is located in Table 5.1.

Table 5.1. RSM Run Segment Operational Summary

Test Segment Number	Start Date	Start Time	End Date	End Time	Duration (hours)	Glass Temp. (°C)	Noble Metals
1	6/11/96	13:26	6/14/96	9:48	68.4	1150	No
2	6/17/96	9:20	6/20/96	20:34	83.2	****	No
2a	6/17/96	9:20	6/19/96	9:20	48.0	1150	No
2b	6/19/96	9:20	6/20/96	15:32	30.2	1165	No
3	6/24/96	21:08	6/28/96	15:16	90.1	****	No
3a	6/24/96	21:08	6/27/96	22:00	72.8	1150	No
3b	6/27/96	22:00	6/28/96	7:32	9.6	1160	No
3c	6/28/96	7:32	6/28/96	15:16	7.7	1170	No
4	7/22/96	8:12	7/26/96	21:00	108.8	1150	Yes
5	7/29/96	8:25	8/2/96	17:12	104.8	1150	Yes
Test Segment Number	Glass Produced (kg)	Glass Pour Rate (kg/hr)	Waste Prod. Rate (kg/hr)	Oxide Loading (g/L)	Feed Weight (kg)	Feed Rate (kg/hr)	Feed Rate (L/hr)
1	56	0.8	0.3	610	160	2.3	1.5
2	89	1.1	0.4	570	230	2.7	1.9
2a	52	1.1	0.4	570	140	2.9	1.9
2b	33	1.1	0.4	570	85	2.8	1.9
3	84	0.9	0.5	490	240	2.7	1.9
3a	64	0.9	0.4	490	190	2.6	1.8
3b	9.8	1.0	0.5	500	26	2.7	1.9
3c	9.4	1.2	0.6	500	22	2.8	2.0
4	85	0.8	0.4	530	230	2.1	1.5
5	48	0.5	0.2	490	150	1.4	1.0

After reviewing previous testing in the RSM (Cooper et al. 1994), it was apparent that the long interruptions in feed processing (on-line efficiency <80%) were due to the lack of continuous operator support. For this study, three shifts of two operators tended the equipment continuously during each segment. The continuous operator support improved on-line efficiency to nearly 100%, increasing the amount of time the system was at a steady state. The operating theory maintained during each run segment was to establish a constant feed rate that would generate and maintain a cold cap covering 85 to 95% of the melt surface.

Two forms of operational data were collected during each segment, electronic and manual. The DACS recorded operational data at specified intervals based on the level of the data points importance to post test reporting. Feed rate, glass pouring, and cold cap observations were collected manually by operating personnel each hour. Data plots that illustrate trends or variations in operating parameters are included in Appendix A. The kiln and the discharge canister heater were maintained at the operating levels stated in the equipment description Section 3.0 unless otherwise noted in the run descriptions later in this section.

5.1. Test Segment 1

Test segment 1 provided shakedown testing and operator hands on training of the RSM system. The operation of the DACS, feed system, off-gas scrubbing, glass pouring, and sample collection were practiced and optimized. DACS alarm setpoints and events were verified or determined for each of the key operating parameters. Most importantly, the required plenum vacuum was determined. An inadequate melter vacuum caused the loss of off-gas containment, while an excess of vacuum resulted in excessive heat loss and suction of external air through the discharge tube. The optimal range for the melter vacuum was found to be between 2.0 and 2.5 inches of water. Low and high plenum temperature alarms were established to aid operators detection of changes in the cold cap layer. A total of 160 kg of feed (NOM-2 glass formulation) was fed over 68.4 hours and processed at a average glass temperature of 1150°C. The average feed rate during the segment was 1.5 L/hr, while the average glass production rate was 0.8 kg/hr. The average oxide loading of the feed material in this segment was 610 g oxide/L. At the completion of this segment, the operational data was extracted from the DACS to verify ease of data manipulation and completeness.

5.2. Test Segment 2

The duration of test segment 2 was 83.2 hours, during which a total of 230 kg of feed (NOM-2 glass formulation) was processed at a range of temperatures. The average feed rate during the segment was 1.9 L/hr with an average oxide loading of 570 g oxide/L. A

total of 89 kg of glass were produced for an average glass production rate of 1.1 kg/hr. Two glass temperatures (referred to as 2a and 2b) were evaluated during this test segment. The change in glass processing temperatures are depicted in Figure 5.1. Operation data for test segments 2a and 2b is located in Table 5.1. It is important to note that the transition period between changes in the processing temperature, as well as, the data following the return to 1150°C (at an approximate run time of 79 hours) are not included in the run segment summary for 2a and 2b. However, this data is included in the overall values reported for segment 2. Electrode current limits were exceeded when temperatures above 1165°C were attempted. Test segments 2a and 2b both had an average feed rate of 1.9 L/hr. The oxide loading of the feed in segments 2a and 2b was 570 g oxide/L yielding a glass production rate of 1.1 kg/hr for both temperature segments. During segment 2, off-gas composition data was collected. A discussion of the off-gas data is located in section 7.0.

5.3. Test Segment 3

Test segment 3 processed 240 kg of feed (NOM-3 glass formulation) during 90.1 hours of operation. The average feed rate during the segment was 1.9 L/hr with an average oxide loading of 490 g oxide/L. A total of 84 kg of glass were produced for an average glass production rate of 0.9 kg/hr. During segment 3, off-gas composition data was collected. A discussion of the off-gas data is located in section 7.0. During segment 3 glass temperatures were varied to determine temperature effects on processing. Figure 5.2 depicts the changes in the processing temperatures, while Table 5.1 provides a summary for each of the processing temperatures. Run segments 3a, 3b, and 3c were operated at temperatures of 1150°C, 1160°C and 1170°C, respectively. Segment 3a was the majority of the total segment run time operating for 72.8 hours, while segments 3b and 3c operated for 9.6 and 7.7 hours, respectively. For each glass temperature set point, the average feed flow rate was increased to maintain the proper cold cap coverage. The combination of increased temperatures with the increase in feed oxide loading resulted in a significant increase in the glass production rate. The glass production rate for 3a, 3b, and 3c were 0.9, 1.0, and 1.2 kg/hr, respectively.

5.4. Test Segment 4

Noble metals were added to the feed (NOM-3 glass formulation) during test segment 4 and 5. For a discussion of the noble metals addition to the feed, see section 4.0. The feeding duration for segment 4 was 108.8 hours with an average feed rate of 1.5 L/hr. During segment 4, glass temperatures were kept constant at a temperature of 1150°C. Off-gas composition data was collected during this segment and is discussed in Section 7.0. A total of 85 kg of glass were produced for an average glass production rate of 0.8 kg/hr. The kiln temperature was increased to 950°C at an approximate run time of 28.4 hours. The kiln remained at this temperature for the remainder of testing, including test segment 5.

5.5. Test Segment 5

For test segment 5, a total of 48 kg of glass were produced in the 104.8 hours of run time resulting in a glass production rate of 0.5 kg/hr. The average feed rate during the segment was 1.0 L/hr with an average oxide loading of 490 g oxide/L. A glass temperature of 1150°C was maintained through the entire segment. Upon completion of this segment, the RSM was quickly cooled in preparation for destructive analysis, which is discussed in section 8.0.

5.6. Test Segment Comparisons

Electrical problems were encountered during test segment 2. The current limit of the electrodes (2 amp/cm²) was exceeded a number of times during the segment causing the DACS to shut down power to the electrodes. Power was restored after a brief inspection of electrical equipment. Upon completion of segment 2, an acceptable current level was maintained during the idling stage before segment 3. Segment 3 experienced no electrical problems as operations proceeded very smoothly. Current limit problems began again towards the end of segment 4. Electrode current limits were not exceeded in segment 5. However, it appears that a downward trend in power supplied to the melt may have prevented electrode current limits from becoming a problem.

A comparison of the average glass production for segment 3a and segment 4 yields greater than a 10% decrease in glass production rate. A decrease in the production rate was noticed immediately upon addition of the noble metal spiked feed. Likewise, the initial glass resistance during the segment was 0.45 ohms and trended downward to 0.2 ohms by the end of testing. This trend is shown in Figure 5.3. Resistance curves (See Appendix A) for the previous run segments showed an oscillating melt resistance with an average that remained constant throughout the segment. Figure 5.4 shows the glass resistance experienced during segment 5, it also trended downward. The power required to maintain a glass temperature of 1150°C also had a downward trend.

Glass pouring was nearly continuous during segments 1, 2, and 3. Occasionally, glass pouring would stop for a length of time allowing glass to be retained in the melter. The retention would result in an increased glass height in the melter. The glass would eventually pour out in a thick slug at a rapid rate. This rapid pouring of glass would heat the discharge section above its normal operational temperature, thus making it even easier to pour. Glass would pour until the glass level inside the melter was below the discharge tube inlet. When the glass level would drop below this level, ambient air would flow through the discharge tube and cool it rapidly.

Glass pouring during segments 4 and 5 was almost never continuous. The pour stream was very thin and intermittent. In fact, it was so thin that collection of glass samples was very difficult. Glass samples were collected by placing a graphite boat in the pour stream between the glass canister section and the melter discharge section. The space provided for sampling was intentionally kept small to minimize heat losses during sample collection. This small space provided a challenge in removing the glass samples. Operators had some difficulty removing the sample because a glass thread would form as the boat was removed from the pour stream. Also, if the glass sample extended above the height of the divot in the graphite boat it would contact the duraboard which held up the discharge clamshell heater. The ability to collect a glass sample depended greatly on the thickness of the pour stream. During segments 1, 2, and 3, a thicker pour stream provided much easier sample collection. A thicker pour stream would retain enough heat to slump in the graphite boat. A thinner glass pour stream was noticed immediately in segment 4. The thinner pour stream would spiral into the boat freezing almost immediately. Towards the end of segment 4 and throughout segment 5, glass sampling was limited to whenever an adequate pour stream was available. During the majority of segment 5, glass pouring was limited to a random drip.

Figure 5.1. Segment 2 Melt Temperature

Figure 5.2. Segment 3 Melt Temperature

Figure 5.3. Segment 4 Melt Resistance

Figure 5.4. Segment 5 Melt Resistance

6.0 Feed and Glass Analysis

Samples of melter feed and glass were taken periodically during the course of the testing and were submitted for compositional analyses and glass characterization. Limited analyses was performed on feed and glass samples obtained in the equipment shake-down testing, test segment 1. At the completion of run segment 5, a cold cap sample was obtained after the melter was cooled with the cold cap intact. The cold cap sample was submitted for microscopy analyses using optical microscopy and scanning electron microscopy (SEM). The analytical techniques used to characterize the feed and glass samples are described in this section. The results of these analyses are presented in the following sections.

Density Determination of Slurry Samples. The density of slurry samples are measured by weighing the sample in a 15 mL capacity centrifuge tube with graduated volume subdivisions of 0.1 mL. After determining the tare weight of the tube, 10 to 15 mL of slurry are pipetted into the tube. The weight and volume of the slurry are determined and the density is calculated.

Determination of Weight Percent Solids. Weight percent total solids or dissolved solids of slurries or liquids are determined by this procedure. By difference, the undissolved solids fraction can be determined. A five to ten gram sample of slurry is weighed into a tared crucible that has been stored in a desiccator. The crucible is then placed in a conventional drying oven for between 12-24 hours. The oven temperature is maintained at approximately 105°C. Once removed from the oven, the crucible is placed in a desiccator until it has cooled to room temperature. The final weight is then determined and the percent solids calculated.

Determination of Total Oxides. Weight percent total oxides is determined in much the same way as percent solids. However, instead of heating the sample to 105°C, it is heated to 1,000°C. A five to ten gram sample of slurry is weighed into a tared crucible that has been stored in a desiccator. The crucible is then placed in a muffle furnace and the temperature is increased slowly to prevent sample loss.

Fusion. A fusion is a compositional analysis preparation step for solid samples that contain high concentrations of silicates and/or refractory compounds that do not completely or readily dissolve in mineral acids. Each sample was split so that one part could be fused using sodium peroxide in a zirconium crucible and one part could be fused using potassium hydroxide in a nickel crucible. The glass samples were crushed to -200 mesh using a mortar and pestle. Approximately 0.25 g of crushed glass was placed in a metal crucible (zirconium or nickel). The glass and oxidant were mixed and then melted using an electric bunsen burner. The resulting mixture was dissolved in demineralized water and diluted up to 100 mL. The solution is then sent for compositional analysis.

Inductively Couple Plasma (ICP) Analysis. ICP is used to determine the concentration of inorganic analytes in aqueous samples and leachates from solids. ICP was used to analyze aqueous scrub solutions and the solutions resulting from fusions. An ICP unit with Atomic Emission Spectrometry (AES) was used for majority of the samples while a unit with Mass Spectrometry (MS) was used for noble metal analysis.

Ion Chromatography (IC) Analysis of Soluble Ions. Ion Chromatography is used to determine the concentration of several anions (i.e., F^- , Cl^- , NO_2^- , NO_3^- , PO_4^{3-} , SO_4^{2-} , HCO_3^- , and $C_2O_4^{2-}$) in aqueous samples and water leachates of solid and slurry samples. To prepare a samples for analysis, approximately one gram of the supernatant fraction is leached in approximately 100 grams of water. The sample is agitated for one hour and then allowed to settle before an aliquot sample is drawn for IC analysis.

Iron II and Total Iron Ratio Analyses of Glasses. Samples of glass are crushed to achieve a particle size of <200 mesh. They are then dissolved in a non-oxidizing condition using a mixture of sulfuric and hydrofluoric acids. Boric acid is later added to complex the phenanthroline forming an orange-red complex. The complex concentration is determined spectrophotometrically at 510 nm. The colored solution obeys Beer's Law and its intensity is independent of pH from 3 to 9. A pH between 2.9 and 3.5 insures the rapid color development in the presence of an excess of phenanthroline. The total iron in the sample is determined by reducing the ferric ion to a ferrous ion with hydroquinone at room temperature using PNNL Technical Procedure APSL-02, Rev. 0, "Iron II and Total Iron Analysis."

Product Consistency Test (PCT) for Glass Durability Analysis. PCT is the primary method to determine the durability of the final glass product. A glass sample is crushed to a particle size range of 75 to 150 micrometers. Four grams of glass are placed into contact with 40 mL of deionized water for seven days at a temperature of 90°C. The resulting solution is then analyzed for species of interest (sodium, silicon, lithium and boron).

X-ray diffraction (XRD) and SEM Analyses. Glass samples taken of the glass exiting the melter were analyzed by XRD and SEM analyses. Glass samples were crushed to <100 mesh for the XRD analysis. Large pieces were thin sectioned and polished for SEM analysis. The two methods were used to identify phase separation and determine the identities of crystalline phases.

6.1 Results of Feed Compositional Analyses

Melter feed samples were taken routinely from the melter feed container. A daily sample from each test segment was submitted for compositional analysis. The results of the noble metal analyses is discussed separately in Section 6.4. Tables 6.1-6.5 report the

compositional results by test segment and compare the results to the target composition. The sample averages and normalized averages are also shown in the tables.

The reader should note that there is considerable variability in the silica concentration reported for samples taken in test segments 2 and 3. The duplicate analyses were performed on several samples but gave inconsistent results. The variability can be attributed to both sampling and analytical errors (as it pertains to sample preparation). Personnel that performed the feed sample preparation had difficulties in dissolving or fusing the samples. A white precipitate formed in some fusions which usually indicates the presence of insoluble silica. Another possible factor contributing to the discrepancy is related to the homogeneity of the sample taken for analysis. Slurry feed generally has some insoluble solids consisting of silica, alumina, etc. These solids can settle quickly and it can be difficult to keep them suspended in order to obtain a homogeneous sample. The results of test segment 2 and 3 glass compositional analysis shown in Section 6.2 verify that the feed composition was close to the target composition.

More consistent results were obtained for the feed samples in test segments 4 and 5. The measured concentrations of the major oxides in these samples were close to the target values. According to laboratory personnel, the feed samples for test segment 4 and 5 were easier to fuse.

In test segment 4, a mistake was made in the Ru addition resulting in an increase in the target amount of RuO_2 from 0.17 wt % to 0.187 wt %. The Pd and Te concentrations were on target in both test segments 4 and 5. The Ag concentration was lower than the target but the Ag concentration is known to be correct since it was carefully measured and added as a shim chemical.

Miscellaneous sample data is provided in Table 6.6. The physical characteristics such as density, oxide weight percent, oxide loading, and pH are shown in this table. The results have been averaged for each test segment.

Table 6.1. Feed Sample Results for Test Segment 1

Sample ID	NOM-2 Target	Average	Normalized Average
Oxide	Wt % oxide	Wt % oxide	Wt % oxide
Ag ₂ O	0.02	0.00	0.00
Al ₂ O ₃	7.15	11.27	13.68
B ₂ O ₃	9.89	13.34	16.19
BaO	0.24	0.18	0.22
Bi ₂ O ₃	0.02	0.05	0.06
CaO	0.80	1.18	1.43
CdO	0.52	0.77	0.93
CeO ₂	0.05	0.02	0.03
Cl	0.04	0.13	0.16
Cr ₂ O ₃	0.13	0.09	0.11
Cs ₂ O	0.25	0.07	0.08
CuO	0.03	0.02	0.03
F	0.04	0.00	0.00
Fe ₂ O ₃	9.86	15.15	18.38
K ₂ O	0.17	0.64	0.78
La ₂ O ₃	0.20	0.22	0.26
Li ₂ O	6.04	4.77	5.79
MgO	0.48	0.67	0.82
MnO	0.31	0.54	0.65
MoO ₃	0.00	0.00	0.00
Na ₂ O	9.82	14.69	17.83
Nd ₂ O ₃	0.41	0.50	0.61
NiO	0.41	0.42	0.51
P ₂ O ₅	0.42	0.73	0.89
PbO	0.14	0.00	0.00
ReO ₂	0.23	*	*
Sb ₂ O ₃	0.06	*	*
SeO ₂	0.08	*	*
SiO ₂	50.32	14.45	17.53
SnO ₂		0.01	0.01
SO ₃	0.19	0.54	0.65
SrO	0.03	0.07	0.08
TeO ₂	0.06	0.00	0.00
TiO ₂	0.02	0.07	0.08
ZnO	0.02	0.00	0.00
ZrO ₂	1.56	1.83	2.22
Total	100.00	82.43	100.00

* not analyzed

Table 6.2. Feed Sample Results for Test Segment 2

Sample ID	NOM-2 Target	RSM 23	RSM 29	RSM 36	Average	Normalized Average
Oxide	Wt % oxide	Wt % oxide	Wt % oxide	Wt % oxide	Wt % oxide	Wt % oxide
Ag ₂ O	0.02	0.00	0.01	0.00	0.00	0.00
Al ₂ O ₃	7.15	9.50	8.64	8.93	9.02	10.74
B ₂ O ₃	9.89	12.92	11.96	12.89	12.59	14.99
BaO	0.24	0.15	0.16	0.15	0.15	0.18
Bi ₂ O ₃	0.02	0.00	0.00	0.00	0.00	0.00
CaO	0.80	0.72	0.67	0.64	0.68	0.81
CdO	0.52	0.64	0.57	0.61	0.61	0.72
CeO ₂	0.05	0.00	0.00	0.00	0.00	0.00
Cl	0.04	0.15	0.15	0.14	0.14	0.17
Cr ₂ O ₃	0.13	0.08	0.05	0.33	0.15	0.18
Cs ₂ O	0.25	0.24	0.22	0.26	0.24	0.29
CuO	0.03	0.03	0.03	0.03	0.03	0.03
F	0.04	0.00	0.00	0.00	0.00	0.00
Fe ₂ O ₃	9.86	13.71	12.34	14.53	13.53	16.11
K ₂ O	0.17	0.00	0.00	0.00	0.00	0.00
La ₂ O ₃	0.20	0.13	0.10	0.13	0.12	0.14
Li ₂ O	6.04	7.56	6.28	7.52	7.12	8.48
MgO	0.48	0.54	0.49	0.51	0.51	0.61
MnO	0.31	0.41	0.39	0.43	0.41	0.49
MoO ₃	0.00	0.00	0.00	0.05	0.02	0.02
Na ₂ O	9.82	12.39	11.13	12.43	11.98	14.27
Nd ₂ O ₃	0.41	0.43	0.39	0.41	0.41	0.49
NiO	0.41	0.38	0.36	0.38	0.38	0.45
P ₂ O ₅	0.42	0.79	0.73	0.79	0.77	0.92
PbO	0.14	0.00	0.00	0.00	0.00	0.00
ReO ₂	0.23	0.46	0.51	0.53	0.50	0.60
Sb ₂ O ₃	0.06	*	*	*	*	*
SeO ₂	0.08	*	*	*	*	*
SiO ₂	50.32	16.50	30.21	17.49	21.40	25.49
SnO ₂		0.28	0.31	0.31	0.30	0.36
SO ₃	0.19	0.61	0.57	0.61	0.60	0.71
SrO	0.03	0.05	0.05	0.05	0.05	0.06
TeO ₂	0.06	0.00	0.00	0.00	0.00	0.00
TiO ₂	0.02	0.10	0.10	0.10	0.10	0.12
ZnO	0.02	0.05	0.03	0.00	0.03	0.03
ZrO ₂	1.56	2.25	1.97	2.15	2.12	2.53
Total	100.00	81.06	88.41	82.41	83.96	100.00

* not analyzed

Table 6.3. Feed Sample Results for Test Segment 3

Sample ID	NOM -3 Target	RSM 41	RSM 43	RSM 49	RSM 54	RSM 61	Average	Normalized Average
Oxide	Wt % oxide	Wt % oxide	Wt % oxide	Wt % oxide	Wt % oxide	Wt % oxide	Wt % oxide	Wt % oxide
Ag ₂ O	0.03	0.00	0.00	0.01	0.00	0.01	0.00	0.00
Al ₂ O ₃	8.58	10.06	8.46	8.10	8.57	9.28	8.89	8.68
B ₂ O ₃	10.94	13.48	11.61	10.86	10.80	14.44	12.24	11.95
BaO	0.29	0.18	0.15	0.14	0.15	0.15	0.15	0.15
Bi ₂ O ₃	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CaO	0.96	1.31	0.99	1.71	1.11	1.53	1.33	1.30
CdO	0.62	0.73	0.59	0.54	0.59	0.58	0.60	0.59
CeO ₂	0.06	0.00	0.00	0.07	0.06	0.00	0.02	0.02
Cl	0.04	0.18	0.17	1.66	0.30	0.17	0.49	0.48
Cr ₂ O ₃	0.16	0.07	0.06	0.06	0.06	0.06	0.06	0.06
Cs ₂ O	0.30	0.26	0.20	0.28	0.31	0.29	0.27	0.26
CuO	0.03	0.00	0.00	0.03	0.00	0.04	0.01	0.01
F	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe ₂ O ₃	11.83	15.78	12.81	11.80	12.88	12.36	13.13	12.81
K ₂ O	0.21	0.03	0.00	0.02	0.03	0.01	0.02	0.02
La ₂ O ₃	0.24	0.15	0.12	0.11	0.12	0.12	0.12	0.12
Li ₂ O	0.99	1.39	1.20	1.15	1.17	1.21	1.22	1.19
MgO	0.57	0.59	0.53	0.51	0.53	0.52	0.53	0.52
MnO	0.37	0.48	0.38	0.36	0.38	0.37	0.40	0.39
MoO ₃	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00
Na ₂ O	18.26	22.35	18.78	19.66	20.13	18.11	19.81	19.33
Nd ₂ O ₃	0.49	0.48	0.41	0.44	0.44	0.43	0.44	0.43
NiO	0.49	0.33	0.35	0.33	0.32	0.34	0.34	0.33
P ₂ O ₅	0.50	0.74	0.70	0.78	0.70	0.62	0.71	0.69
PbO	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PdO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ReO ₂	0.27	0.21	0.23	0.21	0.23	0.26	0.23	0.22
RuO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sb ₂ O ₃	0.07	*	*	*	*	*	*	*
SeO ₂	0.10	*	*	*	*	*	*	*
SiO ₂	41.09	33.49	24.40	36.18	34.53	63.47	38.41	37.49
SnO ₂	0.00	0.27	0.20	0.28	0.29	0.29	0.27	0.26
SO ₃	0.23	0.51	0.38	0.46	0.47	0.35	0.44	0.42
SrO	0.04	0.06	0.06	0.05	0.06	0.06	0.06	0.06
TeO ₂	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TiO ₂	0.03	0.10	0.09	0.08	0.09	0.09	0.09	0.09
ZnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ZrO ₂	1.94	2.45	2.06	2.07	2.25	1.97	2.16	2.11
Total	100.04	105.69	84.92	97.96	96.56	127.15	102.46	100.00

* not analyzed

Table 6.4. Feed Sample Results for Test Segment 4

Sample ID	NOM-3 Target	RSM 67	RSM 75	RSM 89	RSM 102	RSM 116	Average	Normalized Average
Oxide	Wt % oxide	Wt % oxide	Wt % oxide	Wt % oxide	Wt % oxide	Wt % oxide	Wt % oxide	Wt % oxide
Ag ₂ O	0.27	0.13	0.11	0.08	0.08	0.21	0.12	0.13
Al ₂ O ₃	8.54	7.75	7.68	7.78	7.49	7.79	7.70	8.16
B ₂ O ₃	10.88	10.09	10.04	9.94	9.45	10.16	9.94	10.53
BaO	0.29	0.13	0.14	0.13	0.13	0.12	0.13	0.14
Bi ₂ O ₃	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CaO	0.96	0.60	0.60	0.59	0.56	0.52	0.57	0.61
CdO	0.62	0.55	0.54	0.53	0.50	0.55	0.54	0.57
CeO ₂	0.06	0.11	0.08	0.08	0.03	0.03	0.06	0.07
Cl	0.04	0.24	0.24	0.22	0.22	0.23	0.23	0.24
Cr ₂ O ₃	0.16	0.08	0.05	0.05	0.05	0.06	0.06	0.06
Cs ₂ O	0.29	0.23	0.22	0.22	0.20	0.22	0.22	0.23
CuO	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
F	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe ₂ O ₃	11.77	11.82	11.57	11.67	11.09	11.91	11.61	12.31
K ₂ O	0.21	1.55	1.66	1.73	1.85	1.84	1.73	1.83
La ₂ O ₃	0.24	0.13	0.11	0.13	0.11	0.12	0.12	0.13
Li ₂ O	0.99	0.97	0.95	0.96	0.90	0.98	0.95	1.01
MgO	0.57	0.55	0.54	0.53	0.53	0.52	0.54	0.57
MnO	0.37	0.34	0.35	0.35	0.34	0.37	0.35	0.37
MoO ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na ₂ O	18.17	17.47	17.47	17.05	16.36	18.13	17.30	18.34
Nd ₂ O ₃	0.49	0.45	0.44	0.43	0.40	0.43	0.43	0.45
NiO	0.49	0.79	0.35	0.35	0.32	0.34	0.43	0.45
P ₂ O ₅	0.50	0.63	0.60	0.64	0.61	0.61	0.62	0.66
PbO	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PdO	0.05	0.04	0.04	0.04	0.03	0.03	0.04	0.04
ReO ₂	0.27	0.21	0.22	0.24	0.20	0.29	0.23	0.25
RuO ₂	0.187	0.18	0.17	0.17	0.16	0.17	0.17	0.18
Sb ₂ O ₃	0.07	*	*	*	*	*	*	*
SeO ₂	0.10	*	*	*	*	*	*	*
SiO ₂	40.89	37.62	37.78	36.64	41.22	36.12	37.88	40.15
SnO ₂	0.00	0.13	0.14	0.00	0.00	0.00	0.05	0.06
SO ₃	0.22	0.37	0.35	0.35	0.37	0.28	0.34	0.36
SrO	0.04	0.05	0.05	0.05	0.05	0.06	0.05	0.06
TeO ₂	0.10	0.06	0.06	0.06	0.07	0.07	0.06	0.07
TiO ₂	0.03	0.08	0.08	0.08	0.08	0.06	0.08	0.08
ZnO	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ZrO ₂	1.87	1.76	1.77	1.76	1.67	1.81	1.75	1.86
Total	100.00	95.18	94.51	92.97	95.16	94.22	94.41	100.00

* not analyzed

Table 6.5. Feed Sample Results for Test Segment 5

Sample ID	NOM-3 Target	RSM 124	RSM 132	RSM 145	RSM 156	RSM 163	Average	Normalized Average
Oxide	Wt % oxide	Wt % oxide	Wt % oxide	Wt % oxide	Wt % oxide	Wt % oxide	Wt % oxide	Wt % oxide
Ag ₂ O	0.27	0.06	0.06	0.09	0.11	0.08	0.08	0.09
Al ₂ O ₃	8.54	7.94	8.00	7.97	7.93	8.15	8.00	8.73
B ₂ O ₃	10.88	10.18	10.31	10.20	0.98	10.27	8.39	9.15
BaO	0.29	0.15	0.15	0.14	0.14	0.14	0.14	0.16
Bi ₂ O ₃	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CaO	0.96	0.60	0.56	0.57	0.72	0.62	0.62	0.67
CdO	0.62	0.57	0.56	0.54	0.53	0.56	0.55	0.60
CeO ₂	0.06	0.09	0.00	0.09	0.08	0.08	0.07	0.07
Cl	0.04	0.26	0.21	0.20	0.23	0.21	0.22	0.24
Cr ₂ O ₃	0.16	0.06	0.06	0.09	0.08	0.08	0.07	0.08
Cs ₂ O	0.29	0.22	0.24	0.23	0.22	0.22	0.23	0.25
CuO	0.03	0.00	0.00	0.03	0.03	0.03	0.02	0.02
F	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe ₂ O ₃	11.77	11.81	11.85	11.72	11.55	12.10	11.81	12.89
K ₂ O	0.21	1.81	1.60	1.55	1.56	1.04	1.51	1.65
La ₂ O ₃	0.24	0.12	0.15	0.20	0.11	0.11	0.14	0.15
Li ₂ O	0.99	0.95	0.98	0.97	0.92	0.99	0.96	1.05
MgO	0.57	0.54	0.53	0.54	0.56	0.56	0.55	0.60
MnO	0.37	0.36	0.36	0.37	0.36	0.37	0.36	0.40
MoO ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na ₂ O	18.17	17.79	17.77	17.45	16.67	17.52	17.44	19.04
Nd ₂ O ₃	0.49	0.45	0.41	0.43	0.42	0.45	0.43	0.47
NiO	0.49	0.33	0.36	0.34	0.33	0.37	0.35	0.38
P ₂ O ₅	0.50	0.60	0.59	0.60	0.64	0.65	0.62	0.67
PbO	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PdO	0.05	0.04	0.04	0.04	0.04	0.04	0.04	0.04
ReO ₂	0.27	0.33	0.31	0.29	0.28	0.30	0.30	0.33
RuO ₂	0.17	0.15	0.15	0.14	0.14	0.14	0.15	0.16
Sb ₂ O ₃	0.07	*	*	*	*	*	*	*
SeO ₂	0.10	*	*	*	*	*	*	*
SiO ₂	40.89	35.64	34.15	36.42	38.24	36.43	36.18	39.48
SnO ₂		0.00	0.00	0.14	0.14	0.14	0.08	0.09
SO ₃	0.22	0.06	0.39	0.37	0.33	0.40	0.31	0.34
SrO	0.04	0.06	0.06	0.09	0.06	0.06	0.06	0.07
TeO ₂	0.10	0.06	0.07	0.04	0.04	0.04	0.05	0.06
TiO ₂	0.03	0.09	0.09	0.09	0.08	0.08	0.09	0.09
ZnO	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ZrO ₂	1.87	1.81	1.75	1.83	1.81	1.86	1.81	1.98
Total	100.00	93.15	91.75	93.79	85.33	94.14	91.63	100.00

* not analyzed

Table 6.6. Miscellaneous Feed Sample Data

	Run Segment 1	Run Segment 2	Run Segment 3	Run Segment 4	Run Segment 5
Density, g/ml	1.5	1.5	1.4	1.4	1.4
Wt. % Solids	51	49	44	47	45
Wt. % Oxides	41	39	34	37	35
pH	7.7	8.3	8.6	8.3	8.1
Oxide Loading, g/L	614	570	492	528	493

6.2 Results of Glass Compositional Analyses

Glass samples were collected periodically by inserting a graphite mold into the melter pour stream and allowing the glass stream to fill the cavity in the mold. A daily sample from each test segment was dissolved using the PNNL fusion method APSL-03 and submitted for compositional analyses by ICP-AES, AA, ICP-MS, and ICP-AES model no. IRIS/AP. Tables 6.7-6.11 report the results by test segment and show the target glass composition. The sample averages and normalized averages are also shown in the tables. The results of the noble metal analysis is discussed in detail in Section 6.4.

In addition to the compositional analyses, the glass samples were also analyzed for their redox state. This analysis was performed by analyzing a dissolved or fused sample of the glass for the Fe^{+2} and the total iron content. The ratio of Fe^{+2} to total iron or $\text{Fe}^{+2}/\Sigma\text{Fe}$ defines the redox state of the glass. As the ratio approaches zero, the glasses are more oxidized. Larger ratio values are more reduced glasses. The redox state of the glasses was not adjusted with any reductant during testing. The results show that the NOM-2 glasses were more reduced than the NOM-3 glass product. The values are shown for each segment in Table 6.12.

Table 6.7. Glass Sample Results for Test Segment 1

Sample ID Oxide	NOM-2 Target Wt %	RSM # 6 Wt %	RSM # 7 Wt %	RSM # 9 Wt %	Average Wt %	Normalized Average Wt %
Ag ₂ O	0.02	0.00	0.01	0.01	0.00	0.01
Al ₂ O ₃	7.15	12.82	10.74	11.23	11.59	12.62
B ₂ O ₃	9.89	8.45	8.21	8.09	8.25	8.98
BaO	0.24	0.11	0.11	0.11	0.11	0.12
Bi ₂ O ₃	0.02					0.00
CaO	0.80	0.86	0.41	0.84	0.70	0.76
CdO	0.52	0.45	0.45	0.45	0.45	0.49
CeO ₂	0.05			0.05		0.00
Cl	0.04	*	*	*	*	*
Cr ₂ O ₃	0.13	0.11	0.11	0.10	0.11	0.12
Cs ₂ O	0.25	*	*	*	*	*
CuO	0.03	0.03	0.01	0.02	0.02	0.02
F	0.04	*	*	*	*	*
Fe ₂ O ₃	9.86	9.02	8.90	8.78	8.90	9.69
K ₂ O	0.17		0.59	0.53	0.56	0.61
La ₂ O ₃	0.20	0.11	0.10	0.10	0.10	0.11
Li ₂ O	6.04	5.54	5.38	5.29	5.40	5.88
MgO	0.48	0.44	0.41	0.45	0.43	0.47
MnO ₂	0.31	0.30	0.30	0.30	0.30	0.33
MoO ₃	0.00					0.00
Na ₂ O	9.82	8.99	8.95	8.78	8.91	9.69
Nd ₂ O ₃	0.41	0.34	0.33	0.35	0.34	0.37
NiO	0.41	0.31	0.31	0.30	0.31	0.33
P ₂ O ₅	0.42	0.58	0.51	0.50	0.53	0.58
PbO	0.14					0.00
ReO ₂	0.23	*	*	*	*	*
Sb ₂ O ₃	0.06	*	*	*	*	*
SeO ₂	0.08	*	*	*	*	*
SiO ₂	50.32	42.61	42.96	43.32	42.96	46.76
SO ₃	0.19	0.27	0.28	0.21	0.25	0.28
SrO	0.03	0.04	0.04	0.04	0.04	0.05
TeO ₂	0.06					0.00
TiO ₂	0.02	0.06	0.06	0.06	0.06	0.06
ZnO	0.02					0.00
ZrO ₂	1.56	1.64	1.54	1.50	1.56	1.70
Total		93.07	90.70	91.38	91.89	100.00

* not analyzed

Table 6.8. Glass Sample Results for Test Segment 2

Sample ID	NOM-2 Target Wt %	RSM 25 Wt % oxide	RSM 28 Wt % oxide	RSM 35 Wt % oxide	Average Wt % oxide	Normalized Average Wt % oxide
Oxide						
Ag ₂ O	0.02	0.01	0.01	0.01	0.01	0.01
Al ₂ O ₃	7.15	6.61	6.75	6.34	6.57	7.00
B ₂ O ₃	9.89	9.29	9.34	8.86	9.16	9.77
BaO	0.24	0.12	0.12	0.11	0.12	0.12
Bi ₂ O ₃	0.02	0.07	0.00	0.00	0.02	0.02
CaO	0.80	0.87	1.09	0.63	0.86	0.92
CdO	0.52	0.44	0.45	0.43	0.44	0.47
CeO ₂	0.05	0.06	0.05	0.02	0.04	0.05
Cl	0.04	*	*	*	*	*
Cr ₂ O ₃	0.13	0.11	0.11	0.11	0.11	0.12
Cs ₂ O	0.25	0.16	0.14	0.12	0.14	0.15
CuO	0.03	0.01	0.03	0.01	0.02	0.02
F	0.04	*	*	*	*	*
Fe ₂ O ₃	9.86	9.77	9.79	9.45	9.67	10.30
K ₂ O	0.17	1.16	1.30	0.79	1.08	1.15
La ₂ O ₃	0.20	0.10	0.10	0.10	0.10	0.11
Li ₂ O	6.04	6.13	6.01	5.64	5.93	6.32
MgO	0.48	0.46	0.47	0.43	0.45	0.48
MnO	0.31	0.30	0.29	0.28	0.29	0.31
MoO ₃	0.00	0.00	0.00	0.00	0.00	0.00
Na ₂ O	9.82	8.91	8.09	8.44	8.48	9.04
Nd ₂ O ₃	0.41	0.37	0.38	0.35	0.37	0.39
NiO	0.41	0.31	0.31	0.31	0.31	0.33
P ₂ O ₅	0.42	0.55	0.52	0.47	0.51	0.55
PbO	0.14	0.00	0.00	0.00	0.00	0.00
ReO ₂	0.23	0.08	0.05	0.09	0.07	0.08
Sb ₂ O ₃	0.06	*	*	*	*	*
SeO ₂	0.08	*	*	*	*	*
SiO ₂	50.32	46.41	47.23	47.19	46.94	50.02
SO ₃	0.19	0.39	0.38	0.35	0.37	0.40
SrO	0.03	0.04	0.04	0.04	0.04	0.04
TeO ₂	0.06	0.00	0.00	0.00	0.00	0.00
TiO ₂	0.02	0.07	0.07	0.07	0.07	0.07
ZnO	0.02	0.01	0.12	0.07	0.07	0.07
ZrO ₂	1.56	1.70	1.50	1.60	1.60	1.70
Total	100.00	94.51	94.73	92.31	93.85	100.00

* not analyzed

Table 6.9. Glass Sample Results for Test Segment 3

Sample ID	NOM-3	RSM 46	RSM 50	RSM 56	RSM 58	RSM 64	Average	Normalized Average
Oxide	Target	Wt % oxide	Wt % oxide	Wt % oxide	Wt % oxide	Wt % oxide	Wt % oxide	Wt % oxide
Ag ₂ O	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Al ₂ O ₃	8.58	7.91	7.97	7.66	7.66	8.16	7.87	8.56
B ₂ O ₃	10.94	10.18	10.10	9.85	10.57	9.43	10.03	10.90
BaO	0.29	0.14	0.14	0.14	0.14	0.14	0.14	0.15
Bi ₂ O ₃	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CaO	0.96	0.99	0.98	0.92	1.06	0.66	0.92	1.00
CdO	0.62	0.54	0.55	0.54	0.53	0.54	0.54	0.59
CeO ₂	0.06	0.00	0.00	0.00	0.00	0.05	0.01	0.01
Cl	0.04	*	*	*	*	*	*	*
Cr ₂ O ₃	0.16	0.17	0.15	0.15	0.14	0.19	0.16	0.17
Cs ₂ O	0.30	0.21	0.25	0.16	0.19	0.21	0.20	0.22
CuO	0.03	0.01	0.01	0.00	0.00	0.01	0.01	0.01
F	0.04	*	*	*	*	*	*	*
Fe ₂ O ₃	11.83	11.94	11.98	11.64	11.63	12.04	11.85	12.88
K ₂ O	0.21	0.08	0.01	0.00	0.00	0.00	0.02	0.02
La ₂ O ₃	0.24	0.11	0.11	0.11	0.11	0.11	0.11	0.12
Li ₂ O	0.99	1.10	1.08	1.04	1.03	1.10	1.07	1.16
MgO	0.57	0.48	0.49	0.45	0.43	0.47	0.46	0.50
MnO	0.37	0.36	0.36	0.36	0.35	0.36	0.36	0.39
MoO ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na ₂ O	18.26	17.23	17.04	16.64	16.89	16.49	16.86	18.32
Nd ₂ O ₃	0.49	0.37	0.38	0.36	0.36	0.37	0.37	0.40
NiO	0.49	0.40	0.39	0.36	0.38	0.37	0.38	0.41
P ₂ O ₅	0.50	0.65	0.67	0.38	0.67	0.61	0.60	0.65
PbO	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PdO	0.00	*	*	*	*	*	*	0.00
ReO ₂	0.27	0.11	0.14	0.13	0.11	0.14	0.12	0.14
RuO ₂	0.00	*	*	*	*	*	*	0.00
Sb ₂ O ₃	0.07	*	*	*	*	*	*	0.00
SeO ₂	0.10	*	*	*	*	*	*	0.00
SiO ₂	41.09	36.78	36.21	37.24	37.45	38.55	37.25	40.48
SnO ₂	0.00	0.26	0.25	0.17	0.25	0.33	0.25	0.27
SO ₃	0.23	0.41	0.41	0.28	0.42	0.44	0.39	0.43
SrO	0.04	0.05	0.05	0.04	0.05	0.05	0.05	0.05
TeO ₂	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TiO ₂	0.03	0.08	0.08	0.08	0.08	0.08	0.08	0.09
ZnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ZrO ₂	1.94	1.94	1.96	1.75	1.89	2.01	1.91	2.08
Total	100.04	92.50	91.77	90.44	92.41	92.91	92.01	100.00

* not analyzed

Table 6.10. Glass Sample Results for Test Segment 4

Sample ID	NOM-3	RSM 77	RSM 92	RSM 105	RSM 117	Average	Normalized average
Oxide	Target	Wt % oxide	Wt % oxide	Wt % oxide	Wt % oxide	Wt % oxide	Wt % oxide
Ag ₂ O	0.27	0.12	0.09	0.10	0.13	0.11	0.12
Al ₂ O ₃	8.54	9.36	10.28	9.20	9.39	9.56	10.26
B ₂ O ₃	10.88	9.71	9.57	9.79	9.87	9.73	10.45
BaO	0.29	0.14	0.13	0.14	0.14	0.14	0.15
Bi ₂ O ₃	0.03	0.07	0.07	0.07	0.00	0.05	0.06
CaO	0.96	1.17	1.12	1.11	0.75	1.04	1.11
CdO	0.62	0.53	0.52	0.53	0.54	0.53	0.57
CeO ₂	0.06	0.00	0.00	0.00	0.00	0.00	0.00
Cl	0.04	*	*	*	*	*	*
Cr ₂ O ₃	0.16	0.12	0.10	0.10	0.10	0.11	0.11
Cs ₂ O	0.29	0.18	0.18	0.19	0.22	0.19	0.21
CuO	0.03	0.04	0.04	0.04	0.01	0.03	0.03
F	0.04	*	*	*	*	*	*
Fe ₂ O ₃	11.77	11.63	11.40	11.62	11.82	11.62	12.47
K ₂ O	0.21	0.00	0.00	0.00	0.01	0.00	0.00
La ₂ O ₃	0.24	0.11	0.11	0.11	0.11	0.11	0.12
Li ₂ O	0.99	0.94	0.93	0.95	0.95	0.94	1.01
MgO	0.57	0.51	0.50	0.51	0.47	0.50	0.53
MnO	0.37	0.35	0.34	0.35	0.35	0.35	0.37
MoO ₃	0.00	0.02	0.02	0.02	0.00	0.01	0.01
Na ₂ O	18.17	16.31	16.20	16.81	17.39	16.68	17.90
Nd ₂ O ₃	0.49	0.38	0.37	0.37	0.37	0.37	0.40
NiO	0.49	0.36	0.34	0.35	0.35	0.35	0.37
P ₂ O ₅	0.50	0.64	0.64	0.66	0.62	0.64	0.69
PbO	0.16	0.00	0.00	0.00	0.00	0.00	0.00
PdO	0.05	0.03	0.03	0.03	0.03	0.03	0.03
ReO ₂	0.27	0.12	0.13	0.14	0.14	0.13	0.14
RuO ₂	0.187	0.11	0.10	0.11	0.10	0.10	0.11
Sb ₂ O ₃	0.07	*	*	*	*	*	*
SeO ₂	0.10	*	*	*	*	*	*
SiO ₂	40.89	36.59	36.52	37.97	36.54	36.90	39.60
SnO ₂		0.42	0.43	0.44	0.36	0.41	0.44
SO ₃	0.22	0.46	0.49	0.48	0.48	0.48	0.51
SrO	0.04	0.05	0.05	0.05	0.05	0.05	0.05
TeO ₂	0.10	0.05	0.05	0.04	0.05	0.05	0.05
TiO ₂	0.03	0.08	0.08	0.08	0.08	0.08	0.09
ZnO	0.02	0.08	0.11	0.10	0.07	0.09	0.10
ZrO ₂	1.87	1.78	1.77	1.84	1.86	1.81	1.95
Total	100.00	92.50	92.77	94.35	93.40	93.26	100.00

* not analyzed

Table 6.11. Glass Sample Results for Test Segment 5

Sample ID	Target	RSM 126	RSM 138	RSM 150	RSM 160	RSM 166	Average	Normalized
Oxide	Wt % oxide	Wt % oxide	Wt % oxide	Wt % oxide	Wt % oxide	Wt % oxide	Wt % oxide	Average Wt % oxide
Ag ₂ O	0.27	0.09	0.08	0.09	0.09	0.08	0.09	0.09
Al ₂ O ₃	8.54	10.17	9.11	10.22	9.40	9.10	9.60	10.21
B ₂ O ₃	10.88	9.90	10.02	9.85	9.95	10.21	9.99	10.62
BaO	0.29	0.14	0.14	0.14	0.14	0.14	0.14	0.15
Bi ₂ O ₃	0.03	0.00	0.07	0.01	0.01	0.01	0.02	0.02
CaO	0.96	0.76	0.81	0.75	0.78	0.81	0.78	0.83
CdO	0.62	0.54	0.55	0.54	0.55	0.57	0.55	0.58
CeO ₂	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cl	0.04	*	*	*	*	*	*	*
Cr ₂ O ₃	0.16	0.16	0.13	0.10	0.10	0.09	0.12	0.12
Cs ₂ O	0.29	0.18	0.21	0.20	0.21	0.20	0.20	0.21
CuO	0.03	0.01	0.02	0.01	0.02	0.02	0.02	0.02
F	0.04	*	*	*	*	*	*	*
Fe ₂ O ₃	11.77	11.86	12.17	11.69	12.02	12.27	12.00	12.77
K ₂ O	0.21	0.00	0.00	0.54	0.52	0.53	0.32	0.34
La ₂ O ₃	0.24	0.11	0.12	0.10	0.12	0.12	0.11	0.12
Li ₂ O	0.99	0.96	0.94	0.93	0.94	0.97	0.95	1.01
MgO	0.57	0.49	0.50	0.49	0.51	0.51	0.50	0.53
MnO	0.37	0.35	0.37	0.36	0.36	0.37	0.36	0.39
MoO ₃	0.00	0.00	0.02	0.02	0.02	0.02	0.02	0.02
Na ₂ O	18.17	17.39	17.25	17.03	17.12	18.05	17.37	18.47
Nd ₂ O ₃	0.49	0.37	0.38	0.38	0.39	0.40	0.38	0.41
NiO	0.49	0.39	0.36	0.35	0.36	0.36	0.36	0.39
P ₂ O ₅	0.50	0.61	0.64	0.62	0.65	0.64	0.63	0.67
PbO	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PdO	0.05	0.03	0.04	0.04	0.03	0.03	0.03	0.04
ReO ₂	0.27	0.16	0.22	0.22	0.25	0.25	0.22	0.23
RuO ₂	0.17	0.09	0.08	0.10	0.09	0.07	0.09	0.09
Sb ₂ O ₃	0.07	*	*	*	*	*	*	*
SeO ₂	0.10	*	*	*	*	*	*	*
SiO ₂	40.89	35.22	36.14	35.58	36.61	37.16	36.14	38.44
SnO ₂	0.00	0.35	0.41	0.39	0.42	0.35	0.38	0.41
SO ₃	0.22	0.45	0.51	0.47	0.51	0.46	0.48	0.51
SrO	0.04	0.05	0.05	0.05	0.05	0.05	0.05	0.05
TeO ₂	0.10	0.04	0.06	0.06	0.06	0.05	0.05	0.06
TiO ₂	0.03	0.08	0.09	0.08	0.08	0.09	0.08	0.09
ZnO	0.02	0.06	0.06	0.05	0.04	0.03	0.05	0.05
ZrO ₂	1.87	1.88	1.89	1.89	1.94	2.06	1.93	2.05
Total	100.00	92.97	93.50	93.40	94.38	96.16	94.08	100.00

* not analyzed

Table 6.12. Redox Measurements of Glass Samples by Test Segment

Segment Number	Sample Number	Segment Description	wt % Fe ⁺²	wt % ΣFe	Ratio Fe ⁺² /ΣFe
2	RSM 25	Nominal condition for glass NOM-2	0.124	7.10	0.0175
2	RSM 31	Nominal condition for glass NOM-2	0.132	6.94	0.0191
3	RSM 60	Nominal condition for glass NOM-3	0.0358	7.66	0.0047
4	RSM 105	Increased silver and noble metal, NOM-3	0.0734	8.52	0.0086
4	RSM 115	Increased silver and noble metal, NOM-3	0.0835	9.05	0.0092
5	RSM 155	Increased silver and noble metal, NOM-3	0.0601	8.68	0.0069

6.3 Glass Characterization

During the course of RSM operations, samples from the glass pour stream were routinely taken for glass characterization. The glass characterization results described in this section include; PCT, XRD, and electrical conductivity.

The chemical durability of the glasses produced by the melter was determined by a 7-day PCT using the technical procedure MCC-TP-19, Rev. 0, "Leach Test Using the PCT Test Method." The 7-day PCT was performed on glass samples taken each day of operation. The test segment averages of the PCT results are compared to the results obtained with crucible melts of the same glass composition and with the limits established by the DWPF Environmental Assessment (EA) glass in Table 6.13. The glass that was processed in the melter consistently had higher release rates than the crucible glass but were well within the EA glass limits. The average difference in release rates between the crucible melts and the RSM segment glasses was 105%. In both the NOM-2 and NOM-3 glass formulations, boron had the largest increase in release rate with an increase of 133% and 165% for the NOM-2 and NOM-3 glass, respectively.

During test segment 4 and 5, the NOM-3 waste was spiked with noble metals, tellurium, and silver. A comparison of test segments 3 and 4 show a decrease in the durability of the glass product with the addition of noble metals to the NOM-3 melter feed. The PCT results of the glasses produced in test segment 5 suggest a continuation of this trend. As additional spiked melter feed was processed, the durability of the glass product decreased.

During both test segment 2 and 3, processing temperatures were elevated to determine the effect of increased temperature on melter performance and product quality. Elevated processing temperatures appear to have had no significant effect on the PCT results.

Table 6.13. PCT Leach Results for Selected Glasses

NOM-2	Crucible melts ⁴ (g/m ²)	Segment 2 Average (g/m ²)	EA Glass ⁵ (g/m ²)	
Si	0.20	0.35	2.0	
B	0.30	0.70	8.4	
Na	0.24	0.44	6.7	
Li	0.37	0.85	NA	
pH	10.51	10.38		
NOM-3	Crucible melts ³ (g/m ²)	Segment 3 Average (g/m ²)	Segment 4 Average (g/m ²)	Segment 5 Average (g/m ²)
Si	0.16	0.24	0.28	0.32
B	0.35	0.93	1.77	2.07
Na	0.38	0.82	1.39	2.00
Li	0.26	0.49	0.78	1.17
pH	10.69	10.65	10.97	11.22

Samples taken from the top of the glass canisters produced in test segments 2, 3, and 4 were submitted for electrical conductivity testing using PNNL Technical Procedure PSL-417-ELC, "Electrical Conductivity Measurement Procedure." The conductivity measurements were conducted for a range of temperatures, from 850°C to 1200°C. The temperature had to be elevated slowly above 1150°C because several glasses reboiled. The results of the electrical conductivity tests of the glass product for segments 2, 3, and 4 are shown in Figure 6.1.

As shown in Figure 6.1, the electrical conductivity of NOM-2 glass is approximately 7.5 S/m higher than that of the NOM-3 glass at a processing temperature of 1150°C. This data confirms that the glass composition was responsible for the operational difficulties that were encountered in processing the NOM-2 glass formulation. The conductivity of the glass caused over-current conditions, shutting down the system. Current limits were also approached during the end of segment 4 and all of segment 5. The higher electrical conductivity of NOM-2 and NOM-3 with noble metals additions required higher currents to maintain a target processing temperature. NOM-3 with noble metal additions had an electrical conductivity approximately 5 S/m higher than that of the baseline glass formulation. However, this fact alone does not fully explain the operation difficulties encountered in test segment 5 which were discussed in detail in Section 5.0. As the noble

⁴ Vienna, J.D., M.J. Schweiger, D.E. Smith, H. Li, and P. Hrma. 1996. DRAFT: Phase I Privatization High-Level Waste Glass Data Support Interim Data Package, Pacific Northwest National Laboratory, Richland, Washington.

⁵ Jantzen, C.M., et al. 1993. "Characterization of the Defense Waste Processing Facility (DWPF) Environmental Assessment (EA) Glass Standard Reference Material." WSRC-TR-92-346 Rev. 1, Westinghouse Savannah River Co., Aiken, South Carolina.

Figure 6.1. Measured Electrical Conductivity of Product Glasses

metal spiked feed was processed, a conductive layer formed in the bottom 1 cm of the RSM. This layer lead to current “channeling” which is further discussed in Section 8.0.

The samples submitted for XRD analysis were grab samples taken during the course of RSM operations from the glass pour stream. The crystalline phases identified by XRD are shown in Table 6.14. The primary crystalline phase identified in nearly all the samples is Al_2O_3 . In the samples in which alumina is present, the crystalline volume percentage ranges from 1 - 5%.

The presence of alumina and silica crystals in the glass product is unlikely. The samples were obtained by lowering the discharge canister section and placing a graphite boat in the pour stream between the Pyrex viewport and duraboard used to hold up the discharge heater. The gap was intentionally kept small to preserve temperatures in the melter kiln and the discharge canister. This gap was small enough that a sample that was not fully contained within the graphite boat would frequently contact the duraboard. A thin pour stream would cool rapidly during sample collection, not allowing it to slump into the graphite sample boat. Duraboard has a typical composition of 70% Al_2O_3 and 26% SiO_2 . It is believed that the crystals of alumina and silica are not present in the glass product,

but are a result of the contact with the duraboard. This hypothesis is further backed by the SEM sample analysis discussed in Section 6.4. The SEM samples are prepared by mounting the sample and polishing the surface to be analyzed. This preparation removed the surface that would have been affected by the duraboard contact. No evidence of silica or alumina crystals was encountered during SEM analysis.

A minor phase with several unidentified peaks was encountered in all of the samples from the noble metals segments. A comparison of these results with that of the SEM results discussed in Section 6.4 leads to the conclusion that some of the unknown peaks are the result of the presence of RuO₂ crystals.

Table 6.14. Crystalline Phases Identified by XRD

Run Segment	Sample #	Crystallinity vol %	Primary Phase	Crystalline Fraction	Secondary Phase	Crystalline Fraction
2	RSM 31	<5	Corundum, Al ₂ O ₃	0.95	Quartz, SiO ₂	0.05
	RSM 35	1	Quartz, SiO ₂	1	none	--
3	RSM 58	<1	Quartz, SiO ₂	1	none	--
	RSM 64	0	Fully amorphous	--	--	--
4	RSM 77	3	Corundum, Al ₂ O ₃	0.95	Six (6) additional weak peaks were unidentifiable	0.05
	RSM 92	3	Corundum, Al ₂ O ₃	0.85	Five (5) additional weak peaks were unidentifiable	0.15
	RSM 105	2	Corundum, Al ₂ O ₃	0.8	Six (6) additional weak peaks were unidentifiable	0.2
	RSM 117	3	Corundum, Al ₂ O ₃	0.75	Four (4) additional weak peaks were unidentifiable	0.25
5	RSM 126	3	Corundum, Al ₂ O ₃	0.95	Three (3) additional weak peaks were unidentifiable	0.05
	RSM 138	3	Corundum, Al ₂ O ₃	0.95	Four (4) additional weak peaks were unidentifiable	0.05
	RSM 150	5	Corundum, Al ₂ O ₃	0.95	Five (5) additional weak peaks were unidentifiable	0.05
	RSM 160	2	Corundum, Al ₂ O ₃	0.95	Three (3) additional weak peaks were unidentifiable	0.05
	RSM 166	1	Corundum, Al ₂ O ₃	0.6	Four (4) additional weak peaks were unidentifiable	0.4

6.4 Noble Metals Analyses

Ruthenium, palladium, and increased amounts of silver and tellurium were added to the NOM-3 melter feed in test segments 4 and 5. A decision was made not to include rhodium. This decision was based on the availability of rhodium, its high cost, and the minimal impact associated with not including rhodium in testing. Rhodium will substitute itself in the place of ruthenium in the RuO_2 crystals. Prior testing (Cooper et al. 1994) verified that precipitation and accumulation of noble metals can occur in the RSM system. Alloys of Pd/Ag/Te and Ru crystals were observed in the previous RSM testing as a continuous phase precipitated on the bottom of the melter indicating silver could enhance or effect precipitation.

Noble metal analyses were performed using an ICP-AES (for Ru and Ag), ICP-MS, and ICP-AES model no. IRIS/AP. While all three methods showed similar trends (the concentration of the noble metals in the glass samples were generally less than in that in the feed samples), the ICP-MS feed results were closest to the target values and showed less scatter. The ICP-MS results were used to calculate the accumulation of noble metals. The analytical results from samples of glass produced by the melter were compared to the analytical results of feed samples. The difference in these two amounts was considered the amount retained or accumulated in the melter. A calculation of the percent retained was made for each of the four elements and is shown in Table 6.15.

Table 6.15. Calculated Accumulation in the Melter of Ag, Ru, Pd, and Te

Run Segment	Ag Accumulation (%)	Ru Accumulation (%)	Pd Accumulation (%)	Te Accumulation (%)
4	12.72	38.38	16.44	27.05
5	-7.32	41.4	15.35	8.97

While the accumulation of the noble metals, ruthenium and palladium, was similar in both test segments, the amount of silver and tellurium retained in the melter decreased in run segment 5. Perhaps the trend can be explained by significant operational differences between the two run segments. As the resistance and power dropped, the cold cap became much thicker in run segment 5 and the glass became more oxidizing. Redox measurement of glass samples taken during each segment indicate that segment 4 was slightly more reducing than segment 5.

SEM/EDX analysis was performed on the glass samples acquired during both test segments to determine the qualitative composition of any visible inclusions or crystals. The SEM/EDX photos and scans of the glass samples are shown in Figures B.1 - B.12 located in Appendix B. The SEM/EDX data indicated the presence of ruthenium crystals in each sample either in a needle or block geometry. Palladium was scarce and was only

visible in four of the glass samples. The spherical shape of the palladium or palladium/tellurium particles most likely indicate a metallic nature. The particles were all similar in size. Several larger Ru crystals were observed at the beginning of test segment 4.

One sample taken at the end of run segment 4 contained 100 nm dia. silver spheres and very little ruthenium. Interestingly, this sample coincides with the melter experiencing very high current densities. It is unknown at this point if enough silver spheres were available to influence the melt conductivity or if the silver precipitation was caused by the high currents. Table 6.16 summarizes the SEM/EDX observations for each sample.

Table 6.16. SEM Observations of Selected Glass Samples

Sample	Date	SEM/EDX Observations	Particle Size
Run Segment 4			
RSM 85	07/23/96	Ru crystals, Ru blocks	most particles 1-5 μm some were 5-10 μm
RSM 93	07/24/96	Ru crystals, Pd/Te spheres	Ru 1-5 μm Pd/Te 1-2 μm
RSM 112	07/25/96	Ru crystals	1-5 μm
RSM 120	07/26/96	Ag spheres, very little Ru crystals	Ag 100 nm Ru 2-3 μm
Run Segment 5			
RSM 125	07/29/96	Ru crystals, Pd spheres	Ru 1-5 μm Pd 1-2 μm
RSM 135	07/30/96	Ru crystals	1-5 μm
RSM 148	07/31/96	Ru crystals	1-5 μm
RSM 158	08/01/96	Ru crystals, Pd/Te spheres	Ru 1-5 μm Pd/Te 1-2 μm
RSM 165	08/02/96	Ru crystals, Pd/Te spheres	Ru 1-2 μm Pd/Te 1-2 μm

6.5 Results of Cold Cap Analyses

Cold cap samples were retrieved at the completion of RSM testing as described in section 8.0 (Destructive Melter Examination). This section discusses preliminary results from an analysis of the cold cap samples. A detailed analysis to identify critical or rate limiting processes was beyond the scope of the RSM studies. The detailed analysis of this cold cap, and others, is planned for a future study to be published elsewhere. Once critical and rate limiting processes are identified, simple laboratory tests will be designed to model the processes. Results from these laboratory tests will be used to identify the melter key melter parameters that need to be controlled to increase melter throughput.

Visual inspection of the cold cap revealed a one dimensional chemical and physical structure. Five distinct layers were observed within this cross section and are discussed briefly below and in greater detail later in this section:

- (i) Top Layer - The top portion of the cold cap consisted mostly of unreacted dried feed materials (100 μm diameter SiO_2 sand, waste material simulant, and composition trimming additives such as H_2BO_3 , Li_2CO_3 , and NaCO_3).
- (ii) Light Colored Salt Layer - A light colored layer was found to start roughly 10 mm below the top of the cold cap and extended down for an additional 2.5 mm. It is presumed that this layer consisted of a salt, marking the layer location as an isotherm for salt accumulation.
- (iii) Reaction Layer - Just below the salt layer was a region that is similar in appearance to the top portion of the cold cap.
- (iv) Dark Brown Glassy Foam - Starting at roughly 5 mm below the bottom of the salt layer, this region begins to darken in color, and leads seamlessly into a region of darker brown glassy foam.
- (v) Glassy Layer With Undissolved Feed Material - Below the roughly 2.5 mm of glassy foam was a layer of glass swirled with dissolving feed plumes and dense to the naked eye.

Samples from each region within this typical cold cap cross section were analyzed by optical microscopy (OM), scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDX), and x-ray diffraction (XRD). Results from these analyses are discussed for each layer. Compositional analysis was performed using inductively coupled spectroscopy/atomic emission spectroscopy (ICP/AES) and ion chromatography (IC) (both KOH and Na_2CO_3 fusions were used to prepare samples for analysis). Tables 6.17 through 6.19 summarize the compositional analyses for each of the layers and are shown below. Table 6.17 provides anion concentrations, Table 6.18 shows oxide composition based on the feed, and Table 6.19 shows oxide composition based on the

glass (i.e., the values are normalized to exclude components that do not end up in the final glass).

Table 6.17. Anion Concentrations (wt % of material) in Cold Cap Layer Samples

layer	F ⁻	Cl ⁻	NO ₂ ⁻	NO ₃ ⁻	PO ₄ ⁻	SO ₄ ⁻	(COOH) ₂ ⁻	Total
i	0.00	0.08	0.30	7.39	0.00	0.00	0.22	7.99
ii	0.00	0.31	1.17	35.80	0.73	0.49	0.65	39.14
iii	0.00	0.01	0.01	0.21	0.02	0.00	0.00	0.25
iv	0.00	0.00	0.00	0.03	0.01	0.00	0.00	0.04
v	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 6.18. Oxide Compositions of Cold Cap Layer Samples (Feed Basis)

	i	ii ^{(a)*}	ii ^{(b)*}	iii	iv	v
Al ₂ O ₃	2.83	2.62	3.62	7.61	8.36	8.49
B ₂ O ₃	3.57	6.84	9.97	7.48	10.19	10.51
Fe ₂ O ₃	4.19	3.44	5.24	9.41	11.76	12.37
K ₂ O	0.70	0.61	0.00	0.54	0.00	0.56
Li ₂ O	0.34	0.48	0.70	1.04	1.08	1.06
Na ₂ O	6.18	19.80	26.45	12.54	17.84	19.38
P ₂ O ₅	0.23	0.00	0.25	0.48	0.54	0.55
SO ₃	0.14	0.52	0.51	0.29	0.39	0.38
SiO ₂	15.57	12.93	6.55	46.50	37.81	37.71
ZrO ₂	0.63	0.50	0.78	1.48	1.91	2.01
Others	1.32	1.46	1.73	3.73	3.92	4.28
Total	35.70	49.20	55.80	91.10	93.80	97.30

*two samples of layer ii were analyzed due to the inhomogeneity in the layer

Table 6.19. Oxide Compositions of Cold Cap Layer Samples (Glass Basis)

	i	ii ^{(a)*}	ii ^{(b)*}	iii	iv	v	target
Al ₂ O ₃	7.9	5.3	6.5	8.4	8.9	8.7	8.54
B ₂ O ₃	10.0	13.9	17.9	8.2	10.9	10.8	10.88
Fe ₂ O ₃	11.7	7.0	9.4	10.3	12.5	12.7	11.77
K ₂ O	2.0	1.2	0.0	0.6	0.0	0.6	0.21
Li ₂ O	1.0	1.0	1.3	1.1	1.2	1.1	0.99
Na ₂ O	17.3	40.2	47.4	13.8	19.0	19.9	18.17
P ₂ O ₅	0.6	0.0	0.4	0.5	0.6	0.6	0.50
SO ₃	0.4	1.1	0.9	0.3	0.4	0.4	0.22
SiO ₂	43.6	26.3	11.7	51.0	40.3	38.8	40.89
ZrO ₂	1.8	1.0	1.4	1.6	2.0	2.1	1.87
Others	3.7	3.0	3.1	4.1	4.2	4.4	5.96

*two samples of layer ii were analyzed due to the inhomogeneity in the layer

6.5.1 Top Layer (i)

During continuous melter feeding, the top of the cold cap is replenished with the feed slurry. The water content of the slurry is sufficient to maintain a nearly constant temperature of roughly 100°C within the feed slurry pool on top of the cold cap surface. At this temperature, the feed species mostly remain in the form used for preparation (e.g. SiO₂, AlO(OH), Na₂B₄O₇·5H₂O, and disassociated alkali). No reactions other than the loss of water occur until alkali (mostly sodium) nitrates begin to melt between 200° and 300°C. Table 6.17 lists the anion concentrations found in cold cap samples from each visible layer. The concentration of nitrate dominates the light colored salt layer.

Figures 6.2, 6.3, and 6.4 show an SEM micrograph and EDX spectra of a sample from the top layer. The SEM reveals a porous mixture of dried, unreacted feed in the form of a gel surrounding SiO₂ sand grains. The EDX spectra from this sample show the large (~70 µm) dense material is the sand while the loose gel like material contains Fe, Ca, Ni, P, Al, and Na. Large, continuous pores exist in this layer, which allow gasses generated during glass melting reactions to escape to the melter plenum space.

A top layer sample analyzed by XRD showed an amorphous hump with an estimated 50 vol % amorphous phase. Figure 6.5 shows the XRD spectra with the amorphous hump subtracted. The major peaks have been identified as the following phases: SiO₂ (80 wt %), NaNO₃ (20 wt%), and traces of Na₂B₄O₇·5H₂O, Fe₂O₃, AlO(OH). Results from SEM, EDX, and XRD indicate that a large fraction of the simulated waste and composition trim materials were present in the form of amorphous gels, likely formed during feed preparation.

Figure 6.2. SEM, EDX Scan #4 for Top Layer Sample.

Figure 6.3. SEM, EDX Scan #5 for Top Layer Sample.

Figure 6.5. X-Ray Diffraction Spectrum (Amorphous Lump Subtracted) of Top Layer Sample.

6.5.2. *Light Colored Salt Layer (ii)*

Progressing down from the top layer, water content decreases and the oxides within the feed are exposed to temperatures above 100°C. As the feed oxides reach higher temperatures, alkali salts melt to form a "primary" low viscosity melt. As shown by Bunting and Bieler (1969) and Hrma et al. (1991), these primary melts tend to drain until they reach a temperature region in which they vigorously react with solid components, resulting in the evolution of gasses. During steady state operation, the solid feed material passes through this salt layer and reacts with molten salts. This produces a partly reacted feed of the same composition as the original batch with the exception of volatile species produced by these reactions.

Compositional analysis of a sample from this layer using IC showed a significant increase in salt concentrations (see Table 6.17) within this layer. Relative to the top layer, the salt layer is enriched in phosphate and sulfate and depleted in chloride, nitrite, and oxalate. Phosphates and sulfates do not decompose below 300°C while chloride, nitrite and oxalate either decompose or are volatilized.

The alkali (Na, Li, and K) react with the feed materials in this layer as discussed by Hrma (1988) and Vienna et al. (1994). Sodium enrichment in the salt layer is confirmed by the data in Table 6.18 and 6.19. Within experimental error, all but the salt layer have similar composition on a glass basis. There is no evidence of large scale demixing within the cold cap, which would lead to destabilization of the steady state.

Figure 6.6 and 6.7 show an SEM micrograph and an EDX analysis of a salt layer sample. This micrograph shows a dense agglomerate of SiO_2 sand surrounded by NaNO_3 phase which was molten during glass melting. This phase is very low in viscosity and allows any generated gasses to escape easily. The relative density of glass forming constituents to the molten salt phase is low in this region.

Area for EDX Scan #2

Figure 6.6. SEM, EDX Scan #1 for Salt Layer Sample.

Figure 6.7. SEM, EDX Scan #2 for Salt Layer Sample.

Analysis of a salt layer sample by XRD showed an amorphous hump with an estimated 40 vol % amorphous phase in the sample. Figure 6.8 shows the XRD spectra (with the amorphous hump subtracted) for a salt layer sample. The major peaks have been identified as the following phases: NaNO_3 (60 wt %), SiO_2 (30), with traces of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$, Fe_2O_3 , $\text{Na}_8[\text{AlSiO}_4]_6[\text{B}(\text{OH})_4]_2$, and $\text{Li}_2\text{Al}(\text{ClO}_4)_5$. Comparison of these data with XRD analysis of the top layer further quantify the enrichment of NaNO_3 in this layer.

6.5.3 Reaction Layer (iii)

While most of the nitrate reacts in the salt layer, a fraction of nitrate also reacts in the primary reaction layer just below the salt layer. Chloride, nitrite, and a portion of the phosphate also participate in this reaction layer. According to Smith et al. (1995) NaNO_3 reacts in two phases in Hanford HLW feed. The first phase occurs between 200° and 530°C and the second between 620° and 780°C for untreated waste (i.e., no reductant additions). These temperature ranges vary with anion concentrations in the feed.

Analysis of a reaction layer sample by XRD showed an estimated 55 vol % amorphous phase. Figure 6.9 shows the XRD spectra for a reaction layer sample with the amorphous hump subtracted. Approximately 80 wt % of the crystalline phase is unreacted silica sand. In this layer, several intermediate crystalline phases were identified. A complex alumino-boro-silicate, $\text{Na}_8[\text{AlSiO}_4]_6[\text{B}(\text{OH})_4]_2$, comprises 10 wt % of the crystalline phase and traces of lithium-alumino silicates (possibly containing phosphate) were detected. Traces of unreacted hematite (Fe_2O_3) were found along with spinel, $(\text{Ni},\text{Fe})(\text{Cr},\text{Fe})_2\text{O}_4$, which made up 5 wt % of the crystalline phases.

Figure 6.8. X-Ray Diffraction Spectrum (Amorphous Lump Subtracted) of Salt Layer Sample.

Figure 6.9. X-Ray Diffraction (Amorphous Lump Subtracted) of Reaction Layer Sample.

6.5.4 Dark Brown Glassy Foam Layer (iv)

The dark brown glassy foam layer consisted of a glassy phase entrapping a large volume (relative to the glassy phase) of gas bubbles. Figure 6.10 is an optical microscopy scan of a sample from this layer and shows the pockets of trapped gas bubbles. The bubbles range in size from less than 0.5 mm to over 4 mm and are postulated to have been larger and more abundant at the glass melting temperature. The melt is a complete glass phase in this layer. The high viscosity of the glass causes the entrapment of gasses evolved in melting reactions. A foam layer in glass melting is responsible for lowering the heat transfer to the cold cap above and hence may lower the melting rate. Conversely, the action of bubble formation and motion causes mixing and drawing of feed plumes which may increase the batch to glass conversion rate. There is an ideal set of conditions which the foam should meet for optimum melting kinetics as discussed by Vienna et al. (1994).

In the foamy glass layer, the last vestiges of salt have been reacted. The nitrate decomposed by reaction with glass forming oxides while the phosphate forms into the amorphous phase and partly into a complex crystalline phase. Analysis of the foamy glass layer by XRD showed an estimated 90 vol % amorphous phase in the sample. Figure 6.11 shows the XRD spectra with the amorphous hump subtracted. Undissolved SiO_2 is still a major crystalline phase (65 wt %). The second major phase is a complex aluminosilico-phosphate, $\text{Na}_6\text{CaAl}_6\text{Si}_6\text{O}_{24}(\text{PO}_4)_2$, which forms 25 wt % of the crystalline matter. Hematite was no longer identified. Spinel, $(\text{Ni,Fe})(\text{Cr,Fe})_2\text{O}_4$, made the remaining 10 wt % of crystalline material.

Magnification 12X

Figure 6.10. Optical Microscopy of Dark Brown Layer Sample.

Figure 6.11. X-Ray Diffraction (Amorphous Lump Subtracted) of Dark Brown Layer Sample.

In the foamy glass layer, the amorphous phase is no longer made of the feed material gel, but consists of highly viscous glass forming boro-silicate melt. Figure 6.12, 13, and 14 show the SEM/EDX analysis of a foamy melt sample. According to SEM micrograph the amorphous phase consists of two regions separated by clear interfaces. The connected region is silicate glass while the dispersed phase, 50 to 100 μm size, is an alumino-borate phase. Undissolved ZrO_2 was also identified by SEM.

6.5.5 Glassy Layer With Undissolved Feed Material (v)

The glassy layer is 98 vol % amorphous according to XRD analysis shown in Figure 6.15. The crystalline phase consists of RuO_2 (identified by XRD) and spinel (detected by OM and SEM). Figures 6.16 shows the OM view of this layer while Figures 6.17, 18, 19, and 20 show results from SEM/EDX. As can be seen by OM, the glass contains spinel, noble metals, and undissolved feed which are drawn and attenuated by the convective flow of glass in the region.

Figure 6.13. SEM, EDX Scan #2 for Foamy Glass Layer Sample.

Figure 6.15. X-Ray Diffraction (Amorphous Lump Subtracted) of Glass Layer Sample.

Magnification 15X

Figure 6.16. Optical Microscopy of Glass Layer Sample

Figure 6.17. SEM, EDX Scan #7 for Glass Layer Sample.

Figure 6.18. SEM, EDX Scan #8 for Glass Layer Sample.

Figure 6.19. SEM, EDX Scan #9 for Glass Layer Sample.

Figure 6.20. SEM, EDX Scan #10 for Glass Layer Sample.

7.0 Off-Gas Characterization

The off-gas stream was sampled daily during test segments 2, 3 and 4. Continuous monitoring for selected non-condensable species was performed for eight hour time periods. In addition, a filter sample (to collect particulate) was obtained for a two-hour period each day. The filter samples were taken upstream of the venturi scrubber while continuous gas monitoring was performed downstream of the scrubber and mist eliminator as shown in Figure 7.1.

The results of the non-condensable gas monitoring are shown in Figures C.1 through C.23, located in Appendix C, and are summarized in Table 7.1. Air from the film cooler and inleakage account for greater than 99% of the total off-gas flow rate (varied between 5.8 and 7.0 moles/min). The total flow rate was determined by using a helium tracer injected upstream of the venturi scrubber. The gas was sampled downstream of the scrubber as shown in Figure 7.2 to ensure that the helium was well-mixed with the melter off-gas.

Table 7.1. Average Values of Non-Condensable Off-Gases Generated in Test Segments 2, 3, and 4

	Processing Temperature °C	H ₂ moles/min	O ₂ moles/min.	N ₂ moles/min.	CO moles/min.	CO ₂ moles/min.	NO _x moles/min.	Total moles/min.
Segment 2	****	<2.00E-04	1.52	5.35	0.00076	0.038	0.041	6.96
2a	1150	<2.00E-04	1.35	4.75	0.001	0.040	0.038	6.18
2b	1165	<2.00E-04	1.58	5.56	0.001	0.037	0.042	7.22
Segment 3	****	<2.00E-04	1.25	4.63	0.00022	0.025	0.048	5.95
3a	1150	<2.00E-04	1.29	4.78	0.00028	0.025	0.048	6.14
3b	1160	<2.00E-04	1.17	4.33	0.00002	0.023	0.045	5.56
3c	1170	<2.00E-04	1.16	4.31	0.00010	0.024	0.048	5.54
Segment 4	1150	<2.00E-04	1.25	4.66	0.00004	0.021	0.042	5.97

Hydrogen and nitrous oxide levels were below detection limits. The hydrogen detection limit is 2.00E-04 moles H₂/min. The nitrous oxide detection limit is 4.00E-03 moles/min and also depends on the carbon dioxide concentration. Carbon monoxide was occasionally above detection limit (CO detection limit is about 100 ppm or 4.00E-03 moles/min). Most of the recorded data varied between zero and 50 ppm. There may have been some CO present in the off-gas stream but because of the low concentrations the data is questionable. It is worth noting that test segment 4 data reported very little CO compared to test segments 2 or 3. This difference could be attributed to a small shift in the behavior of the GC or could be an actual difference due to lower feed processing rates.

Figure 7.1. Aerosol Sampling Train

Figure 7.2. Gas Sampling Train

The carbon dioxide data included both the CO₂ generated by the melter and that present in the inleakage air. Air is typically reported to contain 330 ppm carbon dioxide (CRC Press, Inc. 1994). The measurements of the air in the room containing the RSM contained 370 ± 20 ppm. The air inleakage rate ranged from about 5.0 to 7.5 moles per minute during the tests. The carbon dioxide flow resulting from this air, then, was between 0.0015 and 0.003 moles/min, which is on the order of 5% to 10% of the observed CO₂ flow with the majority of CO₂ generated by the melter in processing the feed.

The particulate content of the off-gas stream was measured by capturing particulates and submicron aerosols on filters samples. Decontamination factors (DF) can be estimated based on the chemical composition of the captured particles. The DF were calculated by dividing the mass of the element entering the melter by the mass of the element leaving the melter. The data shown in the table includes all elements that were detected as present in both the feed and off-gas samples. The average DF for test segments 2, 3, and 4 are shown in Table 7.2.

There were significant differences in the DF values from the first sample period to the final sample period in each segment. This is not unexpected because changes like this have been observed in many previous HLW melter runs. With the variability of the data, it is difficult to compare the results. This difference could be partly a result of sampling or analytical error, but is most likely a result of changes in melter operating parameters. For several samples that show significant variation within the same run segment, the operation data was examined and no explanation was obvious. In addition, the small size of the RSM leads to feed carryover which in turn affects the calculated DF.

An attempt was made to compare the DF values in Table 7.2 to DF obtained from previous HLW melter runs, which are also shown in the table. Two typical runs, PSCM-23 and LFCM-8, were chosen for comparison (Goles et al. 1989; Perez et al. 1994). Several elemental RSM DF such as calcium, chlorine, lithium, and sodium were similar to the DF calculated for the HLW runs. Four major elements which had higher DF for this run included aluminum, boron, iron, and silica.

Table 7.2. Estimated Decontamination Factors

Test Segment	2a 1150°C	2b 1165°C	3a 1150°C	3c 1170°C	4 1150°C	PSCM-23	LFCM-8
Element	DF	DF	DF	DF	DF	DF	DF
Ag	*	*	169	94	274		60
Al	22600	30700	23200	20000	49800	1000	319
B	9470	12700	14000	14000	23200	390	
Ba	5500	5770	7100	7650	10900	980	647
Ca	912	1070	1100	1140	670	4700	694
Cd	1150	1570	1620	834	4978		250
Cl	7	11	*	*	45	6.6	4
Cr	140	274	745	176	374	440	317
Cu	642	779	191	134	1850	680	541
F	*	*	*	*	*	9.2	4
Fe	18900	14300	13500	16100	22000	870	739
La	8870	9280	10800	9500	19400		
Li	1420	2060	1680	1220	3770	1500	
Mg	1320	1670	1220	1080	2050	4300	
Mn	8850	8290	7460	7360	10700	900	778
Mo	32	46	*	*	*	110	196
Na	290	386	423	317	872	340	
Nd	7630	9370	7960	8160	14400	1200	879
Ni	2310	3030	2580	2070	6240	99000	722
P	958	1350	772	636	1460	2600	54
S	49	94	64	37	161	6.4	10
Si	70200	60380	130900	153000	74500	15000	884
Sr	7390	4950	7290	8850	10100	840	736
Ti	37500	41400	23100	25700	42800		
Zn	708	958	*	*	*	960	390
Zr	19300	18700	19300	22600	31900	890	792

* Below detection limit in feed sample

-- Below detection limit in off-gas sample

The film cooler and off-gas piping was examined after completion of all test segments. The film cooler was coated almost to the point of plugging with deposited material. A sample of the deposit was obtained and analyzed with ICP and IC. The results are shown in Table 7.3 and Table 7.4. Some of the deposit can be attributed to entrained feed but as expected, the analysis of the deposit showed relatively high amounts of the more volatile species such as sodium, boron, and chlorine.

Table 7.3. Analysis of Film Cooler Deposit (Oxide Basis)

Oxide	Wt %	Oxide	wt %
Ag ₂ O	0.11	MnO	0.20
Al ₂ O ₃	2.30	MoO ₃	0.09
B ₂ O ₃	7.40	Na ₂ O	19.88
BaO	0.08	Nd ₂ O ₃	0.22
CaO	0.27	NiO	0.21
CdO	0.50	P ₂ O ₅	0.35
Cl	5.21	PbO	0.15
Cr ₂ O ₃	0.49	SiO ₂	2.34
CuO	0.01	SnO ₂	0.21
F	0.00	SO ₃	3.75
Fe ₂ O ₃	6.41	SrO	0.03
K ₂ O	0.00	TeO ₂	0.25
La ₂ O ₃	0.08	TiO ₂	0.03
Li ₂ O	1.45	ZnO	0.02
MgO	0.28	ZrO ₂	0.82

Table 7.4. Anion Content of Film Cooler Deposit

Anion	Wt. %	Anion	Wt. %
F	0.00	PO ₄	0.00
Cl	5.21	SO ₄	4.08
NO ₂	0.00	(COOH) ₂	10.83
NO ₃	4.47		

8.0 Destructive Melter Examination

8.1 Melter Sectioning

After completion of the final test segment, the RSM was cooled with the intent to preserve the cold cap. To stop the cold cap from melting into the glass pool, the RSM was cooled as quickly as possible. Power was turned off to the electrodes, the kiln, the glass discharge tube heater, and the discharge canister heater. The wire cage enclosing the electrical connections and the duraboard insulation was removed from the top of the kiln. A fan was positioned so that air blew down into the kiln enclosure and out of the discharge section. Simultaneously, water was fed to the melter until the glass temperature dropped below 700°C.

After the RSM was disconnected from instrumentation and services, the lid was removed and the residual cold cap examined. The majority of the cold cap was preserved. Figure 8.1 shows the quenched cavity. A sample was obtained of the cold cap layer with a 1 in. core drill. Analysis of the cold cap was performed and was discussed in detail in section 6.5.

Prior to sectioning the RSM, a castable refractory was poured on top of the cold cap to stabilize the melt cavity during cutting operations. A band saw with a diamond blade was used to section the melter in half through the vertical plane which cuts through each electrode. The section that contained the discharge tube was halved again to produce a total of three sections (one half and two quarter sections). Figures 8.2 and 8.3 show the sectioned melter.

Some material loss was observed in the wall thickness of each electrode. The electrodes were a uniform 0.65 cm thickness prior to testing. After the test, the electrodes tapered from the original thickness of 0.65 cm to 0.42 cm on the bottom. The loss of electrode material could be attributed to the high current densities ($> 2 \text{ amp/cm}^2$) that were observed in test segment 2 and for part of test segment 4. The local current densities were probably very high during the later portions of segment 5 because the current was channeled or skewed to the bottom of the melter and could have also attributed to the material loss.

Both electrodes contained thermowells on the back side of each paddle. The thermowells were intact and did not contain any glass. Figure 8.2 shows the electrodes in the half section of the melter. An electrode was removed from one of the quarter sections and carefully examined. A copper colored coating was visible on both the front and back of the paddle.

Figure 8.1. Quenched Cold Cap Surface

Figure 8.2. Destructive Examination of Melter

Figure 8.3. Discharge Section of Melter

The glass in the melt cavity was a mixture of yellow/brown and black swirled together. The swirls show the convective currents that were present when the melter was quenched. Voids or bubbles were visible along the face of the electrode paddles and at the discharge tube indicating that reactions and/or gas generation were taking place at these points. Material loss was also apparent on the end of the discharge tube that was submerged in the molten glass. The cause of the material loss is not clear.

The bottom of the melt cavity did not contain a readily apparent metal layer such as the one found in 1992 RSM testing (Cooper et al. 1994) and the bottom K-3 refractory was eroded up to a 1 cm depth. Similar amounts of corrosion were also seen in the 1992 RSM testing. Corrosion seems to be related to the noble metals layer because the K-3 crucible in both tests (1992 and 1996) appeared to be intact under the electrodes. Several theories have been proposed to explain the increased corrosion. One explanation is metal down-drilling in which metals drill holes in melter bottom refractory. This theory is not supported by experimental data since a metal phase layer was apparent in the 1992 but not visible in the 1996 RSM test. Another theory that seems more plausible is that the more conductive bottom sludge experiences a higher current density resulting in localized high temperatures. The higher temperatures would then result in an increased corrosion rate.

The continuity was checked between the two electrodes and other areas in the cooled melter by applying a voltage and measuring the resistance using a Megger. A conductive layer of approximately 1 cm thick resides on the floor of the melter resting between the two electrodes. The conductive layer extends to both electrodes. The resistance checked from electrode to electrode measured $\sim 10\text{K } \Omega$ implying that joule-heating was primarily taking place in this conductive sludge layer. This "channeling" of current allowed the top section of the melter to cool while the 1150°C temperature was maintained by localized heating. The overall cooling of the melt reduced glass production rates in the final run segment to 50 % of the production rate observed for the baseline glass tested in segment 3.

These results also confirm the operational observations of shorting between the Inconel electrodes. The overall resistance between the electrodes decreased from an average of 0.4Ω in test segment 3 (the baseline run without noble metals) less than 0.25Ω in segment 5.

8.2 Glass Tank Sample Analyses

Samples were taken from the bottom center of the melter at several elevations, next to the north electrode, and below the discharge section. The locations of these samples are shown in Figure 8.4. These samples were submitted for SEM and XRD analyses. Two of the samples were also submitted for compositional analysis using an ICP-MS.

Note : Location and depths of samples
 RSM 170-Glass/K3 interface
 RSM 171-Center line toward north electrode
 RSM 172-Next to north electrode
 RSM 173-Centerline 0.5" above glass/K3 interface
 RSM 178-Towards discharge

Figure 8.4. Destructive Analysis Sampling Point

Scanning electron microscopy analysis of the melter samples all showed varying amounts of Ru crystals. Segregated areas as large as 200 μm of Ru were observed on the bottom center of the melter along with other Ru crystal shapes such as long needles and small blocks. Pd/Te spheres were also located in this phase. Pd/Te/Ag and/or a Pd/Ag alloys were found in the samples taken next to the north electrode and in the center of the melter 1 cm above glass/K3 interface.

While no distinct phases were observed, the concentration and particle size of RuO_2 increased with depth in the melter. The size of the particles found in the melter samples were much larger than the particles that were observed in the routine glass samples. Large segregated areas of RuO_2 were detected in the bottom of the melter that were at least twenty times the size of the particles found in the poured glass. The size of the Pd/Te spheres were approximately five times the size of the Pd spheres seen in the glass samples poured from the glass discharge. As postulated by Cooper et al. (1994), settling of the Pd alloys are a mechanism for accumulation.

The results of the SEM analysis are summarized in Table 8.1. The SEM/EDX photos and scans of the glass tank samples are shown in Figure B.13 through B.22 located in Appendix B.

Table 8.1. SEM Analysis of Melter Glass Samples

Sample Number	Location	Observations	Particle size
RSM 170	Center at glass/K3 interface	Segregated areas of Ru, Ru in various crystal shapes, Pd/Te spheres surrounded by Ru crystals	Ru area 200 μm , Ru needles 100 μm , Ru blocks 5-10 μm , Pd/Te spheres 10-20 μm
RSM 171	Centerline toward north electrode	Ru in various crystal shapes, Pd/Te spheres surrounded by Ru crystals	Ru needles 100 μm , Ru blocks <10 μm , Pd/Te spheres 10-20 μm
RSM 172	Next to north electrode	Clusters of Ru crystals, Round spheres of Ag/Pd surrounded by inclusions of Ru	Ru area 50 μm , Ru needles 50 μm , Ru blocks 5-10 μm , Ag/Pd/Te spheres 5-10 μm
RSM 173	Center 0.5" above glass/K3 interface	Segregated areas of Ru, Ru in various crystal shapes, Ag/Pd/Te spheres surrounded by Ru crystals	Ru area 50 μm , Ru needles 50 μm , Ru blocks 5-10 μm , Ag/Pd/Te spheres 5-10 μm

The XRD analysis identified the primary crystal phase detected in each sample as RuO_2 and/or PdO_2 . XRD analysis suggested that either or both crystal structures were possible. SEM analysis confirmed that all of the Pd particles were probably metallic in phase since the particles were spherical in shape and alloyed with Te and/or Ag. The SEM results suggests that the primary crystal phase was indeed RuO_2 . The largest amount of crystals by volume were observed in the sample, RSM 178, taken on the bottom center of the melter slightly toward the discharge tube. Approximately 10 vol % of crystals were found in this location. The majority, 95 %, of crystals were composed of RuO_2 . A small

amounts of spinel-type crystals were also detected at this location. Similar results were seen in the sample, RSM 172, taken at the bottom of the melter next to the north electrode. The sample, RSM 173, taken in the center of the melter but 0.5 in. from the glass/K3 interface showed only 1 vol % of crystallinity composed of RuO_2 . No spinel-type crystals were detected at this location. The reduced amount of crystallinity at 0.5 in. above the glass/K3 interface suggests the crystalline noble metal layer primarily settled on the bottom of the K3 crucible in a layer less than 0.5 in. thick. The results of the XRD analysis are summarized in Table 8.2.

Table 8.2. XRD Analysis of Melter Glass Samples

Sample Number	Sample Location	Crystallinity vol %	Primary Phase	Crystalline Fraction	Secondary Phase	Crystalline Fraction
RSM 172	Next to north electrode	5	RuO_2 and/or PdO_2	0.85	Spinel-type - copper magnesium manganese oxide	0.15
RSM 173	Center 0.5" above glass/K3 interface	1	RuO_2 and/or PdO_2	1	none	--
RSM 178	Bottom center toward discharge	10	RuO_2 and/or PdO_2	0.95	Spinel-type - copper magnesium manganese oxide	0.05

In support of both the SEM and XRD results, the compositional analysis of two of the samples also showed increased amounts of noble metals in the bottom sludge layer. A sample taken at a 1 cm elevation showed a significant decrease in Ru and Pd concentrations in comparison to the bottom sludge layer sample. This analysis indicates Ru and Pd were settling out in a layer less than 1 cm thick. The amounts of Ag and Te detected in these samples did not indicate any significant retention in this layer.

Table 8.3. Compositional Analysis of Samples Obtained in the RSM

Sample Number	Sample Location	Ag wt %	Ru wt %	Pd wt %	Te wt %
172	Next to front face of the north electrode	0.08	1.45	0.20	0.06
173	Center, 0.5 in. above glass/K3 interface	0.09	0.06	0.03	0.05
Target in Glass	--	0.25	0.13	0.04	0.08

9.0 Comparison of 1996 and 1992 RSM Results

In FY 1992, testing in the RSM was conducted to assess noble metal behavior as a function of different operating conditions (e.g., elevated feed concentrations, elevated operating temperatures, differing glass redox conditions). The RSM operated for 48 days and produced 531 kg of glass, which is equivalent to 153 tank turnovers. A complete description of this work can be found in Cooper et al. (1994).

Contained in this section is a brief summary of the observations and analytical data resulting from the 1992 test and a comparison to the data obtained in the FY 1996 RSM test. Since the basic melter is the same for both sets of tests (i.e., the RSM system), differences between the two tests can be discussed in terms of operating conditions and glass formulations. A number of systems besides the RSM have been used for testing on HLW simulants (both with and without noble metals); however, comparison of the 1996 RSM results to these other tests would require a discussion of each of these other systems that is beyond the scope of this report.

Table 9.1 shows the major components of the glass formulations used for the 1992 and 1996 RSM runs. Significant compositional differences can be seen due to the fact each formulation was designed for a different purpose. In 1992, the glass formulation tested was a fully pretreated feed for the proposed Hanford Waste Vitrification Plant. The 1996 glass formulation was designed specifically to incorporate for the HLW in the tanks identified in the RFP issued for Phase 1 Privatization.

The noble metal concentrations, except for rhodium, in the 1996 test were approximately 80% of the concentrations found in the 2X run segments performed in the RSM in 1992 and 50% higher than the 1992 nominal run segments. The concentrations of silver and tellurium in the 1996 RSM test were much higher than the levels tested in 1992.

Table 9.1. Glass Formulation Comparison Between 1992 and 1996 RSM Tests

Major Oxides	1992 RSM Target wt %	1996 RSM Target wt %
Al ₂ O ₃	2.71	8.58
B ₂ O ₃	14.04	10.94
Fe ₂ O ₃	8.10	11.83
Li ₂ O	4.98	1.00
Na ₂ O	7.55	18.26
SiO ₂	52.29	41.09
ZrO ₂	4.30	1.94
Noble Metal/Other Oxides		
Ag ₂ O	0.015	0.27
PdO ^(a)	0.035 (0.070)	0.05
RuO ₂ ^(a)	0.11 (0.22)	0.17
TeO ₂	0.03	0.10
Rh ₂ O ₃ ^(a)	0.015 (0.30)	(b)

(a) 1992 RSM test included segments utilizing twice the nominal noble metal concentration

(b) 1996 RSM test did not use rhodium for testing

9.1 Melter Destructive Analysis

- 1992 - Vertical cuts through the cooled RSM created three pieces for observation (one intact halve and two quarters). The cut to create the halves was made through the center of the electrodes while the cut for the quarters went directly through the discharge section. For each of the three pieces, a metal layer (between 2 and 4 mm thick) was observed between the electrodes on the floor of the melter. The melter refractory was also corroded severely on the floor between the electrodes. The corrosion was as bad as 1.27 cm which corresponds to 37.6 cm/yr.
- 1996 - The RSM was quenched while processing to preserve the cold cap. The same cuts were made through the cooled RSM as in the 1992 test. The bottom of the melt cavity did not contain a readily apparent metals layer such as the one found in 1992 RSM testing (Cooper et al. 1994) but the bottom sludge or lower 1.0 cm of glass was found to be conductive when checked with a Megger. Inspection of the refractory showed accelerated corrosion of the K3 on the bottom of the melter between the electrodes. The original thickness of the bottom K-3 refractory was eroded up to 1 cm.

9.2 Electrode Corrosion

- 1992 - Destructive analysis showed that approximately one-third of an electrode had been eroded during the course of the test segments. The other electrode showed minor levels of corrosion. Analytical results from the glass samples do not indicate elevated levels of Inconel components, so it is postulated that the electrode was eroded continually or at least not all at once during one test segment. This was true for both the glass samples taken at the end of each test segment as well as for a melter bottom sample taken during destructive analysis. The absence of spikes or sudden changes in the electrical data also supports the hypothesis of a continual electrode erosion.
- 1996 - The electrodes were intact though some material loss was observed in the wall thickness of each electrode. The face of the electrodes were a uniform 0.65 cm prior to testing. After the test, the electrodes tapered from the original thickness of 0.65 cm to 0.42 cm. The loss of electrode material could be attributed to the high current densities ($>2 \text{ amp/cm}^2$) that were observed in two run segments. Both electrodes contained thermowells on the back side of each paddle.

9.3 Phase Separation

- 1992 - A single glass sample was analyzed upon the completion of a given test segment (sample was taken from the top of the pour canister). Four glass samples taken during the destructive analysis of the melter were also analyzed. SEM/EDX showed presence of metallic noble metals for test segments involving reducing glasses. Small spheres (<1 micrometer) were seen for a redox potential of $0.019 \text{ Fe}^{2+}/\Sigma\text{Fe}$ while slightly larger spheres (1 to 5 micrometers) were seen of a redox potential of $0.251 \text{ Fe}^{2+}/\Sigma\text{Fe}$. Ruthenium oxide needles were present in all of the samples except for one (pure ruthenium and ruthenium alloys were observed from the test segment with a redox potential of $0.251 \text{ Fe}^{2+}/\Sigma\text{Fe}$). Small (1 to 2 micrometer) palladium spheres were also observed for the test segment involving elevated levels of silver and tellurium.

With respect to non-noble metals, iron, chromium, and nickel spinels were found in samples from the test segment involving a $0.019 \text{ Fe}^{2+}/\Sigma\text{Fe}$ and for the first test segment with a feed containing a "2X" noble metal concentration. The spinels were not present in samples from the "2X" test segment that also contained elevated silver and tellurium levels. Iron, chromium, and nickel were also not present (as spinel or metal) in samples from the high redox ($0.251 \text{ Fe}^{2+}/\Sigma\text{Fe}$), high temperature (1200°C), and "2X" noble metal concentration test segment.

- 1996 - Nine glass samples were analyzed upon the completion of the noble metal test segments. The redox potential of these glasses was not adjusted and varied from

0.0069 to 0.0092 $\text{Fe}^{2+}/\Sigma\text{Fe}$. The SEM/EDX analysis performed on the glass samples acquired during both test segments indicated the presence of ruthenium crystals in each sample. Palladium was scarce and was only visible in four of the glass samples. The spherical shape of these palladium or palladium/tellurium particles most likely indicate a metallic nature. One sample taken at the end of run segment 4 contained 100 nm dia. silver spheres and very little ruthenium. None of the glass

11.0 QA Statement

This work was conducted under quality impact level III per PNNL's quality assurance manual PNL-MA-70.

Appendix A

Melter Process Data

Figure A.1. Segment 1 Resistance and Power

Figure A.2. Segment 2 Resistance and Power

Figure A.3. Segment 3 Resistance and Power

Figure A.4. Segment 4 Resistance and Power

Figure A.5. Segment 5 Resistance and Power

Figure A.6. Segment 1 Volts and Amps

A.6

Figure A.7. Segment 2 Volts and Amps

Figure A.8. Segment 3 Volts and Amps

Figure A.9. Segment 4 Volts and Amps

Run Segment 5: 7/29/96 -- 8/2/96

Run Segment 5: 7/29/96 -- 8/2/96

Figure A.10. Segment 5 Volts and Amps

Figure A.11. Segment 1 Melt and Plenum Temperature

Figure A.12. Segment 2 Melt and Plenum Temperature

Figure A.13. Segment 3 Melt and Plenum Temperature

Figure A.14. Segment 4 Melt and Plenum Temperature

Run Segment 5: 7/29/96 -- 8/2/96

Run Segment 5: 7/29/96 -- 8/2/96

Figure A.15. Segment 5 Melt and Plenum Temperature

Figure A.16. Segment 1 Plenum Vacuum and Off-Gas Line Temperature

Figure A.17. Segment 2 Plenum Vacuum and Off-Gas Line Temperature

Figure A.18. Segment 3 Plenum Vacuum and Off-Gas Line Temperature

Run Segment 4: 7/22/96 -- 7/26/96

Run Segment 4: 7/22/96 -- 7/26/96

A.19. Segment 4 Plenum Vacuum and Off-Gas Line Temperature

Run Segment 5: 7/29/96 -- 8/2/96

Run Segment 5: 7/29/96 -- 8/2/96

Figure A.20. Segment 5 Plenum Vacuum and Off-Gas Line Temperature

Figure A.21. Segment 1 Feed Tank Weight and Feed Pump Output

Figure A.22. Segment 2 Feed Scale Weight and Feed Pump Output

Run Segment 3: 6/24/96 -- 6/28/96

Run Segment 3: 6/24/96 -- 6/28/96

Figure A.23. Segment 3 Feed Scale Weight and Feed Pump Output

Figure A.24. Segment 4 Feed Scale Weight and Feed Pump Output

Figure A.25. Segment 5 Feed Scale Weight and Feed Pump Output

Appendix B

SEM Analysis of Glass Samples

Figure B.1. SEM, EDX Scan #1 for RSM-85. RSM-85 collected July 23, 1996.

Figure B.2. SEM, EDX Scan #1 for RSM-93. RSM-93 collected July 24, 1996.

Figure B.3. SEM for RSM-112. RSM-112 collected July 25, 1996.

Figure B.4. SEM, EDX Scan #1 for RSM-120. RSM-120 collected July 26, 1996.

Figure B.5. SEM, EDX Scan #1 for RSM-125. RSM-125 collected July 29, 1996.

Figure B.6. SEM for RSM-135. RSM-135 collected July 30, 1996.

Figure B.7. SEM for RSM-148. RSM-148 collected July 31, 1996.

Figure B.8. SEM, EDX Scan #1 for RSM-158. RSM-158 collected August 1, 1996.

Figure B.9. SEM, EDX Scan #2 for RSM-158. RSM-158 collected August 1, 1996.

Figure B.10. SEM, EDX Scan #3 for RSM-158. RSM-158 collected August 1, 1996.

Figure B.11. SEM, EDX Scan #1 for RSM-165. RSM-165 collected August 2, 1996.

Figure B.12. SEM, EDX Scan #2 for RSM-165. RSM-165 collected August 2, 1996.

Figure B.13. SEM, EDX Scan #1 for RSM-170. RSM-170 collected August 19, 1996.

Figure B.14. SEM, EDX Scan #2 for RSM-170. RSM-170 collected August 19, 1996.

Figure B.15. SEM, EDX Scan #3 for RSM-170. RSM-170 collected August 19, 1996.

Figure B.16. SEM, EDX Scan #4 for RSM-170, RSM-170 collected August 19, 1996.

Figure B.17. SEM, EDX Scan #1 for RSM-171. RSM-171 collected August 19, 1996.

Figure B.18. SEM, EDX Scan #2 for RSM-171. RSM-171 collected August 19, 1996.

Figure B.19. SEM, EDX Scan #3 for RSM-171. RSM-171 collected August 19, 1996.

Figure B.20. SEM, EDX Scan #1 for RSM-172. RSM-172 collected August 19, 1996.

B.21

Figure B.21. SEM, EDX Scan #2 for RSM-172. RSM-172 collected August 19, 1996.

Figure B.22. SEM, EDX Scan #1 for RSM-173. RSM-173 collected August 19, 1996.

Appendix C

Off-Gas Data

Segment 2 (6/18/96)

**Figure C.1. NO_x and CO_2 Gas
Generation in Segment 2 - 6/18/96**

Segment 2 (6/19/96)

Figure C.2. NO_x and CO₂ Gas
Generation in Segment 2 - 6/19/96

Segment 2 (6/20/96)

Figure C.3. NO_x and CO₂ Gas
Generation in Segment 2 - 6/20/96

Segment 2 (6/18/96)

Figure C.4. N_2 and O_2 Gas
Generation in Segment 2 - 6/18/96

Segment 2 (6/19/96)

Figure C.5. N_2 and O_2 Gas
Generation in Segment 2 - 6/19/96

Segment 2 (6/20/96)

Figure C.6. N₂ and O₂ Gas
Generation in Segment 2 - 6/20/96

Segment 3 (6/26/96)

**Figure C.7. NO_x and CO₂ Gas
Generation in Segment 3 - 6/26/96**

Segment 3 (6/27/96)

**Figure C.8. NO_x and CO₂ Gas
Generation in Segment 3 - 6/27/96**

Segment 3 (6/28/96)

Figure C.9. NO_x and CO₂ Gas
Generation in Segment 3 - 6/28/96

Segment 3 (6/25/96)

Figure C.10. N_2 and O_2 Gas
Generation in Segment 3 - 6/25/96

Segment 3 (6/26/96)

Figure C.11. N_2 and O_2 Gas
Generation in Segment 3 - 6/26/96

Segment 3 (6/27/96)

Figure C.12. N_2 and O_2 Gas
Generation in Segment 3 - 6/27/96

Segment 3 (6/28/96)

Figure C.13. N₂ and O₂ Gas
Generation in Segment 3 - 6/28/96

Segment 4 (7/22/96)

Figure C.14. NO_x and CO_2 Gas Generation in Segment 4 - 7/22/96

Segment 4 (7/23/96)

Figure C.15. NO_x and CO₂ Gas Generation in Segment 4 - 7/23/96

Segment 4 (7/24/96)

Figure C.16. NO_x and CO_2 Gas Generation in Segment 4 - 7/24/96

Segment 4 (7/25/96)

Figure C.17. NO_x and CO_2 Gas Generation in Segment 4 - 7/25/96

Segment 4 (7/26/96)

Figure C.18. NO_x and CO_2 Gas Generation in Segment 4 - 7/26/96

Segment 4 (7/22/96)

Figure C.19. N₂ and O₂ Gas
Generation in Segment 4 - 7/22/96

Segment 4 (7/23/96)

Figure C.20. N_2 and O_2 Gas
Generation in Segment 4 - 7/23/96

Segment 4 (7/24/96)

Figure C.21. N₂ and O₂ Gas
Generation in Segment 4 - 7/24/96

Segment 4 (7/25/96)

Figure C.22. N₂ and O₂ Gas
Generation in Segment 4 - 7/25/96

Segment 4 (7/26/96)

Figure C.23. N₂ and O₂ Gas
Generation in Segment 4 - 7/26/96