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Research-Scale Melter Test Report

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MASTER

EP

Summary

The Melter Performance Assessment (MPA) activity in the Pacific Northwest Laboratory's (PNL)^(a) Hanford Waste Vitrification Plant (HWVP) Technology Development (PHTD) effort is intended to determine the impact of noble metals on the operational life of the reference HWVP melter. As a part of this activity, a parametric melter test was completed using a Research-Scale Melter (RSM). The RSM is a small, approximately 1/100-scale melter, 6-in.-diameter, that allows rapid changing of process conditions and subsequent re-establishment of a steady-state condition. The test matrix contained nine different segments that varied the melter operating parameters (glass and plenum temperatures) and feed properties (oxide concentration, redox potential, and noble metal concentrations) so that the effects of these parameters on noble metal agglomeration on the melter floor could be evaluated.

The RSM operated for 48 days and consumed 1,300 L of feed, equating to 153 tank turnovers. The run produced 531 kg of glass. During the latter portion of the run, the resistance between the electrodes decreased. Upon destructive examination of the melter, a layer of noble metals was found on the bottom. This was surprising because the glass residence time in the RSM is only 10% of the HWVP plant melter. The noble metals layer impacted the melter significantly. Approximately 1/3 of one paddle electrode was melted or corroded off. The cause is assumed to be localized heating from short circuiting of the electrode to the noble metal layer. The metal layer also removed approximately 1/2 in. of the refractory on the bottom of the melter. The mechanism for this damage is not presently known.

Samples taken from the bottom of the RSM contained a 2 to 4-mm layer of precipitated noble metals. Scanning Electron Microscopy/Energy Dispersive X-Ray (SEM/EDX) analyses of the layer found that it consisted of metallic particles (10 to 20 μm) of a Ru/Rh alloy surrounded by two separate, continuous phases. One of these continuous phases was an alloy of metallic Pd/Ag/Te with a small amount of Ru metal. The other continuous phase was pure RuO_2 . It is assumed that the layer was made up of RuO_2 needles and alloys of Pd/Rh/Ag/Te until the last segment of the run which was run under reducing conditions ($\text{Fe}^{+2}/\Sigma\text{Fe} = 0.25$). This reduction of the RuO_2 has significance with respect to HWVP operation. At $\text{Fe}^{+2}/\Sigma\text{Fe} = 0.19$ palladium alloy spheres were formed. At $\text{Fe}^{+2}/\Sigma\text{Fe} = 0.25$ there were no visible RuO_2 crystals. All of the RuO_2 at this point was apparently reduced to metal. This was not expected to occur so close to the plant redox operating limit. The upper redox operating limit for the plant is $\text{Fe}^{+2}/\Sigma\text{Fe} = 0.23$. Under these conditions, the flocs of RuO_2 could reduce to metallic ruthenium and alloy with rhodium. This would increase the rate of noble metals sedimentation and thus shorten the life of the melter.

(a) PNL is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

Mass balance calculations indicate that approximately 5% of the noble metals present in the feed precipitated to the floor of the melter during the segments of the test with nominal noble metals concentration. Approximately 46% of the noble metals precipitated during the segments of the test with double nominal noble metals concentration and uncertainty.

Samples taken from the glass exiting the RSM were analyzed by optical and scanning electron microscopy for the presence of noble metals. The particles observed averaged 10 μm in diameter with many agglomerates in the 100 to 200 μm range. The agglomerates were mainly RuO_2 needles or rods attached end-to-end at random angles to form fractal or "hair ball"-like flocs. The average size of these flocs increased substantially during the segments of the run when the concentration of noble metals in the feed was doubled. This indicates a nonlinearity of floc size to noble metals concentration. The noble metal agglomerates were much larger than those observed during the gradient furnace testing (GFT), which indicates that a significant amount of agglomeration occurs in the melt pool even though the average residence time of the RSM was only 5 hours. The glass samples taken from the canisters were nonhomogeneous with respect to noble metals concentrations. Observation of the thin-sectioned samples with the naked eye could detect dark streaks that were found to be areas of concentrated RuO_2 agglomerates. The reason for these streaks is not presently known.

As stated earlier, the RSM test was parametric with respect to plenum temperature, glass temperature, glass oxide loading, redox state, and noble metals concentration. The effect of glass temperature on the melter operation was pronounced. At the lower setting of 1,050°C, the feed could barely be processed through the melter, and at the higher temperature of 1,200°C, the feed processed much faster than at the nominal setting of 1,150°C. The effect of plenum heating was minor.

Pre-test, preliminary post-test, and post-test computer model simulations of the RSM were completed using the Transient Energy, Momentum and Pressure Equations Solutions in Three Dimensions (TEMPEST) computer code. Simulations were run with symmetric electrodes in their "as built" state and with asymmetric electrodes in the end-of-test "as observed" state. Both fully coupled (several hours) and longer time uncoupled (several days) simulation sets were computed. For the asymmetric electrode simulations, an enhanced conductivity sludge layer was included. Electric conductivity of the layer was varied by nearly four orders of magnitude. Significant differences were seen in the electric parameters for the feed (cold cap) cases relative to the idling state. Current flux on the electrode face showed a six-fold increase caused by the simulated sludge layer. The maximum current density observed with the shortened electrode was 4.4 A/cm^2 . The current density for the symmetric electrode case was 0.98 A/cm^2 . The current density measured during the RSM test under similar conditions was 1.1 A/cm^2 . The maximum current density recommended for the plant melter is 1 A/cm^2 . The convection patterns predicted by TEMPEST were nearly identical to those observed in the RSM during post-test destructive examination of the melter (as indicated by swirls in the glass). This is significant because it represents the first experimental confirmation of predicted glass melt convection.

The power controller was tested for both bulk-averaged temperature and single-point thermocouple temperature control. These tests showed that there can be rather marked differences in the average temperature relative to the controlling thermocouple temperature.

Fully coupled momentum, energy, species, and electric field calculations are computer-time intensive. An accelerated modeling approach was used in which large particles (400 μm) were assumed. Simulation of a fully coupled (albeit accelerated) transition to an idle state showed a much increased settling rate. This accelerated settling approach needs to be investigated further to determine whether a confirmed basis for time scaling can be determined. Even without a time scaling factor, the results of the accelerated model were very useful. The geometry of the settled noble metals layer on the bottom of the melter was similar to that predicted by the TEMPEST computer code.

Particle size and shape data from the GFT and RSM were analyzed to determine sphericity, porosity, and hindrance effects on particle settling rates. Long-term (up to three weeks), uncoupled particle transport calculations were conducted to investigate concentration variations using "real" data to determine settling rates. Results show that concentration variations that occur in the uncoupled state over relatively long periods of time are relatively small. This is, in general, consistent with experimental observations.

Comparison of predicted RSM melter operational parameters (power, voltage, current, and resistance) agree to within 13 to 50% of measured values. Measurements have as much as $\pm 18\%$ variations. Predicted temperatures are in qualitative agreement with limited temperature probing near the melter floor and near electrode forces. A predicted (3 day) retention of 7% of noble metals is in both qualitative and quantitative agreement with nominal (1X) noble metals test segments. Additional confirmation of property data used in the computer models with experimental data is needed. This is especially true for the concentration dependence for electrical conductivity and viscosity, for which there is no data on HWVP glass.

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Abbreviations and Acronyms

AA	Atomic Adsorption
AES	Atomic Emission Spectrometer
CO	Carbon Monoxide
CPU	Central Processing Unit
DOE	U.S. Department of Energy
DWPF	Defense Waste Processing Facility
EDS	Energy Dispersive Spectrometry
EDL	Engineering Development Laboratory
EDX	Energy Dispersive X-Ray
ESM	Engineering-Scale Melter
FY	Fiscal Year
GFT	Gradient Furnace Testing
HCN	Hydrogen Cyanide
HEME	High-Efficiency Mist Eliminator
HEPA	High-Efficiency Particulate Air
HWVP	Hanford Waste Vittrification Plant
IC	Ion Chromatography
ICP	Inductively Coupled Plasma
IDMS	Integrated DWPF Melter System
I/O	Input/Output

KfK	Kernforschungszentrum Karlsruhe
KOH	Potassium Hydroxide
L/D	Length to Diameter
MS	Mass Spectrometer
MPA	Melter Performance Assessment
NCAW	Neutralized Current Acid Waste
NM	Noble Metals
PHTD	PNL HWVP Technology Development
PID	Proportional Integral Derivative
PNL	Pacific Northwest Laboratory
PSCM	Pilot-Scale Ceramic Melter
RSM	Research-Scale Melter
SCR	Silicon Controlled Rectifier
SEM	Scanning Electron Microscopy
SRAT	Slurry Receipt Adjustment Tank
SRTC	Savannah River Technology Center
TEMPEST	Transient Energy, Momentum and Pressure Equations Solutions in Three Dimensions
TO	Total Oxides
WHC	Westinghouse Hanford Company
WVDP	West Valley Demonstration Project
XRF	X-Ray Fluorescence

Contents

Summary	iii
Acknowledgements	vii
Abbreviations and Acronyms	ix
1.0 Introduction	1.1
1.1 Needs/Issues	1.1
1.2 Background	1.2
1.3 Overview of Melter Performance Assessment Approach	1.3
1.4 Specific Objectives Related to Needs/Issues	1.8
1.5 Report Outline	1.8
2.0 Conclusions and Recommendations	2.1
2.1 Conclusions	2.1
2.2 Recommendations	2.4
3.0 Experimental Methods	3.1
3.1 Test Objectives	3.1
3.2 Description of Test Matrix	3.2
3.3 Equipment and Operations	3.2
3.3.1 Feed Preparation Procedure	3.3
3.3.2 Research-Scale Melter	3.11
3.4 Analytical Techniques	3.21
3.4.1 Anion Analysis	3.21
3.4.2 Cation Analysis	3.22
3.4.3 Microscopy Analyses	3.22
3.4.4 Glass Redox Potential	3.23
4.0 Results of Experimental Run	4.1
4.1 Pretest Feed Preparation	4.1
4.1.1 SRAT Preparation	4.1
4.1.2 Off-Gas Measurements	4.3
4.2 Run Description	4.12
4.2.1 Feed Preparation	4.12
4.2.2 Melter Processing	4.13
4.2.3 Summary of Interruptions	4.21
4.3 Test Results	4.23
4.3.1 Melter Joule Heating Resistance Data	4.23
4.3.2 Barium Tracer Test Results	4.26
4.3.3 Post-Test Destructive Melter Examination	4.27
4.3.4 Sample Analytical Results	4.29
4.3.5 Noble Metal Particle Characterization	4.49
4.4 Input to Computer Modeling	4.49

5.0	Discussion of Experimental Run Results	5.1
5.1	Post-Test Results	5.1
5.1.1	Noble Metal Behavior in Glass Product	5.1
5.1.2	Noble Metal Behavior in Bottom Samples	5.6
5.1.3	Joule Heating Resistance and Noble Metal Retention Data	5.8
5.2	Electrode Failure	5.8
5.3	Comparison RSM Results with Other Melter Runs	5.12
5.4	Lessons Learned	5.15
6.0	Computer Modeling	6.1
6.1	Tempest Computer Program Description	6.3
6.1.1	Species Transport - Continuum Approach	6.4
6.1.2	Species Transport - Particle Tracker Approach	6.4
6.1.3	Electric Field Equations - AC Model	6.5
6.2	Computer Submodel Connections	6.6
6.2.1	Enhanced Electrical and Thermal Conductivities	6.7
6.2.2	Glass Viscosity	6.8
6.2.3	Particle Settling	6.11
6.2.4	Power Controller	6.18
6.3	RSM Computer Model Description	6.19
6.3.1	Geometry and Simulation Considerations	6.19
6.3.2	Properties Used in Simulations	6.20
6.4	Computer Results	6.28
6.4.1	Simulation Matrix	6.30
6.4.2	Average Power, Voltage, Current, and Resistance Results	6.34
6.4.3	Transient Power and Temperature Results	6.35
6.4.4	Transient Fully Coupled Noble Metals Transport Without Pouring	6.49
6.4.5	Transient Fully Coupled Noble Metals Transport With Pouring	6.62
6.4.6	Particle Settling Submodel Testing	6.67
7.0	References	7.1
Appendix A:		
	Feed Preparation Off-Gas Data (Figures A.1 to A.11)	A.1
	Electrode Resistance Data After Filtering (Figures A.12 to A.20)	A.12
	Optical and SEM Micrographs of Glass Samples (Figures A.21 to A.54)	A.21
Appendix B: Raw Melter Processes Data		B.1
Appendix C: Feed Rheology		C.1

Figures

1.1	Noble Metals Assessment Strategy	1.4
3.1	Precipitation Solids Settling Behavior	3.8
3.2	RSM Configuration	3.12
3.3	RSM Electrodes	3.13
3.4	RSM Position in Kiln	3.14
3.5	Service Locations for RSM Test	3.15
3.6	Feed Nozzle	3.17
3.7	Discharge Trough	3.19
3.8	Muffle Furnace Surrounding Glass Canister	3.20
4.1	RSM Barium Tracer Test	4.28
4.2	Post-Test Melter Examination	4.31
4.3	Part of Melter Showing Erosion of Discharge Tube	4.33
4.4	Nickel Content in Glass, Weight % Elemental	4.43
4.5	Chrome Content in Glass, Weight % Elemental	4.44
4.6	Location of Samples Taken from Melter Tank	4.46
5.1	Noble Metals in Glass Product by Segment	5.2
5.2	Resistance Between Electrodes and Noble Metal Accumulation Over Entire Melter Campaign	5.9
5.3	Scenario for Electrode Erosion	5.11
6.1	Theoretical Ratio of Electrical Conductivity for a High Conductivity Discrete Particle Distributed in a Continuous Medium	6.9
6.2	Schematic of the RSM Before and After Testing	6.21
6.3	Comparison of Temperature Dependence of Electric Conductivity Correlations and Data	6.24
6.4	Temperature Dependence of Thermal Conductivity Used in RSM Computer Modeling	6.25
6.5	Temperature Dependence of Density Used in RSM Computer Modeling	6.26
6.6	Temperature Dependence of Viscosity Used in RSM Computer Modeling	6.28
6.7	Power, Average Melt Temperature, and Thermocouple Temperature Response to Electric Conductivity and Controller Scheme	6.38
6.8	Power, Average Melt Temperature, and Thermocouple Temperature Response to Electric Conductivity and Controller Scheme Showing an Underdamped Thermocouple Control	6.40
6.9	Power, Average Melt Temperature, and Thermocouple Temperature Response to Electric Conductivity and Controller Scheme Showing the Response in Transition from a Feeding to an Idle Situation	6.41
6.10	Power, Average Melt Temperature, and Thermocouple Temperature in Response to a Transition to Thermocouple Control in a Melt with an Enhanced, Nonconvecting Sludge Layer	6.42

6.11	Power, Average Melt Temperature, and Thermocouple Temperature in Response to a Transition to Thermocouple Control in a Melt at Idle State with an Enhanced, Nonconvecting Sludge Layer	6.43
6.12	Power, Average Melt Temperature, and Thermocouple Temperature in Response to a Transition to Thermocouple Control in a Melt in a Feed State with 0.58 kg/h Pouring and a Simulated Sludge Layer with a Reference Electric Conductivity of 15.2 S/m	6.45
6.13	Power, Average Melt Temperature, and Thermocouple Temperature in Response to a Transition to Thermocouple Control in a Melt in a Feed State with 0.58 kg/h Pouring and a Simulated Sludge Layer with a Reference Electric Conductivity of 678 S/m	6.46
6.14	Power, Average Melt Temperature, and Thermocouple Temperature in Response to a Transition to Thermocouple Control in a Melt in a Feed State with 0.58 kg/h Pouring and a Simulated Sludge Layer with a Reference Electric Conductivity of 6.78×10^4 S/m	6.47
6.15	Power, Average Melt Temperature, and Thermocouple Temperature as a Function of Reference Electric Conductivity in a Simulated Nonconvecting Sludge Layer	6.48
6.16	Power, Average Temperature, and Thermocouple Temperature for Feed Case with Fully Coupled Noble Metals Particle Transport and Accelerated Settling	6.50
6.17	Power, Average Temperature, and Thermocouple Temperature for a Transition to Idle Case with Fully Coupled Noble Metals Particle Transport and Accelerated Settling	6.51
6.18	Electric Parameters for a Feed Case with Fully Coupled Noble Metals Particle Transport and Accelerated Settling	6.53
6.19	Electric Parameters for a Transition to an Idle Case with Fully Coupled Noble Metals Particle Transport and Accelerated Settling	6.54
6.20	Normalized Electric Current Flux on the Face of One Electrode for a Feed Case with Fully Coupled Noble Metals Particle Transport and Accelerated Settling	6.55
6.21	Normalized Electric Current Flux on the Face of One Electrode for a Transition to an Idle Case with Fully Coupled Noble Metals Particle Transport and Accelerated Settling	6.56
6.22	Velocity Vectors Comparison for the Feed and Transition to Idle Case	6.58
6.23	Isotherms Comparison for the Feed and Transition to Idle Case	6.59
6.24	Volume Fraction Comparison for the Feed and Transition to Idle Case	6.60
6.25	Time Buildup of Simulated Noble Metals in the Sludge Layer for the Transition to Idle Situation	6.61
6.26	Perspective View of Solids Distribution Near the Melter Floor for the Feed Case . . .	6.63
6.27	Perspective View of Solids Distribution Near the Melter Floor for the Idle Case	6.65
6.28	Simulated Noble Metals Mass at the Melter Floor and Total Mass in the System for a Simulated Noble Metals Feed Rate of 0.0511 kg/h and Glass Pour Rate of 0.49 kg/h	6.68

6.29	Species Volume Fraction at the Melter Floor and at the Diptube Entrance and Total Mass in the System for a Simulated Noble Metals Feed Rate of 0.0511 kg/h and Glass Pour Rate of 0.49 kg/h	6.69
A.1	Gas Generation Data from Formating Batch RSM-1	A.1
A.2	Gas Generation Data from Formating Batch RSM-2	A.2
A.3	Comparison of RSM-1 and RSM-2 Formating: CO ₂ Data	A.3
A.4	Comparison of RSM-1 and RSM-2 Formating: N ₂ O Data	A.4
A.5	Comparison of RSM-1 and RSM-2 Formating: NO _x Data	A.5
A.6	Comparison of RSM-1 and RSM-2 Formating: H ₂ Data	A.6
A.7	Typical Lab-Scale CO Data	A.7
A.8	RSM-1 CO Data	A.8
A.9	RSM-2 CO Data	A.9
A.10	Gas Chromatograph Carbon Monoxide Data	A.10
A.11	Carbon Monoxide Data for RSM-1 and RSM-2	A.11
A.12	Resistance Between Electrodes (Segment Number 1)	A.12
A.13	Resistance Between Electrodes (Segment Number 4)	A.13
A.14	Resistance Between Electrodes (Segment Number 5)	A.14
A.15	Resistance Between Electrodes (Segment Number 6)	A.15
A.16	Resistance Between Electrodes (Segment Number 7)	A.16
A.17	Resistance Between Electrodes (Segment Number 8)	A.17
A.18	Resistance Between Electrodes (Segment Number 9)	A.18
A.19	Resistance Between Electrodes (Segment Number 10)	A.19
A.20	Resistance Between Electrodes (Segment Number 11)	A.20
A.21	SEM/EDX of Glass from Segment 1	A.21
A.22(a)	SEM/EDX of Glass from Segment 4	A.21
A.22(b)	SEM/EDX of Glass from Segment 4	A.22
A.23	SEM/EDX of Glass from Segment 4	A.22
A.24	SEM/EDX of Glass from Segment 4	A.23
A.25	SEM/EDX of Glass from Segment 5	A.23
A.26	SEM/EDX of Glass from Segment 6	A.24
A.27	SEM/EDX of Glass from Segment 7	A.24
A.28(a)	SEM/EDX of Glass from Segment 7	A.25
A.28(b)	SEM/EDX of Glass from Segment 7	A.25
A.29	SEM/EDX of Glass from Segment 8	A.26
A.30	SEM/EDX of Glass from Segment 8	A.26
A.31(a)	SEM/EDX of Glass from Segment 9	A.27
A.31(b)	SEM/EDX of Glass from Segment 9	A.27
A.32	SEM/EDX of Glass from Segment 9	A.28
A.33	SEM/EDX of Glass from Segment 10	A.28
A.34	SEM/EDX of Glass from Segment 10	A.29
A.35	SEM/EDX of Glass from Segment 10	A.29
A.36(a)	SEM/EDX of Glass from Segment 11	A.30
A.36(b)	SEM/EDX of Glass from Segment 11	A.30

A.36(c)	SEM/EDX of Glass from Segment 11	A.31
A.36(d)	SEM/EDX of Glass from Segment 11	A.31
A.36(e)	SEM/EDX of Glass from Segment 11	A.32
A.37(a)	SEM/EDX of Glass from Post-Test Sample C1	A.33
A.37(b)	SEM/EDX of Glass from Post-Test Sample C1	A.34
A.38(a)	SEM/EDX of Glass from Post-Test Sample C1	A.35
A.38(b)	SEM/EDX of Glass from Post-Test Sample C1	A.36
A.38(c)	SEM/EDX of Glass from Post-Test Sample C1	A.37
A.39(a)	SEM/EDX of Glass from Post-Test Sample C2	A.38
A.39(b)	SEM/EDX of Glass from Post-Test Sample C2	A.39
A.40(a)	SEM/EDX of Glass from Post-Test Sample C2	A.40
A.40(b)	SEM/EDX of Glass from Post-Test Sample C2	A.41
A.41	SEM/EDX of Glass from Post-Test Sample C3	A.42
A.42(a)	SEM/EDX of Glass from Post-Test Sample C3	A.43
A.42(b)	SEM/EDX of Glass from Post-Test Sample C3	A.44
A.43(a)	SEM/EDX of Glass from Post-Test Sample C4	A.45
A.43(b)	SEM/EDX of Glass from Post-Test Sample C4	A.46
A.44	SEM/EDX of Glass from Post-Test Sample C4	A.47
A.45(a)	SEM/EDX of Glass from Post-Test Sample C4	A.48
A.45(b)	SEM/EDX of Glass from Post-Test Sample C4	A.49
A.46(a)	Optical Micrographs of Glass from Segment 1	A.50
A.46(b)	Optical Micrographs of Glass from Segment 1	A.50
A.46(c)	Optical Micrographs of Glass from Segment 1	A.51
A.47(a)	Optical Micrographs of Glass from Segment 4	A.51
A.47(b)	Optical Micrographs of Glass from Segment 4	A.52
A.47(c)	Optical Micrographs of Glass from Segment 4	A.52
A.48(a)	Optical Micrographs of Glass from Segment 5	A.53
A.48(b)	Optical Micrographs of Glass from Segment 5	A.53
A.48(c)	Optical Micrographs of Glass from Segment 5	A.54
A.49(a)	Optical Micrographs of Glass from Segment 6	A.54
A.49(b)	Optical Micrographs of Glass from Segment 6	A.55
A.49(c)	Optical Micrographs of Glass from Segment 6	A.55
A.50(a)	Optical Micrographs of Glass from Segment 7	A.56
A.50(b)	Optical Micrographs of Glass from Segment 7	A.56
A.50(c)	Optical Micrographs of Glass from Segment 7	A.57
A.51(a)	Optical Micrographs of Glass from Segment 8	A.57
A.51(b)	Optical Micrographs of Glass from Segment 8	A.58
A.51(c)	Optical Micrographs of Glass from Segment 8	A.58
A.52(a)	Optical Micrographs of Glass from Segment 9	A.59
A.52(b)	Optical Micrographs of Glass from Segment 9	A.59
A.52(c)	Optical Micrographs of Glass from Segment 9	A.60
A.53(a)	Optical Micrographs of Glass from Segment 10	A.60
A.53(b)	Optical Micrographs of Glass from Segment 10	A.61

A.53(c)	Optical Micrographs of Glass from Segment 10	A.61
A.54(a)	Optical Micrographs of Glass from Segment 11	A.62
A.54(b)	Optical Micrographs of Glass from Segment 11	A.62
A.54(c)	Optical Micrographs of Glass from Segment 11	A.63
B.1	Resistance Between Electrodes (Segment Number 1)	B.1
B.2	Melt Temperature (Segment Number 1)	B.2
B.3	Plenum Temperature (Segment Number 1)	B.3
B.4	Glass Pour in 15-Min Interval (Segment Number 1)	B.4
B.5	Resistance Between Electrodes (Segment Number 4)	B.5
B.6	Melt Temperature (Segment Number 4)	B.6
B.7	Plenum Temperature (Segment Number 4)	B.7
B.8	Glass Pour in 15-Min Interval (Segment Number 4)	B.8
B.9	Resistance Between Electrodes (Segment Number 5)	B.9
B.10	Melt Temperature (Segment Number 5)	B.10
B.11	Plenum Temperature (Segment Number 5)	B.11
B.12	Glass Pour in 15-Min Interval (Segment Number 5)	B.12
B.13	Resistance Between Electrodes (Segment Number 6)	B.13
B.14	Melt Temperature (Segment Number 6)	B.14
B.15	Plenum Temperature (Segment Number 6)	B.15
B.16	Glass Pour in 15-Min Interval (Segment Number 6)	B.16
B.17	Resistance Between Electrodes (Segment Number 7)	B.17
B.18	Melt Temperature (Segment Number 7)	B.18
B.19	Plenum Temperature (Segment Number 7)	B.19
B.20	Glass Pour in 15-Min Interval (Segment Number 7)	B.20
B.21	Resistance Between Electrodes (Segment Number 8)	B.21
B.22	Melt Temperature (Segment Number 8)	B.22
B.23	Plenum Temperature (Segment Number 8)	B.23
B.24	Glass Pour in 15-Min Interval (Segment Number 8)	B.24
B.25	Resistance Between Electrodes (Segment Number 9)	B.25
B.26	Melt Temperature (Segment Number 9)	B.26
B.27	Plenum Temperature (Segment Number 9)	B.27
B.28	Glass Pour in 15-Min Interval (Segment Number 9)	B.28
B.29	Resistance Between Electrodes (Segment Number 10)	B.29
B.30	Melt Temperature (Segment Number 10)	B.30
B.31	Plenum Temperature (Segment Number 10)	B.31
B.32	Glass Pour in 15-Min Interval (Segment Number 10)	B.32
B.33	Resistance Between Electrodes (Segment Number 11)	B.33
B.34	Melt Temperature (Segment Number 11)	B.34
B.35	Plenum Temperature (Segment Number 11)	B.35
B.36	Glass Pour in 15-Min Interval (Segment Number 11)	B.36

C.1	Rheograms for Feeds with 500 g TO/L and Nominal Noble Metals Concentration . . .	C.2
C.2	Rheograms for Feeds with 400 g TO/L and Nominal Noble Metals Concentration . . .	C.3
C.3	Rheograms for Feeds with 400 g TO/L and 500 g TO/L and Nominal Noble Metals Concentration	C.4
C.4	Rheograms for Feeds with 400 g TO/L and 2X Noble Metals Concentration	C.5
C.5	Rheograms for Feeds Agitated in the Laboratory with 400 g TO/L and 2X Noble Metals Concentration	C.6

Tables

1.1	Gradient Furnace Testing Results	1.7
3.1	RSM Test Matrix	3.3
3.2	HWVP Target Glass Composition	3.5
3.3	RSM Feed Make-up Materials and Amounts	3.7
4.1	RSM-1 SRAT Feed Analysis Results	4.2
4.2	Mixed Hydroxide Slurry Elemental Analysis	4.3
4.3	RSM-2 SRAT Feed Analysis	4.4
4.4	Moles of Gas Released During RSM-1	4.6
4.5	Moles of Gas Released During RSM-2	4.6
4.6	RSM Run Summary	4.15
4.7	RSM Alarm Conditions	4.22
4.8	Cold Cap Losses During Each Segment	4.24
4.9	Description of Typical RSM Outages	4.24
4.10	Melter Resistance Data for Each Segment	4.26
4.11	Anion Concentration in Melter Feed	4.35
4.12	ICP-AES Glass Product Analyses	4.36
4.13	ICP-MS Glass Product Analyses	4.38
4.14	XRF Glass Product Analyses	4.40
4.15	Average Cation Analysis of Glass Product	4.42
4.16	Fe ⁺² /ΣFe Iron for Glass by Segment Number	4.45
4.17	Bottom Sample Analysis Results for ICP-MS	4.47
4.18	Bottom Sample Analysis Results for XRF	4.48
4.19	Results of SEM, EDX, and Optical Microscopy Observations	4.50
4.20	Measured Particle Size Distributions	4.52
5.1	Percent of Noble Metals Retained in the Melter	5.4
5.2	Noble Metal Distribution in Bottom Samples	5.7
5.3	Summary of HWVP Noble Metals Runs	5.13
5.4	Comparison of Noble Metals Content in Melter Glass	5.15
6.1	Measured Particle Size Distributions	6.12
6.2	Particle Shape Factors and Sizes for GFT RuO ₂ Particles	6.14
6.3	Values of F for RSM Particles	6.16
6.4	Settling Velocity Distributions for RSM and GFT Particles	6.18
6.5	Summary of RSM Computer Model Simulation Cases, Steady-State Thermal Parameters	6.33
6.6	Summary of RSM Computer Model Simulation Cases, Steady-State Electric Parameters	6.36
6.7	Summary of RSM Test Segment, Average Power, Voltage, and Current	6.37
6.8	Relative Heat Loss Summary	6.67
6.9	Times Required to Reach Constant Concentration	6.70
6.10	Local Concentration Constants for the Melter Floor in Front of the Electrodes	6.72

6.11	Local Concentration Constants for the Tops of the Electrodes	6.72
6.12	Local Concentration Constants for Areas of Decreased or Initial Concentration	6.72
6.13	Maximum Volume Fractions Reached in Test Runs	6.73
6.14	Local Concentration Constants for the Melter Floor in Front of the Electrodes, with Hindered Settling	6.73
6.15	Local Concentration Constants for the Tops of the Electrodes, with Hindered Settling	6.73
6.16	Local Concentration Constants for Areas of Decreasing or Constant Concentration, with Hindered Settling	6.74
C.1	Feed pHs During RSM Test	C.5

1.0 Introduction

The reprocessing of nuclear fuel generates a form of high-level radioactive waste that will be treated further to produce a stable, low-solubility glass suitable for geologic or long-term disposal. In many countries, including the United States, current plans call for vitrification of the high-level and transuranic fraction of these wastes to form a borosilicate glass that is resistant to radioactive damage and leaching. At the Hanford Site, wastes have been generated over the span of 45 years from fuel reprocessing and other operations. These wastes, like other nuclear fuel reprocessing wastes, contain platinum group metals, also known as noble metals. The solubility of noble metals (e.g., palladium, rhodium, and ruthenium) in glass-forming melts is typically extremely low. Undissolved metallic particles can agglomerate, creating regions of heterogeneous nucleation, which influence the viscosity and uniformity of the glass in the melter. The size and behavior of the noble metal particles in the glass tank determines whether a significant quantity of the metal will settle to the floor of the melter or be carried out in the discharged glass. Many of the noble metal oxides and alloys are excellent electrical conductors and are corrosive to melter refractories. If a sufficient quantity of noble metals settles to the melter floor, the lower electrodes could be electrically shorted. If this occurs, the noble metal accumulation would need to be removed or the melter would have to be replaced.

The Melter Performance Assessment (MPA) activity in Pacific Northwest Laboratory's (PNL) Hanford Waste Vitrification Plant (HWVP) Technology Development (PHTD) effort is intended to determine the impact of noble metals on the operational life of the reference HWVP melter. The performance assessment approach is based on a plan formulated in fiscal year (FY) 1990,^(a) the premise of which is that a noble metals assessment cannot be made at full scale. A full-scale assessment cannot be conducted at this time for two reasons: 1) a full-scale melter will not be available until the HWVP performs cold testing (not expected to occur until the late 1990s), and 2) costs for noble metals are high. For example, based on a cost estimate developed in FY 1991, a 30-day run in a full-scale melter would require almost \$4M worth of noble metals alone. The approach taken is to rely on smaller test systems and augment testing with laboratory and computational modeling work. This approach is discussed in detail in Section 1.3, "Overview of Melter Performance Assessment Approach."

1.1 Needs/Issues

The objectives of Research-Scale Melter (RSM) testing are "to obtain data that assist in providing an understanding of noble metals behavior in conjunction with feed and glass chemistry to predict melter performance. Studies of test parameters, including glass melter temperature, residence time, plenum temperature, and glass redox will be performed" (Kruger 1991). To perform this scope of

(a) Nakaoka, R.K., and D.M. Strachan. 1990. *DRAFT: Melter Performance Evaluation Report*. Milestone Report HWVP-90-1.2.2.04.08B, Pacific Northwest Laboratory, Richland, Washington.

work, a small joule-heated melter system was designed in FY 1990 and constructed in FY 1991. Approximately 50 days of testing were conducted in the RSM in FY 1992 to obtain process and product data as a function of process variables. A description of the objectives related to the needs/issues is contained in Section 1.4.

1.2 Background

Experience at the PAMELA vitrification plant in Mol, Belgium, indicated that the noble metals precipitated from the glass melt during processing and caused electrical shorting in the joule-heated melter. The rate of noble metals precipitation was much higher during idle periods between campaigns.^(a) This presumably is caused by decreased convection in the melt pool during idling. Of the platinum group metals, Pd, Rh, and Ru appear to be the cause because of their low solubility in borosilicate glass and their high electrical conductivity (Volf 1984). These metals enter the feed stream as fission products from weapons production. Rhodium is likely to precipitate as a metal and alloy with Pd, unless Te is present or spinels form. If Te is present in the waste, it will alloy with Pd and exclude Rh. Rhodium is likely to precipitate in solid solution with any spinels that form. Ruthenium is likely to precipitate as RuO₂, of uncertain crystal morphology. The ruthenium dioxide is likely to provide nucleation sites for the formation of spinels and can subsequently dissolve in solid solution with the spinel-forming elements.^(b) Results of extensive work at Kernforschungszentrum Karlsruhe (KfK) indicate that RuO₂ particles are formed during processing and have a tendency to accumulate on the floor of the melter. Precipitated RuO₂ causes the viscosity of the glass melt to change from nearly Newtonian to non-Newtonian in the region of the precipitated RuO₂, leading to a highly viscous glass in areas of low flow in the melter. This may be either a localized or general effect, depending upon the extent of metals precipitation. All of the noble metals and RuO₂ are electrical conductors and tend to distort the power distribution within the melt.

During processing of a simulated waste feed at KfK, a noble metals-enriched sludge was observed on the bottom of the melter. Power from the electrodes became concentrated in this area because of the low electrical resistivity of the sludge. As a consequence, power to the electrodes was reduced to prevent overheating in this region and the feed rate was lowered to maintain acceptable operation of the melter.

Mini-melter tests conducted at Savannah River Technology Center (SRTC) revealed noble metal particles, some as large as several millimeters in diameter, dispersed in the glass.^(b) Preliminary data from the Integrated Defense Waste Processing Facility (DWPF) Melter System (IDMS) product glass examination revealed the presence of 5- to 15- μ m-long RuO₂ needles in 20- to 40- μ m clusters. Samples

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- (a) Collantes, C.E., L.K. Holton, J.M. Perez, Jr., and B.A. Wolfe. 1987. Research Facilities in the Federal Republic of Germany and the PAMELA Facility Workshop: "Vitrification Operational Experience." Foreign Trip Report.
- (b) Nakaoka, R.K., and D.M. Strachan. 1990. *DRAFT: Melter Performance Evaluation Report*. Milestone Report HWVP-90-1.2.2.04.08B, Pacific Northwest Laboratory, Richland, Washington.

taken after further testing of DWPF simulants revealed a dense layer of RuO_2 as well as evidence of Pd, Rh, and (Ni,Mn)(Fe,Cr) spinels. After IDMS testing using an HWVP simulant, further evidence of the compounds listed above were found as well as Rh-nucleated Cr/Ni/Fe spinels and an elongated formation of RuS_2 (Hutson 1992).

Data collected during the Functional and Checkout Testing of Systems testing program at the West Valley Demonstration Project (WVDP) monitored Ru concentration in the glass and feed to the melter, and directly sampled the tank glass and melter sludge deposits. The noble metal sludge that formed at the bottom of the melter contained approximately 10 wt% of the total inventory of Ru fed to the melter (Bowen and Jain 1989).

There is no direct evidence that these same problems will occur in a melter to which Hanford high-level waste is fed. HWVP feed (0.15 wt% noble metals) is projected to have approximately the same noble metals concentrations as was the feed used at the PAMELA Plant (0.14 wt% noble metals).^(a) Based on experience with crystals in melter glass, if the noble metal particles remain small (e.g., < 10 to 20 μm), little accumulation is expected to occur.^(b) It is very important that particle agglomeration not occur, as particle agglomeration would lead to higher levels of noble metal settling in the melter (Cobb and Hrma 1991). Noble metal agglomerations greater than 20 μm have been found in glasses generated during crucible tests at PNL.^(b) Precipitation of noble metals will be a long-term effect; only after a sufficient inventory of feed containing noble metals has been processed through the melter do operating problems arise. Estimating the relative period of time before noble metal effects manifest themselves is the primary objective of the MPA activity.

1.3 Overview of Melter Performance Assessment Approach

To determine whether a noble metals problem will shorten the life of the HWVP melter, an integrated testing and modeling program was deemed to be necessary. The cost of noble metals makes it impractical to conduct large-scale melter tests or perform numerous smaller-scale tests. Therefore, it was decided to conduct tests on three different scales: gradient furnace at laboratory scale, research scale (1/100th), and engineering scale (1/10th). The results of these tests will provide input to computer models and also will be used to evaluate model performance. Ultimately, the computer models and accumulated melter operating experience will be used to assess the performance of the full-scale HWVP melter. The MPA approach is illustrated in Figure 1.1.

(a) Weisenburger, S. "R&D Results for Design of Noble Metals Compatible Electric Waste Glass Melters." U.S. DOE/BMFT Vitrification and Glass Technology Workshop, Aiken, South Carolina, November 10-14, 1989.

(b) Geldart, R.W., S.O. Bates, and S.J. Jette. 1987. *Preliminary Evaluation of Noble Metal Behavior in the Hanford Waste Vitrification Plant Reference Glass, HW-39*. Milestone report HWVP-87-V110202F, Pacific Northwest Laboratory, Richland, Washington.

Figure 1.1. Noble Metals Assessment Strategy

The gradient furnace testing (GFT) apparatus is a laboratory-scale system used to investigate the physical state of the noble metals in the cold cap region and in the melt.^(a) The RSM studies are bench-scale tests that will 1) provide more characteristic melting conditions than the GFT, i.e., the existence of a cold cap and underlying melt pool, and 2) provide data on the effects of process variations on noble metal behavior such as particle size, density, distribution, oxidation state, and agglomeration tendencies. Process variations will simulate the ranges of plant melter operation, such as redox, temperature, slurry properties, etc. The RSM is a cylindrical-cavity melter with a surface area of 0.018 m² (0.7% of the full-scale HWVP melter). Its small size will allow multivariable parametric studies to be completed with a limited amount of feed.

(a) Anderson, L.D., T. Dennis, M.L. Elliott, L.L. Eyler, and P.R. Hrma. 1992. *Laboratory Testing and Computer Modeling of HWVP Melter Feed*. Milestone report C91-04.01B, Pacific Northwest Laboratory, Richland, Washington.

Testing will culminate using the Engineering-Scale Melter (ESM) located at KfK in Germany. The ESM was designed to scale critical dimensions as close to the full scale as possible. The glass surface area (0.28 m^2) is approximately 11% of the proposed HWVP melter. The glass depth of ~31 in. is within the minimum and maximum tank depths of the plant melter so that the glass residence time is prototypic. Chemical and kinetic effects cannot be well simulated or predicted by current numerical models. Therefore, the melter parameters that most affect particle growth will be maintained as closely as possible to full-scale specifications. These parameters are heat transfer conditions, glass residence time, the electrode placement, and overflow location. The residence time, combined with the convective mixing and near surface temperatures, will provide conditions as close to the plant melter as can be achieved at this scale. If a sufficient amount of noble metals are deposited on the melter floor, a decrease in the resistance between the lower electrodes will occur. Very conductive accumulations could ultimately affect the operation of the upper electrodes. For these reasons, the lower electrode height (12 in.) and the separation between the upper and lower electrode set (10 in.) are matched to the plant design.

The GFT^(a) results provide the upper boundary condition for the computer simulation of the melter, i.e., the size, density, and type of particles entering the glass melt through the cold cap. The RSM and ESM tests will characterize the extent of particle agglomeration and settling in the melt chamber.

The gradient furnace cannot completely simulate the cold cap behavior in a melter because of differing geometries and temperature histories. In an actual melter, the feed in the cold cap is exposed to an atmosphere produced by the gases evolved. Different gases are produced in different strata of the cold cap, according to the local temperature and the nature of the gas-generating reactions occurring at that temperature (Schreiber et al. 1990; 1991). Gases evolved at lower layers, where the temperature is higher, leave the cold cap through the upper layers, where they mix with gases generated locally. This complex situation cannot be easily reproduced in a laboratory crucible or boat. Gases from crucibles or boats are those generated locally within the crucible volume, which has a nearly uniform temperature in contrast to the temperature layers of a full-scale melter. Moreover, atmospheric gases can diffuse into the sample and affect the reactions, especially when the sample volume is small.

In addition, feed in a melter will experience heating at some rate as the feed proceeds from the top of the cold cap to the bottom and then into the bulk of the melt. In the gradient furnace, the temperature gradient of the sample is established almost immediately upon placing the crucible into the furnace. Therefore, the material can reach the specified temperature quickly, without experiencing the same heating rate and temperature history it would experience in a melter. However, testing is not intended to ideally simulate the HWVP melter operation, but only to provide an initial boundary condition for the first stage of define Transient Energy, Momentum and Pressure Equations Solutions in Three Dimensions (TEMPEST) computer modeling, as discussed earlier.

(a) Anderson, L.D., T. Dennis, M.L. Elliott, L.L. Eyler, and P.R. Hrma. 1992. *Investigation of Noble Metals Behavior in a Ceramic Melter Cold Cap*. Milestone report PHTD-C91-04.01B, Rev. 0, Pacific Northwest Laboratory, Richland, Washington.

Gradient furnace testing was done using two HWVP feed simulants. The difference between these two feeds was the way the noble metals were precipitated in the simulated Neutralized Current Acid Waste (NCAW). In the first feed, designated HWVP-1, the noble metals were precipitated with the major constituents. In the second feed, designated HWVP-2, the noble metals were precipitated from nitrates along with other nitrates that constitute minor constituents. The purpose of using two feeds was to discern any differences in noble metal properties as a result of neutralization history. The first method (HWVP-1) should be more representative of the history that actual radioactive waste experiences. The HWVP-2 simulation is typical of the way NCAW simulant is currently prepared and is more practical from the standpoint of material control and minimizing losses during slurry manufacture.

In addition to the two HWVP feeds, gradient furnace tests were run using simulants of KfK waste and DWPF feeds to identify any significant differences between these feeds and HWVP feeds. Finally, an isothermal melt was done with HWVP-2 feed for 48 hours at 1,150°C, which are reference conditions for the HWVP melter. This melt provided information concerning the effect of increased melting time and increased temperature on the noble metal particles.

In all the GFT samples, the noble metals separated from the melt as pure metals, metal oxides, or alloys with other noble metals at temperatures higher than approximately 800°C. At the hottest end of each sample, which simulated the bottom of the cold cap and the beginning of the bulk of the melt, particles were generally on the order of 1 μm in the DWPF and HWVP-2 samples and closer to 10 μm in the KfK and HWVP-1 samples. No palladium particles were detected at the hottest end of the HWVP-2 sample.

The input to the initial TEMPEST computer modeling used results from the HWVP-2 feed, because the RSM and ESM will use this same feed. To get this input, the hot end of the sample was sectioned and the number, size, shape, and approximate composition of the particles or agglomerates were determined. The particles at this temperature were assumed to be representative of the particles leaving the cold cap and entering the glass pool. The noble metal particles were classified into three groups based on size and appearance. The group characteristics are presented in Table 1.1. The fact that no palladium and very little rhodium were observed in the glass indicates that very little agglomeration of these metals occurs in the melter cold cap. This, of course, does not mean that agglomeration or alloying of these metals cannot occur in the melt pool.

A 48-hour isothermal (1,150°C) melt of the HWVP-2 feed was done to determine the effect of increased temperature and melt time on the noble metals particles. This was done as a precursor to the RSM test to get an idea of the effect of residence time or soaking on the formation of agglomerates or secondary phases. This melt was thin sectioned and examined by Scanning Electron Microscopy (SEM). Significant growth of an Al-Fe-Ni spinel phase had occurred along the crucible walls. This appeared to be a reaction with the alumina crucible. Needle-like ZrO_2 crystals of up to 50 to 100 μm in length existed along the bottom of the crucible and near the melt surface and, to a lesser degree, in the bulk of the melt. Five-sided crystals consisting of a solid solution of Fe, Cr, Rh, and Ni oxides were also found. They ranged up to 5 μm in diameter. Some of these crystals had small (0.5 μm) spherical

Table 1.1. Gradient Furnace Testing Results

	Group 1	Group 2	Group 3
Shape	solid sphere	"sponge"	"sponge"
Predominant type	RuO ₂	RuO ₂	RuO ₂
Effective particle diameter ^(a)	1.3 μm	3.8 μm	12.4 μm
Ratio of large/small dimension	1.7	1.6	1.9
Particles/melt area (number/mm ²)	34	16.3	0.33
(a) The diameter is calculated using total particle area and assuming a spherical shape of the particle or agglomerate.			

Pd particles adjacent to them. Irregularly-shaped RuO₂ particles ranging from 0.5 to 1 μm were also seen. These results will be compared to the RSM results later in this report.

The RSM, because of its small size, attempted to characterize these effects as a function of melter operating parameters (glass and plenum temperatures) and feed properties (oxide concentration, redox potential, and noble metal concentrations). Because of the short residence time of the RSM, 5 hours, a settled region was not expected to form. However, the glass exiting the melter will be characterized to try to detect changes in noble metal properties as a function of the parameters listed above.

The ESM test was expected to provide similar data to the RSM test, but on a larger, more prototypic scale. A mass balance will be completed throughout the test to see what fraction of the noble metals entering the melter are exiting and what fraction are settling. The residence time of the ESM, 50 hours, will be more prototypic of the full-scale HWVP melter.

By combining the GFT, RSM, and ESM results, the effect of residence time on noble metal agglomeration and precipitation can be correlated. Each series of tests will provide further information for the computer code refinement. Data on the physical properties of the noble metals obtained in the GFT are being used with the TEMPEST computer code to predict the results of the RSM. Data from the RSM will further refine calculations of the ESM in preparation for the HWVP MPA and the ESM runs. At the conclusion of the RSM and ESM runs, the noble metals behavior will be compared with that predicted by TEMPEST and further improvements will be made to the computer models.

As part of the MPA activity, all relevant noble metals data from outside sources will be gathered, reviewed, and compared to PNL data. The sources for this data will include the PAMELA plant and KfK in Germany, Power Reactor and Nuclear Fuel Development Corporation in Japan, and West Valley Nuclear Services and Savannah River Technology Center (SRTC) in the United States. The SRTC processed two batches of simulated HWVP feed containing noble metals in the IDMS in FY 1992. The resulting glass samples were thoroughly examined for noble metals characteristics (Hutson 1992). Several batches of simulated DWPF feed containing noble metals had been previously

processed through the IDMS such that a layer of noble metals has accumulated on the melter floor. This data will be useful for the melter performance assessment both as an aid for the engineering analysis as well as a comparison with the GFT, RSM, and ESM data.

Finally, data from all relevant sources will be used to predict the behavior of noble metals in the full-scale HWVP melter. This will be done using both the TEMPEST model and engineering scale-up analyses. This information will be summarized in the final melter performance assessment report in FY 1994.

1.4 Specific Objectives Related to Needs/Issues

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

- noble metals concentration in the feed
- slurry oxide loading in the feed
- redox ($\text{Fe}^{+2}/\Sigma\text{Fe}$) of the glass
- glass process temperature
- melter plenum temperature.

Process data was used to determine any measurable effects on melter operation, such as glass resistance or process rate. Process data were also used to support continued refinement of the numerical codes. Analytical data were obtained for slurry, glass, and in-melter glass/sludge samples. In addition, post-test examination of the melter was completed to observe sludge or metal deposits.

1.5 Report Outline

This report contains a description of the RSM testing results, the TEMPEST computer code as it relates to the RSM, and some results of RSM computer modeling. Section 2.0 summarizes the conclusions and recommendations drawn from the RSM testing. Section 3.0 covers the experimental methods of the RSM testing. This includes specific test objectives; experimental design of the RSM test matrix; feed preparation, melter, and off-gas system equipment descriptions; and analytical techniques used in analyzing the feeds, glasses, and noble metals sediments. Section 4.0 covers the results of the RSM testing. This section contains a feed preparation summary, test highlights, analytical results from the melter test, and input to the TEMPEST computer modeling. Section 5.0 covers the discussion of the RSM results. This section discusses the behavior of noble metals in the glass product and bottom samples and compares the RSM results with existing data. The results of the RSM computer modeling completed to date are presented in Section 6.0. Section 7.0 contains references. Feed preparation data, RSM electrode resistance plots, and glass sample micrographs are presented in Appendix A. The melter process data plots are presented in Appendix B. Feed rheology experiments are described in Appendix C.

2.0 Conclusions and Recommendations

Conclusions (Section 2.1) and recommendations (Section 2.2) are made based upon results of RSM testing.

2.1 Conclusions

- The effects of noble metals on the RSM were more pronounced than expected. With a short residence time (5 hours), noble metals were not expected to accumulate in the melter based on intuition and an estimation of settling velocities. In fact, a significant amount of noble metals accumulated (~2 to 4 mm thick). The settled layer included RuO_2 , Ru/Rh alloys, Pd/Te/Ag alloys, Pd/Te/Ag/Ru alloys and Fe/Cr/Ni spinels. The majority of the accumulation occurred during the segments with double the nominal amount of noble metals.
- There appears to be a nonlinearity in the relationship between noble metals concentration and noble metals settling in the melter. The feeds with double the nominal noble metals concentration had a much larger effect on the melter than the nominal feeds did. Approximately 45% of the noble metals were retained in the segments with double the nominal amount, compared to 5% retention in the segments containing nominal noble metals.
- The process variations which had an effect on noble metal particle morphology appear to be limited to glass redox, noble metal concentration and silver and tellurium concentration. Under most conditions the only visible noble metal particles the RSM produced were RuO_2 needles which had agglomerated in particles up to 20 μm . When the glass in the melter was reduced to $\text{Fe}^{+2}/\Sigma\text{Fe} = 0.019$ spherical particles of palladium, tellurium and silver were observed along with RuO_2 . When the glass redox reached $\text{Fe}^{+2}/\Sigma\text{Fe} = 0.25$, all of the visible noble metal particles had been reduced to metallic particles and many included alloys of silver, tellurium and copper. When the concentration of noble metals was doubled, the size of the RuO_2 agglomerates grew as large as 200 μm . When silver and tellurium concentrations were doubled in conjunction with doubling the amount of noble metals metallic palladium spheres were observed in the glass.
- Variations in plenum temperature and oxide loading had little discernable effect on noble metal retention with the possible exception of palladium which had higher retention at the higher oxide loading. The addition of extra silver and tellurium also appeared to increase the retention of palladium. This is consistent with the theory of alloying of these materials producing larger particles which settle faster, although, the visible palladium particles did not appear to be alloyed. The effect of glass temperature appeared to be an indirect one. The higher glass temperature reduced the glass and produced spherical metal particles in the glass. This was accompanied, not surprisingly, with increased retention of noble metals. All of these changes were smaller than those observed during the segments with double the amount of noble metals.

- Settled layers of noble metals are very corrosive to the melter's fused-cast refractory. It is not clear whether this is a chemical effect or a thermal effect caused by localized heating.
- Settled layers of noble metals are very damaging to Inconel 690 electrodes. The lower 1/3 of one of the electrodes in the RSM was removed because of overheating caused by short circuiting to the noble metals layer.
- Ruthenium exists as RuO_2 needles under oxidizing conditions in the HWVP glass. These needles agglomerate in the melter pool into random orientations that resemble hair balls. Under reducing conditions ($\text{Fe}^{+2}/\Sigma\text{Fe} = 0.25$), the RuO_2 reduces to metallic ruthenium which then alloys with rhodium metal. This is near the plant operating limit of 0.23 and may pose a problem for the plant.
- As observed during previous PNL melter runs, temperature has a profound effect on the melter processing rate. When the melter setpoint was $1,050^\circ\text{C}$, the feed could barely be processed. When the melter setpoint was $1,175^\circ\text{C}$, the processing rate was 40% higher than at the nominal operating temperature of $1,150^\circ\text{C}$.
- The feed had severe rheology problems when aged. Because of this, the feed system was changed so that new feed was made up every day, and changed to a nominal oxide loading of 400 g/L.
- The current HWVP flowsheet feed processes very poorly. This may or may not be a direct result of the rheology problems mentioned earlier. The feed did not spread over the glass surface well. The cold caps were thick and rigid with very little venting in all segments of the testing. The feed would sinter and form stalagmites from the conical cold cap up to the feed nozzle. Sometimes this would clog the nozzle, requiring shutdown and reaming of the nozzle. This slow processing rate produced a significant hold up for the feed in the cold cap. Tracer tests estimated this to be 2.5 hours.
- The RSM operated semi-autonomously for 2 months with an online efficiency of 80%. The efficiency would have been much higher if the off shifts would have been staffed instead of using a computer control system that would page an on-call engineer if problems arose at night.
- The off-gas information obtained during forming of two batches of feed was similar to that experienced during bench-scale forming runs. However, the nitrous oxide and NO_x concentrations did not peak until well after the formic acid addition was stopped. The off gases generally decrease rapidly when the formic acid addition was stopped during bench-scale runs. The reason for this delay in peaks is not known.

Computer modeling simulations of the RSM operation have been conducted. Pre-test, preliminary post-test, and post-test simulations have been done. These were designed to be numerical experiments to investigate parameters (power, voltage, current, and resistance); particle transport and properties submodels; power control; and sludge layer development. Conclusions reached from these simulations include:

- Predicted operational parameters (power, voltage, current, and resistance) predicted by the computer model agree to within 4 to 50% of RSM measurements. Measurements exhibit as much as $\pm 18\%$ variations.
- Power control to either a bulk-average or a single-point control temperature was demonstrated. The predicted bulk average temperature varied by as much as 70°C from the predicted single-point temperature control value. Maximum temperature predictions vary by as much as 120°C from a control temperature.
- Submodels for concentration-dependent electric conductivity, viscosity, density, and hindered settling have been implemented, tested, and shown to work. Fully coupled calculations have shown expected physical effects of these submodel couplings.
- Gradient furnace testing and RSM particle characterizations from glass sample microscopy are very useful to the computer modeling. Microscopy results have been used to determine effects of particle porosity and sphericity on terminal settling velocities.
- Predicted glass convection patterns are in remarkably good agreement with streak patterns observed in post-test melter examination. This is very significant in that it is the first experimental confirmation of computer prediction of glass convection patterns in an operational melter.
- Using an accelerated analysis methodology, development of a sludge layer containing a very high concentration of noble metals was successfully computed.
- Predictions indicate that an enhanced noble metals sludge layer develops more readily in an idling melter than a feeding melter with or without pouring. This is because without the cold cap, temperatures differences inducing buoyancy-driven flow are less.
- In a combined fully coupled/uncoupled analysis, a 7% retention of simulated noble metals particles was computed in a three day simulation. This is in both qualitative and quantitative agreement with test data (5% retention of noble metals).

2.2 Recommendations

- The HWVP operating limits for redox and possibly temperature should be reviewed based on the findings of this work. It appears that the reduction of noble metals to their metallic state can occur within the current plant operating limits. This will result in increased noble metal accumulation in the melter.
- The RSM is a flexible and low-cost tool for testing requiring continuous processing in a joule-heated melter. If future testing is needed, the RSM infrastructure installed for this testing should be considered.

- Glass properties (viscosity and electrical conductivity) as a function of noble metals concentration and temperature should be measured for use in TEMPEST computer modeling and will be needed for MPA analysis.

3.0 Experimental Methods

The following sections discuss the layout of the RSM run and the procedures used in completing the test. The data obtained from these operations are presented in Section 4.0.

3.1 Test Objectives

Per the FY 1991 PNL statement of work, the objectives of RSM testing were "to establish operating parameters for engineering-scale melter tests at KfK and evaluate glass containing noble metals. Obtain data that provide an understanding of noble metals behavior in conjunction with feed and glass chemistry to predict melter performance...conduct studies of test parameters, including glass melter temperature, residence time, plenum temperature, and glass redox." (Kruger 1991). To perform this scope of work, a small joule-heated test system was designed in FY 1990 and constructed in FY 1991. Approximately 8 weeks of testing were conducted in the RSM in FY 1992 to obtain process and product data as a function of process variables.

The relevant slurry and process variables were varied through the ranges of the HWVP operating limits (WHC 1992). The following variables were investigated:

- noble metals concentration in the feed - nominal for the HWVP is 0.15 wt% noble metals in the glass
- slurry oxide loading in the feed - nominal for the HWVP is 500 g TO/L. The design range is 400 to 600 g TO/L.
- redox ($\text{Fe}^{+2}/\Sigma\text{Fe}$) of the glass - the acceptable range for the HWVP glass is $\text{Fe}^{+2}/\Sigma\text{Fe} = 0.005$ to 0.23.
- glass process temperature - the nominal operating temperature for the HWVP is 1,150°C. The limits are 1,050°C and 1,170°C.
- melter plenum temperature - minimum operating plenum temperature for the HWVP is 650°C.

Process data were used to determine any measurable effects on melter operation, such as glass resistance or process rate. Process data were also used to support continued validation and refinement of the numerical codes. Analytical data were obtained for slurry, glass, and in-melter glass/sludge samples. In addition, post-test examination of the melter was done to measure metal deposits.

HWVP process limits have been established for many feed and melter parameters. These include glass temperature, plenum temperature, glass redox, and slurry oxide concentration. Variations of these parameters will alter somewhat the melting and residence time experience of noble metal particles. For

example, the rate of temperature increase and the total time within temperature regimes within the cold cap are dependant on plenum and glass temperature and cold cap thickness. Particle interaction and growth are known to occur in the cold cap and near glass region (Nakaoka et al. 1986,^(a)). To assess the impacts of these parameters on noble metals behavior, testing was conducted at the process limits.

Additional variables that can affect particle size and properties are the level of redox and noble metal concentration in the melter feed. More reducing glasses can lead to reduction of noble metal oxides to metal states. These metals could consolidate, alloy with other metals or act as nucleating sites for spinel growth. Higher concentrations of noble metals provides the opportunity for a greater degree of particle growth.

3.2 Description of Test Matrix

The RSM, because of its small size, was chosen to characterize the effects of noble metals on melter performance as a function of melter operating parameters (glass and plenum temperatures) and feed properties (oxide concentration, redox potential, and noble metal concentrations). Because of the short residence time of the RSM, 5 hours, a settled region was not expected to form based on intuition and an estimation of settling velocities. However, the glass exiting the melter was characterized to detect any changes in noble metal properties as a function of the parameters listed above. The test matrix for the RSM testing is shown in Table 3.1. The glass reduction/oxidation potential was measured by the ratio of ferrous (Fe^{+2}) to total iron (ΣFe). A high redox glass is defined as having $\text{Fe}^{+2}/\Sigma\text{Fe}$ greater than 0.005. Originally, all of the nominal operating conditions chosen for the RSM were those expected for the HWVP. Because of feed rheology problems, the nominal feed oxide loading had to be lowered from 500 g TO/L to 400 g TO/L to permit pumping. Initially, two low glass temperature segments had been prescribed. After the first low temperature segment, it was determined that operating the melter at this low temperature was useless; the melter could barely be fed. The plenum temperatures shown in Table 3.1 are the pretest estimates. The plenum temperatures experienced during the run were much different because of the difficulty placing enough plenum heating capacity in this small melter.

3.3 Equipment and Operations

The equipment and operations necessary for the preparation of the feed and operation of the RSM and off-gas system are described in the following sections.

(a) Sevigny, G.J. 1990. "Foreign Trip Report." Trip taken June 21-June 29, 1990 to KfK Center, Federal Republic of Germany.

Table 3.1. RSM Test Matrix

Segment No.	Description	Noble Metal Concentration	Oxide Loading (g TO/L)	Glass Redox ($\text{Fe}^{+2}/\Sigma\text{Fe}$)	Glass Temperature ($^{\circ}\text{C}$)	Plenum Temperature ($^{\circ}\text{C}$)
1-3	Nominal	Nominal	400	0.005	1,150	550
4	Low glass temperature	Nominal	400	0.005	1,050	550
5	High oxide	Nominal	500	0.005	1,150	550
6	High plenum temperature	Nominal	400	0.005	1,150	650
7	High glass temperature	Nominal	400	0.005	1,200	950
8	Reducing glass	Nominal	400	0.23	1,150	800
9	High NM ^(a) concentration	2X	400	0.005	1,150	800
10	High NM, Ag, Te	2X	400	0.005	1,150	800
11	High NM, Reducing glass, High glass temperature	2X	400	0.23	1,200	800

(a) NM = Noble metals.

3.3.1 Feed Preparation Procedure

The RSM feed was prepared in tank 311 in the chemical make-up room (309) of Building 324. This tank has a 2,700-L capacity and is equipped with steam heating coils, a cold water jacket, a four-bladed agitating impeller, a ventilation blower, and a recirculation loop with an in-line grinder. The feed was prepared in five steps:^(a)

1. Co-precipitate the noble metal and minor component nitrates to hydroxides, in the presence of the insoluble components, and wash until the nitrate concentration target is met.
2. Add mixed hydroxide slurry, followed by the soluble and slightly soluble components.
3. Perform forming and digestion steps.

(a) Letter from D.E. Larson/PNL to R.A. Smith/WHC, "HWVP Feed and Glass Composition Revision Technical Note," May 13, 1991.

4. Add recycle constituents.

5. Add frit constituents.

Each of the feed preparation steps followed the Safe Operating Procedure (SOP 1, Rev. 8, "Chemical Makeup and Storage Safety Rules") and the Job Hazard Breakdowns for the project (JHB-022, "Preparation of Simulated HWVP Melter Feed" and JHB-023, "Chemical Handling During HWVP Feed Preparation"). Finally, the Chemical Safety Protocols and Material Safety Data Sheets were reviewed to understand the hazards and handling procedures for each chemical.

Steps 1 and 2 are those used to obtain the concentrated HWVP Slurry Receipt Adjustment Tank (SRAT) feed simulant. This corresponds to the unformatted waste material in the HWVP feed pre-treatment process. Completing the feed preparation through step 5 generates the simulant material known as NCAW, which is the fully pretreated feed, ready for vitrification in the HWVP melter. The oxide loading target for the SRAT simulant was set at 140 g/L. The oxide loading target for the target melter feed was 500 g/L. The 140 g/L oxide loading for the SRAT was derived such that the final volumes of both the SRAT and the NCAW would be equal.

The oxide target compositions of the SRAT, recycle, and frit are shown in Table 3.2. This table shows that the oxides in the SRAT constitute 28% of the final NCAW oxides. The contribution from the recycle materials is 3.4% of the total oxides and the frit material makes up the final 68.6% of the oxide weight.

The balances of both cations and anions in the feed is critical from a material balance standpoint for feed preparation; however, equally important is the composite behavior of the mixture in terms of rheology and oxidation potential. For example, the precipitation steps were carefully designed to generate the proper sized precipitant solids and the formatting and digestion steps were developed such that the proper reduction of the feed was achieved.

Table 3.3 shows a list of the compounds used to generate the simulant as well as their relative concentrations in the final feed. This list is also divided into the five individual feed preparation steps, as described above. Therefore, the contributions from each constituent for each step are shown.

3.3.1.1 Co-Precipitation of Noble Metal and Minor Component Nitrates

The NaOH solutions for the precipitation and washing steps were first prepared. Solid pellets were used to make both 10-M and 0.1-M solutions. The 0.1-M solution was used for washing the precipitated solids. Next, the constituents for the co-precipitation step were weighed and the dry materials slurried in a ventilation hood to reduce airborne particulates during addition to the tank. Ruthenium (Ru) and rhodium (Rh) nitrates were available in solutions of nitric acid and had elemental concentrations of 1.4% and 9.5% by weight, respectively. Because of the acidity of these solutions, special

Table 3.2. HWVP Target Glass Composition

Oxide	Plant Feed Oxide Concentration (wt%)	Recycle Feed Oxide Concentration (wt%)	Frit Oxide Concentration (wt%)
Ag ₂ O	0.034		
Al ₂ O ₃	2.57	0.14	
B ₂ O ₃	2E-3		14.03
BaO	0.05		
CaO	0.23	0.01	
CdO	0.87	0.11	
CeO ₂	0.18		
Cl	0.08		
Cr ₂ O ₃	0.07		
Ca ₂ O	0.17		
CuO	0.07		
F	0.03		
Fe ₂ O ₃	8.06	0.04	
GeO ₂	4E-5		
K ₂ O	0.06	0.01	
La ₂ O ₃	0.19		
LiO ₂			5.00
MgO	0.10	0.01	
MnO ₂	0.61	0.03	
MoO ₃	0.16		
Na ₂ O	6.10	1.45	
Nb ₂ O ₃	3E-3		
Nd ₂ O ₃	0.99		
NiO	0.66		
P ₂ O ₅	0.25	0.11	
PdO	0.034		
PbO ₂	0.20		
Pr ₂ O ₃	0.04		
Rb ₂ O ₃	0.02		
Rh ₂ O ₃	0.029		
Ru ₂ O ₃	0.106		
Sb ₂ O ₃	2E-3		
SeO ₂	4.5E-3		

Table 3.2. (contd)

Oxide	Plant Feed Oxide Concentration (wt%)	Recycle Feed Oxide Concentration (wt%)	Frit Oxide Concentration (wt%)
SiO ₂	1.14	1.49	49.57
Sm ₂ O ₃	0.02		
SnO	3E-3		
SO ₃	0.19		
SrO	0.03		
Ta ₂ O ₅	1E-3		
TeO ₂	0.028		
TiO ₂	0.19	4E-3	
Y ₂ O ₃	0.02		
ZnO	0.10		
ZrO ₂	4.31		
Total:	28.0	3.4	68.6

care was taken during the weighing and addition steps. Particulate (High-Efficiency Particulate Air [HEPA] cartridge) respirator masks were worn during the handling (in and out of the hood) of all dry components to ensure the safety of the experimentalists.

Before the weighed materials were added to the tank, water was pumped into the tank to reduce the chance of materials sticking to the tank floor and sides. The amount of water added was approximately 25%, by volume, of the desired final feed volume. Next, the noble metal nitrate solutions were added to the feed preparation tank, in the order shown in Table 3.3. The minor component nitrates were then added to the mixture. After this, the tank agitator and the in-line grinder recirculation loop were turned on to enhance mixing. The slurried insoluble components were next added into the tank as shown in Table 3.2. The entire mixture was then left to mix and recirculate for about an hour.

After the material was fully mixed, the recirculation grinder was turned off and a barrel pump was used to transfer the 10-M NaOH solution into the tank in 1-gal increments until a pH of between 10 and 11 was reached. The tank was allowed to agitate and recirculate for 5 to 10 min between additions and for a full 30 min once the target pH was reached, to ensure pH stability. Finally, the agitator was stopped, the total height of the mixture measured, and the solids allowed to settle.

The mixture was left to settle out its solids for 4 days prior to decanting the supernate. During this time the total fluid and solids layer heights were measured. Figure 3.1 shows a plot of the volume percent of the solids layer (or percent total liquid height) versus time for the first feed preparation (RSM-1). This information can be used to identify the resulting precipitant particle size.

Table 3.3. RSM Feed Make-up Materials and Amounts

Molecular Formula of Compound	Primary Ion in Balance	Compound Concentration	Molecular Formula of Compound	Primary Ion in Balance	Compound Concentration
Noble metal nitrates			Solubles and slightly solubles		
Pd(NO ₃) ₂ ·xH ₂ O	Cation	0.33 g/L	CuNO ₃	Cation	1.18 g/L
RuNO(NO ₃) ₃	Cation	1.37 g/L	NaI	Anion	7.49E-6 g/L
Rh(NO ₃) ₃	Cation	0.34 g/L	RbNO ₃	Cation	0.11 g/L
Minor component nitrates			SnSO ₄	Cation	2.39E-2 g/L
			KOH	Cation	0.33 g/L
			NaNO ₂	Anion	33.59 g/L
Cd(NO ₃) ₂ ·xH ₂ O	Cation	10.36 g/L	Na ₂ SO ₄	Anion	1.00 g/L
Ce(NO ₃) ₃ ·xH ₂ O	Cation	2.31 g/L	NaCl	Anion	0.69 g/L
Cr(NO ₃) ₃ ·xH ₂ O	Cation	1.96 g/L	CuSO ₄ ·xH ₂ O	Cation	1.10 g/L
Mg(NO ₃) ₂ ·xH ₂ O	Cation	3.30 g/L	H ₃ BO ₃	Cation	1.45E-2 g/L
Nd(NO ₃) ₃ ·xH ₂ O	Cation	12.42 g/L	Na ₃ PO ₄	Anion	2.86 g/L
Pr(NO ₃) ₃ ·xH ₂ O	Cation	0.58 g/L	Na ₂ CO ₃	Anion	14.84 g/L
Sm(NO ₃) ₃ ·xH ₂ O	Cation	0.27 g/L	Ba(OH) ₂ ·xH ₂ O	Cation	0.52 g/L
Y(OH) ₃	Cation	0.14 g/L	Na ₂ C ₂ O ₄	Anion	1.05 g/L
Zn(NO ₃) ₂ ·xH ₂ O	Cation	1.74 g/L	MoO ₃	Cation	0.80 g/L
AgNO ₃	Cation	0.25 g/L	Sr(NO ₃) ₂	Cation	0.35 g/L
Pb(NO ₃) ₂	Cation	1.38 g/L	Ca(OH) ₂	Cation	1.49 g/L
Insolubles			Sb ₂ O ₃	Cation	8.31E-3 g/L
			SeO ₂	Cation	2.25E-2 g/L
GeO ₂	Cation	2.17E-4 g/L	NaNO ₃	Anion	(balance)
LaF ₃	Anion	0.23 g/L	NaOH	Cation	(balance)
La(OH) ₃	Cation	0.86 g/L	Recycle material addition		
Nb ₂ O ₅	Cation	1.64E-2 g/L	KMnO ₄	Anion	0.31 g/L
NdF ₃	Cation	0.25 g/L	HNO ₃ (15.9 M)	Cation	0.65 g/L
SiO ₂	Cation	5.74 g/L	NaNO ₃	Anion	14.48 g/L
Ta ₂ O ₅	Cation	4.73E-3 g/L	CdO	Cation	0.56 g/L
TeO ₂	Cation	0.14 g/L	Na ₃ PO ₄	Anion	1.29 g/L
TiO ₂	Cation	0.93 g/L	NaCl	Anion	1.85E-2 g/L
Mixed hydroxide slurry			Na ₂ C ₂ O ₄	Anion	2.11 g/L
Al(OH) ₃	Cation	19.75 g/L	Diatomaceous Earth		5.60 g/L
Fe(OH) ₃	Cation	53.97 g/L	Zeolite (IE-96)		2.80 g/L
Ni(OH) ₂	Cation	4.07 g/L	NaOH	Cation	(balance)
Zr(OH) ₄	Cation	27.86 g/L			
Mn(OH) ₂	Cation	3.12 g/L

Figure 3.1. Precipitation Solids Settling Behavior

Once the solids were settled, the supernate was pumped from the tank into individual 55-gal drums. The inlet tip of the barrel pump hose was equipped with a 100 mesh tip for decanting the last few inches of liquid, this helped to keep from decanting solid material along with the liquid. Once the solution was decanted, an aliquot of the supernate was taken and analyzed for its nitrate and sodium concentrations. The SRAT target concentrations for these constituents were 8.1 and 22.7 g/L of feed, respectively. Therefore, the target concentrations of these ions in the precipitated batch had to be adjusted so that when combined with the mixed hydroxide slurry, the targets would be met. As a result, the wash volumes were calculated to meet the proper nitrate and sodium ion target concentrations.

The solids were washed in the tank with a 0.1-M NaOH solution. This solution was added to the tank and agitation started for about 10 min. The agitation was then stopped and the tank material once again left to settle for 3 to 4 days. The supernate was then decanted and another aliquot of supernate analyzed for nitrate and sodium levels to confirm the targets.

3.3.1.2 Addition of the Mixed Hydroxide Slurry and the Soluble and Slightly Soluble Components

Following the noble metals and minor components preparation, the mixed hydroxide slurry containing aluminum, iron, nickel, zirconium, and manganese was added to the mixture. This slurry was 15% solids by weight and had a corresponding density of 1.1 g/mL. Table 3.3 shows the compositions of the major materials in the mixed hydroxide slurry. Once the required amount of slurry was added to the tank, the tank agitator was then turned on and left for the remainder of the feed preparation process. The soluble and slightly soluble components were added, as shown in Table 3.3. These materials were once again pre-slurried in a ventilation hood before addition.

Once all of the components were added to the mixture, the volume was measured to determine the amount of water still required to bring the final volume to its target SRAT/NCAW value. At this point in the feed preparation procedure, the concentrated HWVP simulant portion of the feed was complete; however, the target concentrations of the cations and anions within the mixture were verified by analysis. These analyses included X-ray fluorescence (XRF), atomic absorption (AA), inductively coupled plasma (ICP), and ion chromatography (IC). The possibility of shimming the components was evaluated based on these analytical results.

3.3.1.3 Formating and Digestion of the Simulant

Formic acid was first transferred from its shipping container into a carboy which was plumbed to prevent fumes from escaping the vessel during formating. The acid was available in a 94% (by weight) solution. While working with the formic acid, full safety gear was worn, as described in JHB-022, "Preparation of Simulated HWVP Melter Feed." The carboy was plumbed directly to the tank through polyethylene tubing. The pump used for the transfer was a variable speed peristaltic. Before formating began, the simulant was heated, using the steam coils, in the tank to bring the mixture to a constant 95°C. While the mixture was heating up, the tank blower and venturi scrubber off-gas system were turned on. Approximately 21 psig of steam was required to bring the tank contents to a constant 95°C.

The total amount of formic acid required was based on 30 mL of formic acid per liter of SRAT. The formic acid was added to the slurry at a rate of 3×10^{-4} L/min/L of SRAT. Before and after the formic acid addition sequence, a couple of gallons of water were pumped through the line to prevent initial and residual reactions in the feed tube. During formating the tank view port lid was removed periodically to check for foaming within the mixture. Additionally, the pH of the tank contents was measured over time during formating and digestion. Once the formic acid was added to the tank, the temperature was increased to between 100 to 102°C (approximately 30 psig of steam) and the mixture was allowed to "digest" for 4 hours. After this digestion period was complete, the solids concentration was measured (approximately, by total slurry level) and further boil-down was performed if required. The steam to the coils was then turned off and the water cooling jacket turned on. This helped cool the tank to room temperature (with the blower still sweeping the off-gas). Once the temperature was decreased, an aliquot of the slurry was taken for nitrate concentration analysis, $\text{Fe}^{+2}/\Sigma\text{Fe}$ redox analysis, solids weight composition, and pH measurement.

A series of gas analyzers was used to measure the generation rates of specific gases evolved during formic acid addition (formating) and the subsequent digestion of two batches of RSM feed, designated RSM-1 and RSM-2. The generation rates of CO_2 , CO, NO_x , N_2O , and H_2 were measured. The gas analysis system consists of four Optical Filter Corporation (model IR-703D) gas-specific infrared absorbance analyzers (CO_2 , CO, N_2O , and CH_4/HCOOH), an electrochemical cell oxygen monitor (Optical Filter Corporation model IR-2200), a Beckman Industrial model 951A NO/NO_x analyzer (chemiluminescent), and a Microsensor Technology Incorporated model M200D gas chromatograph (used to monitor H_2 , He, O_2 , N_2 , and CO). Data from these analyzers were collected by a computerized data acquisition system. The instantaneous readings from each instrument (excluding the gas

chromatograph) were stored by the data acquisition system once every 15 sec during testing. The gas chromatograph sampled at a rates between 1.25 and 2.25 min.

A calibrated mass flow controller was used to inject a known flow rate of ultra-high purity helium into the off-gas line prior to the gas entering the venturi scrubber. This was done to provide a measure of the flow rate in the off-gas pipe. A sample of the off-gas was continuously drawn from the off-gas pipe downstream of the venturi scrubber. The injected helium was determined to be adequately mixed with the gas in the off-gas pipe. Furthermore, whether the venturi scrubber was operating did not affect the measured helium concentration. The helium flow rate was set at 2.0 sLpm for RSM-1 and 4.0 sLpm for RSM-2.

The sample gas withdrawn from the off-gas line was passed through a Drierite desiccant column (anhydrous CaSO_4) and a particulate filter before being supplied to the off-gas analyzers. The desiccant was needed to protect the instrumentation from any internal water condensation. It is possible that the desiccant may have absorbed some of the NO_2 from the off-gas. The venturi scrubber probably removed some NO_2 as well.

Based on the analyzer accuracies specified by the manufacturers combined with the uncertainties introduced during data analysis, the off-gas data are expected to be accurate to within $\pm 5\%$. This estimate does not include any inaccuracies introduced by events external to the analyzers (e.g., stripping of NO_2 by the venturi scrubber).

3.3.1.4 Addition of Recycle Constituents

The next step for the feed preparation was to weigh out and add the recycle constituents. Each constituent (see Table 3.2) was pre-slurried before addition. Note, however, that the KMnO_4 was pre-slurried and added separately because it is such a strong oxidizer. At least an hour after all of the recycle constituents were added, another aliquot of slurry was taken for measuring solids weight composition, sodium and nitrate ion concentrations, and pH.

3.3.1.5 Addition of Frit Constituents

Once the recycle addition was complete, the material was pumped from the tank into individual barrels corresponding to each of the 12 RSM run segments. Frit was not added until just before the feed was fed to the melter, because prolonged storage of HWVP feeds with frit has been known to affect rheology behavior (Hutson 1992). Once frit was required, it was added as 68.6 wt% (on an oxide basis) of the feed material.

Along with frit addition, each feed segment batch was modified based on any segment changes prescribed during the run. Such changes included sugar addition, noble metals addition, and silver and tellurium additions. See Section 3.2 for more detail on these additions.

3.3.2 Research-Scale Melter

The RSM's primary component was an electrically joule-heated melter, internally positioned in an electrically heated ceramic kiln. The melter shell was of cylindrical geometry with a 10-1/4-in.-OD and was constructed of 1/8-in.-thick Inconel 601. Ceramic paper and Alfrax 66 lined the inner portion of the melter shell and provided insulation, structural support, and prevention of molten glass migration to the steel.

The glass containment refractory was an 8-in.-OD x 6-in.-high cylinder of K-3 block. The melt cavity was a 6-in.-ID x 4-3/4-in.-deep cylinder with a nominal volumetric capacity of 1.33 L under an operating plenum vacuum of 1.5-in. H₂O. The configuration of the RSM's refractories and insulation are shown in Figure 3.2.

The joule heating was provided to the RSM from two top-entering paddle electrodes fabricated from 1/4-in. Inconel 690 plate. The electrodes had a square face with dimensions measuring 3 in. x 3 in. The arms of the electrodes extended 17-3/4 in. and measured 1 in. in width. Detailed dimensions of the electrodes are presented in Figure 3.3.

The electrodes were allowed to rest on the bottom surface of the melt cavity and were located 4-3/8 in. apart. The arms of the electrodes extended out of the melt region, through the plenum space, and through the lid. The electrodes were isolated from the lid providing oversized lid penetrations through which the electrodes protruded and by filling the unoccupied space with Alfrax 66. This provided sufficient electrical isolation and vertically stabilized the electrodes.

The plenum region temperatures were varied by using a 1-in.-diameter, 15-in.-long silicon carbide bayonet-style heater with an effective heating length of 5 in. The heating element protruded through the lid and was suspended from a 9-in. length of 2-1/2-in. stainless steel, thick wall tube such that the end of the heater sat 2 in. above the melt level. A ceramic sleeve was inserted to isolate the heating element from the riser pipe and lid.

The RSM sat inside an electrically heated firebrick kiln. The inner geometry of the kiln was an octagon with a diameter of 16 in. and a height of 16 in. During the test, the kiln was maintained at an approximate average of 1,050°C. The melter was elevated on two firebricks. This configuration is presented in Figure 3.4.

The melter lid was a single unit secured to the melter which covered the entire interior cavity. It was 12 in. in diameter and was fabricated from 1/2-in. Inconel 601 plate. The lid was electrically isolated from the main body of the melter by two alternating layers of ceramic paper and mica gaskets. All services to the RSM ran to connections on or through the lid including the feed port, located in the center. The locations of specific services for the test are indicated in Figure 3.5.

Figure 3.2. RSM Configuration

Figure 3.3. RSM Electrodes

Figure 3.4. RSM Position in Kiln

Figure 3.5. Service Locations for RSM Test

3.3.2.1 Temperature Instrumentation

To monitor the internal operating temperatures during the test, calibrated type K thermocouples with Inconel 601 sheathes were installed. The thermocouples were placed in appropriate positions to measure and record pertinent test parameters throughout the overall system. These temperature values were logged in the system's data acquisition computer (described in Section 3.3.2.6). Bulk glass temperatures were measured continuously by one thermocouple, 1/4 in. above the melt cavity floor on the back side of an electrode. This thermocouple was contained inside an Inconel 690 thermowell. The thermowell was welded to the back side of one of the electrodes. This thermocouple provided the majority of the glass temperature data because no other continuous thermocouple point was present in the cavity. Additional glass temperature data was collected intermittently during the test from a probe thermocouple to assess temperature profiles at varying elevations in the melt region. This thermocouple was inserted through a 1-in. opening in the lid normally used as the view port, located adjacent to the electrode with the thermowell. Temperature indication in the plenum space was provided by one thermocouple fixed approximately 4 in. above the surface of the nominal glass level.

3.3.2.2 Feed Delivery System

The original RSM system had a feed tank that would hold enough feed for 1 week of operation (roughly one segment). The feed was to be made up from formatted waste (with recycle) by adding frit and water. Before the test was started, it was discovered that the melter feed developed severe rheology problems as it aged. After 1 week, the feed would be too thick to pump using the existing feed delivery system. In light of the rheology problems, it was decided to scale down the feed tank so that fresh feed would be made up once or twice per day depending on the processing rate. During the test approximately 35-L batches of fritted melter slurry were prepared in the storage vessel located on the second floor of EDL-102 in Module 18. The vessel was a high density polyethylene carboy with a maximum volumetric capacity of 50 L. The slurry was agitated using two laboratory bench-top mixers mounted 90 degrees apart over the carboy. Feed was made up by taking the tank level of the melter feed tank, calculating the amount of feed to be made up, pumping in the appropriate amount of waste plus recycle mixture, adding frit, and then adding makeup water. This could all be completed in about 10 min so that the feed pump did not have to be shut off and the composition of the feed going to the RSM was not affected.

The melter feed tank was positioned directly above the RSM to facilitate the primary delivery method for the slurry—gravity feed. Feed was transported to the peristaltic metering pump in stainless-steel tubing. The peristaltic pump was manually controlled to regulate flow rate to the feed nozzle. The feed nozzle, (shown in Figure 3.6) extended 4-1/2 in. into the plenum with the nozzle tip 3 in. above the cold cap. During processing, the feed nozzle was water cooled to prevent premature drying of the feed. Periodic water back-flushing in conjunction with reaming of the tubing was required to eliminate obstructions caused by agglomerations of material in the lines.

The proper feed rate to the melter was determined through observation and evaluation of the extent of cold-cap coverage of the melt. This was augmented by calculating the feed consumption based on the

Figure 3.6. Feed Nozzle

feed tank dropout. The level in the tank was monitored by use of a calibrated measuring stick where varying levels on the stick corresponded to known volumes of liquid in the vessel.

3.3.2.3 Glass Discharge System

A continuous gravity-controlled overflow design was used for simplicity. The discharge trough (see Figure 3.7) was constructed entirely of 1/2 in., schedule 160, Inconel 690 pipe. The vertical internal portion of the discharge trough was submerged in the glass while the other leg protruded out of the side of the melter at a 15-degree downward slope. Once the level of glass rose to the point that exceeded the highest point of the trough slope, glass discharge would occur. The exterior portion of the discharge trough was seal-welded to the melter wall to prevent leakage at the interface. In addition, a vertically oriented extension arm that stretched to the bottom of the melter was attached to assist in reducing horizontal motion of the pouring glass stream. The edge of the external trough was chamfered at 60° to avert glass wicking and distortion of the pour stream.

Glass flowed from the tip and free fell 8 in. through a 4-1/2-in. penetration in the floor of the kiln then through a 4-in. Pyrex glass view pipe into a 4-L stainless-steel canister. The discharged glass was exposed to the ambient kiln temperature of 1,050°C to prevent the glass from solidifying in the trough. The 4-L canister that captured the glass was surrounded by a 12-in.-high x 12-in.-diameter muffle furnace operated at 750°C (see Figure 3.8). To determine glass pour rate, the 4-L stainless-steel canister was located on a small platform scale to constantly measure the weight of glass being poured.

3.3.2.4 Power Control System

The electrodes and plenum heater were controlled by silicon-controlled rectifiers (SCR). The SCRs acted as a switch to turn the line voltage on and off to the load at the specified firing angle. The longer fraction of time they were engaged, the greater amount of power which was directed to the load. This power output was controlled by a signal from the RSM's centralized data acquisition computer and remote input/output (I/O) Plexer communication boards. The proportional integral derivative (PID) control was executed by the process control software, Cim-Pac. The software received critical input signals from the melter's power instrumentation and output corresponding command signals. While in typical automatic mode, the temperature of the specific control point which the element was heating was relayed to the computer and the complementary alteration was output to the SCR. In addition, the control system possessed a manual mode capability for emergency situations.

3.3.2.5 Off-Gas Treatment

The gases and airborne effluent generated by the RSM vitrification process were contained and treated by the off-gas system. During operations vacuum in the melter was maintained at 1-1/2 in. water column through the combination of a manually adjusted air bleed valve and an air injection point. Air injection was regulated by a computer-controlled, diaphragm-operated valve. The vacuum

3.19

Figure 3.7. Discharge Trough

Figure 3.8. Muffle Furnace Surrounding Glass Canister

condition in the RSM plenum was detected through a pressure tap penetration and sensed by a pressure transducer that simultaneously relayed a corresponding signal to the data acquisition and computer control system.

The port entrance for the off-gas was a 2-1/2-in. penetration in the melter lid. Initially, effluent was extracted from the plenum space and passed through a porous metal film cooler. The film cooler was constructed from 2- μ m, 316 stainless steel to ensure a sufficient pressure drop that would cause a laminar air flow along the interior of the line. It was determined after preliminary testing that a film cooler was absolutely vital to sustaining an open off-gas pipe in addition to reducing the temperature of the produced effluent.

The off-gas was then routed through a venturi scrubber to provide further cooling and remove the majority of condensables and particulate material. The solution derived from this procedure was recirculated in a continuous loop which passed through a small shell and tube heat exchanger to transfer the heat from the melter off-gas. When the scrub liquid became so contaminated as to loose efficiency, it was drained into Tank 20 in the Tank Pit below EDL-102 and fresh water was added. From the scrubber, the off-gas was run through a High-Efficiency Mist Eliminator (HEME) to remove condensed phase aerosols. After this, the off-gas was pulled through the auxiliary off-gas blower in the service tunnel and finally exhausted through a bank of HEPA filters on the path out the 324 Building stack.

3.3.2.6 Data Acquisition

Data acquisition and melter control were performed with a computer data acquisition and control system. The system was designed for autonomous usage and possessed features for acquiring data, computing values based on the data, logging data electronically in history files, and controlling the melter, including all of the associated alarm functions. The fundamental pieces of hardware used for receiving input and emitting output signals to and from instrumentation were two Dutec multichannel, analog, digital I/O Plexer boards. All incoming temperature, electrical, pressure, and scale signals were terminated at these boards as well as all control and digital output signals necessary for automation. The boards, in turn, communicated via RS2-32 protocol with a 286 AT computer operating under a process control software package, Cim-Pac. Attending test personnel were able to interface with the system and make observations or modifications as necessary.

3.4 Analytical Techniques

The analytical techniques used to characterize the feed and glass samples from the RSM run are described below.

3.4.1 Anion Analysis

Selected RSM feed samples were analyzed for anions using ion chromatography procedure APSL-12, "Using the Dionex DX-300 Series Ion Chromatography System." The samples were prepared by mixing 1 g feed slurry with 100 g deionized water, shaking the mixture for 1 hour to allow leaching of the water-soluble ions, settling the mixture, and sampling the supernatant. The leachate was analyzed using a Dionex DX-300 ion chromatograph equipped with Dionex AI-450 software. Dilute sodium hydroxide was used as the eluent. The results were reported as grams per liter of slurry for fluoride, chloride, nitrite, nitrate, sulphate, and phosphate. The results of these analyses are reported in Section 4.3 of this report.

3.4.2 Cation Analysis

The RSM feed and glass samples were analyzed for cations using ICP. The feed samples were analyzed using an ICP with an atomic emission spectrometer (ICP-AES) detector. The glass samples were analyzed by both ICP-AES and ICP mass spectrometer (ICP-MS).

The feed samples were prepared for ICP-AES using a digestion technique. The feed was dissolved in sulfuric acid over night. If the dissolution was not complete, the sample was heated until all the solids had dissolved. The digested sample was injected into a Jarrel-Ash model 975 Plasma Atomcomp ICP using PNL procedure PNL 7-40.27, Rev. 0, "Using the Spectro 901 Spectrometer." The results were reported in grams element per liter of feed solution.

The glass samples were prepared for ICP analysis (both AES and MS) using a fusion/dissolution method (PNL Technical Procedure APSL-03, "Fusion Procedure"). Each glass 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. Two fusions were done because zirconium and sodium cannot be obtained from the sodium peroxide fusion, and nickel and potassium concentrations cannot be obtained from the potassium hydroxide fusion. The glass samples were crushed to -140 mesh using a mortar and pestle. Approximately 1/4 g of crushed glass was placed in a metal crucible (zirconium for the sodium peroxide fusion and nickel for the potassium hydroxide fusion). The glass and oxidant were mixed and then melted using an electric bunsen burner. The resulting mixture was then dissolved in demineralized water and diluted up to 100 mL. This solution was then sent to the ICP. The ICP-AES analysis was done using a Jarrel-Ash model 975 Plasma Atomcomp (PNL Procedure 7-40.27, Rev. 0, "Using the Spectro 901 Spectrometer"). The ICP-MS was done using a VG PQII+ spectrometer and Technical Procedure PNL-ALO-280, "Inductively Coupled Plasma Mass Spectrometer (ICP-MS) Analysis."

3.4.3 Microscopy Analyses

Samples taken of the glass exiting the melter as well as samples from the melt pool at the end of the test were analyzed by optical microscopy and SEM. To prepare samples for these analyses, the glass was mounted on a slide, thin-sectioned, and polished. Each thin section was examined initially with an

optical microscope (Olympus model PM63) equipped with an image analyzer (Leco model 2001). The samples were examined in both reflected- and transmitted-light modes. The reflected-light analysis was done to identify the size of the noble metal particles on the surface of the slide and to characterize the particle size distribution. The transmitted light analysis was done to get a three-dimensional image of the particles so that the porosity and morphology could be measured.

The polished, thin-section samples were also examined using SEM to identify the elements present in the noble metals particles. The glass samples taken from the glass exiting the melter were examined using an SEM in backscatter mode. The composition of the particles were then determined by energy dispersive spectrometry (EDS) using a Link Spectrometer at 20 kV. Selected particles were examined, characterized, and photographed. The samples from the bottom of the melter at the end of the run were examined using a JEOL model JSM-U3 with a TN880 energy dispersive spectroscopy analyzer.

3.4.4 Glass Redox Potential

The reduction/oxidation potential of glass samples from each segment was analyzed by measuring the ferrous-to-total-iron ratio using PNL Technical Procedure APSL-02, Rev. 0, "Iron II and Total Iron Analysis." In this method the glass samples are dissolved in a non-oxidizing condition using a mixture of sulfuric and hydrofluoric acid. Boric acid is added to complex the excess fluoride ion. The ferrous ion in the solution is chelated by three molecules of phenanthroline, forming an orange-red complex. The colored solution obeys Beer's law; its intensity is independent of pH from 3 to 9. A pH between 2.9 and 3.5 ensured 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. The operating $\text{Fe}^{+2}/\Sigma\text{Fe}$ range for the HWVP will be 0.005 to 0.3 (WHC 1992). All but two of the RSM run segments were oxidizing ($\text{Fe}^{+2}/\Sigma\text{Fe} = 0.005$). The two segments with reducing glass ($\text{Fe}^{+2}/\Sigma\text{Fe} = 0.23$) were Segment 8 and Segment 11.

4.0 Results of Experimental Run

The following sections present the results and discussion for the pretest feed preparation, run description, post-test operations, and computer modeling input.

4.1 Pretest Feed Preparation

The original feed preparation scheme was comprised of generating 1,335 L of NCAW and adding additional material (such as noble metals) to the segment fractions which required them. However, because of a concentration discrepancy, two times the prescribed amount of ruthenium nitrosyl nitrate was added to this batch. To reconcile the problem, enough of this unformatted material was removed from the tank so that materials in addition to ruthenium could be added to meet the targets shown in Table 3.3. The portion left in the tank was then formatted first, with the high ruthenium, and used for the double noble metal concentration segments.

This error presented an interesting opportunity to formate two separate large-scale feed batches and measure the off gas from each. Certain noble metals are suspected of catalyzing the forming reactions to produce higher amounts of hydrogen and other gases. Therefore, by formatting a high ruthenium batch (RSM-1) and a nominal noble metals batch (RSM-2) in the same large-scale system, data could be taken to help quantify some of the catalysis claims.

4.1.1 SRAT Preparation

The initial feed batch had a target SRAT/NCAW volume of 1,335 L. Once enough material was removed for RSM-2, the RSM-1 feed volume was 945 L. The augmented feed for RSM-2 had a total volume of 960 L. The amounts and methods of material additions during the feed preparation are discussed in Section 3.3.1. Once the SRAT portions of the feed batches were complete, these slurries were analyzed for cation and anion concentrations for comparison with the target values. The feed batch for RSM-1 was analyzed by XRF, ICP, and AA. The results of these analyses are shown in Table 4.1. This table shows the target concentrations, concentrations obtained from each analytical technique, as well as a comparison of each analysis with the target concentration. Note that the entered concentration (or target concentration) may vary slightly from previously described targets. This is because the feed was slightly diluted or concentrated. Therefore, the relative targets for each constituent remain constant. Despite the number of elements analyzed, the tabulated results show that for one element, a difference in analytical methods can drastically affect the concentration obtained. For example, the analyses for zinc shows over an 8% difference in the analytical values from XRF and ICP alone.

Despite the variation in the analytical results, the numbers for ruthenium and zirconium were used on a semi-quantitative basis. The ruthenium number for this batch shows a concentration twice that of the target. This discrepancy revealed the error in the ruthenium addition as discussed previously.

Table 4.1. RSM-1 SRAT Feed Analysis Results

Element Symbol	Entered Concentration (g/L)	XRF Elemental Concentration (g/L)	AA Elemental Concentration (g/L)	ICP Elemental Concentration (g/L)	XRF % Deviation from Target	AA % Deviation from Target	ICP % Deviation from Target
Pd	0.143	0.126			-11.5		
Ru	0.435	0.929			113.6		
Rh	0.120	0.112			-6.7		
Cd	3.761	3.644		3.665	-3.1		-2.6
Ce	0.744	0.647			-13.0		
Cr	0.254			0.242			-4.9
Mg	0.312		0.347	0.368		11.3	17.8
Nd	4.248						
Pr	0.186						
Sm	0.093						
Y	0.090	0.095			6.4		
Zn	0.381	0.512		0.606	34.3		59.0
Ag	0.158	0.181		0.194	14.2		22.6
Pb	0.863	0.792		0.840	-8.2		-2.6
Ge	0.000						
La	0.693	0.566			-18.4		
Nb	0.011	0.010			-15.3		
Si	2.673	6.223	6.471	1.239	132.8	142.1	-53.7
Ta	0.004						
Te	0.113	0.099			-11.8		
Ti	0.555	0.436		0.095	-21.4		-83.0
Al	6.806	5.596	6.739	5.943	-17.8	-1.0	-12.7
Fe	28.10	25.87	24.27	23.94	-7.9	-13.6	-14.8
Ni	2.565	2.271		2.132	-11.5		-16.9
Zr	15.90	11.48		11.45	-27.8		-28.0
Mn	1.921		1.660	1.785		-13.6	-7.1
Cs	0.804	0.714			-11.2		
Rb	0.064	0.058			-8.9		
Sn	0.013	0.003			-76.5		
K	0.232						
Cu	0.279	0.272		0.284	-2.3		1.8
B	0.003						
Ba	0.224	0.186		0.216	-16.9		-3.3
Mo	0.529	0.540		0.494	2.1		-6.7
Sr	0.143	0.138		0.148	-3.0		3.7
Ca	0.801	2.312		1.197	188.5		49.4
Sb	0.007						
Se	0.016	0.015			-6.9		
Na	21.72		15.88	22.05		-26.9	1.5

Secondly, the zirconium came from the mixed hydroxide slurry, which proved to be slightly low in this material. The analysis of the mixed hydroxide slurry is shown in Table 4.2. This information was used to generate an amount of solid zirconium hydroxide that was used to shim this concentration closer to its target.

The second SRAT simulant (RSM-2) was analyzed by ICP only. This was because of the large amount of analytical scatter observed in the RSM-1 analysis. The results of this analysis are shown in Table 4.3. Note that this analysis could not really provide much more information than a semi-quantitative analysis of the feed. For example, the values shown for silicon, titanium, boron, and silver suffer gross analytical errors because of the sample fusion and large amounts of elemental interferences. As a result, the concentration accuracies for both feeds relied mostly on the accuracies of the supplied feed constituents and careful weigh-out and additions of the individual materials.

4.1.2 Off-Gas Measurements

The generation rates of CO₂, CO, NO_x, N₂O, and H₂ were measured for both of the forming runs. The instantaneous readings from each instrument (excluding the gas chromatograph) were stored by the data acquisition system once every 15 s during testing. During RSM-1, the gas chromatograph sampled at a rate of once every 2.25 min. This frequency was increased during RSM-2 to about once every 1.25 min. Total off-gas flow during forming of both batches was 12 to 16 scfm. The data provided evidence that an additional gas is being generated in significant quantities. The data indicate that the gas is probably either hydrogen cyanide or hydrogen azide, although the data are not conclusive.

The data from the off-gas analyzers were being recorded at least 15 min prior to initiating formic acid addition. This was done to establish a baseline zero gas generation rate. At time = 0 min, formic acid addition began. Once forming was complete, the slurry temperature was raised from 95°C to approximately 100°C for 4 hours (slurry digestion). Temperature was controlled by manually adjusting the flow and pressure of steam to the steam coils inside the forming vessel.

RSM-1 forming took place between time = 0 and = 127 min. At approximately = 107 min, the formic acid addition rate was accidentally increased by approximately a factor of two for about 1 min. This was noticed and the formic acid flow was temporarily terminated at time = 108 min. The

Table 4.2. Mixed Hydroxide Slurry Elemental Analysis

Element Symbol	Target Concentration (g/L)	XRF Concentration (Ag Source) (g/L)	AA (g/L)	XRF % Deviation from Target	AA % Deviation from Target
Al	9.57		10.69		11.8
Fe	42.95	41.56	36.53	-3.2	-15.0
Ni	3.85	3.57		-7.4	
Zr	21.85	17.61		-19.1	
Mn	3.09		2.66		-13.9

Table 4.3. RSM-2 SRAT Feed Analysis

Element Symbol	Entered Concentration (g/L)	ICP Concentration (g/L)	% Deviation from Target
Pd	0.122		
Ru	0.373		
Rh	0.103		
Cd	3.224	3.34	3.48
Ce	0.638		
Cr	0.218	0.22	-1.22
Mg	0.268		
Nd	3.642		
Pr	0.159		
Sm	0.079		
Y	0.077		
Zn	0.327	0.53	37.79
Ag	0.136	0.18	22.39
Pb	0.740	0.78	5.19
Ge	0.000		
La	0.594		
Nb	0.010		
Si	2.292	0.71	-222.78
Ta	0.003		
Te	0.097		
Ti	0.476	0.08	-494.98
Al	5.835	5.75	-1.47
Fe	24.087	22.70	-6.11
Ni	2.199	2.02	-8.85
Zr	13.632	12.20	-11.74
Mn	1.647	1.72	4.23
Cs	0.689		
Rb	0.055		
Sn	0.011		
K	0.199		

Table 4.3. (contd)

Element Symbol	Entered Concentration (g/L)	ICP Concentration (g/L)	% Deviation from Target
Cu	0.239	0.25	4.48
B	0.002	0.16	98.60
Ba	0.192	0.19	-0.89
Mo	0.453	0.39	-16.28
Sr	0.122	0.13	6.61
Ca	0.687	0.75	8.39
Sb	0.006		
Se	0.014		
Na	18.619	21.20	12.17

increased formic acid addition rate resulted in increased gas generation, which apparently increased the height of the foam layer inside the tank so that some of the slurry foam was drawn out of the tank and into the venturi scrubber liquid. Formic acid addition was restarted at time = 114 min and continued until time = 127 min. pH measurements were not taken during the forming of RSM-1.

Also of interest during RSM-1 was a large spike in the rate of gas generation that occurred at time = 181 min. This spike also resulted in foam carryover into the venturi scrubber liquid. The steam flow was terminated at time = 365 min. and the collection of gas data continued until time = 404 min.

RSM-2 forming took place between time = 0 and time = 127 min. The formic acid flow was constant throughout this period. The slurry temperature was then raised and digestion continued until time = 369 min. During RSM-2, pH measurements were taken at approximately 10-min intervals. Syringe samples of the off-gas were also taken at time = 112 and time = 123 min. These samples were later analyzed by a magnetic sector mass spectrometer.

The off-gas data are provided in Figures A.1 through A.11 in Appendix A. Figures A.1 and A.2 provide the generation rates of the various gases versus time. As stated above, time = 0 corresponds to the initiation of formic acid addition. Figures A.3 through A.6 are graphs that compare the gas generation profiles from RSM-1 and RSM-2 for each gas. Figures A.7 through A.11 describe the data obtained from the carbon monoxide analyzer.

4.1.2.1 Total Generation of Various Gas Species

The gas generation rate data (Figures A.1 and A.2) were integrated to obtain the total quantities of each gas generated. These data are presented in Tables 4.4 and 4.5.

Table 4.4. Moles of Gas Released During RSM-1

Gas	Formating (t = 0 to 127 min)	Digestion (t = 127 to 405 min)	Total
CO ₂	180	60.5	241
N ₂ O	3.7	50.3	54
NO _x	8.0	15.2	23
H ₂	0.0029	0.024	0.027

Table 4.5. Moles of Gas Released During RSM-2

Gas	Formating (t = 0 to 127 min)	Digestion (t = 127 to 369 min)	Total
CO ₂	195	73	268
N ₂ O	17	59	76
NO _x	10.7	20.2	31
H ₂	0.081	0.257	0.338

No conclusive evidence was obtained during either test that indicated significant quantities of carbon monoxide were being generated. See Section 4.1.2.3 for further discussion of the carbon monoxide data.

The NO_x data must be applied cautiously because the actual generation was probably greater than what was measured because of the stripping of NO₂ into the venturi scrubber liquid. Sampling of the recirculating venturi scrubber liquid was conducted with the intention of measuring the nitrate anion concentration to quantify the NO₂ stripping. However, foaming inside the tank resulted in the contamination of the scrubber liquid with slurry, thereby rendering further samples questionable.

4.1.2.2 Comparison of RSM-1 Data With RSM-2 Data

The carbon dioxide generation rate data for both tests are shown in Figure A.3 in Appendix A. The agreement between the data is good. The large spike in the RSM-1 CO₂ data at about 107 min was caused by the accidental increase in the formic acid addition rate. The remaining differences in the two curves may be attributed to a combination of slurry temperature effects, slurry chemistry effects (e.g., RSM-1 feed contained 2X ruthenium), and the fact that more formic acid was added during RSM-2.

The nitrous oxide data are given in Figure A.4 in Appendix A. There are significant qualitative differences between the two curves. The RSM-2 curve is similar in shape to those observed during

lab-scale forming tests (1.5 L). The RSM-1 curve, however, contains a large spike at about 180 min. It is not known why this occurred. It is noteworthy that during lab-scale forming tests, the nitrous oxide and NO_x generation rates usually decrease rapidly after the end of formic acid addition. During both RSM runs, however, the peak N_2O and NO_x generation rates were encountered *after* forming was completed. The spike in the RSM-1 N_2O data occurred nearly an hour after formic acid addition was terminated. The reason for this qualitative difference in nitrogen-containing off-gas is not known, but may relate to the differences in the mixing times between lab-scale and research-scale experiments (see Section 4.1.2.3 for further discussion).

The NO_x generation data are given in Figure A.5 in Appendix A. The NO_x generation rates reported in Figure A.5 are probably somewhat lower than the actual generation rates. This is caused by the stripping of NO_2 from the off-gas by both the venturi scrubber liquid and the desiccant column used to dry the gas before it entered the gas analyzers. The difference between the RSM-1 and RSM-2 curves in Figure A.5 is probably caused by the increased rate of formic acid addition used during RSM-2. There is evidence from lab-scale testing that increasing the rate of formic acid addition tends to result in both larger generation rates and in a larger proportion of the nitrite anions being reacted to form NO_x rather than N_2O . The ratio between NO_x and N_2O generation rates is also thought to be influenced by the carbonate anion concentration, but both RSM-1 and RSM-2 slurries should have contained similar carbonate anion concentrations.

Lab-scale tests using slurries nearly identical to those used in the RSM tests have demonstrated that the NO_x generated during forming is initially released from the slurry as nitric oxide (NO). Nitrogen dioxide (NO_2) is subsequently formed via the gas-phase reaction of nitric oxide with oxygen.

The hydrogen generation data are presented in Figure A.6 in Appendix A. Relatively small amounts of hydrogen were generated during both tests. Hydrogen generation at these levels would not be expected to result in an explosive off-gas mixture under prototypic forming conditions. The fact that the RSM-2 hydrogen peak occurs prior to the RSM-1 peak is probably caused by the higher rate of formic acid addition used in RSM-2. The gas chromatograph was configured for a hydrogen generation detection limit of about 0.0002 moles/min during RSM-1 and about 0.001 moles/min during RSM-2. The difference was necessitated by the desire to acquire data at a higher frequency during RSM-2. In view of this, the step-functions apparent in the RSM-2 hydrogen data are not actual; they are an artifact of the gas chromatograph setup.

4.1.2.3 Carbon Monoxide Data Analysis

In previous forming tests on noble metal feeds, no significant amounts of carbon monoxide (CO) have been detected. If present, carbon monoxide should be detected by both the CO infrared absorptance analyzer and the gas chromatograph. Analysis of the infrared CO analyzer data is complicated by the fact that the CO analyzer responds to both carbon monoxide and nitrous oxide.^(a)

(a) Nitrous oxide has an infrared absorptance peak at about $2,200\text{ cm}^{-1}$, which is close enough to the CO analyzer's operating frequency of $2,117 \pm 40\text{ cm}^{-1}$ to result in some interference.

The response of the CO analyzer to N₂O has been found to be linearly related to the nitrous oxide concentration. When analyzing the CO analyzer data from previous, lab-scale tests, the effect of nitrous oxide interference was mathematically removed and the remaining CO data were within noise level of 0% (Figure A.7 in Appendix A). However, removal of the nitrous oxide interference from the CO analyzer data collected during the RSM tests resulted in a measurement equivalent to 0.5 to 1.2% CO (Figures A.8 and A.9 in Appendix A).

The gas chromatograph^(a) did not indicate that significant amounts of CO were present (see Figure A.10 in Appendix A). This discrepancy was noticed after the RSM-1 data were analyzed. In an effort to resolve this problem, two gas samples were taken in glass syringes during RSM-2. The syringe samples were taken when the CO analyzer indicated CO concentrations of 0.43% and 1.02%, respectively (time = 112 and = 129 minutes). The samples were analyzed approximately 24 hours later by a magnetic sector mass spectrometer.

The mass spectrometer found no CO in either syringe sample. Because of interference from nitrogen, the mass spectrometer detection limit for CO was 0.3 to 0.5% for these samples. According to the infrared CO analyzer, there should have been about 1.0% CO in the second syringe sample. The mass spectrometer analysis certainly should have detected CO had it been present at 1.0%.

Because neither the mass spectrometer nor the gas chromatograph indicated that significant amounts of CO were present, other explanations were explored. It was suggested that an error in the calibration of either the infrared CO analyzer or the infrared nitrous oxide analyzer could have resulted in the observed "CO" data. For example, if the nitrous oxide analyzer was erroneously calibrated to produce artificially low readings, the "corrected" CO analyzer data would be artificially high. The calibration of the nitrous oxide analyzer was verified before both tests as well as after RSM-2 and found to be accurate to within 0.02%. The accuracy of the factory-certified N₂O calibration gas was verified by the onsite Mass Spectrometer Laboratory using the same mass spectrometer mentioned previously. The calibration of the CO analyzer, the gas chromatograph, and the CO gas standard were all similarly verified. In addition, if an analyzer calibration error were at fault, the corrected CO data would be expected to exactly track the N₂O data.^(b) This did not happen. Thus, the possibility of a calibration error being responsible for the observed "CO" peak has been discounted.

It is probable that the unexplained reading on the CO analyzer was caused by interference from some as-yet-unidentified gas. The CO analyzer is tuned to measure infrared absorbance within a frequency band of $2,117 \pm 40 \text{ cm}^{-1}$. In an effort to identify candidate gases, a brief review of published infrared absorbance spectra was performed.

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- (a) It was hypothesized that carbon monoxide and nitrous oxide may be reacting inside the gas chromatograph column (to form nitrogen and carbon dioxide). If this were the case, carbon monoxide would not have been detected because of the large excess of nitrous oxide. Tests were performed, however, that verified the ability of the gas chromatograph to measure 100 ppm-1.0% quantities of CO in the presence of 0 to 4.0% nitrous oxide.
 - (b) If both the "corrected" CO data and the nitrous oxide analyzer data were plotted versus time, both plots would show identical trends.

Ammonia was ruled out for two reasons. First, the desiccant used to dry the gas sample entering the analyzers is very efficient at absorbing ammonia gas. The desiccant was observed to remove >99% of the ammonia from a 0.89% ammonia in nitrogen gas standard. Second, the infrared absorbance spectra of ammonia does not show any significant absorption in the frequency band of the CO analyzer (Reding and Hornig 1951). Sulfur dioxide (Shelton and Nielsen 1953) and hydrogen sulfide (Bailey et al. 1936) were similarly ruled out based on a lack of absorbance near $2,117\text{ cm}^{-1}$. Furthermore, sulfur dioxide should have been detected by the mass spectrometer analysis of the syringe samples. (The mass spectrometer is unable to detect hydrogen sulfide). Lack of absorbance at or near $2,117\text{ cm}^{-1}$ also forced the elimination of methane (CH_4), hydrazine (H_2NNH_2), nitric oxide (NO), nitrogen dioxide (NO_2), carbon dioxide (CO_2), and formic acid (HCOOH) (Pouchert 1985).

A review of the infrared absorbance spectra of many common functional groups revealed that absorbance around $2,117\text{ cm}^{-1}$ could be expected for molecules containing either triple-bonded atoms (e.g., CO or molecules containing $\text{-C}\equiv\text{C-H}$) or atoms bonded by adjacent double bonds (e.g., nitrous oxide (CRC Press Inc. 1982).

Hydrogen cyanide has a primary absorbance peak at $2,097\text{ cm}^{-1}$ (Allen et al. 1956). This is within the frequency range of the infrared CO analyzer. Hydrogen cyanide (HCN) contains a triple bond between carbon and nitrogen. Hydrogen cyanide is thought to be a possible forming reaction product. The mechanism for its formation could involve the reactions (Fuson and Snyder 1942, p. 102):

It is not known whether the mass spectrometer is capable of detecting HCN. It is possible that HCN readily absorbs into the trace amounts of water present inside the vacuum chamber of the mass spectrometer, thereby preventing its detection. This is the reason that hydrogen sulfide is not detectable by the mass spectrometer. The hypothesis that HCN is not detectable by the mass spectrometer was not tested because of the lack of an available HCN gas sample for analysis.

Volatile alkynes (e.g., acetylene C_2H_2) contain triple-bonded atoms, but a review of the infrared spectra revealed that most alkynes^(a) have only a very weak absorbance near $2,117\text{ cm}^{-1}$. Furthermore, nearly all the alkyne spectra examined contained a strong absorbance at about $3,000\text{ cm}^{-1}$, which is within the frequency range of the infrared methane analyzer ($3,020 \pm 40\text{ cm}^{-1}$). If gaseous alkynes were present in the off gas, the methane analyzer should have shown a response. The methane analyzer indicated <0.01% at all times during both forming tests, so it is highly unlikely that the CO analyzer was responding to an alkyne.

(a) Acetylene, for example, does not have an absorbance at $3,000\text{ cm}^{-1}$. However, it does not have any significant absorbance near $2,100\text{ cm}^{-1}$ either.

A further possibility is that the carbon monoxide analyzer was responding to hydrogen azide (HN_3). Azides have a strong $\text{N}=\text{N}=\text{N}$ absorptance at about $2,130\text{ cm}^{-1}$. Hydrogen azide (Eyster 1940) (also known as hydrazoic acid) has a very strong absorptance at $2,141\text{ cm}^{-1}$ (Dows and Pimentel 1955). Methyl azide also has a peak absorptance at $2,141\text{ cm}^{-1}$ but is ruled out because the infrared methane analyzer would have responded to the C-H absorptance. As noted previously, no significant response was observed on the methane analyzer.

A possible mechanism for the formation of HN_3 has not yet been identified. HN_3 can be produced by reacting nitrous oxide (N_2O) with sodium amide (NaNH_2) and an acid. The formation of NaNH_2 , however, requires a very strong reductant. Sodium amide is typically produced by reacting pure ammonia with a metallic sodium at 300°C (Handbook of Preparative Inorganic Chemistry 1963). It is suspected that the strongly reducing conditions required to generate HN_3 may be beyond those encountered during forming. Furthermore, NaNH_2 reacts violently with water to produce NaOH and NH_3 . If any NaNH_2 was generated during forming, it would be much more likely to react with water than with any dissolved N_2O . Based on this information, it appears unlikely that HN_3 would be generated during forming.

Based on reviews of the infrared spectra of many possible gaseous reaction products, it appears most likely HCN was generated during both RSM forming tests. In the absence of further data, however, it is not possible to prove this assertion. Future testing should include provisions for resolving this issue.

It is interesting that the unidentified gas has never been observed during lab-scale tests (1.5 L of feed) in which nearly identical simulant was formed. This implies that the mechanism for the unidentified gas relies upon some type of scale-up effect. Possible scale-up effects include the relatively poor mixing of the slurry at the larger scale and heat distribution effects caused by the differing means by which the slurry was heated.

The single vertical impeller in the 1.5-L lab-scale vessel is a very efficient mixer compared to the impeller in the $>1,000\text{-L}$ forming tank. Qualitative observations of the rate of fluid surface motion in both tanks suggest that the mixing time for the lab-scale vessel is on the order of 1 s; the 1,000-L forming tank mixing time is on the order of 10 s.

During forming, this difference in mixing affects the slurry in the larger tank such that it has regions of relatively high formic acid concentration for longer times than in the 1.5-L vessel (e.g., near the point of formic acid addition). These areas of low pH in the RSM slurry could give rise to reactions not observed in the lab-scale slurry where the formic acid distribution is more uniform and quicker.

The other difference between the lab-scale vessel and the RSM forming tank is the means by which the slurry is heated. In the lab-scale setup, the slurry is contained in a 2-L glass vessel which is heated by an external, electric heating mantle. The power delivered to the heating mantle is thermostatically controlled based on the slurry temperature. This configuration results in uniform heat distribution over the inner surface of the vessel.

The temperature of the RSM slurry, by contrast, is heated by steam coils partially submerged^(a) in the slurry. Approximately 30 psig of steam, was delivered to these steam coils to maintain the slurry temperature. The heat from the steam coils is added to the slurry over a comparatively small surface area, so the slurry temperature near the steam coil surfaces is likely to be significantly higher than the bulk slurry temperature.^(b) However, the more important effect may be the heating of slurry by the exposed steam coils. The mixing of the slurry was observed to splash slurry onto the steam coils above the slurry surface. The temperature obtained by these exposed coils is not known, but it is likely that it approached the temperature of 30 psig steam, which is about 275°F. The forming reactions that are possible in HWVP feed slurries at such high temperatures have not been studied, so it is possible that such reactions might include the generation of HCN, hydrogen azide, or some other gas.

The hypothesis that the dehydration of slurry splashed onto the exposed steam coils led to the generation of the unknown gas is favored over other possible mechanisms at this time. Dehydration of slurry containing formamide (HCONH_2), as shown above, results in the production of HCN. This mechanism explains why the unknown gas was not observed during lab-scale testing. Slurry dehydration on the heated surfaces has not been encountered during lab-scale testing. Further testing will likely be required to determine the mechanism for formation and the identity of the unknown gas, but it is currently thought that the unknown gas was HCN generated by the dehydration of formamide on the exposed steam coil surfaces.

A sample of the venturi scrubber liquid from RSM-1 was analyzed for cyanide anion by a titration method. Cyanide was not found to be present in the sample at concentrations above the detection limit of approximately 10 ppm. This does not rule out the possibility that HCN was generated. HCN is infinitely soluble in water, but it is a very weak acid ($\text{pK}_a = 9.31$). To effectively scrub and retain HCN, the scrub solution must have a pH of 10 or higher. Otherwise, any HCN that is scrubbed will quickly be stripped from the scrub liquid as the gas phase HCN concentration drops. The pH of the venturi scrubber liquid was on the order of 5 to 5.5 during testing because of acidification of the liquid resulting from NO_2 scrubbing. Because of this, it is unlikely that significant quantities of HCN would have been retained in the venturi scrubber liquid.

If it is determined during future testing that significant HCN generation does take place, it will be important to determine the conditions under which this generation takes place and how much is evolved. Such data are important as they may impact the design and permitting of the HWVP. Based on the data currently available, it is not possible to provide an estimate for the quantity of gas generated (even if it is assumed that the gas was HCN). If further testing indicates that the gas was HCN, the response of the infrared CO analyzer to a known concentration of HCN will be measured. These data will allow an estimate to be made of the quantity of HCN generated during RSM forming.

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- (a) The tank in which the RSM slurries were formed is designed to hold more liquid than was used in either RSM test. As a result, there was not enough slurry to completely submerge the steam coils under the slurry.
- (b) However, the fluid surrounding the submerged steam coils is not likely to exceed the slurry boiling temperature of about 102°C.

If the formamide dehydration mechanism for HCN generation proves correct, serious consideration should be given to monitoring the melter off gas during future tests using feed containing noble metals. The feed is expected to be completely dehydrated in the melter cold cap. This would likely result in quantitative conversion of any formamide to HCN.

4.2 Run Description

The RSM noble metals test comprised 48 days of melter operation divided into nine segments. The test was divided into segments so that a parametric evaluation of the effects of various operating conditions on noble metals effects could be evaluated. These parameters included melter operating parameters (glass and plenum temperatures) and feed properties (oxide concentration, redox potential, and noble metal concentrations). The target operating conditions for the test segments were discussed previously in Section 3.2. Significant deviations were made from the original run plan for various reasons. These changes were also discussed in Section 3.2.

4.2.1 Feed Preparation

The original RSM system had a feed tank that would hold enough feed for 1 week of operation (roughly one segment). The feed was to be made up from formatted waste (with recycle) by adding frit and water. Before the test was started, it was discovered that the melter feed developed severe rheology problems as it aged. After 1 week, the feed would be too thick to pump using the existing feed delivery system (see Section 3.3.2.2 for a description of the feed delivery system). In light of the rheology problems, it was decided to scale down the feed tank so that fresh feed would be made up once or twice per day depending on the processing rate. Feed was made up by taking the tank level of the melter feed tank, calculating the amount of feed to be made up, pumping in the appropriate amount of waste plus recycle mixture, adding frit, and then adding makeup water. This could all be completed in about 10 min so that the feed pump did not have to be shut off and the composition of the feed going to the RSM was not affected. This method of frequent feed batching coupled with changing the reference oxide concentration to 400 g TO/L seemed to avert the feed rheology problem (although the symptoms were being treated and not the problem). This method of feed makeup also made the process more labor-intensive. Approximately 65 batches of feed were made up during the run, resulting in 1,300 L (343 gal) of feed. This is a large amount of feed, considering that the melter is only 6 in. in diameter.

Mass balances around the RSM and the melter feed tank were conducted regularly to ensure that frit was not settling on the bottom of the feed tank. Tank dropouts were compared with the amount of glass poured over a given time period to ensure that the oxide loading of the feed was correct. The feed was always on specification within 5%.

Feed samples were drawn from the final fritted material at the beginning of each segment and at intermittent times during each segment. The feed characterization results are presented in Section 4.3. In general, the composition of the feed remained constant over the course of the test and varied only in oxide loading, redox states, and noble metals concentrations as prescribed in the original test design.

4.2.1.1 High Redox Segments

Two test segments were completed with reducing feed. Segment 8 contained high redox feed at the nominal noble metals concentration and Segment 11 contained high redox feed at 2X noble metals concentration. To determine the amount of reductant (sugar) required to reduce the feeds to the upper HWVP limit ($\text{Fe}^{+2}/\Sigma\text{Fe} = 0.23$), feed samples were drawn and vitrified in a crucible at varying sugar concentrations. The resulting glasses were analyzed to assess the redox level. Based on the results of these tests, it was decided to spike the feed for Segment 8 with 6.8 g/L of sugar. The sugar addition in Segment 8 did not significantly affect the measured redox of the glass. In fact, the redox ratio of the high temperature segment (Segment 7) was more reduced than was Segment 8. This was surprising because it was expected that the laboratory tests using a crucible exposed to air would be more oxidizing than the melter cold cap. Just the opposite was observed.

In hindsight, the RSM was more oxidizing than the crucible most likely because the cold cap was very thick during normal operation as discussed in Section 4.3.2. This provided a substantial residence time for the dried feed in the melter plenum, which should have been very oxidizing. Because of these observations, the quantity of sugar added to the feed for Segment 11 was increased to 15 g/L. This amount, which was based on engineering judgement, was very close to the correct amount. The ferrous-to-total-iron ratio of the glass during Segment 11 was measured to be 0.25. The target was $\text{Fe}^{+2}/\Sigma\text{Fe} = 0.23$.

4.2.1.2 Barium Tracer Test

In run Segment 11, a spike barium hydroxide was introduced to feed as a tracer to evaluate the mixing in the RSM. Barium was selected because of its low concentration in the nominal glass and its high analytical resolution. Barium was added to the feed as 2.47 g $\text{BaOH} \cdot 8\text{H}_2\text{O}$ per liter of feed at 400 g TO/L. This equates to an increase of 0.25 wt% Ba in the glass. The results of the tracer test are discussed in Section 4.3.2.

4.2.1.3 High Silver and Tellurium Segments

The concentrations of silver and tellurium were increased twofold in Segment 10 to evaluate their effect on noble metals precipitation. Silver and tellurium have been observed to alloy with palladium in HLW glasses. The methods of addition were discussed in Section 4.1.

4.2.2 Melter Processing

Originally, each RSM test segment was to last 5 to 7 days or until a steady state was achieved. Although operation of each segment was performed continuously, constant feed and glass discharge, the duration of each segment was determined by the interval of time required for the melter to reach steady state and then process 3 to 5 tank turnovers. This manner of operation was sufficient to satisfy melter-related objectives and to extract the related information.

To evaluate the effects of fluctuations in the melter, variations were restricted to a single factor at a time. The pervasive operating theory during the test was to establish a constant feed rate that would generate and maintain a cold cap of 85 to 95% on the melt surface. The coverage was monitored and regulated at initiation of each segment by test personnel. A target cold cap was not excessively thick. In reality, the cold caps were very thick and rigid. A more thorough description of the cold cap conditions experienced during the run is contained in Section 4.2.2.2.

Upon completion of the start-up sequence for each segment, efforts were focused toward establishment of steady-state conditions. Glass sampling was done in conjunction with feed sampling to assist in mass balances. Additional temperature and electrical resistance data values were recorded to compile an accurate description of the segment.

The processing time of each segment is shown in Table 4.6. As indicated by the table, Segments 1 through 3 were combined into one long segment so that a good baseline segment which started on July 29 and ended on August 12, was very successful, as indicated by the 89% online efficiency. This long segment was also needed to work out the "bugs" in the system, primarily the feed system. When operating steadily, the melter processed feed at 1.4 L/h for a 400 g TO/L feed. This equates to a glass production rate of 0.57 kg/h (32 kg/h/m²). The normalized glass production rate is below the HWVP reference rate of 40 kg/h/m².

Segment 4 was a low glass temperature (1,050°C) test. The segment started on August 12 and ended on August 19. It was very difficult to process the feed at the lower temperature of this segment. The average glass production rate dropped by 40% to 0.88 L/h or 0.35 kg/h (19 kg/h/m²). This is similar to results obtained from a previous test at PNL, Pilot-Scale Ceramic Melter (PSCM) PSCM-24. During the PSCM test, the temperature had to be increased to 1,075°C to even be able to feed the melter (Elliott et al. 1991). The online efficiency for this segment of the RSM run dropped to 75% because of overfeeding and increased feed blockages. At lower feed rates, the velocity in the feed lines decreased, which allowed the frit to settle and cause blockages. This segment took almost 7 days to complete because of the difficulties encountered trying to reach steady state without overfeeding the melter or plugging the feed line.

Segment 5 was a high oxide loading test. The segment started on August 19 and ended on August 22. Originally, the feed oxide loading was scheduled to be 600 g TO/L for this segment. When it was decided to change the nominal oxide loading to 400 g TO/L, the high oxide segment was dropped to 500 g TO/L. Surprisingly, this feed plugged the lines less than during the low temperature segment. The online efficiency was 89%. The feed became very thick only 12 hours after it was made up. The agitators in the melter feed tank were having a difficult mixing the slurry. The average glass feed rate was 1.31 L/h. This equates to a glass production rate of 0.66 kg/h (37 kg/h/m²).

Segment 6 was a high plenum temperature test. It started on August 22 and ended on August 25. A silicon carbide bayonet heater was installed in the RSM plenum. It did not have a large effect on the plenum temperature, raising it from about 690°C to about 750°C. This is not surprising because the RSM sat in a kiln that provided heat in the plenum region. The melter operated very steady during this

Table 4.6. RSM Run Summary

Segment Number	Start Date	Start Time	End Date	End Time	Total Time		Total Feed On (h)	Seg. Wt	% Efficiency	Oxides (g/L)	Noble Metals	Redox (g sugar/L)	Glass Temp (°C)	Platinum Temp (°C)	Glass (kg)	Feed (L)	Normal Feed Rate (L/h)	Average Glass Prod. (kg/h)
					Days	Hours												
1	7/29/92	19:05	8/12/92	9:55	13.6	327	289	0.29	89	400	1 X	Nom.	1,150	588	164	409	1.41	0.57
4	8/12/92	10:00	8/19/92	8:20	6.9	166	124	0.15	75	400	1 X	Nom.	1,050	542	43.8	109	0.88	0.35
5	8/19/92	8:25	8/22/92	0:25	2.7	64	57	0.06	89	500	1 X	Nom.	1,150	692	37.4	75	1.31	0.66
6	8/22/92	0:30	8/25/92	16:19	3.7	88	78	0.08	89	400	1 X	Nom.	1,150	766	41	102	1.32	0.53
7	8/25/92	16:25	8/27/92	19:00	2.1	51	42	0.05	82	400	1 X	Nom.	1,200	868	34.2	86	2.05	0.82
8	9/8/92	10:00	9/11/92	18:10	3.3	80	80	0.07	99	400	1 X	HI-(6.8)	1,150	812	52.7	132	1.65	0.66
9	9/11/92	18:15	9/17/92	15:55	5.9	142	99	0.13	70	400	2 X	Nom.	1,150	752	63.1	158	1.59	0.64
10	9/17/92	16:00	9/22/92	17:25	5.1	121	84	0.11	69	400	2 X	Nom.	1,150	716	50.2	125	1.50	0.60
11	9/22/92	17:30	9/26/92	6:30	3.5	85	75	0.08	88	400	2 X	HI-(15)	1,200	762	44.6	111	1.48	0.59
Average Online Efficiency = 83 % Net Operating Days = 47 Total Mass of Glass Produced = 531 kg Total Volume of Feed Consumed = 1,308 L																		

segment with very few interruptions from burst feed lines. The online efficiency was 89%. The average glass feed rate was 1.32 L/h. This equates to a glass production rate of 0.53 kg/h (29 kg/h/m²).

Segment 7 was a high glass temperature segment with plenum heating. It started on August 25 and ended on August 27. To start the segment, the glass temperature was brought up slowly from 1,150°C to 1,200°C. This was done too quickly at first and the melter foamed (reboiled) because of the change in oxygen potential. Upon reboil, the power to the electrodes was immediately shut off. When the foam subsided, the power was brought back up slowly until the temperature was 1,200°C. The melter was much more dynamic at this temperature. The cold cap was thinner and more flexible with good venting. At one point the glass production rate was up to 1.4 kg/h (80 kg/h/m²). This is twice the HWVP reference rate.

Because of its small size, the RSM was unstable and difficult to control at the higher temperature of this segment. The plenum temperature would go into high alarm when a vent formed within view of the plenum thermocouple. After about 8 hours of operation at 1,200°C, the control system shut down power to the electrodes because of high glass and plenum temperature alarms. It appears that this was a foaming event. By the time that the shift engineer got to the melter, it had cooled to 1,030°C. The melter was brought slowly back up to temperature, but this time the set point was lowered to 1,170°C. This was done because it was realized that the location of the glass thermocouple might not be the hottest place in the glass pool. The large increase in power (up to 5 kW) and the brightness of the melt were key indication of this.

The thermocouple was replaced and the glass pool was probed with a second thermocouple. This probing found that when the glass thermocouple (located on the back of one of the electrodes) was reading 1,150°C, the front face of the electrode was reading 1,170°C, and the center of the glass pool was reading 1,185 to 1,190°C. By setting the glass set point at 1,170°C, the melt pool temperature would be at approximately 1,200°C. At this setting, the melter was stable.

This segment was ended when the building was evacuated because of an unrelated incident. The melter ran steadily on its own until it ran out of feed approximately 6 hours after the evacuation. When the feed ran out, the plenum temperature rose until the high temperature alarm tripped. When this happened, the feed pump and plenum heater were turned off and the melter idled until entry to the building was gained 4 days later. The segment was ended at this point because the melter had been operating steadily before the shutdown. The online efficiency for this segment was 82%. During steady operation, the average glass feed rate was 2.05 L/h. This equates to a glass production rate of 0.82 kg/h (46 kg/h/m²). This is the only segment of the run that produced glass above the nominal rate for the HWVP.

Segment 8 was a high glass redox test with plenum heating. The feed makeup for this segment was discussed earlier in Section 4.2.1.1. There was a long delay (11 days) between the two segments. This was caused by both the building evacuation and some repairs that needed to be made to the RSM. The segment was started on September 8. About 7 hours into the segment the glass thermocouple became

unstable and had to be replaced. The highest temperature recorded was 1,320°C, but this excursion was very brief. After reviewing the data, it does not appear that this excursion caused any change in the electrical characteristics of the melter. When the melter returned to steady state, the resistance returned to the same value as before the excursion. After these initial problems, the melter ran very steady with only a few interruptions during the next 3 days. The segment ended on September 11. The online efficiency for this segment was 99%. During steady-state operation, the average glass feed rate was 1.65 L/h. This equates to a glass production rate of 0.66 kg/h (37 kg/h/m²).

The last three segments of the RSM run all had 2X the nominal concentration of noble metals in the feed. Segment 9 was the first of the 2X noble metals tests. All conditions were nominal except that the concentrations of ruthenium, rhodium, and palladium were doubled. The segment was started on September 11. The melter ran fine for the first 1-1/2 days of the segment. At this time the melter kiln relay tripped, which resulted in the shutdown of the melter for almost 1 day. The melter was restarted on noon on September 14. There were intermittent feed outages (every 2 to 8 hours) from the feed line clogging. Most of the outages were fixed quickly to get the melter back online. The segment ended on September 17. The online efficiency for this segment was only 70% because of the kiln failure. During steady-state operation, the average glass feed rate was 1.59 L/h. This equates to a glass production rate of 0.64 kg/h (35 kg/h/m²).

Segment 10 was similar to Segment 9 except the tellurium and silver concentrations were doubled as well as the noble metals concentrations. The feed line clogged frequently during the entire segment. Most outages were short but a few were 4 to 8 hours. It was not until September 21 that a continuous feeding period was established for long enough to complete the segment. The segment ended on September 22. The online efficiency for this segment was only 69%. During steady operation, the average glass feed rate was 1.50 L/h. This equates to a glass production rate of 0.60 kg/h (33 kg/h/m²).

Segment 11 was a worst-case scenario. The feed contained 2X noble metals, the glass redox was increased to the HWVP limit, and the glass temperature setpoint was increased to 1,200°C. The segment began on September 22. Late in the day on September 23, the building power was lost for 2 hours. The melter cooled but was able to be restarted. Feeding was resumed on September 24. The melter was not nearly as dynamic as the previous high-temperature segment even though the setpoint was higher. A probe of the glass temperatures showed that the glass in the center of the melter on the bottom was 1,135°C when the electrode thermocouple read 1,200°C. The temperature 1 in. up from the bottom in the center of the cavity was 1,132°C. In front of the electrode, the temperature was 1,185°C. In hindsight, this was probably caused by the fact that there was a layer of metals on the bottom of the melter. Most of the current was being conducted through the layer, but all of the joule heating was taking place in the gap between the electrode tips and the metals layer. The center of the layer was cool because it was a short circuit and, therefore, no heat was generated there. This explains why the melter was less dynamic than during the earlier high-temperature segment; most of the melt pool was much cooler than the controlling thermocouple. The bulk glass was only at 1,135°C.

The barium tracer test was also part of Segment 11. The feed preparation for this test is discussed in Section 4.2.1.2. The tracer was started on September 25. The results of this test are discussed in Section 4.3.2. The segment ended on September 22. This completed the RSM test. The online efficiency for the last segment was 88%. During steady operation, the average glass feed rate was 1.48 L/h. This equates to a glass production rate of 0.59 kg/h (33 kg/h/m²). This lower processing rate also indicates that the melt pool was much cooler than indicated by the controlling thermocouple.

4.2.2.1 Establishment and Control of Equilibrium

A vital component to the RSM testing was its subdivision into segments based on changes in process parameters. To acquire relevant data from these changes, a steady state had to be established to collect information that reflected solely the result of the variance. During the beginning phase of each segment, test operators set the nominal glass temperature in the proportional integral control point consistent with the test segment. Once the value had been fixed, the controller would modify the power input accordingly and hence sustain a steady state for power and temperature. This procedure was extended to control of the temperatures experienced in the melter plenum space. A silicon carbide bayonet heater was used to compensate for heat loss in the region as a result of cold cap coverage and to boost temperatures during the high-temperature segment. These were very effective methods of producing accurate and reliable temperatures.

Another critical point in establishing equilibrium was selecting a feed rate that neither overfed nor underfed the melter. The metering pump speed was manually adjusted according to two observed values, plenum temperature and coverage efficiency. The desired feed rate was one that yielded a cold cap of roughly 85 to 95% area and an ambient plenum temperature of 750°C under stable conditions. Typically, the setting of the pump was at 3.5, which equated to a mean feed rate of 1.5 L/h, 90 L/h/m². This is close to reference plant rate of 80 L/h m². When the feed was processing poorly, the glass surface would be almost completely covered with very little visible glass. Sometimes the feed would continue to process under these conditions, but many times the plenum temperature would continue to fall and the feed would have to be shut off until the cold cap had partially burned off. The feed would then be turned back on at a lower rate.

4.2.2.2 Cold Cap and General Observations

The cold cap was a central focus point for control of the melter. The aim was to create a cold cap of 85 to 95% coverage of moderate flexibility and minimal depth. In addition, an optimal cold cap possessed visible molten glass portions with good venting. Because of the heightened viscosity of the melter feed, the cold caps during the RSM run were very rigid in comparison with past HWVP tests. The increased level of viscosity also contributed to drier, denser cold caps. This produced a mounding phenomena directly beneath the site of flow from the feed nozzle that resembled a volcano. Over time this mound would build up in a stalagmite and rise to a height where it would either collapse or result in a feed nozzle blockage.

To minimize the feed nozzle obstructions, the feed rate was interrupted via a timed relay. The relay permitted slurry to flow for a specified interval and then disrupted power to the pump for a short period of time. In essence, an oscillating pulse was generated that tended to reduce feed blockages. As stated earlier, this was a stop-gap method of keeping the melter operating. It was treating the symptoms, not the problem.

The cold cap remained thick and rigid throughout all of the test segments. The high temperature segments had cold caps which appeared to be slightly thinner because of the higher melting rate, but were still very poor cold caps compared to those seen in previous HWVP testing. The consistently poor cold caps did not allow any conclusions to be drawn about the behavior of noble metals as a function of cold cap behavior.

4.2.2.3 Glass Discharge and Canister Handling

Glass was discharged from the RSM continuously via a gravity overflow design. Excess glass dripped from the RSM's discharge trough, through a 4-in. x 4-in. penetration in the floor of the kiln that was held at a temperature of 1,020 to 1,050°C. This was the desired temperature range to conduct pouring and prevent the formation of frozen glass obstructions. The molten glass was collected in 4-L, 304-L stainless-steel canisters within a clam shell style muffle furnace that was operated at 750°C. This was done to slump the glass in the canister. During preliminary shakedown testing, the necessity of this design became evident, as discharged glass would form a solid column back into the kiln and clog the discharge section.

The glass canister was located on a platform load cell to measure the mass of the poured glass. A continuous monitoring signal from the scale was transmitted to the data acquisition and control system, which calculated the change in glass mass ("delta") over the previous 15-min time period. This data point was used to assess the continuous operation of the melter system by searching for low delta values and actuating the appropriate alarm sequence. The scale also indicated the time for canister removal and exchange when the over-weight alarm was tripped. The alarm was set to 10.0 kg.

The canister removal procedure involved several steps. Vacuum in the plenum space was increased from 1 in. to 3 in. to pause the glass pour stream. Once the glass flow had halted, the power to the muffle furnace was deactivated. The scale and canister were withdrawn from below the melter and the adapting Pyrex and insulation were removed. The number, time, and weight of the full canister was recorded in the test log for future reference and mass balance analysis. The full canister of molten glass was removed and placed for interim cooling adjacent to the melter. An empty can was then inserted and the assembly reinstalled under the melter. The vacuum was then reset to 1 in. By halting the pouring in this manner, the melter usually took about an hour to start pouring glass again because of cooling of the overflow. This is indicated in the data by a low scale delta for a period of time after a canister changeout. During the last three segments of the run, the glass was not halted during canister changeout. This resulted in the dripping of a small amount of glass, but this was much better than stopping the glass flow.

Canisters were changed in conjunction with feed preparation, one preceding the other. In all, 69 canisters were produced with a total mass of 531 kg. The average glass production rate ranged from 0.35 to 0.8 kg/h (19 to 44 kg/h/m²). The online efficiency for the run was 81%. This is surprisingly high considering that the melter was monitored remotely. During the night, the average response time was 1 hour from the time that the control computer dialed the person on-call until the time the melter was restarted. If the off-shifts would have been manned, the online efficiency would have been much higher. Detailed data for each segment are shown in Table 4.6.

4.2.2.4 Glass Probing, Electrical Impedance Measurement, and Sampling

Glass sampling was performed in two ways: samples were taken on an intermittent basis or according to a sampling schedule. Such a schedule was used specifically during the barium tracing segments. Typically, a sample was removed at the onset of a new test segment to establish a baseline composition of the glass and as a means for comparison through the progression of a segment. Upon completion of a segment a sample was taken to ascertain final composition. This data was amassed for development of a noble metal particle tracking computer model as well as a check of the constituents of the final glass form.

The glass sampling method was relatively simple. On sampling occasions, glass discharge was permitted to continue during canister change. While the canister assembly was removed dripping glass was collected, packaged and labeled. The sample number and time was then documented in the run book's sample log.

Electrical resistance of the glass and the formation of a conductive sludge layer of metals were of special interest. A portion of the investigation into this area was to measure the impedance in the molten glass and to gather accurate temperature profiles in the melt pool. Resistance was measured theoretically, by manipulating the data from the main electrode instrumentation; current and potential. Using Ohms Law, $R = E/I$, the value was calculated by a programmed algorithm in the data acquisition computer and logged. Consequently, real-time information about the resistance between electrodes was available.

Periodically, a probe thermocouple was inserted into the melt to obtain temperature profiles. These temperatures were to determine varying temperatures across different regions in the melt cavity. Furthermore, the information was to validate the hypothesis generated about run conditions. The area of prime interest was the bottom level of the cavity directly between both electrodes. During Segment 10 (9/19/92), the melt pool temperature was probed with a thermocouple. The melter was controlling at 1,150°C based on the temperature at the back of one of the electrodes. The temperature at the bottom, center of the melter was 1,189°C. At 1 in. off the bottom, the temperature was 1,128°C. This indicates that most of the heating was coming from the bottom of the melter because of a partial short circuiting from a metals layer.

During Segment 11 (9/25/92), a similar probe was performed. The melter was controlling at 1,200°C. A probe of the glass temperatures showed that the glass in the center of the melter

on the bottom was 1,135°C when the electrode thermocouple read 1,200°C. The temperature 1 in. up from the bottom in the center of the cavity was 1,132°C. In front of the electrode with the thermowell, the temperature was 1,185°C. In hindsight, this was probably caused by a layer of metals on the bottom of the melter. Most of the current was being conducted through the layer, but all the joule heating was taking place in the gap between the electrode tips and the metals layer. The center of the layer was cool because it was a short circuit and, therefore, no heat was generated there. This explains why the melter was less dynamic than during the earlier high-temperature segment; most of the melt pool was much cooler than the controlling thermocouple. The bulk glass was only at 1,135°C.

4.2.3 Summary of Interruptions

This section describes the alarm system that alerted off-shift personnel of operating problems. Types of operating interruptions and corrective actions are also described.

4.2.3.1 Alarm Configuration

Because of the extensive time involved to perform all aspects of the RSM testing, an elaborate distributive control system was developed to automate the equipment. The objective was to allow autonomous operation during the off shift. The operators' main activities were changing glass canisters, preparing fritted slurry, making test observations, and performing general repairs as necessary. The control scheme was created to completely operate all elements of the system including power, temperature, off-gas vacuum, and feed rate (after manual set point). To achieve this, Cim-Pac software was used in conjunction with a string of analog and digital I/O Plexor boards and the data acquisition system. The details regarding the equipment and associated system are defined in Section 3.3.

Elimination of required presence time by operators mandated a sophisticated and smart alarm system with outside communication capabilities. A series of potential failure modes were identified and linked to a sequence of corrective events to abate any detrimental outcomes. These actions prevented damage of the test equipment, preserved personal and environmental safety, and alerted an on-duty shift operator of the problem. Thus an operator was able to respond and resolve the situation. When a monitored alarm point exceeded its predisposed value, the event items were triggered and an auto-dialer called a personal pager phone number. The on-duty operator, in possession of the pager, responded immediately to correct the condition. A description of the alarm conditions, levels, and corresponding events are shown in Table 4.7.

4.2.3.2 General Overview

The approach assumed in conducting the RSM testing was to maintain a steady-state operating condition with constant cold cap coverage and glass discharge. Interruptions in the constant liquid feeding of the melter were to be averted so as not to disturb the melter's equilibrium. However, breaks in operations were inevitable based on feed nozzle blockages or alarm events that terminated feeding. Therefore, the goal was to minimize the duration of feed shutdown and the resulting cold cap burn-off. A direct measure of blockages and alarm conditions was the number of cold cap losses. The loss of cap

Table 4.7. RSM Alarm Conditions

Num	Alarm Point	Alarm Condition	Alarm Setting	Process Condition Tigger	Response Event
1	Melter plenum temperature	High	750°C	Loss of cold cap	Stop feed pump, alert operator
2	Melter plenum temperature	Low	500°C	Overfed	Alert operator
3	Melter plenum vacuum	High	3" H2O	Loose film cooler air	Alert operator
4	Melter plenum vacuum	Low	0.5" H2O	Blocked off-gas pipe	Alert operator
5	Glass temperature	High	1,165°C *	Loss of control, bad thermocouple	Stop feed pump, terminate power, alert operator
6	Glass temperature	Low	1,125°C **	Loss of control, bad thermocouple	Stop feed pump, alert operator
7	Electrode current	High	120 Amps	Loss of control	Stop feed pump, terminate power, alert operator
8	Electrode current	Low	< 2 Amps	Power interrupted	Stop feed pump, terminate power. alert operator
9	Plenum heater current	High	8 Amps	Loss of control	Terminate power to heater, alert operator
10	Plenum heater current	Low	< 1 Amp	Power interrupted	Terminate power to heater, alert operator
11	Kiln temperature	Low	900°C	Kiln element failure	Alert operator
12	Scale weight	High	10 Kg	Full glass canister	Alert operator, change canister
13	Scale weight delta	Low	< .15 Kg/h	Ceased feed, obstructed	Stop feed pump, alert operator

coverage frequency varied across segments. These interruptions and the other operational problems are represented in Tables 4.8 and 4.9.

One unique incident occurred during RSM testing which induced a prolonged cessation of testing and an unforeseen idle period. The event was an accident in another part of the 324 Building. The occurrence on Thursday, August 27 (during Segment 7), forced an emergency evacuation of the facility without the opportunity to halt and secure the melter system. Uncertain conditions in and around the 324 Building precluded all access into the 324 Building until 2 days later. At that time, the facility was entered and the melter was secured. Testing resumed operation on Monday, August 31, once the risk to personnel had been mitigated. At that point, Segment 7 was decided to be terminated and the next segment was started.

4.3 Test Results

The following sections describe the results of the post-test evaluation of the melter data.

4.3.1 Melter Joule Heating Resistance Data

During the operation of the melter, the RSM voltage and current supplied to the melter were being monitored continuously. Using this data, the apparent resistance of the material being joule heated could be calculated by dividing the RSM voltage by the RSM current. The resistance data were displayed and logged along with the other important process parameters. This value was watched during the run for any sign of decrease in the resistance value. There were no indications during the run of any rapid changes in resistance other than those caused by the planned changes in glass temperature control setpoint for certain segments. There was, however, a general decrease in the melt resistance over time of about 40%.

Several factors could have affected the indicated resistance value: "noise" in the voltage and current data, glass melt bulk temperature variations, glass melt temperature distribution changes, and glass melt level. Changes caused by bulk glass melt temperature are simply a result of the glass resistivity changing as a function of temperature. It is also possible for the temperature sensed in a single point to remain constant, as in the RSM's electrode temperature used to control joule heating, while the temperature distribution around that point changes, causing a change in the melt resistance. This effect was observed in the RSM during the operation. When a cold cap was started on the melt surface, the top of the glass was chilled and the resistance increased accordingly. Other similar effects related to variations in the cold cap during processing can cause the resistance to vary, particularly in a melter this small.

Table 4.8. Cold Cap Losses During Each Segment

Segment	Cold Cap Losses	Losses/Day
1	19	1.4
4	16	2.3
5	6	2.2
6	9	2.4
7	18	8.6
8	15 ^(a)	4.5
9	25	4.2
10	19	3.7
11	13	3.7
(a) Building evacuation occurred.		

Table 4.9. Description of Typical RSM Outages

Interruption Description	Cold Cap Observation	Corrective Actions
Feed nozzle blockage	Burn off, high plenum temperature	Clean nozzle passage, water flush tubing, restart
Tube blockage	Burn off, high plenum temperature	Clean tubing, water flush, restart
Ruptured metering pump tubing	Burn off, high plenum temperature	Replace pump tubing, water flush tubing, restart
Glass discharge blockage	Reduced to 0 to 10% coverage	Temporarily cease feed, remove glass obstruction
High melt temperature	Thin, active cold cap, foaming	Reduce power control set point, continue feed
Thermocouple failure	Normal cap, unstable temperature indication	Cease feed, stop power, replace thermocouple, restart
Over-fed conditions	Thick, dense, dark cap; low plenum temp	Cease feed or reduce pump speed
Off-gas line blockage	Normal cap, low plenum vacuum (< .5" H ₂ O)	Cease feed, replace film cooler, restart
Pressurized melter plenum	Low plenum vacuum (< .5" H ₂ O)	Adjust vacuum control, restart
Low scale delta	Burn off	Clean tubing, remove obstruction, restart

Another observed effect was related to the glass height in the melter. Because the overflow was gravity driven, the stable glass height in the melter during idling was simply the point of hydrostatic equilibrium. During processing, however, the cold cap on the melter would cause the top of the glass surface to become cooler and therefore more viscous. This would make the glass in the discharge tube cold enough that it would have difficulty flowing. As time would go on with feed going to the melter and no glass flowing out, the melt level would eventually rise and the discharge tube would become immersed in hotter glass until the glass would begin to flow and the system would come to a mass flow equilibrium. This would cause a variation in the glass level in the melter. Because the electrodes are paddles that are never fully immersed in glass, the resistance between them would change as the amount of material available to conduct electricity went up and down.

As a result of these variations, any effort to inspect the resistance data over time to determine whether the melt resistance changes because of metals settling on the bottom must attempt to account for them. To accomplish this, the glass temperature, plenum temperature, feed pump status, and glass pour rate for each test segment were plotted and a range for each of the process variables was determined that appeared to represent "normal processing" for each segment. The resistance data for each of the test segments were then filtered so that if all these parameters were not within the bounds set for them, the resistance data were ignored. Using this new filtered data, the average resistance were determined, a linear regression was performed, and the slope of the regression line was determined. The average resistances and computed slopes are shown in Table 4.10 along with the computed standard error for those slopes.

The average resistances for Segments 1 through 8 do not indicate any appreciable differences in the melt resistance. Segment 4 was a low glass temperature segment, which accounts for the high average resistance value during this segment. A curious result is that the high glass temperature segment (7) had an average resistance that was just as high as the nominal segment. It was expected that this segment would have a resistance significantly lower than nominal. The resistivity data for this glass (using the electrical conductivity data in Section 6.3.2) indicates that the resistance should have gone up by about a factor of 1.5 for a temperature change from 1,150 to 1,050°C. This is approximately what was observed in Segment 4. Using this same data, one would expect a decrease by about a factor of 1.17 to a resistance of about 0.31 for a 1,200°C segment. The fact that it did not may indicate that something had changed in the system between Segment 4 and 7.

Inspection of the raw data for this segment indicates that the joule heating power was very unstable, with periods where the amperage on the electrodes was high (as much as of 120 amps). At these high amperages, it is possible that the current transformer was not behaving linearly. This behavior has been observed before when amperages near the upper rated limit were placed on current transformers using phase angle SCR. The current transformer output may have been indicating that the current was lower than the real current, causing the calculated resistance to be larger than the real resistance.

The important aspect of the average resistance data is that the resistance remained very near nominal during almost all the segments containing the nominal noble metal amounts, but the resistance dropped significantly during the segments with double the noble metals.

Table 4.10. Melter Resistance Data for Each Segment

Segment No.	Description	Average Resistance (ohm)	Resistance Change Rate (ohm/day)	Std Error of Change Rate (ohm/day)
1	Nominal	0.36	-0.0017	0.000130
4	Low glass temperature	0.51	-0.0078	0.000687
5	High oxide	0.37	+0.0108	0.000850
6	High plenum temperature	0.34	-0.0168	0.000946
7	High glass temperature	0.37	+0.0177	0.00475
8	High redox	0.36	-0.0055	0.00120
9	High NM concentration	0.32	-0.0178	0.000280
10	High NM, Ag, Te	0.24	-0.0064	0.000310
11	High NM, redox, glass temperature	0.22	+0.0037	0.000509

The rate-of-change results indicate that some of the resistance changes are actually in the positive direction. There are two questions associated with the interpretation of the rate-of-change data. The first is whether the rates computed by the least-squares method are real and significant. The standard error is one measure of the error in the rate-of-change data. In all the test segments, the magnitude of the standard error is much lower than that of the parameter itself. This would indicate that the rates are significant; however, it is still possible for these rates to appear real when they are not, if certain types of errors exist. The discussion of these errors or the statistical analyses to determine if they exist are beyond the scope of this work.

Perhaps the most appropriate method to assess the validity of these rates is simply to inspect the data and the line produced by the least-squares method. Figures A.12 through A.20 in Appendix A show the filtered data used to compute the slope and the least-squares curve fit. An inspection of these plots indicates that the data for test Segments 1 and 4 don't appear to support any assertion that the resistance is changing. The data for Segments 5 and 6 are of higher quality and may well indicate a detectable change in the resistance. The data for Segments 7 and 8 are quite sparse and probably don't allow any conclusions to be drawn about resistance changes during these segments. The last three segments have relatively good data and the curve fit to this data is believable.

4.3.2 Barium Tracer Test Results

During the final segment of the RSM test, extra barium was added to the feed in a step change as a tracer to determine the mixing characteristics of the melter. The barium was added in the form of hydrated barium hydroxide and was intended to produce a 0.25 wt% increase of barium in the glass. This amount was chosen to induce an easily detectable change in barium concentration in the glass

product. The nominal glass composition target was 0.045 wt% barium (0.05 wt% BaO). The glass samples analyzed by ICP-AES and ICP-MS from testing segments with this nominal amount of barium indicated an average barium content of 0.049 wt%. Following the step change in the feed composition, glass samples were taken from the melter pour stream at approximately 1-hour intervals. These samples were analyzed for their barium content using both ICP-AES and ICP-MS.

Figure 4.1 shows the results of these analyses as a function of time after the barium was added to the melter feed tank. The melter pour rate data from the glass canister scale was used to generate a curve of the theoretical barium content of the glass product coming from the melter assuming that the melter was a well stirred tank and that the melter feed rate was varying directly with the melter feed rate. The calculation was performed for a cylindrical tank 6 in. in diameter, 3 in. deep and using a glass specific gravity of 2.5. This curve was found to fit the data well if it was assumed there was a 2.5-hour lag time between a change in the melter feed composition and a change in the glass product composition. This curve is also shown on Figure 4.1.

The source of this apparent lag time is probably the cold cap in this melter, which was quite thick relative to the glass depth when compared with larger melters. A 2.5-hour lag time would represent about 1.9 kg of glass, 4.7 L of feed, or 1.6 in. of glass depth in the melter at the average processing rates over the period of time the test was performed (1.87 L of feed/h or 0.75 kg/h of glass). Calculations for the lag caused by the length of the feed line from the melter feed tank to the melter indicate that this contribution is small (~ 0.1 hour). Some of the lag time is probably caused by the abnormally large cold cap that was present in the melter; the remainder is probably in the relatively cold portion of the glass just under the cold cap, which is too viscous to mix.

While a 2.5-hour lag is quite large and difficult to justify based on the size of the melter and observations made during processing, it must be remembered that this is the result of fitting the available data to an idealized model of a plug flow reactor followed by a continuously stirred tank reactor. Undoubtedly, this idealized situation did not exist in reality; however, it appears to be undeniable that there was a significant lag time between the melter feed tank and the mixing portion of the melter. This would indicate that the noble metals particles coming into the melter probably spent a relatively large amount of time in the cold cap and the viscous portion of the top of the glass melt.

4.3.3 Post-Test Destructive Melter Examination

After the completion of the last test segment, the melter was left idling at temperature for several days to allow any further settling of noble metal particles from the glass to take place. The joule heating was then stopped, the kiln shut off, and the insulation removed from the top of the kiln. This was done to cool the melter as quickly as possible and preserve the melt cavity in the condition it was in at the time the melter was shut off. The cooled melter was then sawed in half in the vertical plane which cuts through the center of each electrode.

Figure 4.1. RSM Barium Tracer Test (Ba wt% in glass vs. time)

An inspection of the melter showed that a large piece of one electrode was gone, the other electrode had lost some material (but much less than the other electrode), and that there was a layer of metal on the bottom of the melt cavity. This is shown in Figure 4.2. One of the halves was then taken and halved again to produce a quarter which cut directly through the discharge section. This quarter had a metal layer on the bottom and showed that a portion of the discharge tube in the melt cavity was eroded. This quarter is shown in Figure 4.3.

The electrode that had lost the most material originally had its lower end resting on the bottom of the melt cavity refractory. About one-third of the length of this electrode was missing. The other electrode was not missing any of its length, but the square end of the electrode had been rounded and the thermowell for the melt temperature thermocouple had leaked glass into it through a small crack in the bottom. The only visible portion of the electrodes was the plane through which the first cut was made. The remaining portions of the electrodes were not visible and their condition could not be determined.

The metal layer on the bottom of the melt cavity was between 2 and 4 mm thick. The layer appeared discontinuous in the planes through which it was cut with non-metallic portions interspersed between metal sections. The metal layer was thicker in the plane that cut the electrode centers than it was in the plane cutting the discharge section. There were clumps of metal which were significantly larger than the average layer thickness in front of the electrodes and below the discharge tube. The metal layer in the plane cutting through the electrodes was checked for electrical continuity using a hand-held multimeter at room temperature. This indicated that a section of the melter bottom approximately 4 in. in diameter had a low resistance (~ 0.4 ohm). The resistance checked from electrode to electrode was essentially infinite. This would imply that joule heating of the glass was taking place in front of the electrodes, but that a large portion of the melt tank bottom was shorted out at the time the melter was shut off.

The bottom of the melt cavity where the metal layer was present was eroded as much as 1/2 in. from its original thickness. It appeared to be eroded the worst where the metal layer was found and relatively untouched where there was no metal layer. This would imply that the erosion mechanism was in some way related to the presence of the metal.

The glass found in the tank had two distinct colors (black and green) swirled together in patterns that appeared to be indicative of convective mixing. The quarter containing the discharge section seemed to contain a convective roll cell in the location predicted by computer modeling (see Section 6.0). The colors in the glass may have been caused by compositional differences in the glass or by different devitrification patterns.

4.3.4 Sample Analytical Results

Samples of feed and glass were taken during the course of the run and were submitted for compositional analyses after the completion of the run. Samples were also taken from the melt cavity following the destructive examination of the melter. The results of these analyses are presented in the sections below. Specific information about the methods used are reported in Section 3.5.

4.3.4.1 Feed Sample Analyses

Samples were taken from the melter feed tank periodically during the melter run. One of these samples from each segment were submitted for IC analysis to identify anion concentrations in the feed. Table 4.11 reports the results for the samples that were analyzed according to the test segment during which they were taken. The target values for some of the anions are also given in the table. In the case of NO_3 and NO_2 , the targets are not given because these values are not just a function of the amount of these ions added during feed makeup, but also the forming process which changes their amounts. The analyses indicate that the fluoride analyses are below target. This is most likely caused by fluoride being added as rare earth (lanthanum and neodymium) fluorides. These fluorides are not water soluble and are therefore underpredicted by the IC method. The other ions are probably off target from small amounts of contamination in the feed makeup materials that were not accounted for and contaminants in the process water used for feed makeup.

During melter feed makeup, the pH of the feed was measured a number of times. The pH was always within the range of 9.9 to 10.6.

4.3.4.2 Glass Product Sample Analyses

The glass produced by the melter was collected in stainless-steel beakers. Following the melter run, the canisters that were the last ones poured in each section had a sample of glass taken from the top of the glass pour. These samples were submitted for glass composition analyses by ICP-AES, ICP-MS, and XRF. The results of these analyses are reported for each test segment by cation for each method in Tables 4.12 through 4.15.

Not every element is available by each method, either because of limitations inherent to the method itself, limitations particular to the equipment used, or the suspect quality of the data produced by the analyses. In the case of the two ICP methods, the glass must be fused before it can be analyzed by these methods. To analyze for all the elements, including the ones which are used during the fusions (see Section 3.5.2), two fusions must be done. One fusion uses Na_2O_2 and the other potassium hydroxide (KOH). For some of the elements, the two fusion analyses seemed to produce a consistently higher value for the Na_2O_2 fusion. This difference is most likely caused by the inability of the KOH fusion to put those elements fully into solution, or possibly interelement interference from the sodium in the sample. The data reported for each element are the average of the two fusion values.

Table 4.15 reports the average of all the analyses on an oxide bases and compares them to their target values.

Because the melter inspection found a large portion of the electrode missing, analyses were inspected more closely for the presence of Inconel components in the glass product. The composition of Inconel 690 is approximately 60-30-10 Ni-Cr-Fe. Because of this, the reported values for Ni and Cr were plotted versus time during the run to see whether there were any indications of abnormally high values for these components at any particular time. The analyses are shown in Figures 4.4 and 4.5 along with their glass target values.

Figure 4.2. Post-Test Melter Examination

Figure 4.3. Part of Melter Showing Erosion of Discharge Tube

Table 4.11. Anion Concentration in Melter Feed (all values in g/L of feed)

Segment Number	Fluoride	Chloride	Nitrite	Sulfate	Phosphate	Nitrate
Target	0.111	0.345	N/A	0.547	1.93	N/A
1	0.0365	0.723	10.1	1.23	3.23	19
4	0.0352	0.699	9.98	1.24	2.86	19
5	0.0350	0.793	11.0	1.32	3.56	21
7	0.0279	0.633	9.14	1.10	2.95	17
8	0.0337	0.655	9.91	1.17	3.27	19
9	0.0409	0.650	9.30	1.13	2.87	15
11	0.0497	0.728	9.54	1.14	3.38	15

The analyses for Cr indicate that the data are consistently high for the duration of the run with no discernable peaks. The Ni data indicate that the glass was consistently low in nickel for the duration of the run, again with no discernable peaks. The glass tank refractory also has a very high chrome content. This may explain the chrome content of the glass, because we know that the melt tank bottom was eroded during melter operation. Based on this, it does not appear that the electrodes were melted off at any single point during the melter run. It is possible they were eroded over the course of the run or that they were melted at some time during the melter equipment testing and debugging period that preceded the run.

In addition to the compositional analyses, the samples were also analyzed for their redox state. This analysis is done by analyzing a fused sample of the glass for the Fe^{+2} and the total iron. The ratio of Fe^{+2} to total iron defines the redox state of the glass. The values are shown for each segment in Table 4.16.

Two of the test segments were planned to be reduced to a value of $0.23 \text{ Fe}^{+2}/\Sigma\text{Fe}$. Sucrose (as table sugar) was used as a reductant. The amount to add to the feed was determined by a set of crucible melts which were performed with varying amounts of sugar and then analyzed for redox. These melts yielded the value of 7 grams of sugar per liter of feed. The results for the first segment with reduced glass (Segment 8) indicated that the glass was not as reduced as we had intended. For the next reduced glass segment (Segment 11), the amount of sugar was doubled and the actual value came very near the target.

4.3.4.3 Glass Tank Sample Analyses

The melter tank was sampled in four locations following the destructive melter inspection. Figure 4.6 shows the location of the samples taken. The sample locations were intended to take one from near the center of the bottom of the melt cavity, one from the tank bottom underneath the eroded

Table 4.12. ICP-AES Glass Product Analyses

		Segment Number									
		1	4	5	6	7	8	9	10	11	
		Description									
Element	Target wt% Element	Nominal	Low Glass Temp	High Oxide	High Plenum Temp	High Glass Temp	High Redox	High NM	High NM, Ag, Te	High NM, Redox, & Glass Temp	
Ag	0.028	0.000	0.000	0.050	0.057	0.000	0.050	0.000	0.068	0.040	
Al	1.434	1.780	1.720	1.450	1.610	1.555	1.575	1.590	1.555	1.560	
B	4.358	3.990	3.965	4.130	3.970	3.88	3.945	3.900	4.015	3.995	
Ba	0.045	0.047	0.051	0.046	0.047	0.047	0.047	0.045	0.042	0.279	
Ca	0.172	0.221	0.217	0.222	0.236	0.226	0.232	0.294	0.287	0.288	
Cd	0.858	0.697	0.684	0.630	0.709	0.706	0.742	0.746	0.710	0.717	
Ce	0.147										
Cr	0.048	0.061	0.072	0.055	0.064	0.064	0.060	0.067	0.056	0.071	
Cs	0.160										
Cu	0.056	0.055	0.053	0.049	0.053	0.051	0.054	0.053	0.049	0.049	
Fe	5.666	4.680	4.590	4.235	4.705	4.725	4.770	4.790	4.545	4.515	
Ge	0.000										
K	0.058										
La	0.162										
Li	2.323	2.255	2.205	2.325	2.220	2.330	2.215	2.210	2.255	2.265	
Mg	0.066										
Mn	0.404	0.371	0.366	0.338	0.375		0.385	0.386	0.371	0.374	
Mo	0.107	0.101	0.099	0.100	0.101		0.095	0.085	0.000	0.000	
Na	5.601	6.710	7.070	6.290	6.960	7.270	6.960	6.590	6.040	6.500	
Nb	0.002										
Nd	0.849										
Ni	0.519	0.423	0.410	0.369	0.412	0.459	0.429	0.444	0.409	0.432	

Table 4.12. (contd)

		Segment Number									
		1	4	5	6	7	8	9	10	11	
		Description									
Element	Target wt% Element	Nominal	Low Glass Temp	High Oxide	High Plenum Temp	High Glass Temp	High Redox	High NM	High NM, Ag, Te	High NM, Redox, & Glass Temp	
P	0.157	0.142	0.150	0.127	0.158		0.162	0.133	0.137	0.145	
Pb	0.173										
Pd	0.030										
2X Pd	0.059										
Pr	0.034	23.500	23.100	24.400	23.400	23.4	23.350	23.050	23.050	23.350	
Rb	0.016										
Rh	0.024										
2X Rh	0.049										
Ru	0.086										
2X Ru	0.172										
Sb	0.002										
Se	0.004										
Si	24.402										
Sm	0.017										
Sn	0.003	0.029	0.030	0.027	0.030	0.030	0.030	0.028	0.033		
Sr	0.025										
Ta	0.001										
Te	0.024										
Ti	0.116	0.142	0.142	0.133	0.143		0.143	0.129	0.125	0.128	
Y	0.016										
Zn	0.080										
Zr	3.191	2.550	2.670	2.450	2.590	0.109	2.640	2.980	2.770	2.800	

Table 4.13. ICP-MS Glass Product Analyses

Segment Number											
		1	4	5	6	7	8	9	10	11	
		Description									
Element	Target wt% Element	Nominal	Low Glass Temp	High Oxide	High Phenom Temp	High Glass Temp	High Redox	High NM	High NM, Ag, To	High NM, Redox, & Glass Temp	
Ag	0.028					1.625					
Al	1.434					3.855					
B	4.358	4.905	4.735	4.775	4.165	4.165	4.415	4.635	4.525	4.045	
Ba	0.045	0.048	0.057	0.052	0.052	0.048	0.053	0.051	0.048	0.309	
Ca	0.172	0.419	0.304	0.208	0.263	0.254	0.298	0.209	0.479	0.299	
Cd	0.858	0.763	0.739	0.683	0.722	0.718	0.805	0.842	0.778	0.777	
Ce	0.147	0.149	0.146	0.132	0.140	0.156	0.151	0.151	0.136	0.150	
Cr	0.048	0.072	0.065	0.044	0.058	0.067	0.053	0.042	0.062	0.060	
Cs	0.160	0.143	0.154	0.140	0.154	0.153	0.152	0.158	0.149	0.143	
Cu	0.056	0.065	0.047	0.038	0.044	0.068	0.052	0.035	0.054	0.045	
Fe	5.666	5.590	5.340	4.775	4.995	4.680	5.415	5.625	5.195	4.955	
Ge	0.000										
K	0.058										
La	0.162					0.181					
Li	2.323	2.255	2.240	2.335	2.135	2.280	2.135	2.300	2.220	2.160	
Mg	0.066	0.048	0.033	0.018	0.024	0.117	0.033	0.020	0.039	0.067	
Mn	0.404	0.434	0.418	0.385	0.403	0.432	0.430	0.450	0.421	0.391	
Mo	0.107	0.086	0.094	0.087	0.094	0.092	0.096	0.100	0.093	0.072	
Na	5.601										
Nb	0.002										
Nd	0.849	0.950	0.918	0.737	0.798	0.787	0.835	0.899	0.833	0.767	
Ni	0.519	0.555	0.513	0.422	0.434	0.480	0.510	0.514	0.476	0.388	
P	0.157										
Pb	0.173										
Pd	0.030	0.050	0.054	0.050	0.054	0.032	0.055				
2X Pd	0.059							0.110	0.105	0.055	
Pr	0.034	0.051	0.044	0.037	0.042	0.046	0.047	0.038	0.050	0.044	
Rb	0.016	0.020	0.016	0.013	0.015	0.023	0.018	0.012	0.019	0.016	
Rh	0.024	0.044	0.046	0.051	0.048	0.034	0.051	0.090	0.078	0.063	
2X Rh	0.049										

Table 4.13. (contd)

		Segment Number									
		Description									11
		1	4	5	6	7	8	9	10		
Element	Target wt% Element	Nominal	Low Glass Temp	High Oxide	High Plenum Temp	High Glass Temp	High Redox	High NM	High NM, Ag. To	High NM, Redox, & Glass Temp	
Ru	0.086	0.085	0.084	0.086	0.090	0.086	0.094	0.161	0.154	0.117	
Zr	0.172										
Sb	0.002										
Se	0.004										
Si	24.402					25.100					
Sm	0.017					0.018					
Sn	0.003										
Sr	0.025	0.016	0.014	0.012	0.014	0.029	0.015	0.011	0.016	0.022	
Ta	0.001										
Te	0.024										
Ti	0.116	0.109	0.084	0.060	0.070	0.136	0.085	0.039	0.084	0.094	
Y	0.016	0.017	0.014	0.012	0.013	0.019	0.015	0.011	0.017	0.013	
Zn	0.080										
Zr	3.191	2.860	2.910	2.670	2.950	4.160	2.980	3.260	3.070	3.060	

Table 4.14. XRF Glass Product Analyses

		Segment Number									
		1	4	5	6	7	8	9	10	11	
		Description									
Element	Target wt% Element	Nominal	Low Glass Temp	High Oxide	High Plasma Temp	High Glass Temp	High Redox	High NM	High NM, Ag, Te	High NM, Redox, & Glass Temp	
Ag	0.028	1.900	1.842	1.561	1.715	1.768	1.757	1.704	1.736	1.672	
Al	1.434										
B	4.358										
Ba	0.045										
Ca	0.172	0.902	0.954	0.858	0.963	0.972	0.989	0.972	0.945	0.972	
Cd	0.558										
Co	0.147										
Cr	0.048										
Cs	0.160	0.198	0.198	0.179	0.198	0.198	0.198	0.198	0.189	0.179	
Cu	0.056										
Fe	5.666										
Ge	0.000										
K	0.058	5.435	5.358	4.938	5.365	5.365	5.428	5.428	5.253	5.022	
La	0.162										
Li	2.323										
Mg	0.066										
Mn	0.404	0.127	0.127	0.112	0.127	0.127	0.127	0.142	0.142	0.127	
Mo	0.107										
Na	5.601										
Nb	0.002										
Nd	0.849	1.046	1.037	0.969	1.029	1.037	1.046	1.003	1.020	0.960	
Ni	0.519										
P	0.157										
Pb	0.173										
Pd	0.030	0.064	0.063	0.057	0.061	0.054	0.064	0.115	0.108	0.070	
2X Pd	0.059										
Pr	0.034										
Rb	0.016										
Rh	0.024	0.036	0.036	0.033	0.033	0.032	0.036	0.058	0.054	0.041	
2X Rh	0.049										

Table 4.14. (contd)

		Segment Number									
		1	4	5	6	7	8	9	10	11	
		Description									
Element	Target wt% Element	Nominal	Low Glass Temp	High Oxide	High Plenum Temp	High Glass Temp	High Redox	High NM	High NM, Ag. Te	High NM, Redox, & Glass Temp	
Ru	0.086	0.129	0.120	0.124	0.122	0.113	0.124	0.191	0.187	0.147	
2X Ru	0.172										
Sb	0.002										
Se	0.004										
Si	24.402	24.785	24.598	25.612	24.514	24.448	24.392	24.472	24.794	24.967	
Sn	0.017										
Sa	0.003										
Sr	0.025										
Ta	0.001										
Te	0.024	0.032	0.030	0.028	0.030	0.024	0.029	0.029	0.046	0.018	
Ti	0.116										
Y	0.016										
Za	0.080										
Zr	3.191	3.383	3.457	3.146	3.494	3.516	3.524	3.857	3.753	3.620	

Table 4.15. Average Cation Analysis of Glass Product

Element	ICP-AES wt% Oxide	ICP-MS wt% Oxide	XRF wt% Oxide	Target wt% Oxide	Average Error	Average % Error
Ag	0.059	not analyzed	not analyzed	0.030	97.89	0.029
Al	3.064	not analyzed	3.287	2.710	17.17	0.465
B	12.841	14.343	not analyzed	14.032	-3.14	-0.440
Ba	0.052	0.057	not analyzed	0.050	8.57	0.004
Ca	0.357	0.434	not analyzed	0.246	64.93	0.156
Cd	0.813	0.801	1.082	0.980	-5.56	-0.054
Ce	not analyzed	0.181	not analyzed	0.180	0.45	0.001
Cr	0.093	0.086	not analyzed	0.070	27.95	0.020
Cs	not analyzed	0.160	0.204	0.170	7.18	0.012
Cu	0.065	0.063	not analyzed	0.070	-9.04	-0.006
Fe	6.642	7.510	7.560	8.100	-10.65	-0.863
Ge	not analyzed	not analyzed	not analyzed	0.000		
K	not analyzed	not analyzed	not analyzed	0.070		
La	not analyzed	not analyzed	not analyzed	0.190		
Li	4.828	4.798	not analyzed	5.000	-3.73	-0.187
Mg	not analyzed	0.072	not analyzed	0.110	-34.36	-0.038
Mn	0.593	0.671	not analyzed	0.640	-1.24	-0.008
Mo	0.145	0.137	0.194	0.160	-0.90	-0.001
Na	9.012	not analyzed	9.283	7.550	21.16	1.598
Nb	not analyzed	not analyzed	not analyzed	0.003		
Nd	not analyzed	0.981	1.186	0.990	9.41	0.093
Ni	0.532	0.621	0.619	0.660	-10.50	-0.069
P	not analyzed	not analyzed	not analyzed	0.360		
Pb	0.168	not analyzed	not analyzed	0.200	-16.01	-0.032
Pd	not analyzed	0.056	0.070	0.034	85.42	0.029
2X Pd	not analyzed	0.109	0.112	0.068	63.01	0.043
Pr	not analyzed	0.052	not analyzed	0.040	31.18	0.012
Rb	not analyzed	0.022	not analyzed	0.020	10.33	0.002
Rh	not analyzed	0.056	0.042	0.030	64.52	0.019
2X Rh	not analyzed	0.096	0.063	0.060	32.05	0.019
Ru	not analyzed	0.115	0.161	0.113	22.16	0.025
2X Ru	not analyzed	0.191	0.231	0.226	-6.69	-0.015
Sb	not analyzed	not analyzed	not analyzed	0.002		
Se	not analyzed	not analyzed	not analyzed	0.005		
Si	49.938	not analyzed	52.906	52.200	-1.49	-0.778
Sm	not analyzed	not analyzed	not analyzed	0.020		
Sn	not analyzed	not analyzed	not analyzed	0.003		
Sr	0.035	0.020	not analyzed	0.030	-9.19	-0.003
Ta	not analyzed	not analyzed	not analyzed	0.001		
Te	not analyzed	not analyzed	0.037	0.030	22.96	0.007
Ti	0.226	0.139	not analyzed	0.194	-5.91	-0.011
Y	not analyzed	0.019	not analyzed	0.020	-7.26	-0.001
Zn	0.137	not analyzed	not analyzed	0.100	37.06	0.037
Zr	3.683	4.224	4.766	4.310	-1.99	-0.086

Figure 4.4. Nickel Content in Glass, Weight % Elemental

Figure 4.5. Chrome Content in Glass, Weight % Elemental

Table 4.16. $\text{Fe}^{+2}/\Sigma\text{Fe}$ for Glass by Segment Number

Segment Number	Segment Description	wt% Fe^{+2}	wt% ΣFe	Ratio Total $\text{Fe}^{+2}/\Sigma\text{Fe}$
1	Nominal	0.02	5.322	0.004
4	Low glass temperature	0.021	5.122	0.004
5	High oxide	0.01	4.423	0.002
6	High plenum temperature	0.008	4.968	0.002
7	High glass temperature	0.094	4.88	0.019
8	High redox	0.005	4.944	0.001
9	High NM concentration	0.007	4.994	0.001
10	High NM, Ag, Te	0.012	4.968	0.002
11	High NM, redox, glass temperature	0.094	4.839	0.251

electrode, one from the tank bottom underneath the discharge section, and one from the melt cavity above the bottom of the tank. The samples were removed by a 3/4-in. core drill. These samples were then submitted for analyses by ICP-MS and XRF. In the case of the samples taken from the bottom of the melter tank, only specific elements were analyzed for. These included the noble metals, the first row of transition metals, and silver and tellurium. The sample taken from higher in the glass tank was analyzed for all the elements that a typical glass product sample was analyzed for. The data are reported in Table 4.17 and Table 4.18 for ICP-MS and XRF, respectively.

ICP-AES was not used for these samples because the particular unit available did not have the capability to analyze for noble metals. In the case of ICP-MS, we again put the samples through two fusions; the data reported are the average of the two with the exception of ruthenium, rhodium, and tellurium. In these cases, the sodium peroxide fusion indicated much higher values of these elements.

A visual inspection of the potassium hydroxide fusion samples showed that some material had precipitated to the bottom of the sample container. This material was assumed to be the noble metals and tellurium that were found to be low in the KOH fusion analyses. Consequently, only the Sodium peroxide fusion analyses were used for reporting the data here.

Care should be taken in attempting to compare the results for the samples from the bottom between these two analysis methods. Because the material sampled was inhomogeneous (partially glass and partially metal), different samples sent for different analytical methods should not have the same absolute results. Only the relative distributions of elements in each of the two separate phases could be the same. Because there is no way to tell how much of each phase was in the samples analyzed, any direct comparison is difficult. In the case of the noble metals, the amounts found were far in excess of the glass target values, and the sample from the bulk glass above showed comparatively very little

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Centimeter

Inches

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2 of 4

SAMPLE NUMBER	COORDINATES		
	X	Y	Z
C1	0 - .5	0 - .5	2.5 - 3
C2	0 - .5	0 - .5	0 - .5
C3	0 - 1	.5 - 3	0 - 1
C4	2.5 - 3	0 - .5	0 - .5

Figure 4.6. Location of Samples Taken from Melter Tank

noble metals. Therefore, it is safe to assume that all of the noble metals were from the metal phase. These data clearly indicate that the metal on the bottom of the melter was high in noble metals and tellurium. Not surprisingly, the sample taken from higher up in the tank was low in the noble metals. This would support the belief that these elements settle out of the glass. Silver and tellurium are known to alloy readily with the noble metals, but it appeared that silver was very near target in these analyses.

Table 4.17. Bottom Sample Analysis Results for ICP-MS

Element	Glass Target wt% Element	C-1 Element wt%	C-2 Element wt%	C-3 Element wt%	C-4 Element wt%
Ag	0.028	0.033	0.026		0.025
Al	1.434			1.985	
B	4.358			3.800	
Ba	0.295			0.275	
Ca	0.172			0.256	
Cd	0.858			0.745	
Ce	0.147			0.154	
Cr	0.048	1.121	1.425	0.184	0.222
Cs	0.160			0.126	
Cu	0.056	0.021	0.033	0.046	0.032
Fe	5.666	4.320	4.610	4.010	4.185
Ge	0.000				
K	0.058				
La	0.162			0.175	
Li	2.323			2.175	
Mg	0.066			0.153	
Mn	0.404	0.362	0.386	0.385	0.344
Mo	0.107			0.070	
Na	5.601				
Nb	0.002				
Nd	0.849			0.720	
Ni	0.519	0.905	0.891	0.784	0.645
P	0.157				
Pb	0.173				
Pd	0.059	2.275	0.735	0.013	0.968
Pr	0.034			0.048	
Rb	0.016			0.018	
Rh	0.049	2.490	0.719	0.014	2.110
Ru	0.172	8.150	3.480	0.029	8.360
Sb	0.002				
Se	0.004				
Si	24.402			25.500	
Sm	0.017			0.018	
Sn	0.003				
Sr	0.025			0.029	
Ta	0.001				
Te	0.024	0.772	0.223		0.280
Ti	0.116	0.072	0.084	0.110	0.087
Y	0.016			0.015	
Zn	0.080	0.118	0.116		
Zr	3.191			4.360	

Table 4.18. Bottom Sample Analysis Results for XRF

Element	Glass Target wt% Element	C-1 Element wt%	C-2 Element wt%	C-3 Element wt%	C-4 Element wt%
Ag	0.028				
Al	1.434	2.096	2.450	2.138	1.953
B	4.358				
Ba	0.295				
Ca	0.172				
Cd	0.858	0.753	0.683	1.007	0.700
Ce	0.147				
Cr	0.048				
Cs	0.160	0.141	0.132	0.160	0.141
Cu	0.056				
Fe	5.666	4.113	3.728	5.043	4.155
Ge	0.000				
K	0.058				
La	0.162				
Li	2.323				
Mg	0.066				
Mn	0.404				
Mo	0.107	0.067	0.022	0.127	0.067
Na	5.601	6.617	7.470	6.973	7.211
Nb	0.002				
Nd	0.849	0.789	0.660	0.960	0.806
Ni	0.519	1.045	0.935	0.959	0.872
P	0.157				
Pb	0.173				
Pd	0.059	1.731	2.693	0.027	1.161
Pr	0.034				
Rb	0.016				
Rh	0.049	1.126	1.251	0.011	1.397
Ru	0.172	4.198	5.138	0.048	4.861
Sb	0.002				
Se	0.004				
Si	24.402	24.766	24.173	24.771	25.514
Sm	0.017				
Sn	0.003				
Sr	0.025				
Ta	0.001				
Te	0.024	0.070	0.102	0.021	0.054
Ti	0.116				
Y	0.016				
Zn	0.080				
Zr	3.191	2.458	1.621	3.613	2.502

Chrome and Ni were somewhat elevated in the bottom samples and the melt tank sample, but the chrome was likely from the melt tank refractory which was partially cut into in the case of the bottom samples. The elevated values in the melt tank were likely from erosion of the electrodes during melter idling that occurred for several days following the end of the last segment.

4.3.5 Noble Metal Particle Characterization

At the conclusion of the RSM test, a glass sample from the end of each segment was analyzed for noble metals characteristics (composition, particle size distribution, and morphology). Similar analyses were also conducted on the samples taken from the melter tank upon post-test destructive examination. The results of these analyses are discussed in this section.

The glass samples were analyzed using Scanning Electron Microscopy/Energy Dispersive X-Ray (SEM/EDX) to determine the qualitative composition of the particles. To better characterize the particle morphology and size distribution, optical microscopy analyses were also completed. Using an image analyzer with the optical microscope, the area percentage of clusters on a sample slide could be measured as well as the area percent of RuO_2 needles within the clusters. The area percent of needles on a slide can be obtained by multiplying the two percentages. The results of these analyses are presented in Table 4.19.

The analyses of the samples from the post-test destructive examination of the RSM (C1 through C4) are also included in Table 4.19. The samples from the bottom of the tank (C1, C2, and C4) all have a continuous, but heterogeneous, metallic layer approximately 2 to 4 mm thick. For all three samples, this layer consisted of metallic particles (10 to 20 μm) of a Ru/Rh alloy surrounded by two separate, continuous phases. One of these continuous phases was an alloy of metallic Pd/Ag/Te with a small amount of Ru metal. The other continuous phase was pure RuO_2 . It is not certain that the ruthenium was an oxide. It was assumed to be nonmetallic because of the darkness of the phase and the absence of other elements that would indicate an alloy.

None of the bottom samples, including the C4 directly under the shortened electrode, contained any metallic phases of Inconel constituents. The outer edges did contain Fe/Cr/Ni spinels, but not in the concentrations required to account for the material loss from the electrodes.

4.4 Input to Computer Modeling

The results of the particle size distribution measurements performed using the optical microscope were used as input to the TEMPEST computer models of the RSM. A summary of these data is shown in Table 4.20. For reference, the GFT data is also shown in this table.

Table 4.19. Results of SEM, EDX, and Optical Microscopy Observations (figures referenced are in Appendix A)

Segment	SEM/EDX Observations	Optical Microscopy Observations
1 - Nominal	Sparse RuO ₂ particles, <5 μ m diameter Figure A.21.	Figure A.46 (a), (b), (c).
4 - Low glass temp	Similar to Segment 1 but particles are slightly larger (< 10 μ m) and some contain traces of Rh. Figures A.22, A.23, A.24.	5 to 10 μ m clusters with some up to 16 μ m. 1 area % clusters with 9 area % RuO ₂ within the clusters. Figure A.47 (a),(b), (c).
5 - High oxide	Identical to Segment 1 Figure A.25.	5 to 9 μ m clusters with many smaller particles. 6 area % clusters with 14 area % RuO ₂ within the clusters. Figure A.48 (a), (b), (c).
6 - High plenum temp	Similar to Segment 4 except larger particles, 10 to 20 μ m. Figures A.26.	5 to 10 μ m clusters. 0.07 area % clusters with 13 area % RuO ₂ within the clusters. Figure A.49 (a), (b), (c).
7 - High glass temp	RuO ₂ needles 10 to 20 μ m; Pd, Te, Ag spheres <1 μ m; 2 to 4 μ m Fe, Cr, Ni cubic spinels. Figures A.27 and A.28.	Figure A.50 (a), (b), (c).
8 - High redox	RuO ₂ needles only; most are <5 μ m with a few 20 μ m. Figures A.29 and A.30.	Figure A.51 (a), (b), (c).
9 - 2X noble metals	RuO ₂ needles (most are <10 μ m, a few up to 50 μ m); Fe, Cr, Ni spinels (2 to 3 μ m). Figures A.31 and A.32.	Figure A.52 (a), (b), (c).
10 - 2X NM, Ag, Te	RuO ₂ needles up to 200 μ m. 1 to 2 μ m Pd spheres, no alloying. (see Figures A.33, A.34 and A.35.	Average particle of 12 μ m with clusters up to 60 μ m observed. 2 area % clusters with 6 area % RuO ₂ within the clusters. Figure A.53 (a), (b) (c).
11 - 2X NM, high temp, high redox	Spherical, metallic particles only. Pure Ru, Ag, Pd and alloys of Ru, Ag, Pd, Te, Rh, Cu. Sizes range 1 to 5 μ m. Figure A.36	Figure A.54 (a), (b), (c).

Table 4.19. (contd)

Segment	SEM/EDX Observations	Optical Microscopy Observations
C1 - Post-test sample, under discharge	Metallic layer with Ru, Rh alloy particles; Pd, Ag, Te alloy surrounding phase; secondary phase of pure RuO ₂ (see Figure A.39 (a) and (b). Outer edges of metallic layer have Fe, Cr, Ni spinels with some Pd/Ag spheres Figure A.38 (a), (b), and (c).	
C2 - Post-test sample, center, bottom of melt cavity	Metallic layer with Ru, Rh alloy particles; Pd, Ag, Te alloy surrounding phase with a small amount of Ru; secondary phase of pure RuO ₂ Figure A.39 (a) and (b). Outer edges of metallic layer have Fe, Cr, Ni spinels Figure A.40 (a), and (b).	
C3 -Post-test sample, melt cavity center	Spheres of Ag/Pd with Te Figure A.41. Very sparse Ru metal particles attached to spinels Figure A.42 (a) and (b).	
C4 - Post-test sample, under short electrode	Metallic layer with Ru, Rh alloy particles; Pd, Ag, Te alloy surrounding phase with a small amount of Ru; secondary phase of pure RuO ₂ (Figure A.43 (a) and (b). Outer edges of metallic layer have Fe, Cr, Ni spinels (Figure A.44). Very sparse Ru metal particles attached to spinels (Figure A.45 (a) and (b).	

Table 4.20. Measured Particle Size Distributions

Diameter Range μm	Volume Percent		
	GFT Data	RSM Segments 4, 5, 6	RSM Segment 10
0-1	0.1		
1-3	13.5		
3-5	32.2		
5-7	20.9	11.7	0.1
7-9	0	19.8	0.6
9-11	0	24.3	1.6
11-13	33.4	4.9	2.9
13-15		27.5	2.8
15-17		11.7	2.6
17-19			5.2
19-21			5.7
21-23			1.4
23-25			2.7
25-30			2.7
30-40			16.5
40-50			11.7
50-60			21.4
60-80			22.1

5.0 Discussion of Experimental Run Results

The results presented in Section 4.0 are discussed here.

5.1 Post-Test Results

5.1.1 Noble Metal Behavior in Glass Product

Insight into the noble metal behavior during each test segment of the melter run can be gained by combining the data from the electrode resistance during the segment, the glass compositional analysis, and the glass microscopy analysis. The glass composition data for the noble metals was obtained by the use of both ICP-MS and XRF analyses. The data obtained by the use of ICP-MS appeared to contain a relatively large amount of scatter. An estimate of the uncertainty in these analyses was 20%. The data obtained from XRF had less scatter and was generally considered to be of higher quality, partially because of our previous experience with using this method for the ESM testing at KfK. The data from KfK was all biased above the expected noble metal value but appeared to be repeatable. Because of the bias in the XRF data, it is not possible to simply compare values of weight percent noble metals directly between segments or between analysis methods.

The data are presented in Figure 5.1 showing the amount of noble metal in the glass product from the melter as the percent change between the amount found in the glass from the nominal segment (Segment 1) to each of the subsequent test segments. This calculation is shown for each of the analytical methods employed. This provides a relative comparison of the amount of noble metals coming out of the melter from segment to segment. In the case of the segments with double the concentration of noble metals (Segments 9 through 11), the standard of comparison used was twice the amount in the nominal segment.

The data obtained by ICP-MS show a significant amount of scatter. In some segments, the ICP-MS data indicate that the change in the amounts of the noble metals were in different directions for different metals. The XRF data are much more consistent and generally show less scatter.

The optimum method of determining how much of each noble metal was retained in the melter in each segment would be to compare the analytical results from samples of glass produced by the melter for each segment against the analytical results of a feed sample melted in a crucible. The difference in the two numbers could be considered the amount which was retained in the melter. This approach was not possible using the analytical data which was available. Only XRF was used to analyze feed samples taken during testing and subsequently melted in crucibles. A single melt was performed from samples taken during the 1X portion of the testing and another melt performed using feed samples from the 2X portion of the testing. The XRF data for the glass product from the melter was consistently above target for all of the noble metals. The feed samples which were melted and analyzed by XRF only indicated about one half as much palladium and rhodium as the glass product analyses. The ruthenium

Figure 5.1. Noble Metals in Glass Product by Segment

content in the feed sample was slightly higher than those seen in the glass product analyses. Because the glass product analyses for palladium and rhodium indicated more noble metals coming out of the melter than the feed sample analyses indicated were going in, the method for calculating noble metals retention in the melter cannot be used. No definite explanation for why the analyses of crucible melted feed was so significantly different than those for glass produced from a melter is known. Inspection of the data from the feed sample analyses did not appear to differ from the glass product analyses for any other elements with the exception of sodium. This may be because of the fact that the liquid feed was dried and melted in a refractory crucible that could have absorbed the aqueous portion of the feed (which would have included the soluble sodium) and kept it from melting into the glass. The silica content of the feed sample analyses were nearly identical to those in the glass product analyses. This indicates that the amount of solids in the feed samples (which contains nearly all of the silica in the form of frit) was the same as the average melter feed. It is possible that a surface reaction between the crucible and the glass caused most of the palladium and rhodium to remain in the layer of glass coating the crucible, causing the glass poured from the crucible to be depleted in these elements. Whatever the reason for this discrepancy, an alternative method for estimating the retention of noble metals in the feed was needed. The method which was chosen is described below.

It was assumed that no noble metals were retained during the first segment. This can be justified by the fact that over the length of this segment, no noticeable change in the melt resistance was seen. The XRF analysis for this first segment was then assumed to be the baseline and any difference between the XRF analyses of subsequent segments and this segment were assumed to represent a real change in the data. This method basically assumes that there is a positive bias to the XRF data for all the elements. The XRF data was chosen over the ICP-MS data because it appeared to have less scatter. The difference between segments was therefore assumed to represent a real, absolute change in the amount of noble metals present in the glass and the retention calculated using the target values for the amount of each element in the feed. Using these assumptions a calculation of the percent retained was made for each element and the noble metals as a whole. A sample calculation equation is shown below to demonstrate the method used.

$$\text{Noble Metal Retained}_{\text{seg}} = \frac{\text{NM}_{\text{XRF nominal}} - \text{NM}_{\text{XRF seg}}}{\text{NM}_{\text{target}}}$$

Of course, the nominal values and feed values were doubled for the calculations performed in the segments containing double the nominal amounts of the noble metals. This data is shown in Table 5.1.

These data indicate that there was very little retention of noble metals in the melter through test Segment 8 with the exception of Segment 7. These data are reinforced by the data for the resistance of the melt which was measured during the run. The resistance data did not indicate any discernable decrease in the melt resistance through Segment 8. The melt resistance data for Segment 7 indicated an increase in resistance, although the data were rather sparse and made it difficult to determine whether the resistance was truly changing or not. This segment was the high glass temperature segment; the data for the redox measurement of the glass indicated that it was somewhat reduced at $\text{Fe}^{+2}/\Sigma\text{Fe} = 0.019$. This finding is backed up by the SEM and optical microscopy data for this segment, which

Table 5.1. Percent of Noble Metals Retained in the Melter

Description	Segment Number								
	1	4	5	6	7	8	9	10	11
	Nominal	Low Glass Temp.	High Oxide	High Plenum Temp.	High Glass Temp.	High Redox	High NM Conc.	High NM, Ag, Te	High NM, Redox, Glass Temp.
Pd Retained (%)	0	3	24	12	35	0	24	35	99
Rh Retained (%)	0	0	10	10	17	-3	28	35	63
Ru Retained (%)	0	10	6	8	19	7	40	41	65
Total NM Retained (%)	0	7	10	9	22	3	34	39	72

indicated that this segment contained spheres of palladium alloyed with silver and tellurium. This is further fortified by the fact that this segment was found to have the highest retention of palladium of any of the segments containing nominal amounts of noble metals.

A curious fact is that the high temperature segment (7) was found to be more reducing than the high redox segment (8) in which the feed had sugar added. A possible explanation for this is that the large amount of time that the feed was found to spend in the cold cap (see Section 4.3.2) allowed all of the sugar to oxidize using oxygen from the plenum gases. This would mean that by the time the feed reached the point where it was beginning to melt into the glass, none of the reducing sugar was available to reduce the melt. In fact the data for Segment 8 indicate that it had the lowest total noble metal retention of any segment other than the nominal one, which was assumed to have none. Of course, if the redox measurements are accurate, this segment was basically a second nominal segment, so noble metal retention beyond the amount of Segment 1 would not be expected.

The other segments containing the nominal amounts of noble metals indicated about 7 to 10% retention of noble metals. It is questionable whether this degree of resolution is possible using this data. There may be some effect from aging of the particles in the melter, causing them to get larger. The RuO₂ particles in the glass coming from the melter appeared to be larger in Segments 4 and 6. Segment 5, however, which had the largest retention of Segments 4 through 6, did not appear to have RuO₂ particles any larger than the nominal segment.

When the change was made to twice the nominal amount of noble metals, the retention of noble metals increased dramatically. This was accompanied by a definite decrease in the melt resistance and a large increase in the size of RuO₂ particles in the glass product. Segment 9 (2X noble metals) had the largest rate of decrease in melt resistance of any of the segments.

Segments 10 and 11 had increasingly higher retention of noble metals. Segment 10 (2X noble metals with high silver and tellurium) had an increase in the amount of palladium and rhodium retained and very little change in the ruthenium retention. This would coincide with the postulated effect of alloying of the palladium with the silver and tellurium to produce larger particles with higher settling velocities. The SEM/EDX data for this segment, however, did show the presence of palladium particles, but unalloyed. It is possible that the palladium is normally dissolved in the glass as a metal and that the combination of extra palladium and extra silver and tellurium attempting to dissolve in the glass caused the palladium to reach its solubility limit in the glass and the extra precipitated. Ruthenium had the same retention in Segment 10 as it did in Segment 9. This would also be consistent with the silver and tellurium only affecting the palladium retention, because the ruthenium is present as RuO_2 and theoretically not affected by the silver and tellurium. There is a higher retention of rhodium (approximately 7%) for which an explanation is not readily found. It may simply be beyond the ability of the analytical methods to resolve the change. This segment showed a definite decrease in melt resistance, but at a smaller rate than Segment 9.

Segment 11 (2X noble metals, silver, tellurium and high redox) had the highest overall retention with nearly all of the palladium being retained and around 65% of the rhodium and ruthenium being retained. The SEM/EDX data for this segment indicated that all of the visible particles were spherical and, therefore, most likely metallic. The particle compositions ranged from pure ruthenium, silver, or palladium to alloys containing ruthenium, silver, palladium, tellurium, rhodium and copper. No RuO_2 particles were visible anywhere in the glass product. Given the spherical, metallic nature of these particles, it is not surprising that a large fraction of them were retained. Interestingly, the resistance in this segment did not decrease perceptibly during this segment; in fact, it increased slightly.

It would appear that during the segments containing twice the nominal amount of noble metals, the floor of the melter was being covered by a conductive layer of noble metals. It must be true that the electrode had already melted/eroded by the end of the testing or the melter would have shorted out to the point where operation of the melter would be impossible. As the floor slowly became one continuous layer of conductive material, the resistance dropped. Once this continuous layer was achieved, extra material added to the layer has very little effect on the melt conductivity. Only the effect of the added height of the layer reducing the distance to the electrode can further decrease the resistance.

The difference between the retention of noble metals in the nominal and 2X noble metal segments was dramatic. The nominal segments averaged 5% calculated retention, while the 2X segments averaged 46%. One obvious difference in these segments was the size of the RuO_2 agglomerates. The nominal segments had agglomerates ranging up to 20 μm , while the 2X segments had agglomerates up to 200 μm . It remains to be seen if settling alone can explain the difference in the retention between 1X and 2X segments.

An obvious mechanism for retaining RuO_2 in the melter is the capture of the RuO_2 crystal agglomerates that are commonly seen. In the case of rhodium it is known that it will substitute itself in place of ruthenium in the RuO_2 crystals. In most of the test segments, the calculated retention for rhodium was approximately equal to that of ruthenium. Because the rhodium should have been present

in approximately one-third the concentration of ruthenium, that would mean that about 1/3 of the RuO_2 was really RhO_2 . The SEM/EDX data showed that in every case in which a RuO_2 crystal was seen, rhodium was present. The peaks generated by the EDX analysis for ruthenium and rhodium are very close together, making it difficult to estimate the amount of ruthenium and rhodium present, but there was no doubt that rhodium was present. It is possible that about one-third of the RuO_2 was actually RhO_2 ; this would account for the rhodium retention.

The palladium retention is more difficult to explain. Significant quantities of palladium were calculated to have been retained in the melter in segments where no metallic palladium was seen. Obviously, when palladium is present in either alloyed or unalloyed spherical particles, the settling of these particles is a mechanism for retention. But in cases where the palladium cannot be seen as a separate phase from the glass (SEM should be capable of easily seeing particles less than $0.5\ \mu\text{m}$), another mechanism for retention must be postulated. Segments 5 and 9 showed 24% retention of palladium, though no palladium particles were seen. One could have postulated that this is simply error in the glass analysis; however, Segment 8 had a calculated palladium retention of 0%. As mentioned earlier, Segment 8 was basically another nominal segment because it was intended to be reduced, but turned out to be at a nominal redox state. This would seem to indicate that the calculated retention in the other segments was not just analytical error.

5.1.2 Noble Metal Behavior in Bottom Samples

Bottom samples were taken from the RSM after the melter was sawn in two. These samples were analyzed by ICP-MS and XRF; mentioned results were presented in Section 4.3.4.3. As was mentioned there, the absolute results for these two sets of analyses should not be expected to agree. Because the material being sampled was not homogeneous, and because different pieces of the sampled material were sent to different laboratories for the two analyses, there is no guarantee that the same amount of metal and glass was in each sample. The absolute analytical results and SEM/EDX data have already made it clear that the metals on the bottom were noble metals. For our purposes, the important information is the relative amounts of each of these noble metals and the form they were in.

Table 5.2 gives the distribution of the noble metals in the three bottom samples C-1, C-2, and C-4. The distribution is given for the two analytical methods as well as that calculated from XRF glass product analyses discussed above.

These analyses are in remarkable agreement, considering the possibility for analytical error. The level of agreement between the data for XRF bottom sample analyses and the distribution calculated from the XRF glass product data would tend to reinforce the believability of the mass balance analysis.

The form that of the noble metals on the bottom of the melter posed some interesting questions. There were three distinct phases: a largely continuous phase of what appeared to be RuO_2 , a largely continuous phase of Pd/Ag/Te with small amounts of ruthenium and rhodium in it, and particles of ruthenium and rhodium embedded in the previous phase. The question is, how did the noble metals achieve the final state in which they were found?

Table 5.2. Noble Metal Distribution in Bottom Samples

Element (% of Total Noble Metal)	ICP-MS	XRF	Calculated from Glass Product Data
Palladium	14 %	24 %	23 %
Rhodium	18 %	16 %	15 %
Ruthenium	68 %	60 %	63 %

All the test segments except the last one showed signs of RuO_2 , but always as an agglomeration. Yet the RuO_2 found on the bottom of the melter appeared to be in relatively large pieces of continuous RuO_2 . Of the two metal phases, it would appear that the Pd/Ag/Te phase was molten prior to the melter being cooled (based on its continuous appearance). The presence of the silver in this alloy may have reduced the melt temperature to the point that this phase was molten at the temperatures near the end of the testing. The rhodium/ruthenium phase may have embedded itself in this molten layer as it settled from the melt above. The melting temperature of this phase would almost undoubtedly not be low enough for it to be molten. It is also possible that the metals present separated themselves into two phases after they precipitated onto the bottom of the melter and sat there for many days.

Because only the last test segment was reduced to the point where all of the noble metals in the glass were found as metals, it is possible that prior to the start of this segment, all the ruthenium on the bottom was present as RuO_2 crystal agglomerates. When the last segment occurred, however, the reducing nature of the glass may have reduced this RuO_2 to ruthenium metal. Then in the several days following the test, when the melter was left to idle, the glass melt would have been reoxidizing and may have been oxidizing the ruthenium metal on the bottom to RuO_2 again. This would explain the appearance of the RuO_2 as a largely continuous phase instead of needle-like crystals.

Another interesting phenomenon seen in the bottom of the melter was the corrosion of the melt tank refractory. The corrosion was as bad as 1/2 in. in some places. This would correspond to 3 in. of corrosion over one full year of operation, a rate that could seriously shorten the useful life of an HWVP melter. The corrosion appeared to be related to the presence of noble metals because the melt tank floor underneath the electrode still left touching it had not eroded visibly. The SEM pictures showed that the noble metals did not appear to be actually laying on the refractory but that there appeared to be a thin layer of glassy material between the refractory and the melt. This corrosion may be caused by metal down-drilling or a high temperature condition on the melter bottom.

Metal down-drilling is a phenomenon often seen in commercial glass melters. Metals which inadvertently make their way into melters have been commonly found to drill holes several inches deep in the melter bottom refractories and, in a few cases, have caused melters to fail and drain their contents. There is a considerable amount of work that has been done, and is being done, to attempt to understand the mechanisms which cause this damage. There appears to be two separate mechanisms

which have been identified. One is an attack caused by the metal which can change the structure of the refractory making it more susceptible to corrosion. This effect may be particular to both the metal and the refractory being attacked and can take place without the metal being molten. The other mechanism is a surface tension driven motion in the metal which causes erosion at the refractory to metal interface. This mechanism would require a molten metal.

The high temperature condition on the bottom of the melter could have been caused by a dispersed metal accumulation on the melter bottom. This would cause a higher current density through the area near the bottom of the melter, and this higher current density could cause locally higher heating in the glass portion of the bottom. This higher temperature would then result in an increased corrosion rate.

While there is no way to definitely tell which of these mechanisms was responsible for the corrosion seen in the RSM it would appear that a chemical attack of the refractory is the most likely. The metal visible on the bottom of the melter did not appear to be molten. It was dispersed over the bottom of the melter even though the corrosion had effectively sloped the bottom of the melter to a slight degree. If the metal had been molten, they would have appeared as beads or all have slumped together at the low point of refractory. Because it was not molten, the surface tension driven erosion mechanism could not have been responsible for the corrosion. The chemical attack mechanism could be responsible for the corrosion without the metals being molten. This is also in agreement with the observation in the bottom samples which indicated that there appeared to be a glass layer in between the metal and the refractory. This has been seen before in studies of metal down-drilling of refractories.

5.1.3 Combined Joule Heating Resistance and Noble Metal Retention Data

The resistance measured between the electrodes and the noble metal accumulation in the melter which were presented in Sections 4.3.1 and 5.1.1 are shown in Figure 5.2 are shown over the entire run. In addition, the points during the run at which the glass samples and feed samples were taken for the analyses presented in this report are shown. The time when feed samples were taken for rheology testing are also noted. This data shows the clear correlation between a decreasing resistance in the melter and the change to 2X noble metals. It also shows that there was no detectable decrease in the melt resistance over the 1X noble metal testing section (Segments 1 through 8). The amount of noble metals retained in the melter by the end of the 1X segments was only about 10% of the total noble metals accumulated in the melter by the end of the testing.

5.2 Electrode Failure

The post-test examination of the melter revealed that one of the electrodes had lost nearly one-third of its length.

Figure 5.2. Resistance Between Electrodes and Noble Metal Accumulation Over Entire Melter Campaign

There are two possibilities for the loss of this electrode material. It may have been lost in a relatively short temperature excursion before or during the test, or it may have been slowly eroded away over a period of time during the testing.

If the electrode had melted in a short excursion during the run, it is unlikely that it could have completely oxidized away during the run and left so little of it on the bottom. Though the bottom samples were slightly high in nickel, they did not appear high enough to justify the amount of nickel lost from the electrode. It is also known that there were spinels containing nickel on the bottom of the melter, which may have contributed to the slight increase in nickel in these samples. The chrome values from the bottom samples are not meaningful because the melt tank refractory is largely made of chrome oxide and we know that some of it was included in the samples taken.

As was discussed in Section 4.3.4.2, an inspection of the glass product data for evidence of Inconel constituents did not reveal any points in the test where suspiciously high values of these elements were seen. If the electrode were oxidized continuously during the run, calculations show that it would increase the NiO content of the glass by 0.015 wt%. This small increase would not be detectable in the glass product data. If the electrode were lost only during the high noble metals segments, when a decrease in melt resistance was seen, it would have represented a 0.05 wt% increase in NiO in the glass product. This increase is in the marginally detectable range. It is possible that the electrode was lost in a temperature excursion during the lengthy melter checkout period that preceded the test segments and had largely oxidized away by the beginning of the run. Inspection of the Laboratory Record Books for the project did not reveal any events which could have caused this to happen.

A scenario that could have resulted in the high temperature erosion of the end of this electrode is presented here. If a noble-metal-rich layer were forming on the bottom of the melter and this layer was very conductive but closer to the electrode containing the thermowell, the lowered resistivity near the melt power controlling thermocouple would cause the system to put more amps through this local area to keep the thermocouple at its setpoint. The larger gap of glass between this layer and the other electrode would mean that this higher amperage would result in higher-than-normal power densities in this region. This situation would cause high temperatures at the electrode tip that the amperage would be shorting to.

As the end of the electrode is eroded and moving upward, it would get further away from the conductive sludge layer and, slowly, the percentage of the total current shorting through the sludge layer and to the electrode tip would drop as the percentage of the total current going through the glass melt above increased. Eventually, the electrode tip would move up to the point where it would reach an equilibrium. Once the temperature of the tip of the eroding electrode reached the point where no more erosion occurs, the system stabilized. The stages of this scenario are presented in Figure 5.3.

There is no evidence to establish that this was the mechanism for the electrode failure, it is simply a possibility. At first, it may seem unlikely that a conductive layer forms on the bottom, but is closer to the electrode containing the thermowell than the other electrode. But if the opposite were true, and at any time the sludge layer formed was closer to the electrode without the thermowell, the extra heat

Figure 5.3. Scenario for Electrode Erosion

generated in the local area of the tip of the electrode containing the thermowell would be sensed by the thermocouple. Consequently, the joule heating would be decreased until the electrode temperature was at setpoint again.

5.3 Comparison RSM Results with Other Melter Runs

Work is just being completed on the most important information concerning the processing of NCAW with noble metals in a liquid-fed ceramic melter. To date, tests have been completed on the RSM, the ESM at KfK in Germany, and the DWPF IDMS at the Savannah River Laboratory. All these tests were relatively recent so that the results and conclusions are just now being drawn. A summary of these tests is shown in Table 5.3.

Two batches of NCAW simulant containing noble metals were processed through the IDMS melter during November 1991 through February 1992. Besides the HWVP batches, the IDMS melter has processed a significant quantity of noble metals feeds as shown in the "IDMS-Total" column of Table 5.3. Most of those feeds were prototypic of the DWPF feed. Prior to the HWVP tests, though a significant quantity of noble metals had settled to the floor of the IDMS melter, no change in electrical characteristics was noticed. At the start of the HWVP feed, a slight change in the ratio of the resistances between the upper set of electrodes and the lower set of electrodes was detected. This change was minor, but appeared to be real. Post-test samples taken from the floor of the melter suggest a non-uniform layer of noble metals (mainly RuO_2) and Ni/Fe/Cr spinels. A material balance, based on XRF analyses, suggest that 41 % of the ruthenium, 20% of the rhodium, 8% of the palladium, and 6% of the silver from the HWVP feeds were retained in the melter.

The ESM test was conducted in the summer of 1992 at KfK in Germany. As mentioned in the introduction, this was a one-tenth scale HWVP melter run at nominal HWVP operating and feed conditions. Only preliminary information has been received from the ESM run. This information indicates that approximately 25% of the ruthenium, 25% of the rhodium, and 40% of the palladium were retained in the melter. These percentages appeared to be increasing with time as the run progressed. At the conclusion of the run, a 1 to 3-cm layer of noble metals was found on the bottom of the melter. The layer did not appear to cause an electrical shorting between the electrodes during the run. Based on the results of the RSM run, the latter point is surprising. A layer this thick should cause an electrical disturbance. The results will have to be reviewed by PNL before further conclusions can be drawn.

In reviewing Table 5.3 it becomes clear that the RSM processed many more tank turnovers than the other melters combined. At first glance, this would explain the differences in results between the other melters and the RSM. But this would be based strictly on tank turnovers. What should also be taken into account is the fact that the residence time of the RSM was much less than that of the other melters. That is, the time that the insoluble particles had to settle in the melter cavity was only one-eighth that of either the ESM or IDMS melter. Prior to the RSM run, it was not expected that *any* noble metals would settle in the RSM because of the short residence time. The parametric study was designed to

Table 5.3. Summary of HWVP Noble Metals Runs

	RSM	ESM	IDMS-HWVP Waste	IDMS-Total ^(a)	HWVP Reference ^(b)
Melt pool diameter (m)	0.152 (6")	0.6	0.61	0.61	1.83
Melter surface area (m ²)	0.0182	0.28	0.29	0.29	2.6
Area scale	0.007	0.11	0.11	0.11	1
Melter depth (m)	0.076 (3")	0.78	0.65	0.65	0.86
Melter volume (L)	1.39	245	163	163	2,250
Glass holdup (kg)	3.5	585	408	408	5,600
Reference residence time ^(c) (h)	5	58	42	42	55
Actual residence time ^(d) (h)	5.8	80-100	N/A	N/A	N/A
Length of run (days)	59	60	48 ^(e)	150	511
Glass produced (kg)	531	7,000	3,614	19,769	1.2x10 ⁶
Tank turnovers during run(s)	152	10.5	9	49	219
Average NM concentration in glass ^(f) (wt%)	0.18	0.14	0.17	0.12	0.14
Noble metals throughput ^(f) (kg)	0.96	9.7	6.1	24.5	1,962
<p>(a) Total noble metals runs on the IDMS melter as of April 1993.</p> <p>(b) Based on two years of operation with 70% online efficiency.</p> <p>(c) Assumes 100 kg/h glass production rate from the reference melter.</p> <p>(d) Based on average glass production rate during run neglecting down time.</p> <p>(e) Gross length of the two individual batches. Total length of run from start of first batch to melter to last glass poured was 68 days.</p> <p>(f) Sum of Ru, Rh, and Pd weights as metals.</p>					

investigate noble metals characteristics (morphology and particle size distribution) in the glass product, not in the melt cavity. The fact that a significant layer formed was a complete surprise to the researchers.

The first hypothesis to account for the settled layer in the PSM was the frequent idling periods during the run. Based on TEMPEST computer modeling, the glass convection is much less in an idling melter than in one with a cold cap. This would mean that the worst way to feed a melter would be to have feeding periods followed by long idling periods. This would create a cycle in which metals would be fed to the melter, then the metals would be allowed to settle during idling.

A good example of this phenomenon is the drop in electrode resistance experienced during idling periods for the PAMELA melter in Belgium.^(a) This phenomenon was investigated for the RSM run. No changes could be detected during the idling periods. This is most likely because the RSM has a small length-to-diameter ratio so that the inventory of noble metals in the bulk glass was relatively low (i.e., if all of the noble metals in one tank volume settle, it would not form a layer sufficient to affect the electrode resistance).

From the RSM run data, it appears that there was no change in electrode resistance during the 1X noble metals segments of the run. A steady decline in electrode resistance did not appear until Segment 9, the first segment with 2X noble metals. Some changes were seen early in the run, but this was caused by changes in glass temperature, not a noble metals layer. This topic was discussed earlier in this section and in Section 4.3.1. It is discussed here in relation to other melter runs.

Both IDMS and KfK used 1X noble metals feeds for their HWVP runs. The DWPF feeds previously processed in the IDMS system had noble metals concentrations at or below that of the nominal HWVP feed. Neither the ESM nor the IDMS melter experienced resistance changes anywhere near that of the RSM. At first it would appear that there is an inconsistency here, until it is remembered that the RSM did not show any resistance effects during the 1X noble metals feeds. It is not clear that the RSM would have developed a settled layer if it would have continued to process nominal feed. There appears to be a threshold level of noble metals concentration above which the rate of noble metals layer accumulation dramatically increases. This does not mean that a nominal feed can be processed indefinitely in the HWVP melter without problems. It just indicates that the plant melter will survive much longer with a nominal feed than with a 2X noble metals feed.

To discuss whether or not the waste coming to the HWVP will have nominal quantities of noble metals, the origin of these numbers must first be understood. The "nominal" noble metals concentrations in the double shell tank waste is based on predictions made by a computer code (ORIGEN2) (Croff 1980) that is used to estimate isotopes in spent N Reactor fuel. This nominal noble metals composition is actually a worst-case scenario. The first two double-shell tanks to be treated by the HWVP are 101AZ and 102AZ, respectively. The predicted noble metals concentrations^(b) for these tanks are shown in Table 5.4. As indicated by the table, 101AZ has higher concentrations of noble metals than is currently contained in 102AZ. The 102AZ feed with K Basin Fuel presented in Table 5.4 was the feed scenario used to project the FY 1991 NCAW reference waste simulant that was used for the RSM testing. This assumes that the N Reactor fuel currently stored in K Basin will be reprocessed and the resulting waste will be blended with the current contents of 102AZ. This was proposed before the PUREX Plant was shut down. With no operating reprocessing facility, this scenario now seems unlikely. Assuming that the tanks will be homogeneous, and that the K Basin Fuel will not be blended in 102AZ the RSM 1X feed was a worst-case HWVP feed with respect to noble metals concentration.

(a) Collantes, C.E., L.K. Holton, J.M. Perez, Jr., and B.A. Wolfe. 1987. Research Facilities in the Federal Republic of Germany and the PAMELA Facility Workshop: "Vitrification Operational Experience." Foreign Trip Report.

(b) Conversation with R.A. Watrous of Westinghouse Hanford Company on March 9, 1993.

Table 5.4. Comparison of Noble Metals Content in Melter Glass (wt%)

Noble Metal	101AZ-Current	102AZ-Current	102AZ with K Basin Fuel	K Basin Fuel Alone
RuO ₂	0.06	0.03	0.1	0.55
Rh	0.0125	0.0065	0.021	0.11
Pd	0.0125	0.0065	0.026	0.14
Total	0.085	0.043	0.15	0.80

The assumption of feed homogeneity is still questionable. Because the pretreatment method for the double-shell tank waste is still not set, it is not clear how homogeneous the waste coming to the HWVP will be. If the tank sludge is washed in-tank and then slurried and shipped to the HWVP, it should be fairly well mixed. If the sludge is treated in small batches, the noble metals may segregate because of their high density. If this happens, feeds that are higher than the nominal concentration of noble metals could be sent to the HWVP. As stated earlier, this could severely limit the plant melter life.

5.4 Lessons Learned

The RSM run was a unique melter test in two respects. It was the first time that a melter of this minute scale had been operated at least at PNL, and it was the first time that a melter was operated without full-time operator coverage by using a computer-controlled, autonomous operating system. The system size was intended to minimize the cost of noble metals required to perform a test that involved several melter tank turnovers for 10 to 12 sets of operating conditions. Keeping costs down was also the motivation for the autonomous operating system.

The size of the melter was determined by the availability of an Inconel 601 can and a small pottery-type kiln. The size of the Inconel can constrained the diameter of the melter after the installation of the refractory to 6 in. inside diameter.

A major challenge was the design of a melter lid that could provide a feed nozzle, plenum heater, off-gas line, plenum temperature sensor, plenum vacuum sensing port, viewport, and electrode penetrations inside the 10-in. diameter of the Inconel can. Once the melter was constructed and shakedown testing had begun, it became obvious that the size of the off-gas line (1-in. diameter) would be insufficient to keep particulates from clogging this line in just a few hours of operation. Cleaning the line proved difficult because of the glassy and sticky nature of the material that built up during melter feeding. After some fruitless experimentation with attempts to cool the off-gas temperature at the inlet to the off-gas line, the entire lid was modified to accommodate a sintered metal film cooler. This provided an off-gas line of just over 2 in. and sufficient cooling to drop the off-gas temperature to around 150°C. This modification proved successful; the first film cooler operated for nearly the entire

test before a clog formed. A larger melter would have had less feed entrainment problems and had fewer off-gas clogging problems, which would have significantly shortened the delay in starting the test.

The most significant operational problem during the run was the feed system. The feed used during the system checkout was not the reference NCAW feed. It did not exhibit the feed rheology problems experienced during the run. The feed used during system checkout flowed very well over the cold cap and never caused any feed line clogs during its use. The feed used during the melter run was significantly more difficult to pump; feed line or feed nozzle clogs represented the largest number of feed stoppages (see Section 4.2.2). A larger melter would have required a larger feed rate, which would have undoubtedly meant fewer outages and more stable operation.

The autonomous operating system proved very successful at controlling the operation of the melter and recognizing melter upsets when they occurred. Perhaps its greatest asset was its flexibility. The system was capable of being altered from the keyboard of the controlling computer at any time during the operation of the melter without upsetting the operation. This allowed the operators to construct new alarm conditions or reset current alarm limits, add data acquisition points, and change upset event responses during the run. The only problem associated with the operation of the autonomous system was that the feed line and feed nozzle clogs occurred with such high frequency during some of the run that the operator on call would be required to make two or three trips a night to restart the melter feed.

In general, many of the problems associated with melter operation were caused by the very small melter size. The savings in reduced noble metal costs were easily offset by the increased cost of attempting to make this very small system function well. Having achieved it once, it could be repeated at a lower cost. However, there are very little cost savings, and possibly even an increased cost, to operate a melter this small.

Even with these problems, it would be cost effective to operate a melter the size of the RSM again, should more testing be required. Even though the melter has been removed, the vast majority of the system (off-gas, electrical, feed, and data acquisition and control) still exists. Given the surprising results of this testing (the precipitation of any noble metals), the most advantageous method of performing further testing would be to build one melter for each test segment. Once each segment was completed, the melter could be removed and cut open to preserve the state of the melter bottom as a result of those particular test conditions. Even the melter lid that interfaces with the services could be reused. The extra cost of building these melters is very small, and probably well worth the extra confidence in the data collected. The unfortunate situation in this testing was that the final segment was quite different than the previous segments and may have radically changed the state of the material on the bottom of the melter from what it had been at the end of previous segments.

6.0 Computer Modeling

In the MPA activity, the objective is to determine effects of noble metals on the lifetime of the HWVP melter. Tests (GFT, RSM, and ESM) are being conducted to gain noble metals particle data and melter operational information upon which the MPA will be based. Numerical computer modeling is an integral part of the MPA. The computer modeling and the tests complement each other. The tests provide operational data in a geometrically scaled environment. They also provide data upon which computer submodels can be based. Once confirmed against scaled test data, computer modeling can then provide numerically mocked-up results at full scale.

This section presents the results of the computer modeling effort aimed at simulating the RSM. Included are

- A review of the TEMPEST computer program (Trent and Eyler 1993) (Section 6.1).
- A review of computer submodels needed for simulating RSM operation with noble metals (Section 6.2).
- A description of the computer model and analysis approach to the RSM (Section 6.3) including the geometry and boundary conditions applied (Section 6.3.1) and a survey of the property functions used in the computer models (Section 6.3.2).
- The computed results (Section 6.4) of pre-test, preliminary post-test, and post-test computations. Pre-test predictions are those made prior to RSM testing. Preliminary post-test predictions are those made during and after RSM testing, but prior to complete data reduction. Post-test predictions are those made after RSM test data reduction.
- An extensive analysis of noble metals particle characteristics as they apply to submodels for predicting settling rates (Sections 6.2.3 and 6.4.6).

The review of the TEMPEST computer code includes a description of the equations solved and the coupling of the momentum, energy, species, and electric field equations. The coupling occurs through temperature- and concentration-dependent properties and through local resistance heating. Solving these equations allows for investigating interactions of the convecting glass melt, the cold cap boundary, internal joule heating, and particle advection and settling. Predicting settling and the development of an enhanced conductivity sludge layer on the melter floor is key to the MPA. Fully coupled calculations imply explicit inclusion of all these effects concurrently.

The review of the computer submodels needed for simulating the RSM (and subsequently the ESM and HWVP melters) includes models and bases for noble metal particles enhancing electrical and thermal conductivity in a sludge layer; models and bases for discrete, dispersed particles affecting glass viscosity; and models and bases for particle settling rates. Effects of particle porosity, sphericity, and

hindrance on settling rates are discussed. Information from GFT and RSM glass sample analysis is used as a basis for particle characteristics including porosity, sphericity, and hindrance. The mathematical basis for the power controller is also presented. Its use is successfully demonstrated in several calculations.

Results presented in Section 6.4 show that TEMPEST can successfully compute the RSM operating parameters. In pre-test and post-test predictions, power is predicted to within 13 and 29%; voltage within 30 to 34%; current to within 3 to 13%; and resistance to within 42 to 50%. Power is primarily a function of external boundary conditions. Agreeing with power data to within 13 to 29% is excellent considering that for some segments, RSM power data fluctuated regularly by $\pm 18\%$. Current, voltage, and resistance are all tied together in a very nonlinear fashion. They are affected by the internal electric conductivity distribution which is in turn affected by temperature distribution. The temperature distribution is a function of boundary conditions and internal heating distribution which is a function of electrical conductivity, and so on. Some improvement in predicting the electric parameters may be possible, but it is not, at present, critical to the objectives of simulating the development of the noble metals enriched sludge layer and determining the effects of such a sludge layer on operation. This can be done by examining effects relative to a predicted baseline.

Numerous numerical simulations were conducted to examine parameters of the problem (idle state and feed state; with and without pouring). These simulations successfully demonstrated the correct operation of the power controller in both the bulk temperature mode and the single-point thermocouple mode. Temperature differences in certain simulations are in qualitative agreement with limited temperature probing data. Simulations also successfully examined electrode surface current flux effects with and without presence of a (nearly) purely conducting short, characteristic of the early experiment test segments and the posthumous examination state, respectively. The RSM examination after testing showed a nearly perfect short of pure metal on the floor of the melter. Calculations were also successful with asymmetric electrodes using observed posthumous observations of the RSM.

In fully coupled calculations with settling noble metals particles, the computer model successfully demonstrated the development of an enhanced conductivity layer of sludge by use of an accelerated settling methodology. The success is in demonstrating the complete and full coupling of all the computer submodels. An accelerated settling methodology was used because the fully coupled calculations are very CPU- (Central Processing Unit) time intensive (10 s of hours of computer time per hour of simulation time). Accelerating the settling is a way to test the full coupling in the simulations. Long-term (10 s of days) uncoupled settling calculations with terminal settling rates more prototypic of noble metals particles indicated little development of a sludge layer. This latter result is consistent with deduced experimental observations based on noble metals material balance data obtained from glass sample microscopy and analytical analysis.

Both the continuum and particle tracker approach to modeling noble metals affects in the glass melter have been investigated. After extensive investigations, the particle tracker approach was abandoned because particle path integration accuracy was insufficient to differentiate path inaccuracy

from path deviation because of gravitational settling. The continuum species transport approach has proven successful and quite useful in investigations of enhanced sludge layer effects.

Some critical data are not available. In particular, the particle concentration-dependent effects on electric conductivity and viscosity of noble metals enriched RSM glass have not been measured. In their absence, the limited data available in literature are being used as a guide to determine constants in submodels which describe these effects.

In summary, the numerical modeling results presented in this section:

- Use GFT and RSM particle characterization data as the basis for numerically investigating noble metals particle transport.
- Predict RSM operational performance.
- Evaluate submodels dependent on particle characteristics.
- Demonstrate coupling between TEMPEST submodels, numerical solution, and the analysis procedures.
- Provide the basis for the next step in the activity—modeling of the ESM and HWVP melters.

6.1 Tempest Computer Program Description

The TEMPEST computer program numerically solves a base set of governing transport equations for continuity, momentum, and thermal energy. A separate TEMPEST documentation and evaluation task to MPA is in progress; only a brief overview of TEMPEST is presented here.

The equations solved by TEMPEST are

Continuity:

$$\frac{\partial u_i}{\partial x_i} = 0 \quad (1)$$

Momentum:

$$\rho_0 \left[\frac{\partial u_i}{\partial t} + \frac{\partial (u_i u_j)}{\partial x_j} \right] = -\frac{\partial p}{\partial x_i} + \frac{\partial}{\partial x_j} \left[\mu \frac{\partial u_i}{\partial x_j} \right] + \frac{\partial \mu}{\partial x_j} \frac{\partial u_j}{\partial x_i} + \rho g_i \quad (2)$$

Energy:

$$\rho_0 c \left[\frac{\partial T}{\partial t} + \frac{\partial (u_j T)}{\partial x_j} \right] = \frac{\partial}{\partial x_j} \left[\kappa \frac{\partial T}{\partial x_j} \right] + Q \quad (3)$$

A combination of numerical solution algorithms are used in TEMPEST, depending upon the problem under consideration. These include explicit, semi-implicit, and implicit algorithms. The choice of solution algorithm is dependent upon numerical stability and accuracy considerations and upon the need for computational efficiency (minimizing CPU time).

The transport equations presented above are coupled through material properties. The primary couplings are through temperature-dependent density, thermal conductivity, and viscosity relationships. Coupling also occurs through a resistance heating thermal energy source term arising from the electric field solution in an electrically conducting material. During species transport, additional coupling can occur through concentration-dependent density, viscosity, and thermal and electric conductivity. In the case of melter operation with a noble metals buildup on the melter floor, all these couplings are present and must be considered in the modeling analysis. This is referred to as fully coupled analysis.

6.1.1 Species Transport - Continuum Approach

The continuum approach to modeling species transport involves solving the transport equation for the concentration of a species,

$$\frac{\partial C_k}{\partial t} + \frac{\partial(u_j C_k)}{\partial x_j} = \frac{\partial}{\partial x_j} \left[D_k \frac{\partial C_k}{\partial x_j} \right] + \dot{C}_k \quad (k = 1, 2, 3 \dots) \quad (4)$$

In the continuum approximation, the species concentration may represent a single discrete phase with characteristic particle size. Multiple particle size distributions may be approximated by solving Equation (4) for each of several discrete particle sizes representative of a range within a distribution. Equation (4) may also be solved for discrete species materials, such as Rh, Ru, Pd, Te, or Au or an alloy of these. It can also be used to represent dissolved species if precipitation kinetics were identified as of significance. Thus, the continuum approximation approach offers the advantage of being applicable to a wide variety of cases, assuming appropriate boundary and source/sink information is available from either data or physical models. Also, the entire model is contained in TEMPEST, unlike the particle tracker approach.

6.1.2 Species Transport - Particle Tracker Approach

The particle tracker approach involves solving a Lagrangian equation for the path of individual particles within a convecting melt pool. The general equation is based on a force balance on a single particle,

$$\Sigma F = m \, du/dt = B + W + E_D \quad (5)$$

where m is the particle mass, u is the particle velocity, t is time, B is buoyancy force, W is weight, and E_D is drag force. Each of the terms on the right-hand side are relatable to the particle density, a drag coefficient which is in turn a function of particle shape and size, and the flow field the particle

experiences. The position of the particle with time is obtained by integrating Equation (5) and noting that the position of the particle is obtainable from

$$dx/dt = u \quad (6)$$

In this approach, the fluid velocity moves the particles subject to gravitational and drag forces acting on the particle. The flow field upon which the particles are transported has to be precomputed. If the flow field is steady, this is a rather straight-forward process, except that correct treatment of particles within the very near wall region requires special treatment. If the flow field is unsteady, a rather complicated procedure has to be implemented which involves the use of "recycling" a sequence of flow fields that represent a quasi-periodic flow field, or it requires direct solution of particle tracking within the flow field solution procedures. Submodels for forces on particles are based on data for particle characteristics such as size and shape. Data for these submodels comes from GFT and RSM glass sample analysis.

The particle tracker approach offers advantages in treating specifics of larger particles where inertia or particle-to-particle interactions, such as agglomeration, may be important. The approach suffers from a disadvantage of being computational intensive when sufficient numbers of discrete particles are included so as to be statistically representative. The approach also has the disadvantage of being decoupled from the hydrodynamics of the melt pool. Thus, a procedure must be developed for coupling the predicted effects of particle settling and sludge buildup back into calculation of operation characteristics of the melt pool.

The particle tracker approach was extensively investigated for its application to transport of simulated noble metals particles. The conclusion of these investigations was that the method could not be used in the present work. The computer time required to compute a sufficient number of particles to be significantly representative was excessive. Also, the integration of the circulation path of a single particle in a recirculating flow field could not be calculated accurately enough to distinguish the path position numerical error from path position variation that occurs because of particle settling under the influence of gravity. The particle tracker approach has been abandoned in favor of the continuum species transport approach.

6.1.3 Electric Field Equations - AC Model

Joule heat Q_j as a source in the energy equation is generated by electric currents resulting from potentials applied to a system of electrodes. To compute joule heat efficiently, the potential field $\phi(x,t)$ and the associated electric current flux $I(x,t)$ are factored into a sum of space and time factors as

$$\phi(x,t) = \sum_{n=1}^N f_n(t) \phi_n(x) \quad (7)$$

$$I(x,t) = \sum_{n=1}^N f_n(t) I_n(x) \quad (8)$$

where the spatial current flux is determined from a spatial potential field as

$$J_n(\mathbf{r}) = -\sigma \nabla \phi_n(\mathbf{r}) \quad (9)$$

The spatial potential field is determined from solution of a Poisson equation of the form

$$\nabla[-\sigma \phi_n(\mathbf{r})] = I_{v,n}^0(\mathbf{r}) \quad (10)$$

where $I_{v,n}^0(\mathbf{r})$ is a reference current source (or sink where negative) per unit volume, chosen to be nonzero only within the n-th electrode pair. The cycle-averaged joule heat-per-unit volume is calculated as

$$\begin{aligned} Q_J(\mathbf{r}) &= \langle J(\mathbf{r},t) \cdot J(\mathbf{r},t) / \sigma \rangle \\ &= \sum_{n=1}^N \sum_{m=1}^N F_{mn} J_m(\mathbf{r}) \cdot J_n(\mathbf{r}) / \sigma \end{aligned} \quad (11)$$

where

$$F_{mn} = \langle f_m(t) f_n(t) \rangle. \quad (12)$$

The symbol $\langle \rangle$ indicates a time average of the enclosed quantity. In a glass melter, the electric conductivity, σ , will be spatially varying with temperature and may be spatially varying with noble metals concentration. As a sludge layer develops, the electric conductivity may also be temporally varying.

Use of this model requires specification of a set of F_{mn} values or a combination of time-averaged voltage products, partial powers, and F_{mn} . This formulation allows for phase differences and for non-sinusoidal waveforms in driving a multi-electrode, multi-phase electric system. The number N of spatial potential field solutions required in this representation depends on the number of electrode pairs, the number of electromotive force sources, and their connections.

A more detailed explanation of the electric field solution and analytical basis can be found in Lessor et al. (1991).

6.2 Computer Submodel Connections

Computation of noble metals transport through, and holdup within, the melt pool requires boundary source information at the cold cap/melt pool interface. Particle data from the GFT experiments and slurry feed makeup are the bases for characteristic particle size, shape, and content and material quantity at the cold cap. These data have recently been reported by Anderson et al.^(a) Once in the melt pool, the noble metals material is transported around the melt pool by the buoyancy-induced

(a) Anderson, L.D., T. Dennis, M.L. Elliott, L.L. Eyler, and P.R. Hrma. 1992. *Laboratory Testing and Computer Modeling of HWVP Melter Feed*. Milestone report C91-04.01B, Pacific Northwest Laboratory, Richland, Washington.

convection currents. Glass sample data from the RSM during pouring and from melter posthumous examinations provide data for particle characteristics needed for computational analysis of the RMS. The noble metals particles may undergo physical and/or chemical changes while in the glass melt which may lead to improvements to the modeling at some future date as information on these changes becomes available to the computer modeling task. One such improvement may be the need to model the reduction process of RuO_2 particles to Ru metal. Another may be the need to model the time-rate of growth of particles (agglomeration).

As a noble metals enriched sludge layer develops, several effects can occur that affect melter operations. The primary one is the potential to cause shorting of the electric current between the lower electrode pair. During development of the sludge layer, properties of the sludge layer may vary with time. These properties include viscosity thermal conductivity, and electrical conductivity. Computer submodels are required to represent the concentration-dependent properties. Additionally, because the simulated noble metals particles are heavier than the glass melt, they are subject to gravitational settling. Thus, a particle settling model must be used to describe this effect in the computational analysis.

In the following sections, the mathematical and physical bases for submodels of concentration-dependant properties and particle settling are described.

6.2.1 Enhanced Electrical and Thermal Conductivities

In a melter, noble metals occur as a discrete particle phase in a continuum (glass). The presence of the dispersed noble metals particles can enhance the effective electric and thermal conductivities. Goring and Churchill (1961) provide an excellent review of empirical modeling approaches to this problem in a review of literature back to work done in 1891. In the absence of polarization effects, the electro-static and thermo-static problems are identical.

Both the thermal and electric conductivity of an assumed cubic packed, noncontacting, monodispersed discrete spherical particle phase in a continuous fluid field can be related analytically to the conductivity of the continuous phase, subject to assumptions. Mathematically, Rayleigh's model can be expressed as

$$\frac{\sigma}{\sigma_f} = 1 - \frac{3\nu_p}{\frac{2+\Sigma}{1-\Sigma} + \nu_p - \frac{1-\Sigma}{(4/3)+\Sigma} a\nu_p^{10/3} + \dots} \quad (13)$$

where ν_p is the volume fraction, a is a constant dependent on assumed packing arrangement, and $\Sigma = \sigma_p/\sigma_f$ is the ratio of the electric (or thermal) conductivity of the discrete particle phase to the electric (or thermal) conductivity of the continuous fluid phase. The constant a in Equation (13) takes on different values depending upon the packing arrangement: simple cubic ($a = 1.131$), body centered cubic ($a = 0.129$), or face centered cubic ($a = 0.0752$).

Figure 6.1 presents the theoretical ratio of the enhanced conductivity for infinite Σ for the simple cubic assumption that is the most conservative. Note the large increase in the relative conductivities that results, but that the largest effect according to Equation (13) is at concentrations approaching maximum packing factors. Equation (13) has been implemented into TEMPEST for use with determining the electric conductivity of a developing sludge. This provides one basis for investigating temporal changes in sludge layer conductivities as particles settle and an enhanced conductivity layer develops.

Data from German melter operation experience indicate a factor of 10 to 100 increase in electrical conductivities of a settled sludge layer of noble metals.^(a) A ten-fold increase is at least in qualitative agreement with the upper limit of the curves in Figure 6.1. The concentration at which the ten-fold increase occurs, however, is only about 5 to 6% by volume as compared to 60% by volume for Rayleigh's model (Equation [13]). This occurs because noble metal particles are spiny and porous (see Appendix A). Thus, a more empirically based model has also been implemented in TEMPEST. This model is referred to as a shape function that provides similar variational dependency with concentration as that depicted in Figure 6.1, but offers the computer modeler more flexibility in curve-fitting data as a function of volumetric concentration.

The mathematical approach is to separate the temperature dependence from the concentration dependence as

$$\sigma(T, C_r) = \sigma(T) * f(C_r) \quad (14)$$

where $\sigma(T)$ = temperature-dependent glass conductivity
 $f(C_r)$ = functional concentration dependence
 C_r = ratio of volumetric concentration to maximum volumetric concentration, $(C_v/C_{v,max})$

The concentration-dependent functional form part of Equation (14) allows for expressing the ratio of the maximum conductivity to the reference conductivity as the settled volumetric concentration approaches the maximum settled packing fraction. Note that both the temperature and concentration dependence of the conductivity are modeled in this approach. Rayleigh's model is one which has been implemented in TEMPEST; a power shape function and an exponential form have also been coded. At present, concentration-dependent conductivity data for RSM glass has not been measured. So the choice of a concentration-dependent functional form is somewhat arbitrary.

6.2.2 Glass Viscosity

Molten glass in melters is known to be strongly temperature dependent. The presence of noble metals particles may also lead to a particle concentration dependence. Indications of German melter

(a) Personal correspondence from W. Grünwald of KfK, February 15, 1993 (also see Choi [1992]).

Figure 6.1. Theoretical Ratio of Electrical Conductivity for a High Conductivity Discrete Particle Distributed in a Continuous Medium

operation experience,^(a) published data (Krause and Luckscheiter 1991), and HWVP data (Cobb and Hrma 1991) are that the glass with noble metals particles may behave more like a non-Newtonian fluid than a Newtonian fluid as the volumetric concentration of noble metal particles increases. Plodinec (1986) also presents a summarization of DWPF data on crystalline containing glass which exhibit both Newtonian and non-Newtonian character. For the present work, and for several other waste processing problems, several concentration-dependent Newtonian and non-Newtonian fluid properties models have been implemented into TEMPEST. These offer the modeler a wide range of options for treatment of concentration-dependent viscosity properties.

(a) Weisenburger, S. "KfK Melter Modeling Experience." Presentation to the Noble Metals Workshop, March 16-20, 1992, Richland, Washington. T. Weber, Westinghouse Hanford Company/HWVP, organizer.

In general, effective viscosity in TEMPEST is

$$\mu_{\text{eff}} = f(\mu, \beta) \dot{\gamma}^{g(\beta)}$$

where μ = $\mu(t)$, temperature-dependent dynamic viscosity,
 $\dot{\gamma}$ = strain rate,
 β = ratio of volumetric concentration to maximum concentration ($C_v/C_{v,\text{max}}$),
 $f(\mu, \beta)$ and $g(\beta)$ = functional forms.

For concentration-dependent Newtonian models, the following functional forms are available in TEMPEST:

$f(\mu, \beta)$	$g(\beta)$	Description
$\mu(1 + a_3\beta^{a_4})$	0	Power shape
μa_5^β	0	Exponential shape
$\mu(1 + a_1\beta + a_2\beta^2 + a_3\beta^3)$	0	Cubic power shape

In each of these, μ is treated as temperature dependent.

For non-Newtonian fluids, the following functional forms are available:

$f(\mu, \beta)$	$g(\beta)$	Description
K	m	Power law: Ostwald-DeWaele
$K(1 + a_3\beta^{a_4})$	m	Power law: Ostwald-DeWaele, power shape consistency
Ka_5^β	m	Power law: Ostwald-DeWaele, exponential shape consistency
1	$m(1 + a_5^{-\beta} - a_6^{-\beta})$	Power law: Concentration-dependent behavior index—double exponential form

In these expressions, K is consistency index, m is behavior index, and a_1 to a_6 are constants supplied by the user. To use any of these models effectively, data for the fluid needs to be known. RSM glass samples have not been tested to determine which of these available models best represent the glass' concentration dependence.

6.2.3 Particle Settling

Particles in the melter settle in the Stokes flow (or viscous creeping flow) regime with a particle Reynolds number far less than unity. Although Stokes flow for simple solid particles is well characterized in the literature, calculations of the melter particle settling velocity are complicated by the porosity and nonsphericity of the noble metals particles. Furthermore, it is necessary to choose a model for "hindered settling." This is the decreased particle settling velocity observed at higher solid volume fractions (such as those expected in the packed sludge at the bottom). Settling velocity must go to zero when the particles become so densely packed that no further settling can reasonably be expected.

The particle settling submodels in the TEMPEST computer code accept reference settling velocities as input. The modeler calculates the reference velocities, accounting for nonsphericity and porosity of the particles. These reference velocities are then scaled by TEMPEST to account for the variation of local particle concentration, fluid viscosity, and density in the melter.

The basic equation for the Stokes regime particle settling velocity is

$$V_s = d^2 g (\rho_p - \rho_f) / (18 \mu) \quad (15)$$

Here the diameter d is that of an equivalent spherical particle; the densities, ρ_p and ρ_f , are those of the solid particle and the fluid, respectively. The local dynamic viscosity is μ .

Strictly speaking, Equation (15) holds only for a solid spherical particle which is isolated from other particles. The effects of nonsphericity, porosity, and hindered settling, which are all relevant to the RSM particle behavior, are discussed in following sections. As a reference basis for the discussion, certain observed particle size distributions from GFT and RSM experiments are presented in Table 6.1.

The size distribution is expressed in terms of volume fraction, this being the most appropriate distribution for considering sludge accumulation problems. The volumes are approximate, being based on the volume of spheres having a cross-sectional area equal to the projected area of the observed particles. The GFT data show the smallest particle size and narrowest distribution. The samples from RSM Test Segments 9 and 10 (cans 57 and 63) show a much higher volume fraction of large particles than the earlier samples from Segments 4, 5, and 6 (cans 26, 30, and 35).

6.2.3.1 Nonsphericity

Many of the particles observed in the GFT and RSM tests were not spherical. The GFT data showed a number of particles whose length was two or three times the width (as viewed in two dimensions). A very small percentage of the GFT particles were longer, with length over six times the width. Supporting data can be found in Appendix B of Anderson et al^(a). In the RSM tests, the

(a) Anderson, L.D., T. Dennis, M.L. Elliott, L.L. Eyler, and P.R. Hrma. 1992. *Laboratory Testing and Computer Modeling of HWVP Melter Feed*. Milestone report C91-04.01B, Pacific Northwest Laboratory, Richland, Washington.

Table 6.1. Measured Particle Size Distributions

Diameter Range μm	Volume Percent		
	GFT Data	RSM Data Segments 4, 5, 6 Cans 30, 35	RSM Data Segment 10 Can 63
0-1	0.1		
1-3	13.5		
3-5	32.2		
5-7	20.9	11.7	0.1
7-9	0	19.8	0.6
9-11	0	24.3	1.6
11-13	33.4	4.9	2.9
13-15		27.5	2.8
15-17		11.7	2.6
17-19			5.2
19-21			5.7
21-23			1.4
23-25			2.7
25-30			2.7
30-40			16.5
40-50			11.7
50-60			21.4
60-80			22.1

particles consisted of clusters of small needles. While the needles had large length to diameter (L/D) ratios, the pertinent shape for purposes of settling velocity calculation is the overall shape of the cluster. The observations (given in Appendix A) show that (like the GFT particles) the RSM clusters generally have an L/D ratio of 3 or less.

A settling velocity correction for nonspherical particles can be made. The important variables can be determined by reviewing the derivation of Equation (15). Settling occurs when gravity acts on a particle. A terminal settling velocity is reached when gravitational and drag force on a particle are equal.

$$\text{Drag force} = C_D A_p \rho_f V_s^2 / 2 \quad (16)$$

$$\text{Gravitational force} = g (\rho_p - \rho_f) v_p \quad (17)$$

Here C_D is the drag coefficient, A_p the projected (cross-sectional) area of the particle, and v_p the particle volume. In Stokes flow, the drag coefficient is an inverse function of Reynolds number:

$$C_D = 24 \mu / (V_s d \rho_f) \quad (18)$$

To determine the equivalent spherical diameter d of a nonspherical particle, the important variables are the volume v_p and the surface area s_p of the particle (McCabe and Smith 1976, p. 149). First, the equivalent diameter of the particle is defined as that of a sphere with equal volume. Second, a dimensionless parameter Φ_s (the sphericity) is defined as the ratio of the surface area of the sphere of equal volume to the surface area of the actual particle. With these corrections in place, the equivalent spherical diameter d is defined as

$$d = 6 v_p / (\Phi_s) \quad (19)$$

The drag coefficient is

$$C_D = (4\mu / V_s \rho_f) (\Phi_s / v_p) \quad (20)$$

and the settling velocity is derived as

$$V_s = (g (\rho_p - \rho_f) / (2\mu)) (1 / \Phi_s) (v_p / s_p) (v_p / A_p) \quad (21)$$

The GFT data were first used to find the shape-dependent particle parameters. The particles were treated as cylinders because there was no physical reason to assume they were plates or flakes. The volume-weighted volume-to-area ratio, $(v_p/s_p)(v_p/A_p)$, and sphericity, Φ_s , were calculated and averaged for the three categories of GFT particles defined by Anderson et al.^(a) The results are given in Table 6.2.

The projected (cross-sectional) area was the parameter that was actually measured for each particle, for the RSM as well as the GFT data. The volume to area ratio and the sphericity are quantities calculated only for the GFT data and based on an assumed cylindrical particle shape. The ratio between the measured cross-sectional area and the calculated volume-area ratio do not vary with size because the proportions of the particle were the same with size.

In calculating settling velocities for RSM clusters, the volume-to-area ratio was estimated as being 0.14 times the particle cross-sectional area. Note that sphericity is fairly close to unity, indicating that, on the average, particles are not far from spherical. Because the RSM clusters appear to be in the same range of L/D as the GFT particles, it should be appropriate to use GFT shape factors.

(a) Anderson, L.D., T. Dennis, M.L. Elliott, L.L. Eyler, and P.R. Hrma. 1992. *Laboratory Testing and Computer Modeling of HWVP Melter Feed*. Milestone report C91-04.01B, Pacific Northwest Laboratory, Richland, Washington.

Table 6.2. Particle Shape Factors and Sizes for GFT RuO₂ Particles

Type	Group 1 Solid	Group 2 "Sponge"	Group 3 "Sponge"
Average projected area (μm^2)	1.3	11.3	120
Average $(v_p/s_p)(v_p/A_p)$ (μm^2)	0.174	1.52	16.2
Average sphericity Φ_s	0.84	0.82	0.84

6.2.3.2 Porosity

The noble metal clusters observed in the RSM samples were not simple solid shapes, as tacitly assumed in Equation (21), but highly porous agglomerates of randomly oriented needles. Flow through the pores of these particles must be accounted for in calculating the settling velocity. The literature contains closed-form methods to estimate the settling velocity of high-porosity particles in the Stokes flow regime. Because these methods do not require any adjustable parameters, they are immediately usable in the current study.

The important variables are the cluster's solid volume fraction and the thickness of the needles or rods comprising the particle. From these, the particle permeability (analogous to the permeability of a packed bed) can be estimated. Flow through the cluster can be treated as a case of flow normal to a fiber mat or an array of cylinders, as noted by Masliyah et al. (1987, p. 252). The equation for permeability k is Equation (41) (op. cit.):

$$k = -(a^2 / 8c) * [\ln c + (1 - c^2) / (1 + c^2)] \quad (22)$$

where a is the thickness of the needles making up the agglomerate and c is the volume fraction of the cluster that is solid, equal to $(1 - \text{the void fraction})$.

Given the particle permeability, the drag force for a permeable sphere (relative to that for a solid sphere) can be calculated. A nonspherical particle is treated by using the equivalent diameter d . The parameter β , a dimensionless particle radius, is defined in Equation (4) of Matsumoto and Suganuma (1977) as

$$\beta = \{d / [2 * \sqrt{k}]\} \quad (23)$$

The ratio F of the drag force for the impermeable sphere to that for the permeable sphere can be calculated from Equation (6) of Matsumoto and Suganuma (1977):

$$F = \{\beta / [\beta - \tanh(\beta)] + 1.5 / (\beta^2)\} \quad (24)$$

where $F = (\text{drag force on solid particle}) / (\text{drag on porous particle of same equivalent diameter } d \text{ and bulk density } \rho_p)$

and $F = (\text{settling velocity of porous particle}) / (\text{settling velocity of solid particle of same } d \text{ and } \rho_p)$

The bulk density ρ_s is the linear average of the density ρ_f of the fluid in the particle pores and the intrinsic density of the solid ρ_s , or

$$\rho_p = c \rho_s + (1 - c) \rho_f \quad (25)$$

Use of this formula gives the correct result that when the particle porosity $(1 - c)$ is zero, the particle density is that of the solid, and when the porosity is unity, the particle density is that of the fluid.

It follows that the particle settling velocity, including the effect of porosity, can be expressed as

$$V_s = [gF(\rho_p - \rho_f) / (2 \mu)] (1 / \Phi_s) (v_p / s_p) (v_p / A_p) \quad (26)$$

Equation (26) is the Stokes settling velocity expression (Equation [15]), modified to account for sphericity and porosity. There is no quantified data for the porosity of GFT particles, but some "sponginess," interpreted as a porosity of perhaps 20 to 30%, was noted for the particles in Group 2 and Group 3. This porosity is not high enough to allow significant flow through the particle. However, the porosity of the clusters in the RSM samples was much greater. Viewing the RSM clusters under reflected light, the occluded area fraction of the RSM clusters was between 5 and 17%. Large clusters typically had lower occluded area fractions than small ones, but the correlation between cluster size and occluded area fraction was not very strong. Because the area fraction was determined by reflected light—giving the fraction of cross-sectional area that was solid—the solid volume fraction of a cluster can be taken as about equal to the occluded area fraction.

One GFT particle photo—Figure 3.6 of Anderson et al.^(a)—shows a spiny aggregate, about 16 by 4 μm in size, of RuO_2 needles that are 0.3 to 0.5 μm thick. Other photos (Figures 3.9 and 3.19, op. cit.) show RuO_2 needles that are 0.5 to 1 μm thick. RSM observations (Appendix A) confirm a needle thickness of about 0.5 to 1 μm .

The extent of the effect of flow through a porous particle can be seen in the value of the factor F . Table 6.3 shows some example values of F from Equation (24) that were calculated for parameters within the range of those found in the RSM samples.

It appears that a value of F between 1.0 and 2.0 is to be expected over much of the range of RSM cluster characterization. These values indicate that porosity can make a perceptible difference in the settling velocities of noble metals in the melt.

(a) Anderson, L.D., T. Dennis, M.L. Elliott, L.L. Eyler, and P.R. Hrma. 1992. *Laboratory Testing and Computer Modeling of HWVP Melter Feed*. Milestone report C91-04.01B, Pacific Northwest Laboratory, Richland, Washington.

Table 6.3. Values of F (Porous/Nonporous Settling Velocity Ratio) for RSM Particles

Particle Diam. (μm)	c = 5% solid		c = 17% solid	
	a = 0.3 μm	a = 1 μm	a = 0.3 μm	a = 1 μm
10	1.18	2.08	1.05	1.22
60	1.02	1.09	1.01	1.03

6.2.3.3 Isolated-Particle Settling Velocities

The reference properties that are needed to calculate settling velocities for the variety of particles that might be present in the RSM are as follows:

- Solid density = $\rho_s = 6,970 \text{ kg/m}^3$ for RuO_2
- Fluid density = $\rho_f = 2,170 \text{ kg/m}^3$ for glass @ $1,150^\circ\text{C}$
- Fluid viscosity = $\mu = 8.0 \text{ kg/m s}$ for glass @ $1,150^\circ\text{C}$
- Gravity = $g = 9.8 \text{ m/s}^2$
- Sphericity = $\Phi_s = 0.84$ (from GFT data)
- Volume-to-area ratio = $(v_p/s_p)(v_p/A_p)$
= $0.14 \times \text{cross-sectional area}$ (from GFT data)

The GFT Group 1 particles can be treated as solid RuO_2 with both F and c (the solid fraction) equal to unity, and Equation (26) can be used:

$$\begin{aligned}
 V_s &= [(9.8 \text{ m/s}^2) (6,970 - 2,170 \text{ kg/m}^3) / (2 \times 8.0 \text{ kg/m s})] \\
 &\quad \times (0.14 \times (1.3 \times 10^{-12} \text{ m}^2)) \times (1 / 0.84) \\
 &= 6 \times 10^{-10} \text{ m/s for GFT Group 1 particles}
 \end{aligned}$$

The GFT Group 2 and 3 particles can be treated as solid from the point of view of permeability ($F = 1$), but their lesser bulk density must be considered per Equation (25). A void fraction of 30%, or $c = 0.7$, is used to account for "sponginess."

$$\begin{aligned}
 \rho_p &= 0.7 (6,970 \text{ kg/m}^3) + (1 - 0.7) (2,170 \text{ kg/m}^3) \\
 &= 5,530 \text{ kg/m}^3
 \end{aligned}$$

$$V_s = [(9.8) (5,530 - 2,170) / (2 \times 8)] \times (0.14) (11.3 \times 10^{-12} \text{ m}^2) / 0.84$$

$$= 4 \times 10^{-9} \text{ m/s for GFT Group 2 particles}$$

$$V_s = [(9.8) (5,530 - 2,170) / (2 * 8)] * (0.14) (120 \times 10^{-12} \text{ m}^2) / 0.84$$

$$= 4 \times 10^{-8} \text{ m/s for GFT Group 3 particles}$$

The settling velocity calculations are done in the same way for the RSM clusters, except that the factor F must be calculated. To do this a value of a needle thickness must be assumed.

Table 6.4 shows the settling velocity distribution (by mass fraction) for the cluster particles of RSM Test Segments 9 and 10, assuming two different values of needle thickness, and for the GFT particles. For the GFT, about 65% of the particle mass settles at less than 1×10^{-8} m/s, and none settles as rapidly as 1×10^{-7} m/s. For the RSM, less than 12% of the mass in the clusters settles at 1×10^{-8} m/s or less, and 50% or more settles at roughly 1×10^{-7} m/s or faster. Assuming different needle thickness makes some difference in the velocity distribution; nevertheless, the RSM clusters consistently show higher settling velocity than the GFT particles.

6.2.3.4 Hindered Settling

Should particles settle to the bottom of the melter in significant quantities, their concentration will be great enough to cause their settling velocity to decrease. At some maximum packing factor, the settling velocity becomes zero because no further movement is possible.

The TEMPEST computer code uses three different options to calculate hindered settling and packing effects. In the first option, a constant settling velocity unaltered by particle concentration is used. This option is primarily designed for nonaccumulating, low-concentration species. It could lead to overpacking the cells at the bottom of the melter, raising their solid volume fraction to physically impossible values higher than unity. This option has not been used in the present work. In the second option, a "table" of settling velocities is specified by the user. The input may specify up to five values of particle concentration and the corresponding settling velocity to describe the variation of velocity with concentration. This permits specifying a maximum packing fraction, thus preventing overpacking. Finally, the third option uses a formula relating settling velocity to concentration, providing a continuum of velocities.

The formula used in the third option is taken from Perry and Chilton (1973, pp. 5-64). The hindered settling velocity for particles in the Stokes regime is

$$V_{Sh} = V_s (1 - C_v/C_{v,max})^n \quad (27)$$

Here V_s is the terminal settling velocity at negligible concentration, C_v is the solid (volume) fraction in the suspension, and n is an exponent that depends on the particle flow regime. For Stokes flow, $n = 4.65$, according to Perry and Chilton (1973). TEMPEST allows an exponent n to be chosen by the user. TEMPEST also takes input of V_s and of the maximum packing fraction $C_{v,max}$, at which settling velocity becomes zero.

Table 6.4. Settling Velocity Distributions for RSM and GFT Particles

Mass Percentages of Particles In Each Velocity Range			
Settling Velocity Range (m/s)	RSM Cluster Particles Needle Thickness Equals		GFT Particles
	0.3 μm	1.0 μm	
5×10^{-9}	1.4	0.1	41.2
5×10^{-9} to 1×10^{-8}	11.6	9.4	24.0
1×10^{-8} to 3×10^{-8}	14.6	14.9	0
3×10^{-8} to 5×10^{-8}	14.6	4.2	34.9
5×10^{-8} to 1×10^{-7}	35.8	49.5	0
1×10^{-7} to 3×10^{-7}	21.9	21.9	0

A plausible maximum packing fraction would be about 60% for mono-disposed spherical particles. The atomic packing factors for pure metals range from 0.68 (body-centered cubic) to 0.74 (face-centered cubic). However, a much lower value can be expected for space-filling spiny particles such as found in the RSM. Noble metals concentrations on the order of 5 to 6% (by volume) are reported from the German melter program for sludge samples of noble metals enriched glass.

6.2.4 Power Controller

The power controller used in TEMPEST is based on the PID concept used in the operation of the RSM. The basis for this method is presented by Westsik (1986). The mathematical expression implemented in TEMPEST is

$$P_{\text{tot}} = P_{\text{tot,old}} (1 + \alpha (T_{\text{op}} - T_{\text{ave}})/(T_{\text{ave}} - T_{\text{ref}})) \quad (28)$$

where P_{tot} = the estimated total power
 $P_{\text{tot,old}}$ = the old time power estimate
 α = a relaxation factor
 T_{op} = the desired operation temperature
 T_{ave} = the average temperature desired
 T_{ref} = a reference temperature

The assumption is made that the steady-state bulk average temperature of the melt scales linearly with the joule heat power generation. In practice, a representation of this bulk melt temperature is obtained by either an arithmetic average of point-wise temperatures (replicating point-wise control thermocouples) or as a volume integrated average temperature; both have been programmed into TEMPEST. Both methods have been used successfully in modeling the RSM.

The power controller of Equation (28) is only strictly applicable to single-pair electrode systems and to multiple-pair electrode systems in which current to each electrode pair is adjusted proportionally in each pair. In multiple-electrode systems in which current is adjusted separately for each pair according to a control thermocouple for each pair, the power controller has to be modified. Such a modification is necessary for the ESM and HWVP melters.

6.3 RSM Computer Model Description

The TEMPEST computer program solves the governing conservation equations using finite volume approximations. The mathematical basis is described in Section 6.1. Included in RSM analyses are submodels for property dependencies and noble metals particles transport. Models available are described in Section 6.2.

The RSM geometry, analysis procedures, and material properties used in computing results presented subsequently are presented in this section.

6.3.1 Geometry and Simulation Considerations

The RSM geometry is discussed at length in Section 3.0 of this report. Principally, it consists of small, cylindrical cavity (6 in. ID) containing a single pair of Inconel paddle electrodes (see Figure 3.2) separated a distance of 4-3/8 in. The electrodes, by design, rest on the flat melter bottom. The nominal glass depth is 3-in. Surrounding the cavity is a nominally 1-in. thick shell of K-3 refractory, and a nominally 3/4-in. thick shell of Alfrax. The complete melter is contained in 1/8-in. thick Inconel shell. The whole apparatus is contained in a kiln which maintained the external temperature at a prescribed value. All of these features were included in the computer model.

The discretization of the melter included using a total of 19,364 computational cells. The discretization was done of the full melter (from the modeled cold cap surface down). Because of the location of the pour spout, no symmetry conditions could be used. The smallest computational cell in the melt pool was 0.3-in. thick.

6.3.1.1 Boundary Conditions

The cold cap surface was the upper boundary. Over this surface (assumed flat computationally), specified temperatures were applied to simulate a slurry coverage ($T = 100^{\circ}\text{C}$), a dryout area ($T = 400^{\circ}\text{C}$), and a shining ($T = 900^{\circ}\text{C}$) in approximately cylindrical rings. The slurry coverage area was

nominally specified as 66.3% of the total surface area, the dryout was 15.2%, and the shining was 18.5%. The slurry and dryout areas were modified to 46.3%, and 35.2% of the total surface area in several calculations to investigate the effect the prescribed coverage area had on the simulated melter operational parameters.

The cold cap boundary condition is important to the RSM analysis. Although it is not perfect, using a fixed temperature of 100°C to model the slurry coverage area provides the best estimate for two reasons. One is that boiling of liquid in the slurry feed is a constant temperature process. The other is that the "cold" part of the cold cap boundary provides the correct heat sink temperature for heat generated in the melt and hence best replicates the buoyancy-driving-force temperature difference. In other melter models and earlier modeling work in other programs, other cold cap boundary conditions were experimented with numerically, but none were found to give as good a representation as the three area, fixed temperature condition.

Use of other fixed temperature cold cap boundary surface conditions have been used in other analyses. For example, Choi (1992) used a fix melt pool surface temperature of 1,100°C over 90% of the surface area "to model the cold cap." In evaluating this temperature condition, it was concluded herein that it is more representative of an idling condition without slurry feed than a cold cap/feeding condition. Furthermore, it was concluded that the 1,100°C condition would not represent the correct heat sink temperature, and hence the buoyancy driving force, when a cold cap was present.

The exterior temperature boundary condition on the Inconel melter shell was specified as fixed. In pre-test RSM simulation, exterior surface temperatures of 500°C and 1,000°C were used. The T = 500°C condition was an early (pre-melter construction) design condition. In part, head load analysis from these results led to the conclusion that a 1,000°C exterior surface temperature would have to be maintained by the kiln for joule heat power generated in the melt (and hence electrode surface current flux) to remain within bounds. Thus, pre-test calculations presented herein were computed using the 1,000°C condition on the exterior surface. The refractory blocks the melter sat in the kiln (see Figure 3.2) were modeled as adiabatic surfaces at the melter shell/refractory block interface.

Figure 6.2 presents a schematic of the two principal configurations of the melter and components included in the computer models. The upper half of the figure depicts the "as built" condition in which the paddle electrodes are resting on the floor. The lower half of the figure depicts the posthumous condition observed after completion of the experiment test segments, the melter was cooled down, and subsequently sacrificed (see Section 4.3.3). The location of the single thermocouple used for power control is identified in the figure. In the analysis results presented subsequently, the condition of the shortened electrode is referred to as "asymmetric" electrodes.

6.3.2 Properties Used in Simulations

Density, viscosity, thermal conductivity, and electric conductivity conductivities are required for computational modeling. This section presents the temperature- and concentration-dependent variations and the property model forms used in the pre-test, preliminary post-test, and post-test computer simulations.

Figure 6.2. Schematic of the RSM Before and After Testing

6.3.2.1 Electric Conductivity

Computer simulations of the RSM have been conducted using four representations of electric conductivity. These are identified herein as:

<u>Data Identification Used in Computer Modeling</u>	<u>Description</u>
--	--------------------

RSM/Pre

Data were initially supplied as a temperature-dependent correlation to the computer modeling task.^(a) The correlation for these data is:

$$\ln(\sigma(T)) = A + B/T \quad (29)$$

where A = 9.31
B = -8,469°K
T = temperature (°K)
 $\sigma(T)$ = electric conductivity (S/m)

Pre-test calculations were conducted with these data. They are identified with the label: RSM/Pre.

RSM/Can 21

Data were measured electrical conductivity data obtained using a glass sample cored from RSM canister 21 (end of RSM Test Segment 1). The data were curve fit with Equation (29) to yield:

$$\begin{aligned} A &= 8.703 \\ B &= -7,545^\circ\text{K} \end{aligned}$$

Post-test calculations were conducted with these data. They are identified with the label: RSM/Can 21.

RSM/Can 56

Data were measured electrical conductivity data obtained using a glass sample cored from RSM canister 56 (end of RSM Test Segment 9). The data were curve fit with Equation (29) to yield:

$$\begin{aligned} A &= 9.266 \\ B &= -8,355^\circ\text{K} \end{aligned}$$

(a) Personal communication, M.L. Elliott/PNL to W. Grünwald/KfK-INE, October 23, 1991.

RSM/Alt

These data were supplied in graphical form,^(a) digitized, and entered into TEMPEST in tabular form. The tabulated data used are:

Temperature <u>T (°C)</u>	Electrical Conductivity <u>σ (S/m)</u>
950	6.0
1,000	7.9
1,015	8.6
1,055	10.3
1,100	12.4
1,150	15.2
1,200	18.0
1,210	18.5

Preliminary post-test calculations were conducted with these data. These are identified with the label: RSM/Alt.

Each of the glass electric conductivity data sets are presented graphically in Figure 6.3. The open symbols are measured data points for RSM glass samples from canisters 21 and 56, taken at the end of RSM Test Segments 1 and 9, respectively. Correlations of these data sets agree to within a maximum of 4 percent. Note that of all the RSM data and correlations, except the RSM/Alt data set, agree to within $\pm 5\%$ over the temperature range of 900 to 1,200°C.

In addition to the temperature dependence of electric conductivity, it is necessary to include concentration dependence also. In the fully coupled deposition calculations, the temperature and concentration dependence are separated according to Equation (14). There are no RSM glass data upon which to base the concentration dependence. Thus, it was concluded to use a power shape functional form which is a simplified approximation of the model presented in Figure 6.1. Mathematically, the power shape concentration dependent electric conductivity model used is

$$\sigma(T, C_v) = \sigma(T) * (1 + (a - 1) C_r^b) \quad (30)$$

where $\sigma(T)$ = temperature dependent electric conductivity
 C_r = ratio of volumetric concentration to maximum concentration ($C_v/C_{v,max}$)
 a = maximum conductivity ratio at $C_r = 1$; value used = 10^3 .
 b = curvature shape constant; value used = 3.

(a) Personal correspondence, W. Grünwald/KfK-INE, to M.L. Elliott/PNL, February 1993. Data identified as glass sample 10/92/C/W/32.

Figure 6.3. Comparison of Temperature Dependence of Electric Conductivity Correlations and Data

Without measured data for the concentration-dependent electrical conductivity of RSM glass, the choice of the maximum conductivity ratio, a , is rather arbitrary. A value of $a = 10^3$ was used in combination with a maximum concentration $C_{v,max} = 1$ in selected simulations. Using $C_{v,max} = 1$ can be interpreted as an approximating approach to modeling sludge layer development which is totally composed of transported material. An assumption of $C_{v,max} = 1$ is an upper-bound simulation and is also consistent with simulating development of a pure metal layer on the bottom of the melter. Such a layer was observed in posthumous RSM examinations. Values of $a = 10^2$ and $C_{v,max} = 0.06$ are probably more representative of spiny, porous noble metals particles. These latter values are more representative of data reported by Krause and Luckscheiter (1991). Their electric conductivity data have been used by Choi (1992) who extrapolated it for use in DWPF modeling. Future TEMPEST simulations will incorporate these data.

6.3.2.2 Thermal Conductivity

Thermal conductivity used in RSM computer modeling is presented in Figure 6.4. These data, identified as HW 39, were obtained from an earlier analysis. No concentration dependency of the thermal conductivity was included in the present analysis, although the same modeling approach used for electrical conductivity could be used if there were data to justify it (see Section 6.2.1).

Figure 6.4. Temperature Dependence of Thermal Conductivity Used in RSM Computer Modeling

6.3.2.3 Density

Density as a function of temperature is presented in Figure 6.5. These data, identified as HW 39, were used in RSM computer modeling herein and were obtained from an earlier analysis. For calculations in which noble metal particle transport is done, the density of the mixture of glass and noble metals particles is calculated as a volume-weighted sum of the glass fraction and the solid fraction. The mixture density is

$$\rho_m = (1 - C_v)\rho_g(T) + C_v\rho_s \quad (31)$$

where ρ_m = mixture density
 C_v = volumetric concentration of solid particle phase
 $\rho_g(T)$ = temperature-dependent glass density
 ρ_s = solid particle density

The temperature dependence of the intrinsic density of the noble metals particles, ρ_s , is not presently considered.

Figure 6.5. Temperature Dependence of Density Used in RSM Computer Modeling

6.3.2.4 Viscosity

The temperature dependence of pre-test RSM calculations was determined from a correlation. Subsequent to posthumous examination of the RSM, glass samples were cored from canisters 21 and 56 (end of RSM Test Segments 1 and 9, respectively) and the temperature dependence of the dynamic viscosity was determined in the laboratory. The data used in analysis in the present work are identified as follows

RSM/Pre - These data were supplied as a correlation^(a) given as

$$\ln (\mu(T)) = A + B/(T - T_0)$$

(a) Personal correspondence, M.L. Elliott/PNL to W. Grünwald/KfK-INE, October 23, 1991.

where $\mu(T)$ = dynamic viscosity (Pa-s)
 T = temperature ($^{\circ}\text{K}$)
 A = -7.60
 B = 9,615 $^{\circ}\text{K}$
 T_0 = 397 $^{\circ}\text{K}$

RSM/Can 21 and RSM/Can 56 - These data were determined from experiments^(a) with glass samples cored from RSM glass canisters 21 and 56 (end of RSM Test Segments 1 and 9, respectively). The data are:

T (C)	Viscosity (Pa-s)	
	RSM/Can 21	RSM/Can 56
945	56.0	57.5
996	27.9	28.6
1,045	15.1	16.5
1,097	9.1	9.6
1,147	5.9 $\pm$ 0.2	5.9 $\pm$ 0.2
1,197	4.1	4.1
1,246	2.7	2.7

A comparison of the viscosity data is made in Figure 6.6. Note that the post-test RSM glass sample data are quite close to the pre-test correlation. Most of the calculations presented in subsequent sections are computed with the RSM/Pre correlation.

No RSM data exists to determine concentration dependence of the viscosity. For fully coupled calculations in which viscosity of the glass is assumed to be a function of concentration, the functional form used is a power shape function

$$\mu(T, C_v) = \mu(T) * (1 + (a - 1) * C_r^b) \quad (32)$$

where $\mu(T)$ = temperature-dependent viscosity
 C_r = ratio of volumetric concentration to maximum concentration ($C_v/C_{v,max}$)
 a = maximum viscosity ratio at $C_v = 1$; value used = 10.
 b = curvature shape constant; value used = 3.

(a) Personal correspondence, M.L. Elliott/PNL to L.L. Eyler/PNL, April 12, 1993.

Figure 6.6. Temperature Dependence of Viscosity Used in RSM Computer Modeling

The choice of a maximum viscosity ratio of 10 is based on data for noble metals given by Krause and Luckscheiter (1991). There is no better way to estimate this ratio without measuring it specifically for RSM glass. If this is done, it must be done with glass samples from the pouring process and from the sludge layer. This will ensure that the "correct" noble metals particles are present in the samples.

6.4 Computer Model Results

RSM computer model results fall into three categories: pre-test, preliminary post-test, and post-test. Anderson et al.^(a) present most of the pre-test results. Preliminary post-test calculations are those computations completed during final stages of RSM testing. They were completed prior to completing experimental data reduction. Post-test calculations are those which were completed subsequent to completion of the RSM testing and complete reduction of experimental data.

(a) Anderson, L.D., T. Dennis, M.L. Elliott, L.L. Eyler, and P.R. Hrma. 1992. *Laboratory Testing and Computer Modeling of HWVP Melter Feed*. Milestone report C91-04.01B, Pacific Northwest Laboratory, Richland, Washington.

Computer model calculations were first conducted during the experiment design stage. At that time, it was assumed that the exterior melter surface temperature would be maintained at 500°C in the kiln. The computer results, in part, led to the conclusion that it would be necessary to maintain the exterior melter surface at or above 1,000°C in the kiln. This was because power requirements would be excessive and electrode surface current fluxes would exceed design limitations of the Inconel electrode material at the lower kiln temperature. It was further concluded that the control thermocouple location would be in a relatively cold location and the large temperature gradients would occur across the melt. Additional pre-test predictions were conducted during the RSM Segment 1 tests using an assumed exterior canister surface temperature of 1,000°C. These calculations were conducted in the same time frame that early experiments were being run. These calculations included modeling uncoupled noble metals transport using the species transport approach and the particle tracker approach. These results have been reported by Anderson et al.^(a) and are not repeated in detail herein.

The second set of pre-test predictions which used the $T = 1,000^{\circ}\text{C}$ surface temperature allowed for further development of analysis procedures, including the quasi-steady recycle feature in TEMPEST. One of the principal conclusions of this work was that it is extremely important in computing total power requirements to correctly account for mass source terms which modeled the source of glass under the cold cap during glass pouring simulations. In these calculations, it also became apparent that extremely accurate particle path integrations would be required for the particle tracker approach to modeling noble metals particles to be successful.

These calculations, done between October and December, 1992, led to the conclusion that a single particle's path could not be calculated accurately enough in a circulating flow field to differentiate path integration inaccuracies from a particle's displacement caused by gravitational settling. This conclusion was reached after investigating several path integration schemes (up to and including fourth-order Runge-Kutta) and reviewing other approaches (see Ramsden and Holloway 1990, for example). Thus, the particle tracker approach was abandoned.

Results classified as preliminary post-test are calculations conducted in January and February, 1993. The RSM experiment had been completed in December 1992 and reduced data from these tests was being made available for comparison to the calculations in the same time frame the calculations were being completed. Most of the results included herein are classified as preliminary post-test results. The final set of results included herein were completed at the end of April 1993 when the RSM glass sample data for electric conductivity (see Section 6.3.2.1) and viscosity (see Section 6.3.2.4) became available.

It must be noted that most of the results presented in this section are in the preliminary post-test category. They were computed using the electrical conductivity data identified as "RSM/Alt" in

(a) Anderson, L.D., T. Dennis, M.L. Elliott, L.L. Eyler, and P.R. Hrma. 1992. *Laboratory Testing and Computer Modeling of HWVP Melter Feed*. Milestone report C91-04.01B, Pacific Northwest Laboratory, Richland, Washington.

Figure 6.3 (see Section 6.3.2.1). This data was measured at KfK/INE from glass samples made from feed specified to be identical to RSM feed. Because it was measured data and not a correlation, it was used. When actual RSM measured data became available in April 1993, and found to be in agreement with the earlier RSM correlation, two things were done. It was concluded that 1) post-test results should be computed with the RSM measured data, and 2) the significance of the preliminary post-test results had to be reassessed.

In reassessing the preliminary post-test calculation results, it was concluded that the results were perfectly valid for their purpose. The preliminary post-test calculations, done using RSM/Alt electrical conductivity, were conducted to evaluate modeling approaches and to investigate application of the submodels proposed for use in post-test RSM analysis and in preparation for ESM and HWVP modeling. The calculations were successful in testing particle settling models, sludge layer enhanced conductivity effects, viscosity models, power controller, effects of pouring, feeding, and idling, and prediction of noble metal buildup on the melter floor. The calculations utilized GFT and RSM particle characterization data in these models.

The only preliminary post-test results computed that must be viewed with caution are the operational parameters—power, voltage, current, and resistance. These results must be viewed with caution when compared to measured data because the RSM/Alt electric conductivity is nearly half of that measured later from actual RSM glass samples. However, as a whole, parameterization calculations made to investigate effects of electrode asymmetry, enhanced sludge layer conductivity, feeding versus idling states, and coupled versus uncoupled settling effects are valid when taken as a whole and compared on a relative basis. Furthermore, even though the electrical conductivity of RSM/Alt is nearly half that of measured RSM data, the predicted power results are approximately correct. This is because the calculations are point-temperature controlled and total power in this situation is principally a function of boundary conditions. The internal parameters (voltage, current, and resistance) will not be directly comparable to data, however, because they are an inter-related function of the local electrical conductivity distribution.

6.4.1 Simulation Matrix

A number of pre-test, preliminary post-test, and post-test simulations were conducted. All these simulations were conducted with the three-dimensional computer model of the full RSM using boundary conditions described in Section 6.3.1.1 and properties described in Section 6.3.2. Simulations include the following.

- A bulk-average-temperature controlled simulation was performed, computed to steady conditions using the RSM/Pre correlation for electric conductivity. This was principally a repeat of an earlier analysis to confirm transfer of the analysis from the Cray computers at Los Alamos National Laboratory to an IBM RS9000 Model 580 superworkstation and to confirm computational correctness of the TEMPEST/T2 code version installed on that machine.

- A bulk-average-temperature controlled simulation was performed, computed to steady conditions using the RSM/Alt electric conductivity data. This calculation was done assuming symmetric electrodes, a bulk average glass temperature of 1,150°C, a cold cap boundary condition to the melt, and no glass pouring. This calculation was done primarily to compare to the RSM/Pre results and provide the basis for comparison of subsequent parameterization.
- Several bulk-average-temperature controlled simulations were performed in which the asymmetric electrode condition observed after sacrificing the RSM was modeled. Included in these simulations was a simulated, nonconvecting layer of noble metals enriched glass at the bottom of the melt pool. Four cases were run to near steady-state with the assumed layer. The electric conductivity of the layer was varied from that of the glass to a near-perfect conductor ($1.5 \times 10^1 \leq \sigma \leq 6.8 \times 10^4$ S/m). These simulations were conducted for the purpose of identifying operational features of the asymmetric electrode configuration and the effect of a pure metal layer on the melter floor.
- Each of the above cases were continued to a steady condition using temperature control based upon a single temperature approximating the location of the thermocouple measurement that controlled the experiment. These simulations were to investigate the point-temperature controller and to compare differences between bulk melt temperatures, maximum temperatures, and other differences occurring from bulk average versus point-temperature control.
- Two cases were simulated that approximated a fully coupled melt pool in which noble metals were being transported. In one of these cases, a cold cap boundary condition was imposed on the melt surface; in the other, an idle condition was modeled. Both cases assumed no glass pouring. Fully coupled implies that the viscosity, density, settling velocity, and electric conductivity are dependent upon temperature and volumetric concentration of the noble metals. The purpose of these cases was to investigate the transitory nature of fully coupled settling of noble metals particles into an enhanced conductivity sludge layer.
- Two cases were simulated that approximated both feeding and pouring simultaneously in a fully coupled melter model.
- Long-time (days to weeks) uncoupled noble metals transport simulations were conducted to simulate more closely actual RSM particle transport conditions.

These simulations represent a broad range of investigations into predicting the operational characteristics of the RSM and in demonstrating successful submodel coupling and analysis procedures.

Table 6.5 presents a summary of the thermal conditions for simulations designed to investigate the power controller; the coupled flow, electric and thermal fields; the symmetric and asymmetric electrode configurations; and the effect of a nonconvecting, enhanced conductivity sludge layer. No noble metals transport were included in the simulations presented in Table 6.5 (nor Table 6.6) because, as explained later, the simulations with noble metals transport were conducted using an accelerated settling analysis procedure. Included in the table are

Case Name	Identification used primarily to track computer files for the conditions simulated.
Simulation Time	Simulated time. These calculations were conducted to a time that the power controller indicated that steady conditions had been reached.
Power	Computed total power.
T bulk	Average temperature volume integrated over approximately the central 50% of the glass melt.
TC Sum	Average temperature (linear sum) of four thermocouple locations located in the stalk behind one electrode.
TC Ctrl	This is the single-point temperature located in the stalk behind one electrode. It is the location of the controlling thermocouple.
Tmax	This is the maximum temperature in the glass melt.

There are several general observations that can be made from the results in Table 6.5. In the pre- and post-test cases, (cyln.pre and cyln.post) the total power decreased from 2.09 to 1.79 kW. This resulted from a modification in the cold cap coverage boundary condition (see Section 6.3.1) from a 66% coverage to a 46% coverage. The experimental value for power from RSM Test Segment 1 which most closely approximates these calculations is 1.58 kW. The bulk temperature is within 11°C of the single-point control thermocouple temperature. The maximum glass temperature is typically 60 to 70°C greater than the control-point temperature. The maximum temperature occurs in the center of the glass melt for the symmetric electrode case.

The preliminary post-test cases identified as "cyln.alt" were computed with the RSM/Alt electric conductivity data (see Section 6.3.2.1). Note that the cyln.alt case, bulk temperature control results in virtually the same total power, control point temperature, and maximum temperature as the cyln.pre case, even though electrical conductivity was nearly a factor of two different. This is because the total power is principally a function of external boundary conditions. Also note that the thermocouple controlled case (cyln.alt/feed.3) is virtually the same as the bulk temperature controlled case. It is fortuitous that the bulk temperature and single control-point temperature are quite similar in these cases. This may not be so in the general case.

Table 6.5. Summary of RSM Computer Model Simulation Cases—Steady-State Thermal Parameters

Case Name	Simulation Time (min)	Power (Kw)	Tbulk (C)	TC Sum (C)	TC Ctrl (C)	Tmax (C)	Note
Pre-Test Electric Conductivity, Symmetric Electrodes, No Glass Pouring							
cyln.pre	12.1	2.043	*1,150	1,091	1,152	1,217	Cold cap, RSM/Pre
Post-Test Electric Conductivity, Symmetric Electrodes, No Glass Pouring							
cyln.post	48.8	1.791	1,139	—	*1,150	1,206	Cold cap, RSM/Can 21
cyln.post/idle	50.5	1.217	1,168	—	*1,150	1,201	No cold cap, RSM/Can 21
Preliminary Post-Test Simulations							
RSM/Alt Electric Conductivity, Symmetric Electrodes, No Glass Pouring							
cyln.alt	17.4	2.068	*1,150	1,091	1,152	1,216	Cold cap
cyln.alt/feed.3	40	2.069	1,148	1,089	*1,150	1,214	Cold cap
cyln.alt/idle.0	40	1.424	1,176	1,101	*1,150	1,209	No cold cap
RSM/Alt Electric Conductivity, Asymmetric Electrodes, Enhanced Conductivity Layer ($\sigma = 678$ S/m)							
asym	27	2.269	*1,150	1,173	1,196	1,270	Cold cap, no pour
asym/feed.tc.1	39	1.792	1,086	1,123	*1,150	1,216	Cold cap, no pour
asym/idle	38	1.304	1,136	1,132	*1,150	1,207	No cold cap, no pour
RSM/Alt Electric Conductivity, Asymmetric Electrodes, Enhanced Conductivity Layer, Glass Pouring							
asym/pour.0	20	2.173	*1,150	1,146	1,146	1,227	Layer EC = 15.2 S/m
asym/pour.tc.0	40	2.251	1,157	1,151	*1,150	1,237	Layer EC = 15.2 S/m
asym/pour.1	20	2.271	*1,150	1,174	1,169	1,270	Layer EC = 678 S/m
asym/pour.tc.1	40	1.804	1,083	1,122	*1,150	1,214	Layer EC = 678 S/m
asym/pour.2	20	2.276	*1,150	1,179	1,205	1,279	Layer EC = 6.78×10^4 S/m
asym/pour.tc.2	40	1.729	1,072	1,118	*1150	1,213	Layer EC = 6.78×10^4 S/m
* Indicates controlled temperature							

All of the preliminary post-test cases identified as "asym" are simulation cases conducted to investigate two principal observations from posthumous examination of the RSM: one being that 1/3 of one of the electrodes was gone and the other being that a metal layer (determined to be primarily metallic Ru approximately 3 mm thick) existed across the floor of the melter. Two sets of numerical simulations were conducted to separately investigate these effects.

In one set of simulations, the electrodes were assumed to be asymmetric (one electrode reduced by 1/3 of its original length). The shortened electrode was the one opposite the single control-point thermocouple. In this set of simulations, it was assumed that there was no enhanced conductivity layer on the floor. Note in Table 6.5 for these cases that the single control-point temperature was from 46 to 64°C hotter than the bulk coverage. Also note that the hottest temperature in the glass melt was from 57 to 74°C hotter than the control point. In the numerical simulations, the location of the hottest temperature was directly adjacent to the tip of the shortened electrode. This occurs because of the locally high electric current at this location.

In the last set of simulations listed in Table 6.5 ("asym/pour"), the electrodes were also assumed to be asymmetric. Furthermore, a nonconvecting, enhanced conductivity layer was included in the model and glass pouring was included at a rate of 0.59 kg/h. The nonconvecting layer was modeled to simulate the observed metallic layer on the floor of the melter. The electric conductivity in the nonconvecting layer was assumed to vary from 15.2 S/m (low EC) to 6.78×10^4 S/m (high EC). This latter value is that of Inconel, which was the preliminary assumption about the metal material made from the posthumous examination of the melter. These results are discussed in more detail in subsequent sections. However, it is significant to note here that the general decrease in bulk temperature and the locally high temperatures computed are consistent with the limited thermocouple probing done in the experiments (see Sections 4.2.2.4 and 5.2).

6.4.2 Average Power, Voltage, Current, and Resistance Results

The power, voltage, current, and resistance results predicted for the pre-test, preliminary post-test, and post-test simulation cases are presented in Table 6.6. Table 6.7 presents the corresponding data for each of the 11 test segments of the RSM test. The data in Table 6.7 were obtained by visually averaging the raw data time traces.^(a) Where wild oscillations in the data existed, or where individual sub-segments existed that were identifiable from the data, they are listed separately in the table. Where general indications that a consistent (and mostly linear) trend was identifiable, the beginning and ending values are included in the table.

The most directly comparable predictions in Table 6.6 and data in Table 6.7 are those from pre-test and post-test calculations and data from RSM Test Segment 1. The comparison is summarized as follows.

(a) This was done as part of the numerical modeling task. It is encouraging to note that the resistances "eyeball averaged" in Table 6.7 are completely consistent with those data reduced for time periods during which pouring occurred. These latter data are presented in Table 4.10.

<u>Pre-Test Calculation</u>	<u>Test Segment 1 Experiment</u>	<u>Deviation (Expr-Calc)/Expr</u>
Power P = 2.04 kW	1.58 ± 0.3	-29%
Voltage E = 32.2 V	24 ± 2	-34%
Current I = 63.4 A	66 ± 8	3.4%
Resistance ^(a) R = 0.51 Ω	0.36	-42%
<u>Post-Test Calculation</u>		
Power P = 1.79 kW	1.58 ± 0.3	-13%
Voltage E = 31.1 V	24 ± 2	-30%
Current I = 57.5 A	66 ± 8	12.8%
Resistance ^(a) R = 0.54 Ω	0.36	-50%

(a) Experimental resistance R = measured E/measured I.

The predicted average results are considered to be in excellent agreement with the measured data when consideration is made for the oscillatory behavior of measured results. The measured power for example, showed excursions that were typically in the ± 0.3 kW range, whereas the voltage and current exhibit regular excursions of over $\pm 10\%$ from the average. The 40 to 50% difference in predicted resistance is a little disconcerting, but this may be caused by effects not included in the model. One parameter of significance which has not been varied in the calculations is the glass depth. The calculations were performed assuming a glass depth of 3.6 in. (from the bottom of the melter to the modeled cold cap boundary). While the nominal melt depth is 3 in., the buildup of the cold cap and the thickness of the cold cap relative to the melt depth may be much more significant in a small melter like RSM, than in a larger melter like ESM or HWVP.

It is apparent from looking at the computer simulation results in Table 6.6 and experimental results in Table 6.7 that in the preliminary post-test results there is a consistent offset between the power, voltage, current, and resistance results. These are results identified with RSM/Alt. These results are included here for completeness as they provide results of the numerical experiments that were designed to investigate the affects of asymmetric electrodes, enhanced conductivity layer, and power controller, which are largely parameterization effects and which are largely independent of electrical conductivity. The parameterizations are discussed in more detail in subsequent sections.

6.4.3 Transient Power and Temperature Results

Computed results of several of the preliminary post-test analyses are presented in this section. The purpose of these tests was to numerically investigate the power controller in the bulk average and the single-point temperature mode, the effects of response of the system with and without a simulated sludge layer, and the effects of loss of a portion of the electrode.

Table 6.6. Summary of RSM Computer Model Simulation Cases, Steady-State Electric Parameters

Case Name	Simulation Time (min)	Power (Kw)	Erms (V)	Irms (A)	Resistance (Ω)
Pre-Test Electric Conductivity, Symmetric Electrodes, No Glass Pouring					
cyln.pre	12.1	2.043	32.2	63.4	0.51
Post-Test Electric Conductivity, Symmetric Electrodes, No Glass Pouring					
cyln.post	49	1.79	31.3	57.5	0.54
cyln.post/idle	51	1.22	23.4	52.1	0.45
Preliminary Post-Test Simulations					
RSM/Alt Electric Conductivity, Symmetric Electrodes, No Glass Pouring					
cyln.alt	17.2	2.068	45.5	45.3	1.01
cyln.alt/feed.3	40	2.069	45.8	45.2	1.01
cyln.alt/idle.0	40	1.424	35.1	40.5	0.87
RSM/Alt Electric Conductivity, Asymmetric Electrodes, Enhanced Conductivity Layer ($\sigma = 678$ S/m)					
asym	27	2.269	38.7	58.6	0.66
asym/feed.tc.1	39	1.792	37.4	47.8	0.78
asym/idle	38	1.304	38.7	58.6	0.68
RSM/Alt Electric Conductivity, Asymmetric Electrodes, Enhanced Conductivity Layer, Glass Pouring					
asym/pour.0	20	2.173	42.4	51.2	0.83
asym/pour.tc.0	40	2.251	42.6	52.7	0.81
asym/pour.1	20	2.271	38.7	58.6	0.66
asym/pour.tc.1	40	1.804	37.8	47.8	0.79
asym/pour.2	20	2.276	38.0	59.9	0.64
asym/pour.tc.2	40	1.729	36.8	46.9	0.79

Table 6.7. Summary of RSM Test Segment, Average Power, Voltage, and Current

Test Segment	Duration (Days)	TC Ctrl (C)	Pour Rate (kg/h)	Power (Kw)	Erms (V)	Irms (A)	Resistance (Ω)
1-3	13	1,148	0.5	1.6	24	66	0.36
4	5.5	1,050	0.35	0.6	17	33	0.54
	1.0	1,125	0.35	1.5	25	60	0.41
5	2.6	1,150	0.66	1.5	22	66/59	0.36/0.38
6	2.6	1,150	0.53	1.5	22	62/71	0.38/0.32
7	3.0	1,175	0.82	2.2	27	82	0.31
	6.0	1,150	0.82	1.9	27	72/68	0.37
8	3.0	1,150	0.66	2.0/1.9	27	75/74	0.36/0.37
	3.0	1,150	0.66	1.3	22	62	0.36
9	6.0	1,150	0.64	1.4/1.1	22/16	55/70	0.38/0.27
10	4.5	1,150	0.60	1.0/0.7	14	62/55	0.25
11	1.0	1,175	0.59	1.0	NA	NA	0.22
	2.5	1,200	0.59	1.2/1.1			0.23

During preliminary post-test simulations, the time-dependent response of the computed average power was monitored. The object of investigating this quantity is to evaluate the behavior of the power controller under varying conditions. For these cases, the simulation was computed in steps. The computations were started from a steady-state thermal solution obtained by assuming that the glass was stationary and uniform in temperatures at 1,150°C. This condition provided a good estimate of the initial temperatures in the refractory surrounding the melt pool from which to start the transient-to-steady conditions. In reaching steady state, the bulk average temperature of the glass melt pool was used in the power controller. The bulk average temperature was found to be a more stable and consistent indicator than was a single point temperature measurement. After a steady condition was indicated in the power, restart calculations were conducted. Single-point control temperature was enabled only as a restart to a steady bulk temperature controlled case.

Figure 6.7 presents the power, volume-integration-averaged bulk melt temperature, and the thermocouple temperature. For this test, a feeding situation is assumed (cold cap upper boundary) with no glass pouring in a clean melter (no noble metals). During the first 12.1 min of the results, the electric conductivity of the glass was assumed to be the RSM/Pre data correlation (see Figure 6.3). At 12.1 min, the simulation was restarted using the RSM/Alt data curve for electric conductivity. This calculation was computed to a time of 17.4 min. Note that the initial perturbation requires some time to adjust to the desired average temperature of 1,150°C. For these bulk average temperature-controlled situations, the reference temperature was 1,000°C, the integration time was 0.2 min, and the relaxation factor was 0.8 in the temperature controller Equation (28). During the first 17.4 min of these results,

Figure 6.7. Power, Average Melt Temperature, and Thermocouple Temperature Response to Electric Conductivity and Controller Scheme

the thermocouple result shown (TCouple) is the average of four temperature measurement locations assumed to equally space in the thermocouple stalk located behind one of the electrodes. Thereafter, TCouple is a single-point temperature.

At a time of 17.4 min, the calculation was restarted using a single temperature measurement location as the value to which the power controller should be targeted. The location chosen is at the lower extremity of the thermocouple stalk behind one of the electrodes. For the results shown in Figure 6.7, the reference temperature was set to 800°C, the integration time to 0.1 min, and the relaxation factor to 0.5 in the power controller. This change was made because the parameters used with bulk average temperature control resulted in an underdamped controller which began an uncontrolled oscillatory growth in the power curve. This effect is shown in Figure 6.8. Such an oscillatory underdamped growth has been seen in melter operation.^(a)

Figure 6.9 presents similar controller response to a transition from a feeding (cold cap boundary) to an idle condition. This transition was modeled as a restart to the previous bulk average temperature controlled results at 17.4 min. Note that the thermocouple controlled transient takes a rather long period of time to damp out.

The results presented in Figures 6.10 and 6.11 are similar investigations, but with asymmetric electrodes. The asymmetric electrodes are representative of the end-of-test situation upon which posthumous examination showed a significant loss of electrode material from one electrode and the presence of a "metallic looking" layer on the bottom. Included in these two simulations was a simulated, high electrically conducting layer on the bottom of the melt. A reference value of the 648 S/m at 1,005°C was used as the electric conductivity of the layer. The temperature dependence of the layer was assumed to vary according to that of Inconel. These assumptions were made because a preliminary hypothesis was made that the material was metal from the missing electrode. The first 28 min in each figure were computed using volume-averaged melt temperature for control to 1,150°C. The restart in one case (Figure 6.10) is a transition to a single thermocouple for control. The other case (Figure 6.11) is similar except that at the same time the transition is made to thermocouple control, a transition from a feed (cold cap boundary) to an idle condition is also made. The electric parameters for these cases are listed in Table 6.6 as cases "asym", "asym/feed", and "asym/idle".

In these cases, it is useful to note the differences between the thermocouple temperature and the bulk average temperature. For the feed case, the thermocouple temperature is about 75°C less than the bulk average temperature. For the idle state, the temperatures are very much the same. This is indicative of the temperature distribution in the melt being much more uniform for the idle state. This observation has the implication that there is less temperature difference and hence less driving force for convection. The further implication is that with less driving force and less convection, noble metal particles would have a greater tendency to settle to the bottom of the melt.

(a) Personal communication, M.L. Elliott/PNL.

Figure 6.8. Power, Average Melt Temperature, and Thermocouple Temperature Response to Electric Conductivity and Controller Scheme Showing an Underdamped Thermocouple Control

Figure 6.9. Power, Average Melt Temperature, and Thermocouple Temperature Response to Electric Conductivity and Controller Scheme Showing the Response in Transition from a Feeding (Cold Cap Boundary) to an Idle Situation

Figure 6.10. Power, Average Melt Temperature, and Thermocouple Temperature in Response to a Transition to Thermocouple Control in a Melt with an Enhanced, Nonconvecting Sludge Layer ($\sigma = 678 \text{ S/m}$)

Figure 6.11. Power, Average Melt Temperature, and Thermocouple Temperature in Response to a Transition to Thermocouple Control in a Melt at Idle State with an Enhanced, Nonconvecting Sludge Layer ($\sigma = 678 \text{ S/m}$)

Three additional simulations were computed to investigate the effect of simulated pouring on the computational characteristics of the melter. These cases were computed assuming a feeding condition (cold cap) and glass pouring at a rate of 0.58 kg/h. Again the calculations were computed to a steady condition under bulk average temperature control to 1,150°C and then transitioned to thermocouple control at 1,150°C. The asymmetric electrode configuration was used. A simulated layer of material was assumed to exist on the floor. The electric conductivity of this assumed layer was the parameter varied in each of these three cases.

In the first case, Figure 6.12, the layer was assumed to have an electric conductivity of that of the glass, but was nonconvecting. The comparison value of electric conductivity at 1,150°C is 15.2 S/m from the RSM/Alt data. The second case, Figure 6.13, assumed a reference value of 678 S/m at 1,150°C and a temperature dependence of that of Inconel. The third case, Figure 6.14, assumed that the layer was Inconel, which has an electric conductivity of 6.78×10^4 S/m at 1,150°C. Thus each case increased the electric conductivity of the layer by two orders of magnitude.

In the first case with low electric conductivity in the layer, the bulk average temperature and the thermocouple temperature are nearly the same. In the second and third cases, the thermocouple temperature is higher than the bulk average. This occurs because of the locally high electric current and hence joule heat that occurs just in the corner near the thermocouple location (see Figure 6.2). This is a computational result consistent with limited thermocouple probing in the glass melt (see Section 4.2.2).

The average quantities as a function of the reference electrical conductivity for each of the three cases with the nonconvecting, enhanced conductivity layer are presented in Figure 6.15. The solid symbols are the steady values for the case of bulk average temperature being the controlling temperature. The open symbols are the steady values for the case of a single thermocouple temperature being the controlling temperature.

Note that the ratio of the bulk average temperature cannot be determined because the bulk temperature is a volume integration, and if the volume over which the bulk temperature is changed, the bulk average will change. In the present work, the volume over which the average is computed is approximately the central 50% of the melt. This volume was chosen so as to not skew the result with the inclusion of the colder region directly under the modeled cold cap. Also in the present work, the thermocouple temperature under conditions where the bulk average temperature is the controller is the average of four thermocouple locations equally spaced in the thermocouple stalk. However, for the thermocouple controlled results, in all cases, the thermocouple temperature is a single point value at a location approximating the location of the data measurement.

The purpose of the preliminary post-test numerical experiments presented in this section was to investigate and demonstrate the melter operational response to bulk average and single-point temperature control, the effect of asymmetric electrodes, and the effect of a (assumed) nonconvecting, enhanced conductivity layer of sludge on the floor of the melter. The results show a good degree of success in this regard.

Figure 6.12. Power, Average Melt Temperature, and Thermocouple Temperature in Response to a Transition to Thermocouple Control in a Melt in a Feed State (Cold Cap) with 0.58 kg/h Pouring and a Simulated Sludge Layer with a Reference Electric Conductivity of 15.2 S/m

Figure 6.13. Power, Average Melt Temperature, and Thermocouple Temperature in Response to a Transition to Thermocouple Control in a Melt in a Feed State (Cold Cap) with 0.58 kg/h Pouring and a Simulated Sludge Layer with a Reference Electric Conductivity of 678 S/m

Figure 6.14. Power, Average Melt Temperature, and Thermocouple Temperature in Response to a Transition to Thermocouple Control in a Melt in a Feed State (Cold Cap) with 0.58 kg/h Pouring and a Simulated Sludge Layer with a Reference Electric Conductivity of 6.78×10^4 S/m

Figure 6.15. Power, Average Melt Temperature, and Thermocouple Temperature as a Function of Reference Electric Conductivity in a Simulated Nonconvecting Sludge Layer

6.4.4 Transient Fully Coupled Noble Metals Species Transport Without Pouring

Several simulations were computed to investigate the fully coupled nature of the RSM model. Fully coupled implies that viscosity, density, particle settling velocity, and electric conductivity are all functions of temperature and volumetric concentration according to models discussed in Section 6.2. These calculations were computed by restarting the calculation at a time of 17.4 min where steady conditions had been obtained using the RSM/Alt electric conductivity data for the glass. At the restart, the power controller was transitioned from the bulk average temperature to the single thermocouple temperature corresponding approximately to the data measurement location. Because these were investigations into the nature of the response of the computer model to fully coupling the species transport, the parameters chosen for the submodels are partially based on convenience, partially based on scaling, and partially based on the fact that necessary data were not yet available when the calculation was done. Not all of the RSM experimental data had been reduced, nor had all of the glass samples been analyzed when the calculations were done.

Settling velocity was chosen as being hindered according to the expression given by Equation (27). A terminal Stokes settling velocity of 0.05 mm/s was chosen in conjunction with a maximum packed concentration of 0.6. This terminal settling velocity approximates a rather large particle size of 400 μm of RuO_2 at a density of 6,970 kg/m^3 in a glass with a reference viscosity of 8.065 Pa-s at 1,150°C. Such a large particle has not been observed in the GFT nor RSM data. Use of this large particle size is consistent with the purposes of these simulations and serves to accelerate the coupled physical effects in the simulations for the purpose of the investigations.

Electric conductivity was determined according to Equation (30) with the temperature dependence, $\sigma(T)$, being that of RSM/Alt (see Figure 6.3). The concentration dependence was computed using a maximum conductivity ratio, $a = 10^3$, at $C_r = 1$. The curvature shape function exponent used was $b = 3$. In the ratio of volumetric concentration to maximum concentration, $C_r = C_v/C_{v,\text{max}}$, the maximum concentration, $C_{v,\text{max}} = 1$, was used. Using this value as the maximum concentration of simulated noble metals would be an approximation of a settled layer consisting totally of the transported material. The initial volumetric concentration of the noble metals was specified to be 3%. This relatively large value is consistent with the purpose of accelerating the coupling effects during the simulations.

Two cases were computed with these conditions—a transition to feed (cold cap) case and a transition to idle case. No pouring was assumed. The time-dependent power, bulk average temperature, and thermocouple temperature for these two tests are included in Figures 6.16 and 6.17. Note that the investigations started at 17.4 min. Included in the figures at times less than 17.4 min are the previously computed steady results. Restarting at this point provides a common starting point. The feed (cold cap) case shows very steady average quantities with the bulk average temperature being very similar in magnitude to the controlling thermocouple temperature. The power is maintaining a very steady value at 1.98 kW.

Figure 6.16. Power, Average Temperature, and Thermocouple Temperature for Feed (Cold Cap) Case with Fully Coupled Noble Metals Particle Transport and Accelerated Settling

Figure 6.17. Power, Average Temperature, and Thermocouple Temperature for a Transition to Idle Case with Fully Coupled Noble Metals Particle Transport

The transition to idle case shows quite a different character. The bulk average temperature shows an initial increase above the thermocouple temperature and eventually falls below it. The power behaves much like an exponential decay toward a steady value. Though the power has leveled off, aspects of the particle settling, flow, and thermal fields have not yet reached a final steady state. Prior to looking at the fluid, thermal, and particle species effects, it is useful to examine the electric properties.

Figures 6.18 and 6.19 present the power, voltage, current, and resistance as a function of time for the feed (cold cap) case and the transition to an idle state for the fully coupled noble metals particle simulations without pouring. The voltage, current, and resistance in the feed case remain very constant with time. The transition to the idle case, however, shows a very marked change in these parameters with time. As the power drops off in response to a reduced heat loss to the top melt surface boundary, the voltage and resistance drop off, but the current increases. This effect is a consequence of the settled material building up in a layer on the melter floor causing an increase in electrical conductivity. The increased electrical conductivity of the sludge layer induces a shorting between electrodes, which causes the total current to go up. Near the end of the idle case calculation, material has settled to the floor-adjacent region in sufficient quantity to increase the average electric conductivity in the lower 7 mm to a value of nearly 900 S/m. The reference glass (RSM/Alt) value at 1,150°C is 15.2 S/m.

Figures 6.20 and 6.21 present the normalized electric current flux on the face of one electrode during the simulation cases. The current flux is normalized with the root-mean-square current (I_{rms}) at each time as noted in the legend. For the feed (cold cap) case, there is marginally little difference in the current flux with time. However, for the transition to idle case, the current flux increases dramatically near the floor of the melter. This is caused by the increased electrical conductivity of the sludge layer. For the steady state condition, the current flux can be calculated from the results in Figure 6.21.

For RSM/Pre electric conductivity (12.16 min):

$$I'' = 150 \frac{A}{m^2 - A_{rms}} \cdot 63.4 A_{rms} \times 10^{-4} \frac{cm^2}{m^2} = 0.95 \frac{A}{cm^2}$$

For the RSM/Alt electric conductivity (17.47 min):

$$I'' = 150 \frac{A}{m^2 - A_{rms}} \cdot 45.3 A_{rms} \times 10^{-4} \frac{cm^2}{m^2} = 0.68 \frac{A}{cm^2}$$

For RSM/Alt electric conductivity after the sludge layer has developed (100 min):

$$I'' = 910 \frac{A}{m^2 - A_{rms}} \cdot 49.5 A_{rms} \times 10^{-4} \frac{cm^2}{m^2} = 4.5 \frac{A}{cm^2}$$

Such a locally high current flux of this magnitude would be significantly in excess of design limits ($1A/cm^2$) and may be, in part, an explanation for why material was lost from one electrode (see Section 5.2).

Figure 6.18. Electric Parameters for a Feed (Cold Cap) Case with Fully Coupled Noble Metals Particle Transport and Accelerated Settling

Figure 6.19. Electric Parameters for a Transition to an Idle Case with Fully Coupled Noble Metals Particle Transport and Accelerated Settling

Figure 6.20. Normalized Electric Current Flux on the Face of One Electrode for a Feed (Cold Cap) Case with Fully Coupled Noble Metals Particle Transport and Accelerated Settling

Figure 6.21. Normalized Electric Current Flux on the Face of One Electrode for a Transition to an Idle Case with Fully Coupled Noble Metals Particle Transport and Accelerated Settling

A number of things are happening in the transition to an idle state that cause the coupling effects of particle settling to exhibit a more dominant character than in the feed (cold cap) case. In the idle case, the lack of the cold cap top surface boundary has reduced the net temperature difference between the melt and the boundary (melt surface), which significantly reduces the buoyancy driving force. This in turn reduces the maximum convecting velocity that transports particles around the melter. So in the transition to idle state, there is a greater potential for settling particles to accumulate on the floor. This increase in particle material on the floor causes an increase in viscosity, which, in turn, causes reduced convection currents in the lower region of the melt.

Figures 6.22 to 6.24 present flow field, temperature field, and volume fraction field results that demonstrate this. Presented in these figures are results in the centerplane normal to the electrodes (top half of each figure) and in the centerplane parallel to each electrode (bottom half of each figure). For each grouping, results are plotted at 40, 60, and 80 min. It is obvious that the transition to idle case results in a very quiescent zone in the lower region of the melt which is a consequence of the settling and buildup of simulated noble metals particles coupled to the increased viscosity as a function of increased concentration of material. The predicted counter current flow pattern is very consistent with observed streak lines (Figure 4.3). This is extremely significant because it is the first direct evidence comparison of actual melt flow with a computer prediction.

In the feed case, the maximum glass convection velocity is typically 3.1 mm/s, whereas in the transition to idle case, the maximum velocity magnitude drops as low as 0.013 mm/s before recovering to 0.36 mm/s during the transient. It is important to note that in this simulation the terminal settling velocity of the 400 μm particles of 0.05 mm/s is greater than the maximum flow velocity during portions of the transient. It is hypothesized that in the long term, the result would be the same in any situation where the settling velocity became approximately equal to the velocity magnitude. Such a situation would occur naturally for any size particle very near the melter floor. Thus, if there are settling particles, a high concentration layer will develop. The key to the present work is determining the time rate of such build up of enhanced conductivity noble metals.

Results of an accelerated buildup of simulated noble metals material in the floor adjacent region is given in Figure 6.25. Results in the figure are the amount of mass of simulated noble metals particles in the lower 7 mm of the melt relative to the total mass of simulated noble metals in the whole melt volume. Four cases are shown; three are for a transition to idle state and one is for a feed state. No pouring is assumed. The simulated results are accelerated in that relatively large solid, spherical particles are assumed (~ 135 to $395 \mu\text{m}$) which have particle settling velocities ranging from 0.006 to 0.05 mm/s in glass at $1,150^\circ\text{C}$.

For the largest particles, there is a very definite and significant buildup of an enhanced sludge layer in the transition to idle state. Nearly 70% of the particulate material settles into the floor-adjacent region. This settling accumulation causes increases in viscosity and increases in density, both of which are stabilizing effects. The corresponding increase in electrical conductivity is destabilizing in that it leads to increased local heat generation, higher local temperatures, and hence corresponding temperature-dependent effects on properties.

Figure 6.22. Velocity Vectors Comparison for the Feed (Cold Cap) and Transition to Idle Case

Figure 6.23. Isotherms Comparison for the Feed (Cold Cap) and Transition to Idle Case

Figure 6.24. Volume Fraction Comparison for the Feed (Cold Cap) and Transition to Idle Case

Figure 6.25. Time Build Up of Simulated Noble Metals in the Sludge Layer for the Transition to Idle Situation

It is interesting to note that the largest simulated particles cause a noticeable accumulation effect which continue to grow. Whereas, the lesser-sized particles cause an initial perturbation and then an equilibrium state is reached. These results are important because they demonstrate the successful coupling of all the particle-dependent submodels in TEMPEST.

Figures 6.26 and 6.27 present perspective views of the volumetric concentration of the material adjacent to the floor of the melter at similar times for the feed case and the idle case. Note that the maximum concentration is different in each case. Orientation of the results in the figures is such that the pour spout is in the lower left quadrant. The feed case shows a relatively higher concentration along a line between the electrodes. This is consistent with the predicted flow patterns (Figure 6.22) where the counter rotating cellular flow leaves a stagnant location along this line. The idle case also shows a build up along this line, but shows much more uniformity across the plane.

The portion of heat which is transported through the melter top surface relative to that transported through the melter walls is summarized in Table 6.8. These results are at a time near the final steady condition. The amount of heat being transported through the melter walls was determined by setting the melt top surface to an adiabatic condition.

Note that during operation with a feed, only about 10% of the heat is being lost through the melter walls to a 1,000°C outside boundary condition. The idle case shows a 41% heat loss through the walls for a condition where the top melt surface is assumed to be 900°C. Insufficient data were measured during the experiment to confirm or deny these heat transfer predictions. The temperature data for the outside melter surface provide an indication of the exterior boundary condition. However, the lack of any interior temperature measurements or measurements in the can/refractory wall during the experiment inhibits comparison of the predicted amount of heat being transported through the walls.

6.4.5 Transient Fully Coupled Noble Metals Transport With Pouring

One preliminary post-test simulation was conducted with glass pouring. This simulation was conducted as a complementary numerical experiment to the nonpouring cases discussed in the previous section. In this simulation, a glass pour rate of 0.49 kg/h was used. This pour rate is based on glass density of 2,170 kg/m³ at 1,150°C. A simulated noble metals source rate of 0.0511 kg/h (10.4 wt%) was assumed in the form of 260 μm solid, spherical particles. These assumptions about particle character are made for the purpose of accelerating the numerical experiment as part of the further testing of TEMPEST and the fully coupled submodels.

The calculated results successfully demonstrate the fully coupled character of simulating noble metals transport with glass pouring. This complements the nonpouring results.

Figure 6.28 presents the time variation of total mass, floor region mass, and percent difference between the two. Only 80 min of fully coupled simulation was conducted. At the beginning of the simulation, there is a nonlinear rate of increase in percentage difference between the total noble metals mass in the melt and in the region (6 mm thick) adjacent to the floor. As time progresses, the rate of

(3D) Print: post1 plt ll rsm 3d cvln kfk cup.1 pst.cup.1c file dump #4 (76.2 min.)

SOLIDS VOLUME FRACTION

FEED, 76 min.

6.63

Figure 6.26. Perspective View of Solids Distribution Near the Melter Floor for the Feed (Cold Cap) Case

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SOLIDS VOLUME FRACTION

IDLE, 80 min.

6.65

Figure 6.27. Perspective View of Solids Distribution Near the Melter Floor for the Idle Case

Table 6.8. Relative Heat Loss Summary

Feed (Cold Cap) Case	@76 min	With Melt Surface Adiabatic
Net Heat Out	2,172 W	226 W
Net Heat In	-164	-59
Joule Heat Gener.	1,980	
$\frac{\text{Net Heat Loss Through Walls}}{\text{Total Heat Loss}} = \frac{226}{2,172} 0.104$		
Idle Case	@76 min	With Melt Surface Adiabatic
Net Heat Out	864 W	357 W
Net Heat In	~ 1	~ 1
Joule Heat Gener.	865	
$\frac{\text{Net Heat Loss Through Walls}}{\text{Total Heat Loss}} = \frac{357}{864} 0.413$		

increase of the percentage difference approaches a constant value. At some longer time, a more slowly varying equilibrium would be reached similar to the idle cases of Figure 6.25 that were also accelerated with the use of (assumed) large particles.

Figure 6.29 presents the long-time (three days) continuation results of the calculation computed in the uncoupled mode. This time represents approximately 14 glass turnovers. Apparent in the figure is that asymptotic values of the total simulated noble metals particles is being approached. At the end of three days, a total of 3.68 kg of simulated noble metals had entered the melt through the simulated source at the cold cap. A total of 0.459 kg remain in the melt, resulting in an average concentration of 3.47% by volume. The average concentration at the dip tube exit was 3.24% by volume, corresponding to a 7.1% retention. This value is in qualitative agreement with nominal percent of noble metals retained in the melt as determined from a mass balance from experimental data (see Table 5.1 and associated discussion). This qualitative agreement further demonstrates the success of TEMPEST, associated submodels, and analysis procedures.

6.4.6 Particle Settling Submodel Testing

As was discussed in Section 6.2.3, one of the uncertainties in the RSM modeling is the estimation of the settling velocity. This fundamental property was shown to potentially vary over two orders of magnitude based on measured particle data. Secondly, there is a question about the maximum packing fraction for the settled particulate. This section contains a discussion of the effects of variation in the settling velocity and the maximum packing fraction.

Figure 6.28. Simulated Noble Metals Mass at the Melter Floor and Total Mass in the System for a Simulated Noble Metals Feed Rate of 0.0511 kg/h and Glass Pour Rate of 0.49 kg/h

To test the effect of settling velocity, simulations were completed with settling velocities ranging from 1×10^{-8} m/s to 1×10^{-4} m/s. An option in TEMPEST was used that inhibited any coupling between noble metal particle concentration and the glass physical properties such as viscosity and electrical conductivity, but the particle settling and convection was computed. The flow and temperature fields for these runs were taken from predictions made for the no-pour symmetric RSM configuration with the cold cap, including RSM/Alt electrical conductivity properties.

These particle settling runs provided a test of the of the concentration predictions over that range, under conditions akin to those of RSM operation, but without coupling. This provides part of the basis for determining whether it would be possible to "accelerate" simulations by using settling velocities much higher than those expected. If the concentrations predicted for a settling velocity of 1×10^{-4} m/s and an elapsed time of 1 day turned out to be about the same as those for a settling velocity of 1×10^{-8} m/s and an elapsed time of 10,000 days, this acceleration might be possible. The ability to treat the settling distance (time x velocity) as the single parameter that dominates deposition would allow a considerable savings in computational time.

Total Species Mass in Melter

Species Volume Fraction at Diptube

Species Volume Fraction at Floor

Figure 6.29. Species Volume Fraction at the Melter Floor and at the Diptube Entrance and Total Mass in the System for a Simulated Noble Metals Feed Rate of 0.0511 kg/h and Glass Pour Rate of 0.49 kg/h

Five runs were completed to supply data to test settling velocity effects and the possibility of "acceleration." The runs employed an initial volume fraction C_0 of 0.0004 and an elapsed time of 31,055 min (about 3 weeks). Equation (27) was used to predict hindered settling. A maximum packing fraction of 0.6 and an exponent of 4.65 were assumed. Only the terminal settling velocity was varied in these runs.

On reviewing the results, it was found that the particle volume fractions did not exhibit continuing accumulation or depletion over a long period of time. Rather, they remained constant after a relatively short period. Table 6.9 shows the times required to reach constant concentrations at the floor on a line halfway between the electrodes.

This behavior can be explained as the equilibration of the particle inflow to and outflow from the cell. Inflow results from convection and from settling from the column of cells above the one being monitored, outflow comes purely from convection. Accumulation can only occur in cells that are 1) at a bottom surface; 2) are convergence cells, meaning that all horizontal velocities are into the cell; and 3) have upward vertical flow velocities less than the particle settling velocity. Meeting these conditions means no particle outflow is possible and accumulation must occur. Unless all of these conditions are met, the cell concentration will increase (or decrease) owing to particle outflow until it reaches a constant equilibrium concentration. This is the case in all the cells examined in the settling velocity tests.

The possibility that the local concentration was a function of the local settling velocity was explored in these uncoupled long time calculations. If the settling velocity were the controlling parameter, then the normalized change in concentration would be proportional to the settling velocity.

$$[(C - C_0) / C_0] / V_s = \text{a local concentration constant} \quad (32)$$

Table 6.9. Times Required to Reach Constant Concentration

Initial Settling Velocity (m/s)	Time till Midplane Equilibrium (min)
10^{-8}	28
10^{-7}	260
10^{-6}	820
10^{-5}	1,100
10^{-4}	2,100

Tables 6.10, 6.11, and 6.12 show the results of the five runs in which the settling velocity was varied and the duration of the run held constant. The values shown are the "local concentration constants" calculated in several different locations, which were chosen to represent places where concentration decreased from or held constant at initial values as well as places where concentration had increased.

The values of the "local concentration constants" are an indication of whether the cell concentration increased or decreased, and to what extent. The highest increase in the melter was on top of the electrodes, at their ends—for example, cell (4,14,20). The greatest decrease is in cell (15,14,25), which was at the top of the melter, halfway between the electrodes and next to the wall.

Judging by Tables 6.10 through 6.12, the equilibrium concentrations are not just linearly dependent on the settling velocity. There are evident trends in these "constants" with changes in settling velocity. Whether the "constants" increase or decrease with settling velocity seems to depend on location—presumably on the local flow field. It should be noted that the run made with a settling velocity of 10^{-8} m/s differs the most from the others. This difference almost certainly appears not because of settling velocity dependence but because the four significant figures which are printed to computer output and used in the calculations of the local concentration constants were not accurate enough. Concentration itself varies only in the fourth significant figure at this lowest settling velocity.

It appears that "accelerating the run" is possible for the tested range of conditions but a justifiable time scaling parameter needs to be developed to provide a firmer basis for doing so. Such a basis could be developed from scaling parameters developed from the governing equations of motion.

Several simulations were made to investigate one aspect of the validity of accelerating the coupling calculations as it relates to hindered settling. At the low concentrations used in these runs (an initial volume fraction 0.0004, which is realistic relative to measured RSM data), the maximum equilibrium concentrations reached in uncoupled test runs are well below those at which significant coupling can occur. In these computer runs, the maximum volume fractions attained was on top of the electrodes. The results are tabulated in Table 6.13.

There are at least two possible explanations of why the predicted maximum concentration are lower than observations. First, RSM operation with the cold cap and symmetrical electrodes may not be the mode of operation that causes significant sludge accumulation. The lower fluid velocities during idling may be much more conducive to deposition. Second, some type of particle sticking model may be needed to account for sub-grid-scale velocities that are very low right next to the melter floor, allowing some accumulation from that lowest portion of the bottom cells.

Another set of runs was made to examine the effect of changes in the hindered settling model. The three runs used to supply data for Tables 6.14 through 6.16 employed an initial volume fraction C_0 of 0.03, an elapsed time of 1,440 min (1 day), and a settling velocity of 10^{-4} m/s (calculated at 0.03 volume fraction). Only the hindered settling models were varied. In Case A, a constant settling velocity was used (no hindered settling effect). In Cases B and C, the exponential model for hindered settling

Table 6.10. Local Concentration Constants for the Melter Floor in Front of the Electrodes

Settling Velocity (m/s)	----- Local Concentration Constant x 10 ⁻⁴ -----			
	Cell (6,4,16)	Cell (6,4,15)	Cell (7,4,15)	Cell (29,4,15)
10 ⁻⁸	3.13	3.13	3.13	3.13
10 ⁻⁷	2.13	2.63	2.13	2.63
10 ⁻⁶	2.14	2.65	2.09	2.52
10 ⁻⁵	2.24	2.78	2.19	2.66
10 ⁻⁴	2.96	4.03	3.10	3.82

Table 6.11. Local Concentration Constants for the Tops of the Electrodes

Settling Velocity (m/s)	----- Local Concentration Constant x 10 ⁻⁴ -----			
	Cell (4,14,20)	Cell (4,14,18)	Cell (4,14,9)	Cell (30,14,20)
10 ⁻⁸	9.40	3.13	7.31	3.13
10 ⁻⁷	8.65	3.38	7.40	2.88
10 ⁻⁶	8.74	3.40	7.53	2.85
10 ⁻⁵	9.94	3.21	8.32	2.70
10 ⁻⁴	13.8	1.41	9.20	1.39

Table 6.12. Local Concentration Constants for Areas of Decreased or Initial Concentration

Settling Velocity (m/s)	----- Local Concentration Constant x 10 ⁻⁴ -----		
	Cell (15,14,25)	Cell (15,9,25)	Cell (23,9,14)
10 ⁻⁸	-1.00	-1.00	1.04
10 ⁻⁷	-1.90	-0.88	0.12
10 ⁻⁶	-1.90	-0.94	0.01
10 ⁻⁵	-2.00	-0.93	0.01
10 ⁻⁴	-0.92	-0.62	0.02

Table 6.13. Maximum Volume Fractions Reached in Test Runs

Initial Settling Velocity (m/s)	Maximum Volume Fraction (equilibrium)
10^{-8}	0.00040
10^{-7}	0.00040
10^{-6}	0.00043
10^{-5}	0.00080
10^{-4}	0.0059

Table 6.14. Local Concentration Constants for the Melter Floor in Front of the Electrodes, with Hindered Settling

Case	----- Local Concentration Constant $\times 10^{-4}$ -----			
	Cell (6,4,16)	Cell (6,4,15)	Cell (7,4,15)	Cell (29,4,15)
A	2.99	4.07	3.13	3.86
B	2.12	2.63	2.09	2.52
C	1.93	2.32	1.88	2.23

Table 6.15. Local Concentration Constants for the Tops of the Electrodes, with Hindered Settling

Case	----- Local Concentration Constant $\times 10^{-4}$ -----			
	Cell (4,14,20)	Cell (4,14,18)	Cell (4,14,9)	Cell (30,14,20)
A	14.3	1.41	9.45	1.39
B	4.81	1.39	3.90	1.30
C	3.83	1.37	3.18	1.27

Table 6.16. Local Concentration Constants for Areas of Decreasing or Constant Concentration, with Hindered Settling

Case	-----Local Concentration Constant x 10 ⁻⁴ -----		
	Cell (15,14,25)	Cell (15,9,25)	Cell (23,9,14)
A	-0.92	-0.62	0.02
B	-0.93	-0.62	0.03
C	-0.94	-0.64	0.03

velocity was used, as given in Equation (27), and the exponent was 4.65. The difference was that in Case B, the maximum packing factor was 0.6 and in Case C it was 0.4, giving a greater hindered settling effect in Case C.

Once again, the bases for comparison are the local concentration "constants." It should be noted, though, that the V_s used to calculate the constants was the settling velocity at the initial concentration, 10^{-4} m/s, not the actual local settling velocity, which was often much lower (in Cases B and C).

It is clear that the decrease in settling velocity produced by hindered settling causes a concentration reduction in deposition areas such as the electrode tops. This is no surprise, considering that the local volume fractions predicted without hindered settling (Case A) are 30 to 50%. This is a concentration range where hindered settling would be quite prominent and where its absence (i.e., the constant-velocity model) would not be physically plausible. Cells where the Case A volume fraction is less than 8%, or a local concentration constant of less than 2, show much less effect of hindered settling. It is consistently the case that the greater the effect of hindered settling (Case C > B > A), the lower is the concentration (Case C < B < A).

There is little or no difference between the local concentration constants in Tables 6.10 through 6.12 and those given for Case A (no hindered settling) in Tables 6.14 through 6.16. In all the tabulated cells, whether mass has accumulated or been depleted, whether the concentration is high or low with respect to the maximum packing fraction, there is next to no difference between the local concentration "constant" obtained starting from 0.04% and that from 3% solids. This is consistent with the very low concentrations in the runs tabulated in Tables 6.10 through 6.12; the effect of hindered settling would not have been felt there any more than in Case A. Thus, the initial concentration seems not to affect the particle accumulation/depletion pattern until hindered settling makes itself felt. This observation provides another limitation to "accelerating runs" that needs to be more fully evaluated.

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Appendix A

**Feed Preparation Off-Gas Data
(Figures A.1 - A.11)**

**Electrode Resistance Data After Filtering
(Figures A.12 - A.20)**

**Optical and SEM Micrographs of Glass Samples
(Figures A.21 - A.54)**

RSM-1 (11/19/91)

Figure A.1. Gas Generation Data from Forming Batch RSM-1

RSM-2 (12/18/91)

Figure A.2. Gas Generation Data from Formating Batch RSM-2

CO₂ Data

Figure A.3. Comparison of RSM-1 and RSM-2 Forming: CO₂ Data

N_2O Data

Figure A.4. Comparison of RSM-1 and RSM-2 Formating: N_2O Data

NO_x Data

Figure A.5. Comparison of RSM-1 and RSM-2 Formating: NO_x Data

H₂ Data

Figure A.6. Comparison of RSM-1 and RSM-2 Formating: H₂ Data

Figure A.7. Typical Lab-Scale CO Data

Figure A.8. RSM-1 CO Data

Figure A.9. RSM-2 CO Data

Figure A.10. Gas Chromatograph Carbon Monoxide Data

Figure A.11. Carbon Monoxide Data for RSM-1 and RSM-2

A.12

Figure A.12. Resistance Between Electrodes (Segment Number 1)

A.13

Figure A.13. Resistance Between Electrodes (Segment Number 4)

A.14

Figure A.14. Resistance Between Electrodes (Segment Number 5)

A.15

Figure A.15. Resistance Between Electrodes (Segment Number 6)

A.16

Figure A.16. Resistance Between Electrodes (Segment Number 7)

A.17

Figure A.17. Resistance Between Electrodes (Segment Number 8)

A.18

Figure A.18. Resistance Between Electrodes (Segment Number 9)

Figure A.19. Resistance Between Electrodes (Segment Number 10)

A.20

Figure A.20. Resistance Between Electrodes (Segment Number 11)

Figure A.21. SEM/EDX of Glass from Segment 1

Figure A.22(a). SEM/EDX of Glass from Segment 4

Figure A.22(b). SEM/EDX of Glass from Segment 4

Figure A.23. SEM/EDX of Glass from Segment 4

Figure A.24. SEM/EDX of Glass from Segment 4

Figure A.25. SEM/EDX of Glass from Segment 5

Figure A.26. SEM/EDX of Glass from Segment 6

Figure A.27. SEM/EDX of Glass from Segment 7

Figure A.28(a). SEM/EDX of Glass from Segment 7

Figure A.28(b). SEM/EDX of Glass from Segment 7

Figure A.29. SEM/EDX of Glass from Segment 8

Figure A.30. SEM/EDX of Glass from Segment 8

Figure A.31(a). SEM/EDX of Glass from Segment 9

Figure A.31(b). SEM/EDX of Glass from Segment 9

Figure A.32. SEM/EDX of Glass from Segment 9

Figure A.33. SEM/EDX of Glass from Segment 10

Figure A.34. SEM/EDX of Glass from Segment 10

Figure A.35. SEM/EDX of Glass from Segment 10

Figure A.36(a). SEM/EDX of Glass from Segment 11

Figure A.36(b). SEM/EDX of Glass from Segment 11

Figure A.36(c). SEM/EDX of Glass from Segment 11

Figure A.36(d). SEM/EDX of Glass from Segment 11

Figure A.36(e). SEM/EDX of Glass from Segment 11

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Figure A.37(a). SEM/EDX of Glass from Post-Test Sample C1

Figure A.37(b). SEM/EDX of Glass from Post-Test Sample C1

Figure A.38(a). SEM/EDX of Glass from Post-Test Sample C1

Figure A.38(b). SEM/EDX of Glass from Post-Test Sample C1

Figure A.38(c). SEM/EDX of Glass from Post-Test Sample C1

Figure A.39(a). SEM/EDX of Glass from Post-Test Sample C2

Figure A.39(b). SEM/EDX of Glass from Post-Test Sample C2

Figure A.40(a). SEM/EDX of Glass from Post-Test Sample C2

Figure A.40(b). SEM/EDX of Glass from Post-Test Sample C2

Figure A.41. SEM/EDX of Glass from Post-Test Sample C3

Figure A.42(a). SEM/EDX of Glass from Post-Test Sample C3

Figure A.42(b). SEM/EDX of Glass from Post-Test Sample C3

Figure A.43(a). SEM/EDX of Glass from Post-Test Sample C4

Figure A.43(b). SEM/EDX of Glass from Post-Test Sample C4

Figure A.44. SEM/EDX of Glass from Post-Test Sample C4

Figure A.45(a). SEM/EDX of Glass from Post-Test Sample C4

Figure A.45(b). SEM/EDX of Glass from Post-Test Sample C4

Figure A.46(a). Optical Micrographs of Glass from Segment 1

Figure A.46(b). Optical Micrographs of Glass from Segment 1

Figure A.46(c). Optical Micrographs of Glass from Segment 1

Figure A.47(a). Optical Micrographs of Glass from Segment 4

Figure A.47(b). Optical Micrographs of Glass from Segment 4

Figure A.47(c). Optical Micrographs of Glass from Segment 4

Figure A.48(a). Optical Micrographs of Glass from Segment 5

Figure A.48(b). Optical Micrographs of Glass from Segment 5

Figure A.48(c). Optical Micrographs of Glass from Segment 5

Figure A.49(a). Optical Micrographs of Glass from Segment 6

Figure A.49(b). Optical Micrographs of Glass from Segment 6

Figure A.49(c). Optical Micrographs of Glass from Segment 6

Figure A.50(a). Optical Micrographs of Glass from Segment 7

Figure A.50(b). Optical Micrographs of Glass from Segment 7

Figure A.50(c). Optical Micrographs of Glass from Segment 7

Figure A.51(a). Optical Micrographs of Glass from Segment 8

Figure A.51(c). Optical Micrographs of Glass from Segment 8

Figure A.51(b). Optical Micrographs of Glass from Segment 8

Figure A.52(a). Optical Micrographs of Glass from Segment 9

Figure A.52(b). Optical Micrographs of Glass from Segment 9

Figure A.52(c). Optical Micrographs of Glass from Segment 9

Figure A.53(a). Optical Micrographs of Glass from Segment 10

Figure A.53(b). Optical Micrographs of Glass from Segment 10

Figure A.53(c). Optical Micrographs of Glass from Segment 10

Figure A.54(a). Optical Micrographs of Glass from Segment 11

Figure A.54(b). Optical Micrographs of Glass from Segment 11

Figure A.54(c). Optical Micrographs of Glass from Segment 11

Appendix B

Raw Melter Processes Data

B.1

Figure B.1. Resistance Between Electrodes (Segment Number 1)

B.2

Figure B.2. Melt Temperature (Segment Number 1)

Figure B.3. Plenum Temperature (Segment Number 1)

Figure B.4. Glass Pour in 15-Min Interval (Segment Number 1)

B.5

Figure B.5. Resistance Between Electrodes (Segment Number 4)

B.6

Figure B.6. Melt Temperature (Segment Number 4)

Figure B.7. Plenum Temperature (Segment Number 4)

Figure B.8. Glass Pour in 15-Min Interval (Segment Number 4)

B.9

Figure B.9. Resistance Between Electrodes (Segment Number 5)

B.10

Figure B.10. Melt Temperature (Segment Number 5)

Figure B.11. Plenum Temperature (Segment Number 5)

Figure B.12. Glass Pour in 15-Min Interval (Segment Number 5)

B.13

Figure B.13. Resistance Between Electrodes (Segment Number 6)

B.14

Figure B.14. Melt Temperature (Segment Number 6)

Figure B.15. Plenum Temperature (Segment Number 6)

Figure B.16. Glass Pou. in 15-Min Interval (Segment Number 6)

B.17

Figure B.17. Resistance Between Electrodes (Segment Number 7)

B.18

Figure B.18. Melt Temperature (Segment Number 7)

Figure B.19. Plenum Temperature (Segment Number 7)

Figure B.20. Glass Pour in 15-Min Interval (Segment Number 7)

B.21

Figure B.21. Resistance Between Electrodes (Segment Number 8)

B.22

Figure B.22. Melt Temperature (Segment Number 8)

B.23

Figure B.23. Plenum Temperature (Segment Number 8)

Figure B.24. Glass Pour in 15-Min Interval (Segment Number 8)

B.25

Figure B.25. Resistance Between Electrodes (Segment Number 9)

B.26

Figure B.26. Melt Temperature (Segment Number 9)

Figure B.27. Plenum Temperature (Segment Number 9)

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Figure B.28. Glass Pour in 15-Min Interval (Segment Number 9)

B.29

Figure B.29. Resistance Between Electrodes (Segment Number 10)

B.30

Figure B.30. Melt Temperature (Segment Number 10)

Figure B.31. Plenum Temperature (Segment Number 10)

B.32

Figure B.32. Glass Pour in 15-Min Interval (Segment Number 10)

B.33

Figure B.33. Resistance Between Electrodes (Segment Number 11)

B.34

Figure B.34. Melt Temperature (Segment Number 11)

Figure B.35. Plenum Temperature (Segment Number 11)

B.36

Figure B.36. Glass Pour in 15-Min Interval (Segment Number 11)

Appendix C

Feed Rheology

Appendix C

Feed Rheology

As discussed in the body of this report, the rheology of the RSM feed was very poor. The feed tended to thicken with time, thus becoming difficult to agitate in the melter feed tank. As a result of this thickening, the nominal oxide loading was reduced from 500 g TO/L to 400 g TO/L and the melter feed tank volume was reduced so that feed was made up twice per day. By making up feed twice per day, the thickening of the feed from aging was minimized. To quantify the rheology problems, feed samples were taken during the run and the viscosity was measured using a Haake viscometer with an M5 head. For most segments, a feed sample was taken right before feed makeup and another sample was taken when the makeup of the new batch was complete. This still resulted in an "aged" sample and a "fresh" sample, but the two samples were from different batches. This was done so that the rheograms of the two samples would be generated under the same conditions and at nearly the same time.

The first set of rheograms was generated for Segment 5. This segment had a high oxide loading, 500 g TO/L. A feed sample was taken just before feed makeup when the batch was 10-h old (Feed Sample #13). Another sample was taken right after feed makeup (Feed Sample #14). The rheograms are shown in Figure C.1. The aging effect is very evident in this figure. A Bingham model was used to determine the yield stress and consistency factor of the two curves. Using this model the yield stress of the new feed was 17 Pa and the consistency factor was 0.014 Pa•s. After aging for 10 h the yield stress increased to 21 Pa and the consistency factor decreased slightly to 0.013 Pa•s. The increase in yield stress was a confirmation of what was observed in the melter feed tank, the feed became more difficult to mix and the outer edges of the tank became stagnant as the feed aged.

The second set of rheograms was taken during Segment 7. This feed had the nominal oxide loading for the run, 400 g TO/L. The first sample was taken 8 h after feed makeup (Feed Sample #16). The pH of this feed was 10.16. Another sample was taken after four days of agitation in the melter feed tank (Feed Sample #17). A new feed sample was not taken for this batch. The rheograms are shown in Figure C.2. Using the Bingham model the yield stress of the feed that was 8-h old was 6.8 Pa and the consistency factor was 0.011 Pa•s. After agitating in the feed tank for four days the yield stress decreased to 5.1 Pa and the consistency factor remained constant at 0.011 Pa•s. The confidence in these numbers is not good. The feed was left for four days at the minimum level in the melter feed tank. Because of the low level in the tank, the agitation was not good. It is unlikely that the yield stress would have decreased with time.

Figure C.1. Rheograms for Feeds with 500 g TO/L and Nominal Noble Metals Concentration

To visualize the effect of oxide loading on rheology, the rheograms of the 500 g TO/L new feed from Segment 5 and the 8-h-old feed from Segment 7 are presented in Figure C.3. The consistency factors for the two feeds are similar but the yield stress for the 500 g TO/L feed is substantially higher than the 400 g TO/L feed even though the dilute feed was much older.

The last three segments of the run had feeds that contained two times the nominal concentration of noble metals. The third set of rheograms was taken during Segment 9. This feed had the nominal oxide loading for the run, 400 g TO/L, but had twice the nominal noble metals concentration. The first sample was taken 14 h after feed makeup (Feed Sample #26). The pH of this feed was 10.02. Another sample was taken right after feed makeup (Feed Sample #27). The pH of this feed was 10.02. The rheograms from these feeds are shown in Figure C.4. Again, the aging effect is evident in the figure. The yield stress of the new feed was 1.6 Pa and the yield stress of the feed after 14 h of agitation was 5.4 Pa. The consistency factors of these feeds were not estimated because of the dilatant nature of the fluids. This dilatant nature was the only difference noticed between the nominal noble metals feed and the 2X feed. The yield stresses of the nominal feed after 8 h of agitation and the 2X feed after 14 h of agitation are very close.

Figure C.2. Rheograms for Feeds with 400 g TO/L and Nominal Noble Metals Concentration

After Feed Sample #27 from the 2X noble metals segment was taken from the melter feed tank it was placed in a sealed laboratory flask and agitated with a lab mixer to simulate aging in the melter feed tank. Samples were taken at 24, 48, 120, and 288 h of agitation in the lab apparatus. The rheograms from these samples are shown in Figure C.5. All of the rheograms indicate the same dilatant nature noted in Figure C.4. The difference between the samples agitated in the lab and those agitated in the melter feed tank is the rate that the yield stress increased. The samples agitated in the melter feed tank reached a yield stress of 6 Pa in only 14 h. It took the samples in the lab 288 h to reach this yield stress. The difference between these agitation systems has been noticed in previous experiments conducted at PNL.^(a)

The pH of several feeds were measured during the run. All feeds were within the pH range of 9.85-10.64. There did not appear to be any increase in pH with time. The measured pHs are shown in Table C.1.

(a) Personal communication with Peter A. Smith, PNL.

Figure C.3. Rheograms for Feeds with 400 g TO/L and 500 g TO/L and Nominal Noble Metals Concentration

Figure C.4. Rheograms for Feeds with 400 g TO/L and 2X Noble Metals Concentration

Table C.1. Feed pHs During RSM Test

Segment	Sample	Noble Metals Conc.	Oxide Conc. (g TO/L)	Feed Description	pH
7	15	Nominal	400	7.5 h after frit addition	10.3
7	16	Nominal	400	New feed	10.16
8	N/A	Nominal	400	Before frit addition	10.4
8	N/A	Nominal	400	16 h after frit addition	9.85
9	23	2X	400	New Feed	10.25
9	27	2X	400	New Feed	10.64
10	N/A	2X	400	18 h after frit addition	10.3

Figure C.5. Rheograms for Feeds Agitated in the Laboratory with 400 g TO/L and 2X Noble Metals Concentration

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