

The Behavior and Effects of the Noble Metals in the DWPF Melter System

by

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THE BEHAVIOR AND EFFECTS OF THE NOBLE METALS IN THE DWPF MELTER SYSTEM (U)

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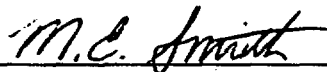
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Abstract

Governments worldwide have committed to stabilization of high-level nuclear waste (HLW) by vitrification to a durable glass form for permanent disposal. All of these nuclear wastes contain the fission-product noble metals: ruthenium, rhodium, and palladium. SRS wastes also contain natural silver from iodine scrubbers. Closely associated with the noble metals are the fission products selenium and tellurium which are chemical analogs of sulfur and which combine with noble metals to influence their behavior and properties. Experience has shown that these melt insoluble metals and their compounds tend to settle to the floor of Joule-heated ceramic melters. In fact, almost all of the major research and production facilities have experienced some operational problem which can be associated with the presence of dense accumulations of these relatively conductive metals and/or their compounds. In most cases, these deposits have led to a loss of production capability, in some cases, to the point that melter operation could not continue.

HLW nuclear waste vitrification facilities in the United States are the Department of Energy's Defense Waste Processing Facility (DWPF) at the Savannah River Site, the planned Hanford Waste Vitrification Plant (HWVP) at the Hanford Site and the operating West Valley Demonstration Project (WVDP) at West Valley, NY.

The Integrated DWPF Melter System (IDMS) is a vitrification test facility at the Savannah River Technology Center (SRTC). It was designed and constructed to provide an engineering-scale representation of the DWPF melter and its associated feed preparation and off-gas treatment systems. An extensive noble metals testing program was begun in 1990. The objectives of this task were to explore the effects of the noble metals on the DWPF melter feed preparation and waste vitrification processes. This report focuses on the vitrification portion of the test program.

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List of Acronyms

AA:	Atomic Absorption
ADS:	Analytical Development Section of SRTC
BDL:	Below Detection Limit
CPC:	Chemical Processing Cell
DWPF:	Defense Waste Processing Facility
DWPT:	Defense Waste Processing Technology Section of SRTC
EDX:	Energy Dispersive X-Ray
HEWC:	High Enrichment Waste Concentrate
HWVP1:	First Run of the HWVP Process Demonstration
HWVP2:	Second Run of the HWVP Process Demonstration
HWVP:	Hanford Waste Vitrification Plant
IC:	Ion Chromatography
ICP:	Inductively Coupled Plasma
ICP-AES:	Inductively Coupled Plasma - Atomic Emission Spectroscopy
ICP-MS:	Inductively Coupled Plasma - Mass Spectrometry
IDMS:	Integrated DWPF Melter System
INE/KfK:	Institute für Nuklear Entsorgungstechnik at Kernforschungszentrum Karlsruhe (Nuclear Fuel Cycle Center)
LEWC:	Low Enrichment Waste Concentrate
LIMS:	Laboratory Information Management System
MFT:	Melter Feed Tank
NCAW:	Neutralized Current Acid Waste
OGCT:	Off Gas Condensate Tank
PHEF:	Precipitate Hydrolysis Experimental Facility
PNNL:	Battelle Pacific Northwest National Laboratory
RWS:	Recycle Waste Stream
SAS:	Steam Atomized Scrubber
SCR:	Silicon Controlled Rectifier
SEM:	Scanning Electron Microscopy/Microscope
SME:	Slurry Mix Evaporator
SRAT:	Sludge Receipt and Adjustment Tank
SRS:	Savannah River Site
SRTC:	Savannah River Technology Center
TEM:	Transmission Electron Microscopy/Microscope
TVF:	Tokai Vitrification Facility (Japan)
WAK:	Waste from the Karlsruhe Reprocessing Plant
WHC:	Westinghouse Hanford Company
WSRC:	Westinghouse Savannah River Company
WVDP:	West Valley Demonstration Project
XRD:	X-Ray Diffraction
XRF:	X-Ray Fluorescence

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1.0 Summary and Recommendations

Numerous governments worldwide have committed to stabilization of high level nuclear waste by vitrification. Many of the facilities use (or will use when completed) the Joule-heated ceramic melter as the means of stabilizing the high-level nuclear waste in a glass matrix. These facilities include the German PAMELA in Mol, Belgium, the Tokai Vitrification Facility (TVF) in Tokai, Japan, the Defense Waste Processing Facility (DWPF) in Aiken, SC, the West Valley Demonstration Project (WVDP) in West Valley, NY, and the planned Hanford Waste Vitrification Plant (HWVP) in Richland, WA.

The PAMELA facility began operation in 1985. The TVF began radioactive operations in 1995. The DWPF began radioactive operations in March, 1996 and has filled more than 200 canisters. The WVDP began operations in July, 1996. The HWVP is in the planning stage.

The noble metals are defined as silver, gold, platinum and the platinum group metals: ruthenium, rhodium, palladium, osmium, and iridium. They are called *noble* because of their resistance to oxidation in contrast to base metals that oxidize when heated in air. They are easily reduced and all occur naturally in their elemental form. Of these, however, only ruthenium, rhodium, palladium, and silver are found in high-level waste as the products of fission reactions. (Note that most of the silver present in the SRS defense waste is from silver saddles used in iodine strippers). They are of concern because the metals and RuO_2 are dense and electrically conductive. They tend to settle to the bottom of melters causing disruption of normal melter electrical currents.

A production-scale melter represents a significant capital investment. Replacement, facility downtime, decommissioning, storage, and melter disposal costs can also be major expenses if production melters become inoperable. It is thus very obvious that the overall lifetime of a production melter should be extended to as long as possible. Almost all of the major production and research vitrification facilities have experienced operational problems which can be traced to the presence of noble metals in the melter. These effects were discovered after the design of the existing DWPF melter. Thus the DWPF melter may be more susceptible to these effects than later melters which attempted to mitigate noble metals electrical effects. These metals and their alloys and compounds have tended to settle to the floor of Joule-heated ceramic melters. An accumulation of these dense, conductive and highly viscous materials can adversely affect the melter operation by decreasing the power release in the bulk glass in the melter thereby decreasing the feed throughput capacity and the ability to maintain operating temperatures. This layer can also cause non-uniform and uncontrollable current distributions at the surface of the electrodes which can lead to physical damage or failure of the electrodes. Over time, with the accumulation of these conductive compounds, some melters have suffered a loss of power release so severe that nominal melter temperatures ($>1100^\circ\text{C}$) could not be maintained. The resulting viscous layer could

also make the draining of the DWPF melter more difficult, but German and Japanese bottom drain configurations have demonstrated an ability to operate under these conditions.

Several large scale melter demonstrations have been conducted in support of the development of the DWPF melter. While some of these operations have included noble metals (mainly Ru) in the slurry feed composition, earlier tests omitted at least one of the following: noble metals in their anticipated chemical forms, potential alloying elements, lead, mercury, or the expected reference combination of reducing and oxidizing agents. Further, previous melter demonstrations with noble metals have not had electrodes similar in geometry to those of the DWPF melter and have therefore not been able to model accurately or predict the electrical response of the DWPF melter to noble metal deposition.

The Integrated DWPF Melter System (IDMS) was designed and constructed to provide an engineering-scale representation of the DWPF melter and its associated feed preparation and off-gas treatment systems. The facility is the first engineering-scale melter system capable of processing mercury and flowsheet levels of halides and sulfates. The IDMS melter also provides meaningful data for predicting the behavior and effects of the noble metals in the DWPF melter.

In order to characterize the behavior of noble metals, 16 runs, using four types of waste sludge simulants containing noble metals have been conducted in the IDMS facility. The sludge simulations were: (1) three runs using a Blend (BL) sludge (a mix of HM and PUREX sludges), (2) four runs using an HM (high noble metals, high aluminum, high viscosity) sludge, (3) seven runs using a PUREX (high iron, low viscosity) sludge, and (4) two runs using the Hanford NCAW sludge.

Specific objectives of this task as defined in the Technical Task Plan^[1] pertaining to melter operation were to:

- 1) demonstrate the long term effects of noble metals on the operating performance of a DWPF-type melter.
- 2) determine the noble metals material balance around the melter system.
- 3) determine the chemical form of noble metals in the glass.
- 4) determine the particle size of noble metals and/or noble metal alloys in the glass.

During the first two runs (BL1, BL2), hydrogen was measured as a feed preparation offgas product. The hydrogen was produced by the noble metal-catalyzed destruction of formic acid during the initial chemical treatment of the sludge simulant. Because of the safety concerns associated with the evolution of hydrogen, the facility was idled while safety-related modifications were made to the feed preparation and process vessel vent system.

The next series of runs (BL3, HM1) were conducted without noble metals or mercury present in the waste sludge simulant. These runs were conducted in order to evaluate the amount of hydrogen which the DWPF could expect during cold simulant testing (which would contain neither noble metals nor mercury).

Following the cold run demonstrations, four runs (HM2, HM3, PX1, PX2) were conducted with HM levels of noble metals (but no mercury). These runs were conducted in order to predict the maximum hydrogen that the DWPF could expect during radioactive operations. It was after these runs that melter floor samples first showed an accumulation of noble metals (mainly RuO_2). The melter also first showed an electrical response to this accumulation during these runs.

Following these runs, two operations (HWVP1, HWVP2) were conducted in support of the design and operation of the Hanford Waste Vitrification Plant. These runs were conducted with a Neutralized Current Acid Waste (NCAW) simulant and contained maximum predicted levels of noble metals (concentrations similar to HM sludge) for that waste. This waste also contained cadmium which is easily reduced to the elemental form.

The next series of runs (HM4, PX3, PX4, PX5, PX6) were conducted to support the adoption of the Nitric Acid Flowsheet coupled with the Late Wash Precipitate Hydrolysis process. These runs contained HM levels of mercury and of noble metals (highest expected for DWPF feed).

Samples have been taken from the melter floor since the introduction of the noble metals. With increasing amounts of noble metals fed to the melter, there has been a corresponding increase in the amount of noble metals, noble metal compounds, and spinels found on the melter floor. Samples taken at the center of the melter and on the outside of the floor diameter (at the face of one of the electrodes) suggest a non-uniform layer of noble metals and Ru/Rh/Ni/Fe/Cr spinels has accumulated. Analysis of these samples revealed a higher concentration of RuO_2 in the samples taken from the outside edges of the melt pool. This suggests that the convective currents in the melter tend to "push" the RuO_2 from the center of the melter (where it enters) to the outside edges. Melter convection currents tend to be downward at the walls away from the electrodes. Samples taken from the center have normally contained Ru and Rh oxides and large amounts of spinels while samples taken from the outer edge have contained fewer spinels, metallic Pd and Pd tellurides, Ru and Rh oxides, and RuS_2 . The presence of the RuS_2 suggests that the temperature at the outer edge may be much lower than that of the bulk melt since this compound decomposes at temperatures $> 1000^\circ\text{C}$. Material balances of these components show a tendency for the noble metals to be retained as $\text{Ru} > \text{Rh} > \text{Pd}$ and Ag. It is estimated that the overall percent accumulations in the IDMS for the noble metals during these runs are 35% for Ru, 21% for Rh, and close to zero percent for Pd and Ag.

In the Research Scale Melter (RSM) studies at PNNL, results suggested that there was a significant nonlinear increase in the amount of noble metal compounds deposited on the melter floor with a 2-fold increase in the nominal noble metal content of the NCAW melter feed simulant. This resulted in a 9-fold increase in the fraction of noble metals that settled.

Noble metal settling is particularly obvious during melter idling (not feeding or pouring). The characteristic settling time seems to be reached between 10 and 20 days of idle time. Approximately 70% of the Ru in the melter at the start of an idling period will settle during this critical settling time period. Ruthenium settling data taken within 20 days (of idling) was used to generate a least-squares relationship for relative Ru concentration in the glass being poured versus idle time for the IDMS melter. The linear region is described by:

$$\frac{[Ru]_t}{[Ru]_0} = 0.9814 - 0.04713 t \quad \text{where } t \text{ is idle time in days}$$

The ultimate relative concentration appears to be between 0.25 and 0.30 indicating that approximately 25 to 30% of the Ru in the melter is of a size or shape that does not settle easily.

As more noble metals were fed to the IDMS melter the upper-to-lower resistivity ratio increased, and therefore current requirement for the bottom electrode pair to maintain the desired melt pool temperature increased as well. Initially a current of 450 amps was necessary to maintain a lower glass pool temperature of 1125°C. At the end of the melter testing, 650 amps were required to maintain a temperature of 1070°C. However, the melter did continue to operate with acceptable performance. There was no decrease in the production capacity of the IDMS melter during the tests. A subsequent inspection of the IDMS melter showed that the bottom electrodes had sustained appreciable damage on their lower portions. This damage was probably due to a high current density caused by noble metals partially shorting out the melter. Globules of noble metals were found at the bottom of the melter.

Since the IDMS melter continued to operate in spite of damage, it is difficult to predict the maximum lifetime of the DWPF melter based on the operational experience of the IDMS melter. However, assuming the DWPF melter will withstand the same conditions to which the IDMS melter has been exposed, estimates of the minimum lifetime have been made.

There are several caveats which should be considered when interpreting these estimations. Firstly, the IDMS melter was subjected to numerous idling periods in excess of 20 days. As stated above, approximately 70% of the noble metals in the melter will settle to the floor during this short idling period.

IDMS Production

1 IDMS glass with HM or NCAW Noble Metals	40,300 lbs
2- IDMS glass with Blend Noble Metals	8,346 lbs
3- Max IDMS glass capacity	1,063 lbs
4- Number of melter HM turnovers (1 / 3)	38 turnovers
5- Number of melter Blend turnovers (2 / 3)	8 turnovers

Equivalent DWPF Production

6- Max DWPF glass capacity	13,136 lbs
7- 38 DWPF Melter turnovers (6 x 38 turnovers)	499,168 lbs
8- DWPF Melter turnovers (6 x 8 turnovers)	105,088 lbs
9- DWPF 100% production rate	228 lbs/hr
10- Target minimum nominal operating time, 2 years @ 70%	511 days
11- Nominal melter turnovers in 511 days	213 turnovers

Equivalent DWPF HM Operating Time

12- Hm sludge Ru content	0.217 wt%
13- Equivalent HM operating time ((7 / 9)/24 hrs per day)	91 days

Equivalent DWPF Blend Operating Time

14- Blend sludge Ru content	0.100 wt%
15- Equivalent Blend operating time ((8 / 9)/24 hrs per day)	19 days

Equivalent Combined Blend Operating Time

16- Equivalent combined Blend operating time (13 + 15)	110 days
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Equivalent Combined Tank 51 Operating Time

17- Tank 51 Ru content ^[30]	0.005 wt%
18- Equiv. Tank 51 operating time (((12 x 13)+(14 x 15))/17)	4,329 days

NOTE: bold numbers in calculations shown [as given in ()'s] show line items used

Recommendation: Based on IDMS data, the settling of the noble metals appears to be much less during periods of feeding and pouring. This impact, however, may be less in the DWPF Melter due to its larger inner diameter. Therefore, the DWPF should avoid periods of idling when operating with melter feeds containing noble metals. A few extended outages appear preferable to several short period outages; thus when outages must be scheduled, for maintenance, etc., all necessary work should be completed within the extended outage in order to avoid short term outages later.

Secondly, this estimation assumes that the noble metals settle linearly with concentration. This is most likely not the case. In tests conducted at PNNL, it was observed that the settling of the noble metals increased nonlinearly with a 2-fold increase in the noble metal content over the nominal NCAW levels. Therefore, the amount of noble metals settling to the floor while feeding "Blend" melter feed will be much higher than that seen with the existing Tank

51 batch 1a sludge. Still more rapid changes can be expected if HM sludge noble metal concentrations are fed to the DWPF.

The first DWPF melter has not experienced any operational problems associated with noble metals deposition to date. However, because of uncertainties in the blending of Tank Farm wastes, it is difficult to predict a minimum lifetime for subsequent sludge batches.

Recommendation: Tank Farm blending strategies should consider the content of the noble metals in the respective waste tanks. The wastes could be blended such that the noble metal contents are evenly distributed and have a content no greater than that predicted for "Blend-type" sludge (Ru about 0.1 wt% of the dried sludge solids to the DWPF). This is advantageous not only in the maximization of the DWPF melter life but also in minimizing hydrogen production in the Chemical Processing Cell (CPC). Alternatively, delaying operations with high concentrations of noble metals (HM sludge) to outlying years until possible modifications can be made to subsequent DWPF melters to make them less susceptible to noble metals deposition problems could be done as well.

An inspection of the IDMS melter after shutdown showed that the bottom electrodes had sustained appreciable damage on their lower portions. The Inconel 690® drain valve and pipe also had extensive corrosion damage. This damage was probably due to a high current density caused by noble metals partially shorting out the melter.

Recommendation: The bottom electrodes of the IDMS melter should be removed from the melter and characterized for change in dimensions and mode of metallurgical attack. Samples previously removed from the bottom of the melter should be measured for viscosity and electrical conductivity. Any deposits remaining under the electrodes should be removed for physical characterization (viscosity, electrical conductivity) and chemical composition.

The ratio of upper-to-lower glass pool resistance has proved to be an effective measure in indicating the accumulation of noble metals on the floor of the IDMS melter. This ratio continue to rise during the noble metals runs, thereby showing that the bottom electrode circuit resistance was being lowered. This implied that a conductive layer of material (noble metals) was forming on the melter bottom. The post shutdown inspection of the melter showed this was indeed the case.

Recommendation: The DWPF should monitor this ratio as an indication of a conductive accumulation on the DWPF melter floor. The individual circuit resistances should also be routinely monitored and trended with time. When feeds with higher noble metals concentrations are used estimates of noble metals settling should be trended. When noble metals accumulations approach 1-2 kg/ft of melter bottom, electrical disruption and electrode attack may occur.

Although there is an obvious trend of international vitrification facilities to move toward sloped bottom melters, this is not necessarily a viable solution for the DWPF should problems develop. Firstly, the technical time and capital invested in the melt cell does not easily allow radical changes in the present melter design. A sloped bottom melter would require a redesign of the drain valve. Fortunately, melter design and testing in Germany and Japan has proceeded to include reliable drain valves that can function with noble metals. Other facilities have moved to sloped bottom melters. The smallest deviation from existing DWPF design and operating practice which appears technically feasible is a combination of 1) a bottom drain assembly of the German or Japanese type, which have been demonstrated to work with noble metals, 2) mechanical removal of melter bottom deposits after melter draining and cooling, and 3) raising and reshaping the bottom electrodes to minimize local current densities.

One modification to the DWPF melter which could be accommodated is the raising of the lower electrodes. It is not known what effect this would have on the operation of the melter with or without a conductive bottom layer. Mathematical models, however, do exist which can be used to predict the effects of such as modification.

Recommendation: Finite element mathematical models should be used to predict the effects of a modified electrode configuration in the DWPF melter.

The West Valley Demonstration melter is designed to be less susceptible to noble metals than the DWPF (which was designed in 1983). The WVDP modifications appear to have been partially successful, yet two-thirds of the electrical resistance in the WVDP melter circuits have been lost after one year of operation with noble metals concentrations comparable to SRS HM waste. WVDP is actively following the electrical response of its melter.

Recommendation: DWPF and SRTC should actively participate in the work at WVDP concerning the electrical response of the WVDP melter, as well as follow their approach to dealing with these issues, which includes the following activities:

- trending of historical operating data;
- updating a computer model for use as a tool in predicting future melter performance, including power needs;
- remote sampling of deposits;
- remote probing the deposits to determine their location and depth; and
- developing remote tools to dislodge deposits of noble metals in situ and performing associated mockups, as applicable.

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2.0 Introduction

2.1 The Noble Metals

The Noble Metals are defined as gold, silver, platinum, and the platinum group metals (ruthenium, rhodium, osmium, iridium, and palladium). Figure 1 shows the position of the noble metals on the Periodic Chart. They are called *noble* because of their resistance to oxidation as compared to base metals that oxidize when heated in air. The noble metals are easily reduced and all occur naturally in their elemental form (usually alloyed with one or more other platinum metals or in gold or silver deposits). However, only ruthenium, rhodium, palladium, and silver are found in high level waste as the products of fission reactions. A brief summary of the chemistry of each of these fission-product noble metals is given below.

25 Mn 55.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.71	29 Cu 63.546	30 Zn 65.38
43 Tc 98.906	44 Ru 101.07	45 Rh 102.905	46 Pd 106.4	47 Ag 107.868	48 Cd 112.40
75 Re 186.2	76 Os 190.2	77 Ir 192.22	78 Pt 195.09	79 Au 196.967	80 Hg 200.59

Figure 1. The Noble Metals

Ruthenium, atomic number 44, is a very rare iron-gray metal with an abundance in the earth's crust near 0.0004 ppm. Ruthenium possesses several interesting chemical features. Firstly, it may assume a wide number of oxidation states (from 0 to +8 are possible). Secondly, it has a tendency, particularly when in the tetravalent state, to form polynuclear complexes with oxide, nitride or hydroxy bridges. And lastly, ruthenium forms more nitrosyl complexes than any other metal.[2] A hydroxynitroyl form is considered to be typical of SRS wastes.

Of its wide number of oxidation states, Ru^{+3} and Ru^{+4} are the mostly likely. In borosilicate glass, the most likely form of ruthenium is RuO_2 [3], though, in very reducing conditions, Ru metal can be formed; while at very oxidizing conditions RuO_4 , an unstable toxic gas, may be formed. RuO_2 is essentially insoluble within the borosilicate glass matrix, even if oxidized.

The electrical conductivity of RuO_2 is comparable to that of the metal at the melter operating temperatures.

Rhodium, atomic number 45, is a very rare silvery-white metal with an abundance in the earth's crust of <0.0004 ppm. Rhodium exhibits far fewer oxidation states than ruthenium. Almost all of its complexes involve either the tri- or monovalent states. In its general chemistry, however, rhodium resembles ruthenium much more than cobalt.

Palladium, atomic number 46, is a silvery-white metal and is much more abundant than either ruthenium or rhodium. Palladium is the only one of the platinum metals that is attacked by nitric acid. Metallic palladium has the unusual ability to absorb hydrogen.^[2] The most common oxidation state of palladium is +2. Palladium is slightly soluble in borosilicate glass and is normally present as Pd metal, PdO , and alloyed with tellurium.

Silver, atomic number 47, is a white metal which is used in jewelry, dentistry, coinage, etc. Most of the silver present in SRS defense waste is the result of the disposal of silver saddles which have been used to scrub radioactive iodine from process stacks. Silver oxide, Ag_2O , is very soluble in borosilicate glass.

Tellurium and selenium, atomic numbers 52 and 34 respectively, are Group VIA nonmetals similar in chemistry to sulfur. They are only slightly conductive and have low melting points and so they, alone, pose no threat to the melter operation. However, they have a strong tendency to react or alloy with the noble metals (esp. with Pd). Thus their chemistry and physical properties are of interest.

Table 1 shows selected properties^[4] for each of these platinum metals as well as for silver and the alloying agents tellurium and selenium.

Table 1. Chemical and Physical Properties of the Noble Metal Properties

Name	Formula	Molecular Wt	Color, Crystalline form	Spec Gravity	m.p. °C	b.p. °C
Ruthenium	Ru	101.07	silver metal, hexagonal (close-packed)	12.45	2427	4119
- (III) chloride	RuCl ₃	207.47	dark brown fluffy, hexagonal	3.11	d > 500	
- dioxide	RuO ₂	133.07	blue, tetragonal	6.97	d	
- tetraoxide	RuO ₄	165.07	yellow needles, volatile	3.29	25.4	40
- disulfide	RuS ₂	165.20	black, cubic	6.14	d>1000	
Rhodium	Rh	102.91	silvery white, face centered cubic	12.41	1966	3727
- chloride	RhCl ₃	209.28	red powder, monoclinic		d 450	subl 850
- (III) oxide	Rh ₂ O ₃	253.81	blue-gray, rhombohedral	8.20	d 1100	
- (IV) oxide	RhO ₂	134.90	brown			
- selenide	RhSe ₂	260.83	cubic			
Palladium	Pd	106.40	silvery-white metal, face centered cubic	12.02	1550	2940
- oxide	PdO	122.40	black powder	8.70	d 870	
- selenide	PdSe	185.36	dark gray, tetragonal		> 960	
- diselenide	PdSe ₂	264.32	olive-gray, rhombic			
- telluride	PdTe	234.01	hexagonal			
- ditelluride	PdTe ₂	361.60	silver crystalline, hexagonal		745	
Tellurium	Te	127.60	white crystalline powder	6.24	450	1009
- dioxide	TeO ₂	159.60	white, tetragonal	5.76	732.6	subl 790
Selenium	Se	78.96	gray-metallic	4.81	221	685
			dark red, monoclinic	4.48	170	
- dioxide	SeO ₂	110.96	white needles, tetragonal	3.95	340	subl 310
Silver	Ag	107.87	white metal, face centered cubic	10.49	960.15	2164
- oxide	Ag ₂ O	231.76	brown-black, cubic	7.22	d 200	

From "Lange's Handbook of Chemistry" 13th Edition, John A Dean, Editor, McGraw-Hill Book Company, New York (1985).

NOTE: "d" - decomposes, subl - sublimates

2.2 Background (International Experience)

The high level nuclear wastes of the United States are quite different from those of other countries. The nuclear wastes which the US is vitrifying are mainly those resulting from the production of nuclear materials for defense purposes. The high level waste in other countries (Federal Republic of Germany, Japan, *etc.*) have resulted from the reprocessing of commercial nuclear fuel (from power reactors). Because of the differences in the waste origins, the expected levels of noble metals in the wastes are also varied. Table 2 shows a comparison of noble metals concentrations for selected German, Japanese, and American wastes. These tests were conducted after the design of the DWPF melter, thus the benefits of these studies have not been incorporated to minimize noble metals effects of DWPF melter operations.

Table 2. Noble Metals in German, Japanese, and American Waste Glasses*

<u>Component</u>	<u>PAMELA LEWC/WAK**</u>	<u>TVF GLASS</u>	<u>SRS/DWPF HM/BLEND</u>	<u>HWVP NCAW'91</u>
Ru	1000/5100	5530	830/350	870
Pd	?/3000	2960	310/160	300
Rh	?/1400	1290	150/ 68	240
Ag	trace	93	20/ 77	320
Total	?/9500	9873	1310/655	1730

* Values in ppm elemental projected in the glass product

**LEWC = Low Enrichment Waste Concentrate

WAK = waste presently stored at the Karlsruhe Reprocessing Plant (Note: the present plans are for this waste to be vitrified at Karlsruhe)

As one can see in this Table, the noble metal content of the commercial waste (the Japanese TVF and the German WAK) is considerably higher than that of the defense wastes (SRS HM and Blend, and the Hanford NCAW). However, as will be explained later, the flat-bottomed PAMELA melter experienced major operational problems which were linked directly to the deposition of noble metals and their compounds while processing the LEWC material. The LEWC material contains a total noble metal concentration (1360 ppm in the final glass) which is very similar to that of the SRS HM (1310 ppm in the glass) and the HWVP NCAW (1730 ppm in the glass).

A general description of the vitrification programs of several nations is summarized below. In each case, any testing with noble metals is specifically discussed.

2.2.1 Testing in Japan

The Japanese Power and Nuclear Fuel Development Corporation (PNC) produced 3.5 tons of simulated waste glass containing 0.74% RuO₂, 0.11% Rh, 0.30% Pd, and 0.02% Ag.^[5,6] The simulant contained no sulfur. The melter feed was an aqueous slurry of borosilicate glass frit and formic acid-denitrated waste. At the end of the test, the electrical field in the flat-bottomed melter was distorted to the point that glass processing could not continue. The deposits on the melter floor were a mixture of RuO₂, and alloys of Pd/Te and Ru/Rh. With these results, PNC redesigned their melter to become more noble metals compatible. Small scale tests led to the design and construction of an engineering scale melter capable of handling noble metals. Tests with this engineering scale melter indicated that the melter

floor required at least a 45° slope if the deposits are to be collected and tapped off through a bottom drain valve.[7] This design has been incorporated into the TVF full scale melter design. Tests conducted in full scale operations have shown that if the bottom section of the melter (just above the drain) is held at a relatively low temperature (800°C) until just prior to initiation of draining, the noble metals discharge efficiency is > 99%.[8] This method is probably not suitable for DWPF wastes because the relatively high concentrations of Cr, Fe, Ni, and Mn would result in accumulations of devitrification products at these low temperatures. These products would block the drain and be difficult to redissolve. Alternatively, PNC electrical modeling has indicated that raising the electrodes off the bottom of the melter by a distance equal to the radius of the melter will assure adequate melter resistance. Two dimensional modeling of this approach with the DWPF melter geometry is discussed in reference 7. The TVF 45° sloped bottom drain melter is shown in Figure 2.

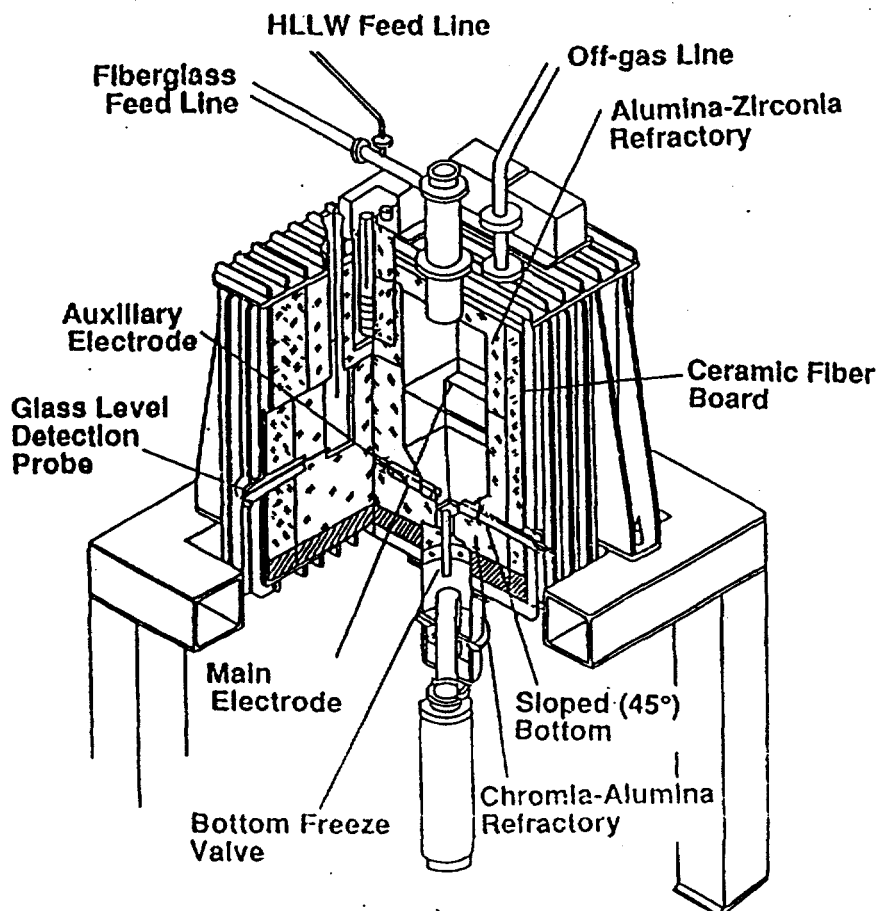


Figure 2. Japanese TVF 45° Sloped Bottom Melter

2.2.2 Testing in the United Kingdom

Although the British have decided to use the French AVM vitrification technology (inductively heated crucible), they have conducted research with small Joule-heated ceramic melters. During a small scale test, 117 kg of simulated waste glass containing 0.6% noble metals was produced by the United Kingdom Atomic Energy Authority (UKAEA).[5] During a 3 month melter idling period the effective melter resistance steadily decreased, until further current increases to maintain temperature became impossible. Melter disassembly and examination indicated that the glass adhering to the bottom 4 cm of the electrodes contained about 15.8% Ru. Ru was primarily present as the metal, and associated with tellurium, but some RuO_2 was also detected. Metallographic and mechanical examination of the electrode indicate that this same lower 4 cm region had operated close to the alloy 690 melting point of 1350°C , and small projections at the melter foot had been partially melted, even though the monitored glass temperatures had never exceeded 1150°C . It was concluded that a 4 cm layer of high electrical conductivity glass formed when Ru collected at the melter bottom, and local electrical resistivity dropped as the layer compacted. Low resistance in this area caused power to concentrate at the bottom of the electrodes, resulting in localized overheating due to a high current density, even at low total power.

2.2.3 Testing in France

The French AVM vitrification technology uses an inductively heated crucible and therefore is not impacted by noble metals deposition as is the Joule-heated technology.

2.2.4 Testing in Germany and Belgium (PAMELA)

Beginning in June, 1985, approximately 47 m^3 of Low Enrichment Waste Concentrate (LEWC) containing 1.5 to 2.2 g/L noble metals were converted into 78 tons of waste glass using a *Kerforschungszentrum Karlsruhe* (KfK) designed flat bottom melter in the *Deutsche Gesellschaft für Wiederaufarbeitung von Kernbrennstoffen mbH* (DKW) PAMELA facility in Mol, Belgium.[9] This melter is shown in Figure 3.

During operation, some of the melter bottom electrodes suffered severe local corrosion. This localized corrosion was the result of significantly overheating the electrodes with excessive local current densities. Probing of the glass determined that a 5 cm thick layer of conductive material at the melter floor was the cause of the shorting. Figure 4 shows the distortion of the electrical field by this layer of noble metals. The figure shows a high current flux between the upper and lower electrodes and low power generation in the upper portion of the melter caused by low local current densities. It also shows the low power generation at the bottom of the melter caused by the high current/low resistance path (noble metals layer).

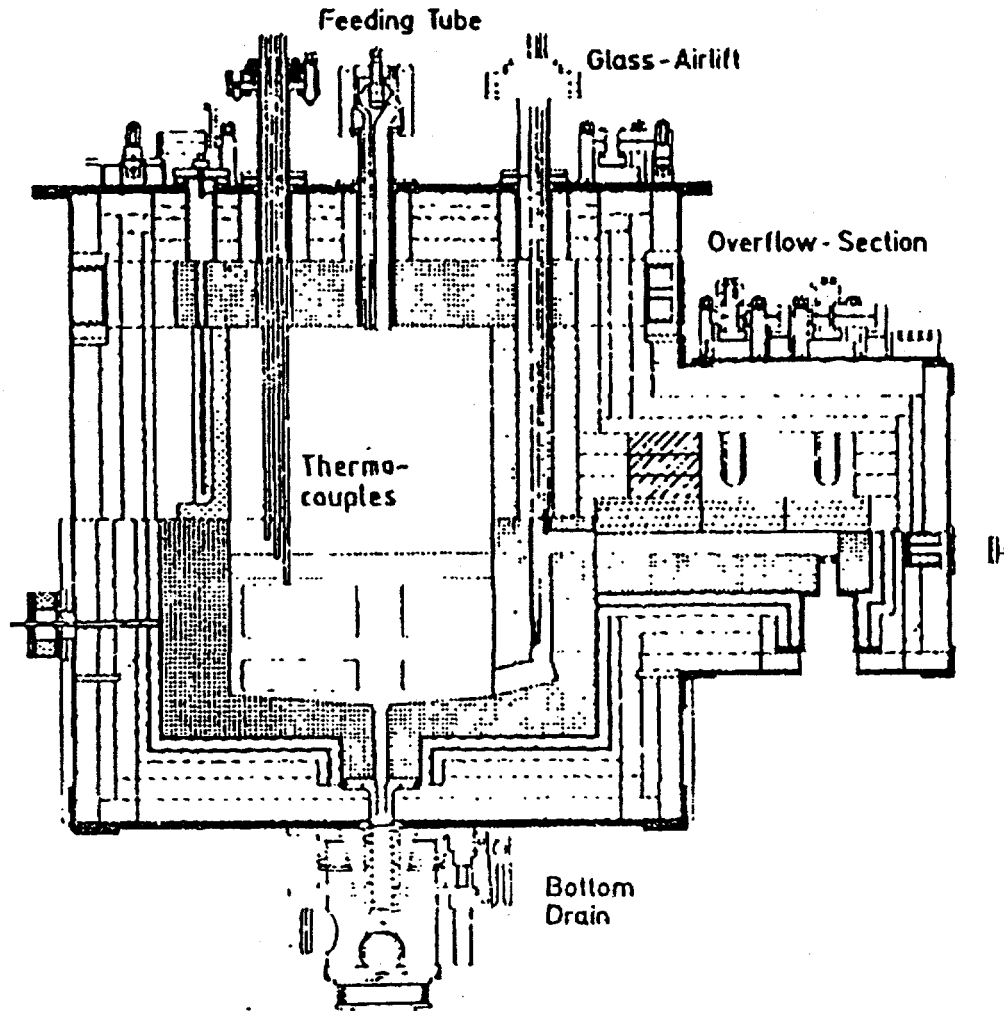


Figure 3. German PAMELA Flat-Bottom Melter

Analysis of samples determined that the deposition on the melter floor was ten times more conductive than the bulk glass and contained 10.4% RuO_2 , 0.3% RhO_2 , 0.05% PdO , 0.02% Se , 0.02% Te , and 0.25% S .^[5] Thus, RuO_2 is believed to be the major cause of the shorting. Attempts to remove of this viscous layer by routine glass pouring via a bottom drain were not successful. However, sparging of the sludge layer was partially successful in resuspending and flushing the deposits; and, operation of the melter continued at a reduced production rate using other electrodes higher in the glass pool. The melter was ultimately replaced in May 1988 due to a corroded wall section in the riser of the glass overflow system.^[9]

In all, the flat-bottomed PAMELA was operated for almost 3 years and produced 220 tons of radioactive waste glass from 47 m³ of LEWC and 218 m³ of High Enrichment Waste Concentrate (HEWC). Note that the HEWC noble metal content was about 10 times less than that of the LEWC.

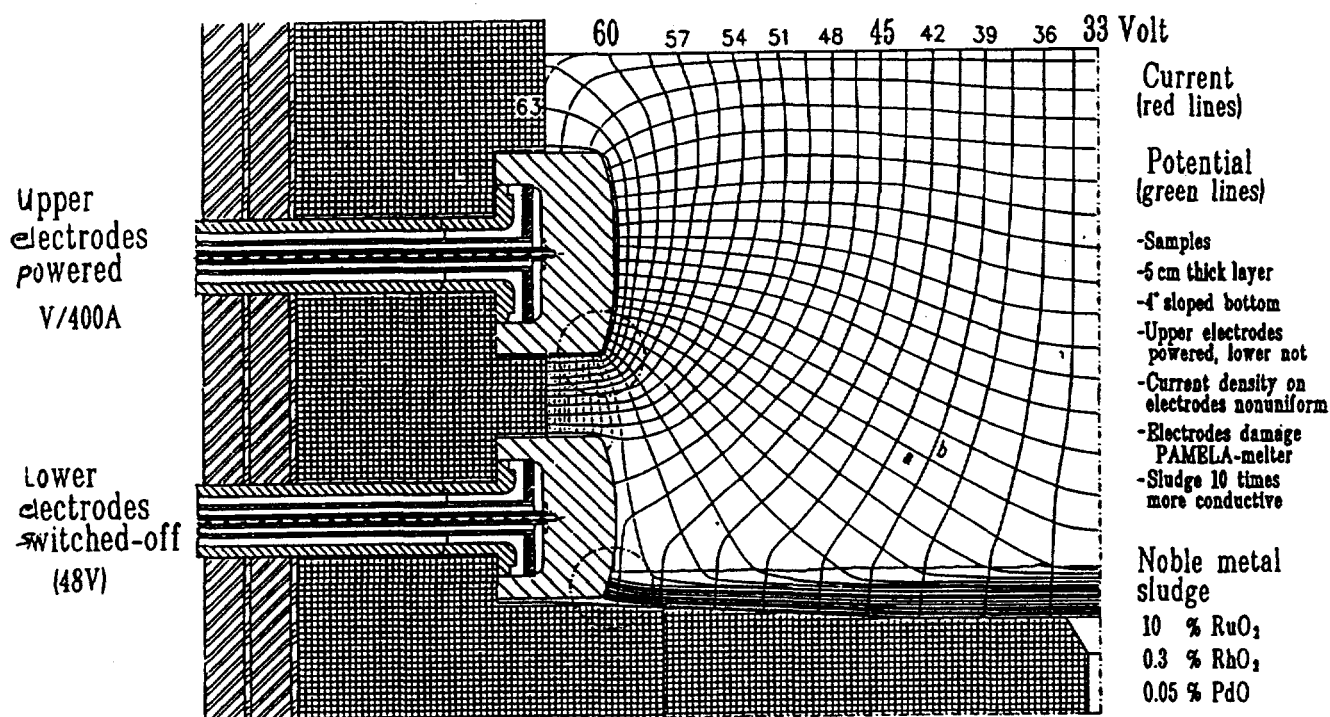


Figure 4. PAMELA Flat-Bottom Melter Showing Distortion of Electrical Field by Noble Metals on Bottom

With the operational problems of the flat-bottomed PAMELA melter, designs for future melters were modified to include noble metals compatibility for wastes from the proposed Wackersdorf Reprocessing Facility (WAK) and were simplified in terms of construction, remote maintenance and decommissioning.[10]

The first technical solution to minimize the effects of noble metal precipitation was the construction of the K-W2 45°-sloped bottom melter. This melter is shown in Figure 5. In tests conducted in a prototype industrial-scale mock up plant, the noble metals discharge efficiency of 25% in the flat-bottomed melter was increased to about 65% in the K-W2 melter. Additional air sparging of the glass pool raised the efficiency to 85-90%. These results suggested that the design of a sloped-bottom melter was a step in the right direction to removal of insoluble melt deposits. However, material was found deposited in the melter corners (where the slope is less than 45°) so the concept was modified to include steeper side walls and localized sparging at the melter bottom, combined with bottom draining. Figure 6

shows location of the deposits at the bottom of the melter. They were found in the relatively stagnant corner areas where the sloped walls intersect to form low dihedral angle corners. Table 3 shows the noble metals concentration in samples taken from the deposits from the locations indicated on Figure 6.

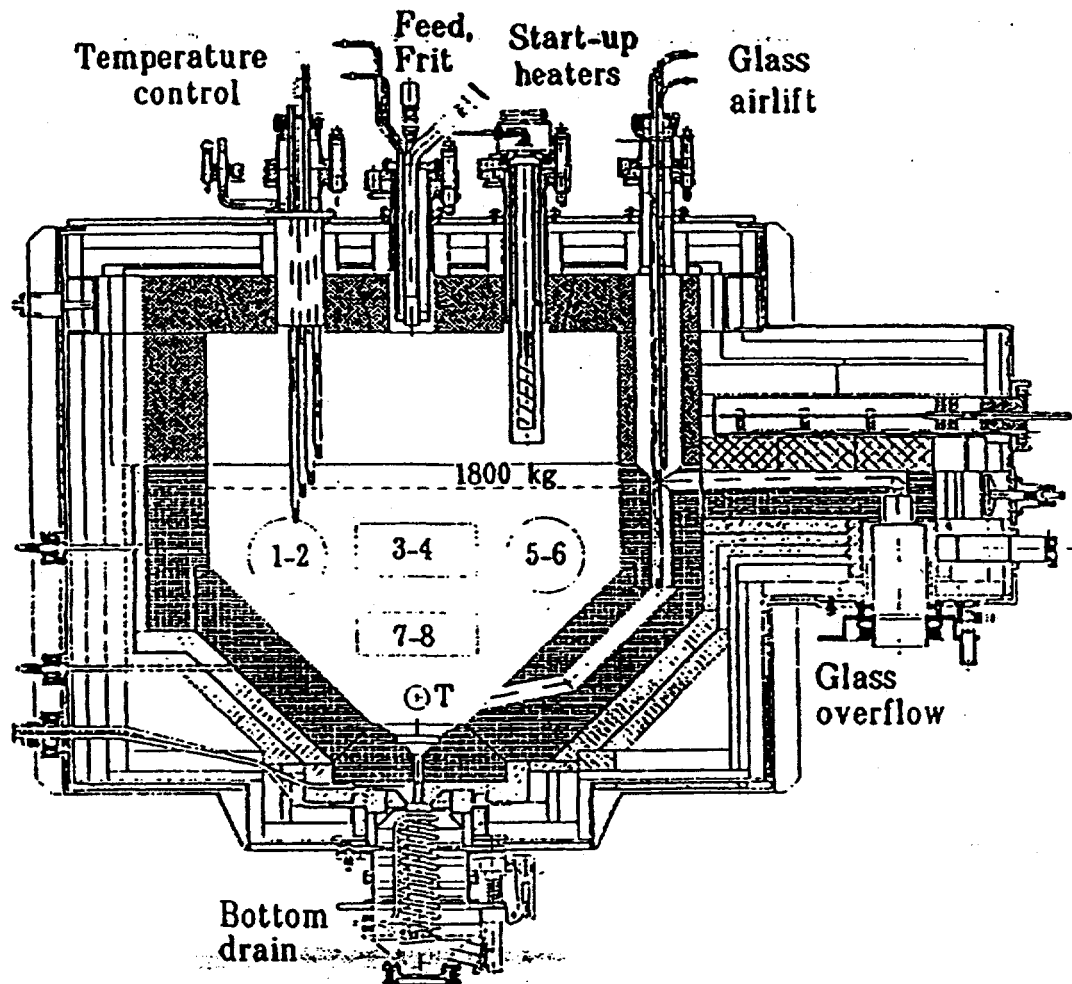


Figure 5. German K-W2 45° Sloped-Bottom Melter

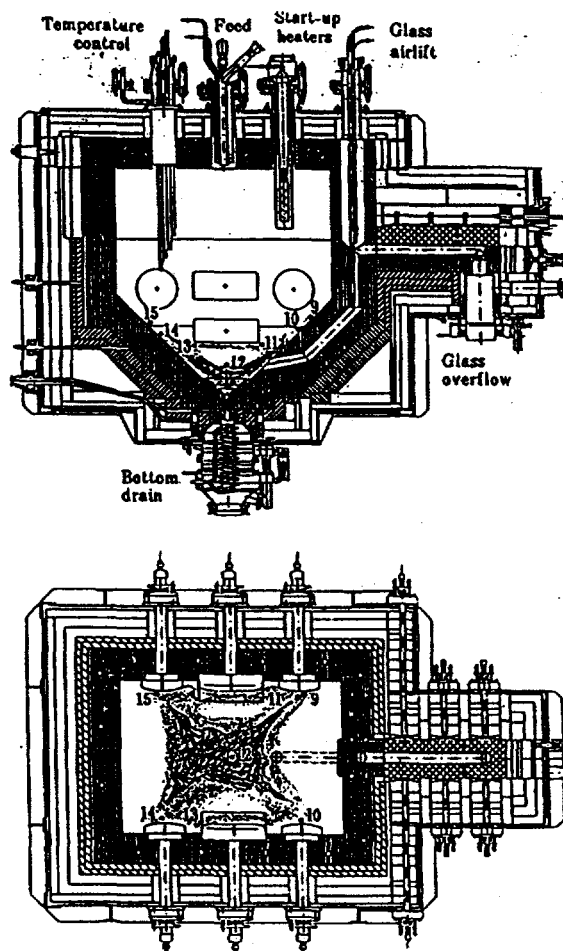


Figure 6. Location of Residue Which Remained in German K-W2 Melter

Table 3. Noble Metals Concentrations in Bottom Residue of German K-W2 Melter

Sample No.	concentration (wt %)		
	RuO ₂	Rh	Pd
9	12.56	0.24	6.05
10	11.83	0.34	5.58
11	12.13	0.50	6.45
12	12.10	0.40	5.37
13	10.00	0.41	6.28
14	11.47	0.42	5.35
15	11.47	0.33	5.29
Nominal glass values	0.69	0.122	0.452

Combining the experiences of the operations of PAMELA and K-W2 melters, the advanced 60°-sloped bottom K-6' melter was designed. This melter is shown in Figure 7. The melter has vertical walls above the main power electrodes. Between the two power electrode sets, the walls are 60° sloped. The lower part of the melting tank has the function of a settling chamber with 75° wall inclination. In inactive testing using the K-6' melter, Ru discharge efficiencies were about 90% for bottom-drained glass pourings but were <60% for overflow pourings.^[10] The present melter in the PAMELA facility is of a design similar to this K-6' melter.

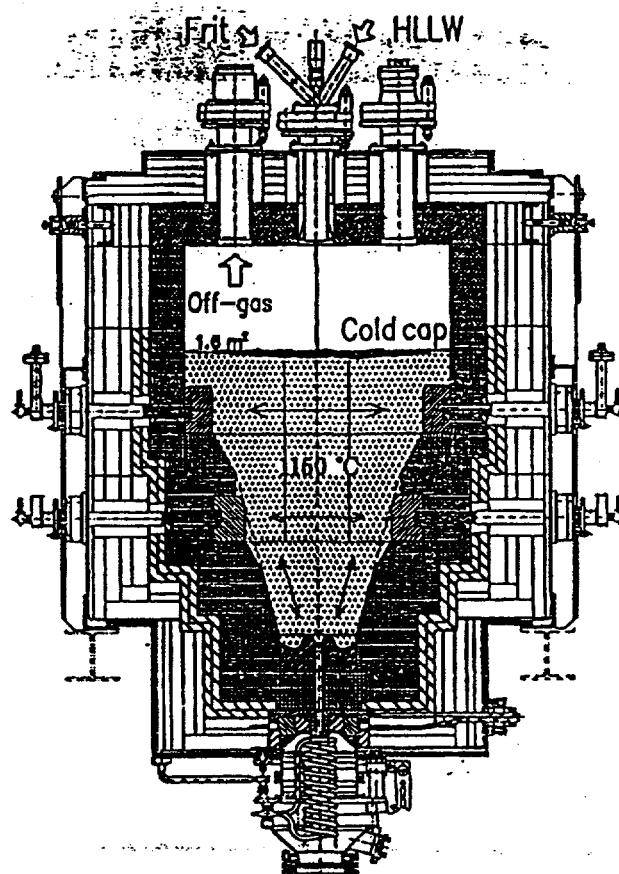


Figure 7. German K-6' 60° Sloped-Bottom Melter

2.3 Background (US Experience)

2.3.1 Testing at the Pacific Northwest National Laboratory

A series of five melting tests were conducted at the Battelle Pacific Northwest National Laboratory (PNNL) with very reducing simulated DWPF melter feeds derived from formate salts. Sulfide nodules from the tank floor at the end of these runs contained 20% of the ruthenium, 25% of the selenium, and 40% of the tellurium fed to the system. The nodule composition was nickel sulfide, Ni_3S_2 , with part of the sulfur replaced by selenium and tellurium. A total of about 45% of the ruthenium fed is believed to have collected at the melter floor, partially as RuO_2 particles. In a similar 30 day campaign in an engineering scale melter, ruthenium was added as RuO_2 , and feed was prepared with mercury and less reducing agent (formic acid). The resulting glass was not strongly reduced, and only small Ru particles 3 to 6 microns in diameter were found on the melter floor. Analysis of the glass concluded that the majority of the ruthenium had remained as finely dispersed RuO_2 , and exited the melter with the glass.[5]

More recent testing by PNNL has included the Research Scale Melter (RSM) in which a variety of conditions were modified to understand their effects on the behavior of the noble metals. These included glass oxidation/reduction REDOX state, bulk glass temperature, noble metal concentration, etc. The tests suggested that there is a significant nonlinear increase in the amount of noble metal compounds deposited in the melter with a 2-fold increase in the nominal noble metal content of the NCAW melter feed simulant.[11]

Settled layers of noble metals damaged the electrodes and refractory at the bottom of the RSM. It is not known if this was due to chemical effects or localized heating effects. The lower 1/3 of one of the electrodes was removed by the effect of a noble metal layer only 0.75 to 1.5 inches deep. The localized refractory loss was 0.5 inch. These effects occurred after only 47 days of feeding, with a 45% loss of resistance across the electrodes. The noble metals were not uniformly deposited. The accumulated noble metals at the conclusion of testing was 1.2 kg/sq. ft. of melter bottom. It was concluded that the likely mode of attack was that the noble metal layer was effectively electrically connected to one of the electrodes, but with a gap between the layer and the other electrode. The net result was the creation of high current densities in the glass adjacent to the electrode that was not connected to the noble metal layer. Either high localized temperatures, or the resulting high current densities at the face of the electrode caused rapid localized attack of the electrodes and refractory damage. The RSM tests also concluded that when Fe(II)/Fe(total) is greater than 0.25, then the Ru will be in its metallic state. PNNL concluded that under these reducing conditions the Ru will alloy with the Rh, and increase the rate of noble metal accumulation, thereby shortening the melter life. Mass balances indicated that the accumulation rate is very sensitive to noble metal concentration: At nominal concentrations only 5% of the noble

metals which were fed to the melter accumulated on the floor of the melter, but at 2X nominal concentrations 46% accumulated. Thus, the tests indicate that a 2X concentration increase can accelerate the noble metal effects by a factor of 9.

PNNL has also sponsored testing in the Engineering Scale Melter (ESM). This work was performed by personnel at the Institute für Nuklear Entsorgungstechnik at Kernforschungszentrum Karlsruhe in Karlsruhe, Germany. These tests, which were run at the nominal NCAW noble metal concentrations, resulted in considerable deposition (mainly RuO_2) on the floor of the 1/10th scale melter. [12,13]

The Engineering Scale Melter was scaled down from DWPF dimensions, with similar electrode configuration and 10% of the melter surface area of the DWPF melter. The octagonal internal shape closely approximated the DWPF cylindrical configuration. Thus the test was conducted with the best physical simulation of the DWPF available. The final mass balance concluded that 35% of the Ru, Pd, and Rh fed to the melter settled to the floor. At the end of the 49 days of tests the resistance to the lower set of electrodes had decreased by 10 to 15%. (IDMS Melter tests required 5 times as much glass processing to produce the same percentage change in electrical resistance, or about 50 melter volumes). At the end of the tests approximately 1.15 kg /sq. ft. noble metals had accumulated in a layer 0.75-1.2 inches deep. Noble metals were fed as soluble compounds, equivalent to : Ru 0.08%, Rh 0.023%, and Pd 0.03% of the glass. These concentrations are similar to DWPF "HM" waste type glasses, and of the concentrations in Hanford "NCAW" waste glasses.

On the basis of The Research Scale and Engineering Scale Melter Tests, PNNL developed both lumped parameter and finite element models of the electrical effects in the melter. They concluded that the expected operating life of a DWPF melter vitrifying feed similar to DWPF HM material would be about 192 days. This limit is based upon electrode transformer current capacity. Based upon this and other experiments it is probable that significant electrode damage would occur under these conditions: This is very close to the time that the IDMS melter showed electrode damage (216 days equivalent combined operating time for IDMS at Blend levels of noble metals). At the current Tank 51 concentration, the IDMS equivalent combined operating time is 4,329 days, so that lifetimes projected from these Tank 51 noble metals concentrations are not representative of DWPF operations with average noble metals content, or higher HM sludge levels.

2.3.2 Testing at the Savannah River Site

Prior to the IDMS melter studies, melting studies were conducted in the SRTC Research Melter (Mini-Melter). In these studies, up to 20% of the noble metals in the simulated DWPF melter feeds were found to settle on the melter floor. However, the glass produced in these tests was very reducing. Further, the Mini-Melter contained almost no natural convection to keep the insolubles suspended in the melt.[14]

2.3.3 Testing at the West Valley Demonstration Project

At the West Valley Demonstration Project (WVDP), the slurry-fed ceramic melter (SFCM) was in test operation from December 1984 to December 1989 to vitrify simulated nuclear waste slurries. In this study, deposition of insolubles and crystallized species on the SFCM floor during the vitrification process were analyzed. The results indicate that the thickness of the sludge layer on the floor of the SFCM was not more than 6 cm deep and consisted mostly of Fe-Cr spinels, and RuO_2 dispersed in a glassy borosilicate matrix. Also, crystalline Ce_2O_3 and undissolved phases consisting primarily of alumina and chromia were present in trace amounts but were inhomogeneously distributed in the glassy matrix on the SFCM floor. Greater than 87% of the RuO_2 fed to the melter was flushed out with normal glass pouring.[17] The SFCM was designed prior to the sloped bottom German and Japanese melters (see Figure 8). It has a unique prismoidal shape with sloping walls and a bottom electrode which was intended to minimize noble metals effects.

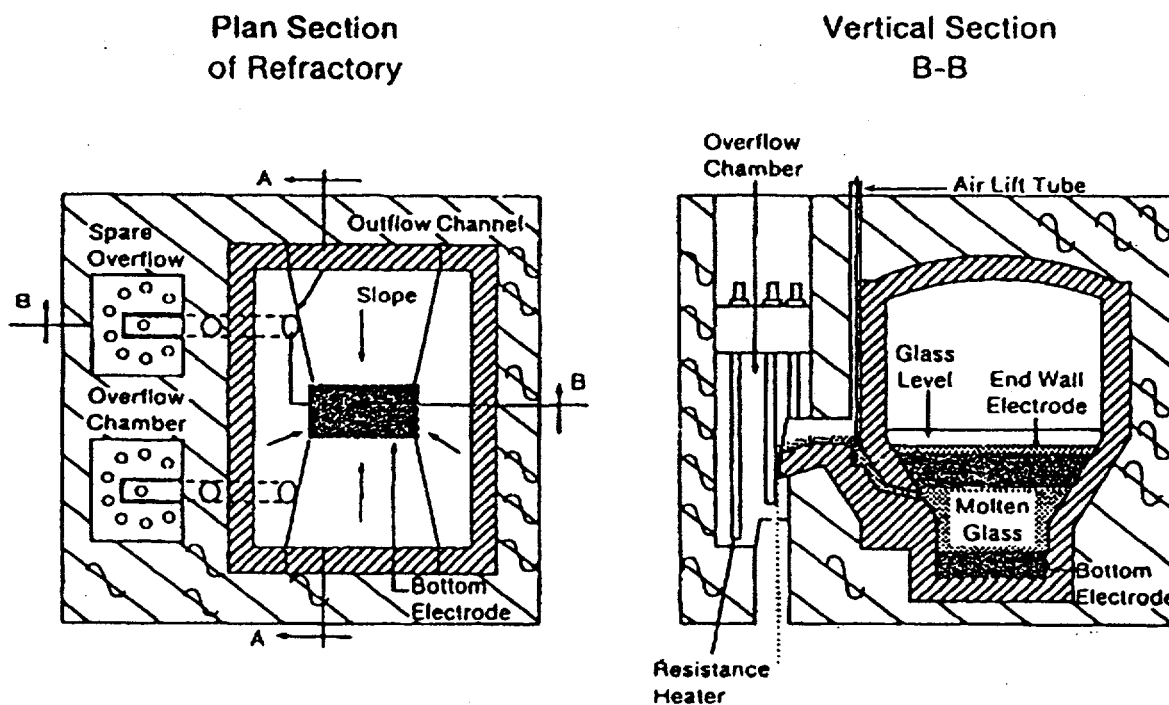


Figure 8. West Valley Slurry Fed Ceramic Melter (SFCM)

Five days of non-radioactive surrogate operations with noble metals were conducted on the WVDP melter before radioactive operations were started. No electrical disturbances were noted during the short test period, but deposits were found on the melter bottom and at the dihedral angle between melter walls, analogous to the German W-4 campaign experience. A preliminary material balance showed that 95% of the Ru had been washed out via the overflow drain.

The expected ruthenium concentration in WVDP radioactive glass is 0.08% by weight based upon fuel burnup fission product yields. Analyses after start of radioactive operations indicate actual values of 0.06 to 0.15%, and are being reviewed. The expected concentration is very similar to DWPF glass if made from HM sludge. After approximately one year of operation a dramatic change in the electrical resistance of the melter was found (fall of 1997) which required adjustment to current control limits to the melter.

Long term trending of historical data from the WVDP melter indicated a downward trend in the electrical resistance between the melter electrodes and skewing of current towards the bottom electrode (Figure 9). The problem is significant enough that a team of vitrification experts was assembled. Preliminary conclusions from this team are as follows. The downward trend in electrical resistance and the skewing of current towards the bottom electrode are most likely caused by deposits of noble metals. The primary effect caused by the accumulation of noble metals is that more current is needed to maintain the same power input into the melter. Trending indicates that sufficient current capacity is available to maintain the present glass production rate at least through June 1998. Part of the detailed action plan includes the need for enhanced monitoring and detection capabilities.

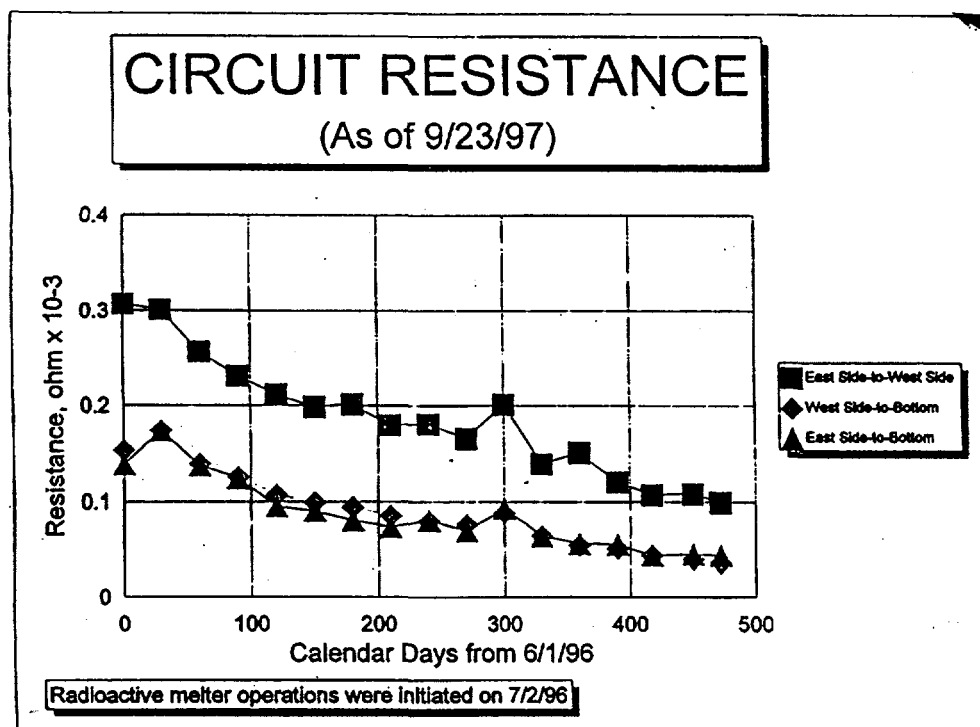


Figure 9. WVDP Melter Circuit Resistance During Radioactive Operations

2.3.4 Path Forward for WVDP Noble Metals Concerns

A team of vitrification experts (assembled by West Valley) gave numerous recommendations for addressing the WVDP noble metals concerns in 1997. They can be summarized as follows:

- assess the adequacy of currently available diagnostic/monitoring capabilities for detecting accumulation of noble metals;
- develop enhanced melter monitoring and detection capabilities with appropriate action limits;
- predict future melter power needs and develop work arounds to meet these needs;
- continue to collect and evaluate data aimed at characterizing the noble metal deposits in the melter;
- develop tools to dislodge the deposits of noble metals in situ;
- develop methods for flushing and draining the melter to remove deposits; and
- develop methods for visually inspecting the melter if it is drained and mechanically dislodging the deposits.

A detailed action plan was developed based on the above which is expected to include the following activities:

- trending of historical operating data;
- updating a computer model for use as a tool in predicting future melter performance, including power needs;
- evaluating alternatives if glass production capacity in the melter become limiting;
- obtaining a sample of the deposits;
- probing the deposits to determine their location and depth;
- developing tools to dislodge deposits of noble metals in situ and performing associated mockups, as applicable;
- following up on initial contacts with international vitrification counterparts; and
- installing a secondary transformer.

These recommendations will be evaluated to determine if they are technically feasible, add to the understanding and control of changes in melter performance, and represent an acceptable risk to ongoing vitrification operations. The implementation of these recommendations will be based on the trending of the data, the development of analytical models to predict long-term melter performance and the need to implement any mitigative actions, if required. Therefore, not all of the above recommended actions may be implemented.

3.0 IDMS / DWPF System Description

This section discusses the IDMS and DWPF equipment associated with the feed delivery and melter systems. For description of other IDMS systems (*e.g.* Feed Preparation, Precipitate Hydrolysis, *etc.*), consult the referenced report.^[17]

3.1 Feed Delivery System

The feed delivery system consists of (1) the Melter Feed Tank (MFT), (2) the melter feed pump, and (3) the melter feed line and feed tube.

The DWPF MFT is a 10,000 gallon Hastelloy C-276 flat-bottomed tank with internal Hastelloy C-276 cooling coils. The DWPF MFT has a 100-horsepower Hastelloy C-276 agitator controlled by a variable speed drive (high speed is 100 rpm). The DWPF MFT agitator has both upper and lower impellers. The upper impeller has three blades of a hydrofoil design while the lower is a four blade flat impeller that acts as a sweeper to keep solids from depositing on the bottom of the tank. The DWPF impellers have a 36-inch diameter.

The IDMS MFT is a 1500 gallon dished-bottom Hastelloy C-276 tank with an internal Hastelloy C-276 cooling coil. Agitation is accomplished via a 15-hp variable speed agitator. The IDMS MFT agitation system is similar to that of the DWPF except the upper impeller of the IDMS MFT agitator is a four blade pitched design with a diameter of 24 inches. During the IDMS Noble Metals testing, the MFT agitator has been operated at a speed such the shear rate matched that of the DWPF MFT. The shear rate is defined as:

$$\text{s.r.} = \frac{\text{Agitator tip speed (ft/sec)}}{\text{Distance from tip to vessel (ft)}}$$

This corresponded to a tip speed of 9.08 ft/sec (87 rpm).

In both the IDMS and DWPF, a recirculation loop feed system is used. In the IDMS, the slurry is recirculated through a 2-inch pipe using a veinless centrifugal pump which is external to the tank. The loop pressure is applied using a venturi-type restrictor at the return to the tank. The loop pressure forces the slurry through a strainer, a 3-way valve, and 50 feet of 0.25-inch ID piping to the melter feed tube. The IDMS feed strainer is a plate with nine 0.0082-inch diameter holes which have a combined cross-sectional area equal to that of the feed line. The flow rate to the melter is measured via a magnetic flow device and is controlled by varying the pump speed.

In the DWPF, the slurry is recirculated through a 2-inch pipe using a vertical centrifugal pump which is internal to the tank. As in the IDMS feed system, the loop pressure in the

DWPF recirculation line is applied using a venturi-type restrictor at the return to the tank. The loop pressure forces the feed slurry through a strainer and 40 feet of 0.43-inch line.

The IDMS melter feed tube extends through the melter lid past the lid heaters and discharges the slurry one foot above the melt pool. Slurry is fed through the innermost pipe of the feed tube which has an ID of 0.18-inch. The slurry feed pipe temperature is maintained at 30-40°C by a cooling water jacket that extends all the way to the feed discharge. Water cooling helps prevent slurry drying and pluggage in the feed tube. The DWPF melter has two feed tubes of approximately 0.43-inch diameter.

3.2 Melter System

The DWPF melter, shown in Figure 10, is a refractory-lined, sealed, stainless steel vessel of 6 feet internal diameter and approximately 7 feet internal height. The 1.5-inch thick vessel shell made of SA 240-304L steel with an OD of 8'-4.5" and an ID of 8'-1.5". It contains no removable parts; all shell components have at least a two-year design life. Nominal melter vessel construction consists of a steel outer vessel with an inner refractory liner for primary glass containment. The outer shell is water-cooled to maintain the outer vessel at or below 50°C. Primary glass containment is achieved by use of 12-inch thick Monofrax K-3 fused cast refractory brick (product of Carborundum Co.).

During operation, the glass is maintained in a molten condition by passing a current from the electrodes through the resistive glass pool. Electrical energy is converted to heat inside the molten glass by Joule's Law:

$$P = I^2 R$$

where P is the heat produced in the glass
 I is the electrode current, and
 R is the resistivity of the glass

As a current is introduced into the glass, the high resistance of the glass converts the electrical energy into heat. The glass is maintained between 1050 - 1170°C.

The DWPF melter electrodes are four uncooled plates fabricated from Inconel 690 of sufficient thickness to last greater than two years. The corrosion rate of the Inconel 690 in the glass pool is expected to be less than 1.8 mils/day. The electrode stems are water cooled.

The DWPF melter vessel shell is penetrated in the vapor space by four pairs of horizontal resistance-type Inconel 690 lid heaters rods. During normal operation, 220 kW of power is supplied to the lid heaters to heat them to 950°C and to maintain the melter plenum vapor space at 650-800°C. This temperature is necessary to maintain the gas above the auto

ignition temperature of organic compounds. Temperature control assures adequate combustion of the organics in the vapors and minimizes chemical attack on the lid heaters.

The DWPF riser heater consists of an Inconel 690 serpentine heater which surrounds the four-inch inside diameter Inconel 690 riser channel. The pour spout heater also consists of an Inconel 690 serpentine heater that surrounds the two-inch diameter of the pour spout channel. Current passing through these strip heaters produces the power to keep the glass flowing through the riser and pour spout channels at a temperature between 1050-1100°C.

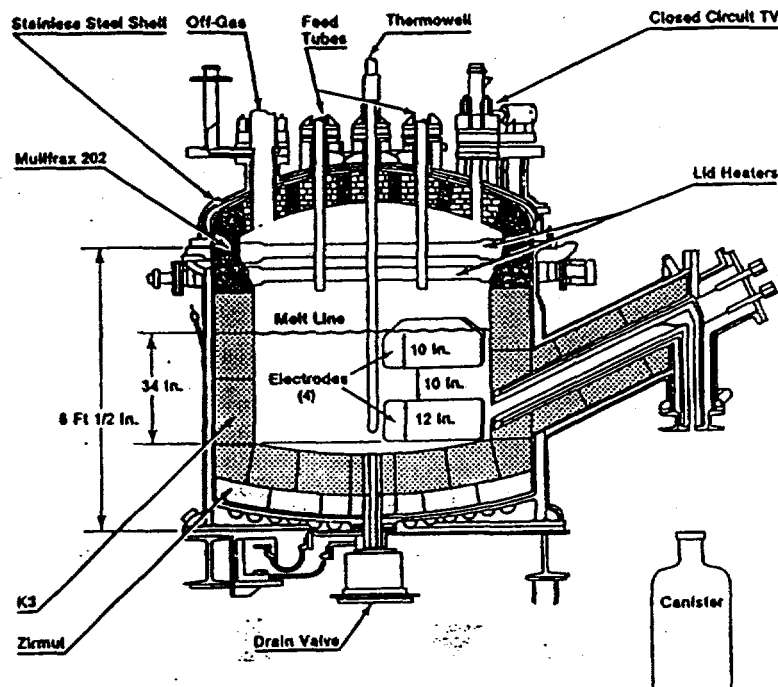


Figure 10. DWPF Melter

The IDMS Melter shell design is basically the same as that of the DWPF Scale Glass Melter (SGM). An additional 12 inches of Monofrax K-3 was added to the lower interior walls of the melt tank to reduce its diameter from 48 inches to 24 inches. This gives a melt pool surface area which is approximately $1/9^{\text{th}}$ that of the DWPF Melter. Melt rate is directly proportional to the surface area. Therefore, the IDMS Melter can be slurry-fed to produce glass at 25 lb/hr, as compared to 228 lb/hr for the DWPF Melter. Table 4 gives a comparison of the two melters. Figure 11 shows a cross-sectional view of the IDMS melter.

Table 4. IDMS/DWPF Melter Comparison

<u>Parameter</u>	<u>IDMS Melter</u>	<u>DWPF Melter</u>
Melt surface area	3 ft ² (0.29 m ²)	28 ft ² (2.61 m ²)
Melt volume	18 ft ³ (0.20 m ³)	87.6 ft ³ (2.48 m ³)
Centerline depth	27 in (69 cm)	37 in (95 cm)
Glass content (max)	1063 lbs (482 kg)	13,136 lbs (5956 kg)
Production rate	24 lb/hr (11 kg/hr)	228 lb/hr (103 kg/hr)
Melt rate	8 lb/hr/ft ²	8 lb/hr/ft ²
Residence time	44 hrs	58 hrs

The melter vessel is lined with K-3 refractory to provide containment of the molten glass. The entire shell is water-cooled to freeze any glass that may penetrate between the refractory blocks before it reaches the shell. Two pairs of diametrically opposed Inconel™ 690 electrodes provide about 35 kW of power to maintain the glass temperature between 1100°C and 1150°C. The A and C electrode stems are water-cooled, and the B and D stems are air-cooled to freeze any glass that could potentially leak out where the stems penetrate the refractory. Air (instead of water) is used on the B and D electrode stems to reduce heat loss in the unheated riser throat region. Each electrode pair (A-B and C-D) is controlled separately to permit diversion of power to the lower or upper melt pool. Table 5 gives characteristics of the IDMS and DWPF full scale electrodes.

Power supplies for the electrodes can provide up to 300 V single phase, but under normal conditions only 53 V single phase will be required. Power to the electrodes is controlled by silicon controlled rectifiers (SCR's) on the primary side of the power supply transformers. Due to the high current (approximately 400 amps), water-cooled cables deliver the power to the electrodes from the secondary side of the transformer.

Two horizontally-entering Inconel™ 690 lid heaters, each made of two elements, provide an additional 60 kW of heat to vaporize water from the slurry feed, melt and the glass, and combust any organics in the feed. These heaters are also the primary source of heat during melter startup. The lid heaters are maintained at 950°C by passing current through the tubes. The surface temperature of the heaters is limited to 950°C because of thermal creep considerations (this is also the case for the DWPF melter lid heaters).

As in the DWPF glass flows from the melter up through a heated riser channel and then down a heated pour spout channel into a canister which holds up to 200 lbs of glass. The riser is a 2-inch diameter Inconel™ 690 pipe surrounded by a serpentine Inconel 690™ heater. The heater is isolated from the Inconel™ pipe and housing with ceramics. The heater is used to maintain the glass in the channel at 1100°C.

The pour spout heater is constructed similarly to the riser heater. It is used to keep the glass above 1050°C to keep it free flowing. Power to the riser and pour spout heaters is controlled by SCR's on the primary side of the power supply transformers.

Pouring is initiated by creating a vacuum at the canister relative to the melter vapor space. A flexible set of stainless steel bellows provides a vacuum seal between the melter and the canister during pouring. These canisters are 31 inches tall and 10 inches in diameter. Although the slurry is fed continuously to the melter, glass is poured in batches. This is due to the fact that the minimum acceptable pour rate to prevent wavering of the pour stream (about 60 lb/hr) is higher than the melt rate of 25 lb/hr for the IDMS Melter.

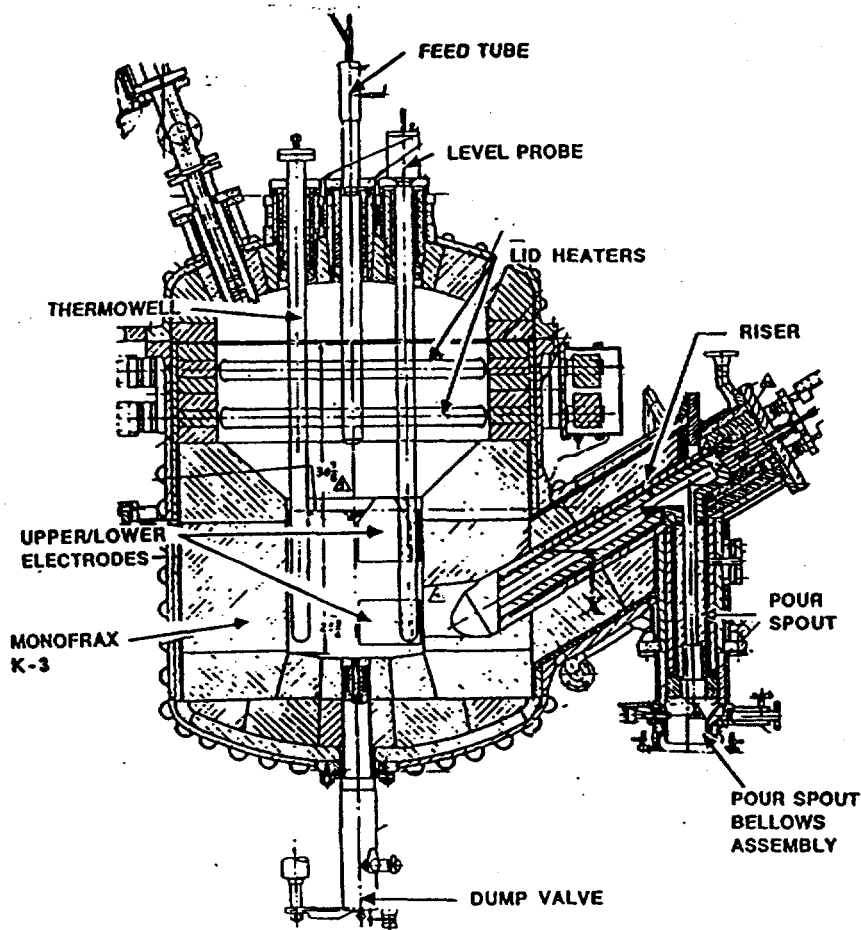


Figure 11. Cross-Sectional View of the IDMS Melter

Table 5. Characteristics of Melter Electrodes

<u>Characteristic</u>	<u>IDMS Melter</u>	<u>DWPF Melter</u>
Upper pair surface area (ft ²)	1.00	9.49
Lower pair surface area (ft ²)	0.74	11.00
Electrode power (kW) *	20.0	80.0
Design current density (amps/in ²)	5.0	5.0
Distance between electrodes:		
- across melter (in)	41.2	56.0
- top and bottom (in)**	6.75	10.0
- and the floor (in)†	2.5	--

* per pair under normal operation

** distance between bottom of top set of electrodes and the top of the bottom set of electrodes

† distance between the bottom of the bottom electrode and the melter floor immediately below

3.3 Melter Offgas System

The IDMS Melter Offgas System is a scaled simulation of the DWPF system. It was designed for an off-gas flow rate of 350 lb/hr entering the SAS's, compared with 1900 lb/hr for the DWPF. The off-gas consists of steam, non-condensable gases from sludge decomposition and volatilization, air from in leakage and purges, mercury vapor, and particulate matter from entrainment. The purposes of the off-gas system are to maintain a negative pressure in the melter plenum, to provide adequate combustion in the melter vapor space, ensure ventilation and treatment of the reaction gases and steam released from the melter, and provide melter pour spout vacuum to initiate and control glass pouring. Since there are no radionuclides present in the IDMS, the demand on the IDMS off-gas system is less than for the DWPF off-gas system. However, to enable adequate evaluation of the processing efficiency, mechanical reliability, corrosion, and fouling of filters, demister pads, and heat exchange surfaces, all of the DWPF processing steps are incorporated into the IDMS. Unlike the DWPF, the IDMS does not have a redundant backup system. Instead, it has a bypass system which can be used if the primary system is not operative.

4.0 Summary of IDMS Noble Metals Runs

The IDMS has conducted a total of 16 noble metal (or noble metal related) runs to date. They have been conducted with four types of simulated waste sludges (Blend, HM, PUREX, and NCAW) and have contained varied amounts of noble metals. Some of the sludge compositions were modified in order to judge the effects of components such as mercury and nitrite. Specific compositions of each of the sludges can be found in Campaign Summary Reports.[17,18,19,20,21,22]

In each run (where noble metals and mercury were added) they were added in the form as shown in Table 6.

Table 6. Additive Form of Noble Metals, etc.

<u>Element</u>	<u>Additive Form</u>	<u>Additive Formula</u>
Ru	Nitrosylruthenium Hydroxide	$\text{RuNO}(\text{OH})_3$
Rh	Rhodium Nitrate	$\text{Rh}(\text{NO}_3)_3 \times \text{H}_2\text{O}$
Pd	Palladium Nitrate	$\text{Pd}(\text{NO}_3)_2 \times \text{H}_2\text{O}$
Ag	Silver Nitrate	AgNO_3
Hg	Mercuric Nitrate	$\text{Hg}(\text{NO}_3)_2$
Se	Selenium Oxide	SeO_2
Te	Tellurium Oxide	TeO_2

Note: Ru added as RuCl_3 in PX6.

A brief summary of each of the runs is given below. The amounts, types, and concentrations of the waste simulants, etc. for each run are given in Table 7.

4.1 Blend with Noble Metals (BL1, BL2)

The first two IDMS runs containing noble metals were made using a Blend-type sludge simulant and are referred to as BL1 (or "Blend-1") and BL2 (or "Blend-2"). In each of the runs "Blend levels" of the noble metals, mercury, TeO_2 , and SeO_2 were added to the sludge simulant. During these runs, hydrogen was measured as an offgas product during the feed preparation process. This hydrogen was due to the noble metal catalyzed decomposition of formic acid. Because of the safety implications of this occurrence, the IDMS facility was put into an extended idling mode while safety upgrades of the facility were completed. Also, because of this, a greater emphasis was placed on research activities involving the feed preparation portion of the operation.[19,23]

4.2 DWPF Cold Runs Demonstrations (BL3, HM1)

After the extended idling period, the operation in the IDMS facility resumed. The next series of runs were conducted to simulate the DWPF cold runs. The purpose was to measure the amount, if any, of hydrogen that could be expected in the DWPF Cold Chemical Runs (in the absence of the noble metals). Thus, these runs did not contain noble metals, mercury, TeO_2 , or SeO_2 . The two runs are referred to as BL3 and HM1 (or "HM-1"). [20]

4.3 DWPF RadOp Design Basis Runs (HM2, HM3, PX1, PX2)

The next set of runs were conducted to provided the DWPF with design information for modifications for radioactive operations (for hydrogen evolution). This set of operations consisted of 2 runs using HM-type sludge and 2 runs using PUREX-type sludge. The runs are referred to as HM2, HM3, PX1 (or "PUREX-1"), and PX2. In each of the runs "HM levels" of the noble metals, TeO_2 , and SeO_2 were added to the sludge simulant. Mercury was not included in any of the runs. The noble metals were added at "HM-levels" in all of the runs because this was the highest concentration and would most likely give the maximum hydrogen evolution.

4.4 Hanford Waste Vitrification Plant Demonstrations (HWVP1, HWVP2)

Following the RadOp Design Basis Runs, two runs were conducted in support of the design and operation of the Hanford Waste Vitrification Plant (HWVP). These runs were conducted with a NCAW waste simulant containing nominal levels of noble metals and are referred to as HWVP1 and HWVP2.[22]

4.5 Nitric Acid Flowsheet - HAN PHA (HM4, PX3)

The next set of IDMS operations were conducted in order to test the "Nitric Acid Flowsheet". This flowsheet was developed as a way to reduce the amount of hydrogen and ammonia which will be evolved during the feed preparation process. The runs used HM and PUREX type sludges with HM levels of noble metals and mercury. In each case, HAN-type PHA was added in the feed preparation process.

4.6 Nitric Acid Flowsheet - Late Wash PHA (PX4, PX5, PX6)

The last IDMS runs demonstrated the use of the "Nitric Acid Flowsheet" with "Late Wash PHA". This operation is currently the reference flowsheet combination employed by the DWPF. Both of these runs used PUREX sludge with HM levels of noble metals and mercury.

Table 7. IDMS Run Summary

Table 1. Summary of Data for the 1992-1993 Period									
Run ID		Sludge Type	PHA Type	Frit Type	Acid Type	Mercury Amounts	NM Amounts	Te, Se Amounts	Glass Prod (lbs)
Blend1	BL1	Blend	HAN	FRIT-202	90% Formic	Blend	Blend	Blend	2970
Blend2	BL2	Blend	HAN	FRIT-202	90% Formic	Blend	Blend	Blend	5376
Blend3	BL3	Blend	HAN	FRIT-202	90% Formic	None	None	None	1595
HM1	HM1	HM	HAN	FRIT-202	90% Formic	None	None	None	3156
HM2	HM2	HM	HAN	FRIT-202	90% Formic	None	HM	HM	2949
HM3	HM3	HM	HAN	FRIT-202	90% Formic	None	HM	HM	3635
PUREX1	PX1	PUREX	HAN	FRIT-202	90% Formic	None	HM	HM	3344
PUREX2	PX2	PUREX	HAN	FRIT-202	90% Formic	None	HM	HM	4232
HWVP1	HV1	NCAW	NA (RWS)	PNNL FY'92	90% Formic	NCAW (none)	NCAW	NCAW	3390
HWVP2	HV2	NCAW	NA (RWS)	PNNL FY'92	90% Formic	NCAW (none)	NCAW	NCAW	4561
HM4	HM4	HM	HAN	FRIT-202	8 M Nitric	HM	HM	HM	3226
PUREX3	PX3	PUREX	HAN	FRIT-202	8 M Nitric	HM	HM	HM	5108
PUREX4	PX4	PUREX	Late Wash	FRIT-202	8 M Nitric	HM	HM	HM	4850
PUREX5	PX5	PUREX	Late Wash	FRIT-202	8 M Nitric	HM	HM	HM	4075
PUREX6	PX6	PUREX	Late Wash	FRIT-202	11 M Nitric	HM	HM	HM	*1693

Sludge Noble Metal, etc. Concentrations

Element	Blend wt%	HM wt%	PUREX wt%	TANK 51 wt%	NCAW wt%
Ru	0.100	0.217	0.028	0.007	0.231
Rh	0.018	0.038	0.008	0.001	0.064
Pd	0.045	0.079	0.026	0.006	0.080
Ag	0.014	0.014	0.014	0.014	0.084
Hg	1.588	3.263	0.102	0.192	0.000
Te	0.022	0.048	0.006	0.00009	0.060
Se	0.002	0.004	0.001	0.0007	0.009

* Only a portion of PX6 was fed to the IDMS melter.

4.7 IDMS Melter Shutdown/Inspection

The IDMS melter was shutdown on June 30, 1995 after operating continuously since October 1988. An inspection of the melter refractory, melter component, and off-gas piping, as well as sampling of the material at the bottom of the melter was done. Aggressive attack of the K-3 refractory occurred at the bottom of the melter drain. The Inconel 690® drain valve and pipe had extensive corrosion. The Inconel 690® upper electrode was in excellent condition above the normal glass level while the bottom of the electrode exhibited some wear. The Inconel 690® lower electrode, continuously in contact with the melt, had lost about 12% of the material from the face of the electrode.

5.0 Behavior of the Noble Metals

5.1 Size, Distribution and Chemical Form

The rate of accumulation of the noble metals in the melter is a function of the size, distribution, and chemical forms of the noble metals and/or the noble metal compounds in the glass. Samples were taken from various points in the melter system in order to understand how the different processing steps affect these parameters. Each of these samples were examined by a variety of analytical methods and are described below.

5.1.1 In the Melter Feed Slurry

In each of the runs, the noble metal compounds were added to the alkaline waste sludge simulant in the SRAT/SME vessel. The palladium, rhodium, and silver were added as nitrate solutions. The ruthenium was purchased as RuCl_3 and was subsequently converted (except for PX6 when it was added as RuCl_3) to a nitrosylruthenium hydroxide ($\text{RuNO}(\text{OH})_3$) slurry (the anticipated form of the ruthenium in the SRS waste). The procedure for this conversion was developed by R. M. Wallace and D. T. Hobbs of the Savannah River Technology Center. While the procedure may not produce a purely nitrosylruthenium solution, it does result in a product which has undergone similar treatment as the actual SRS waste. Selenium and Tellurium were added as dioxides. The resultant waste sludge simulant was acidified with either formic or nitric acid and blended with other simulated wastes (PHA or RWS) and a glass forming frit with the final mixture being the slurry which was fed to the melter.

The size, distribution, and chemical forms of the noble metals in the melter feed slurry are expected to greatly influence the size, distribution, and chemical form in the melter and glass product. The size, distribution, and chemical form of the noble metals in the melter feed are most affected by a combination of the upstream processing steps (especially by the addition of a reductant, formic acid), and the physical treatment of the material in the SRAT, SME, and MFT. The size and distribution of the noble metals are affected by the shearing actions of the vessel agitators and the melter feed pump. Further, the presence of mercury also affects the distribution of some of the noble metals.

Feed slurry samples were taken during periods of continuous melter feeding. These samples were then dried, washed with distilled water, and centrifuged. The resulting insoluble solids were examined by Scanning Electron Microscopy/Energy Dispersive X-Ray (SEM/EDX). These analyses revealed scattered palladium "nuggets" of about $1\text{ }\mu\text{m}$ and, in melter feeds containing mercury, amalgams of Hg/Ag and Hg/Ag/Pd . Although one very small aggregate of Ru/Pd/Ag was seen in the second Hanford NCAW run (HWVP2), no individual or amalgamated Ru or Rh particles were been observed in any of the melter feed slurry insoluble solids. It is suspected that these species, if reduced to the elemental state, form

very small sub-micron particles which cannot easily be found by standard optical microscopy. In general, in the melter feed slurry, the noble metals are present as either very small, finely dispersed particles or as soluble salts.[24,25]

5.1.2 In the Melter Cold Cap

During continuous feeding of the simulant slurry, a "cold cap" region forms on the surface of the molten glass. It is in this area that almost all reduction/oxidation reactions occur and gaseous vitrification products are evolved. After material has been feed to the melter to form a cold cap which sufficiently covers the molten glass, a dip sample of the cold cap region can be obtained. Analysis of these partially vitrified samples have revealed RuO_2 needles of up to 20 μm long present in 20 to 50 μm clusters. The samples have also contained scattered 1 μm AgI salts, RuS_2 , Pd tellurides and selenides, and complex mixtures of Pd/Ag/Te/I/S/Cu. These cold cap samples also provided some evidence as to how this area physically and chemically influences the agglomeration of these species. The SEM micrographs indicated the noble metal compounds (especially the Pd) were preferentially located on the surface of vitrified "gas bubbles". This suggests that the frothing which takes place as a result of vitrification offgases may promote the growth of platinum metal nodules.[24] It has also been suggested that palladium oxides may decompose to metallic Pd and oxygen, with the Pd transported to the melt surface within the oxygen bubble.[26] Once at the melt surface the Pd particles may combine with other free particles to form nodules which will then settle to the melter floor.

Figure 12 shows a SEM micrograph of a melter cold cap sample (H-COLD-0238) showing the partially vitrified sample and the vitrification offgas "bubbles". Figure 13 shows a more detailed micrograph of melter cold cap sample 1-COLD-3690 showing small noble metal particles and salts (RuO_2 , RuS_2 , AgI , AgCl , and other complex mixtures containing Te, Se, I, and Cu).



Figure 12. SEM Micrograph of IDMS Melter Cold Cap Sample (H-COLD-0238)

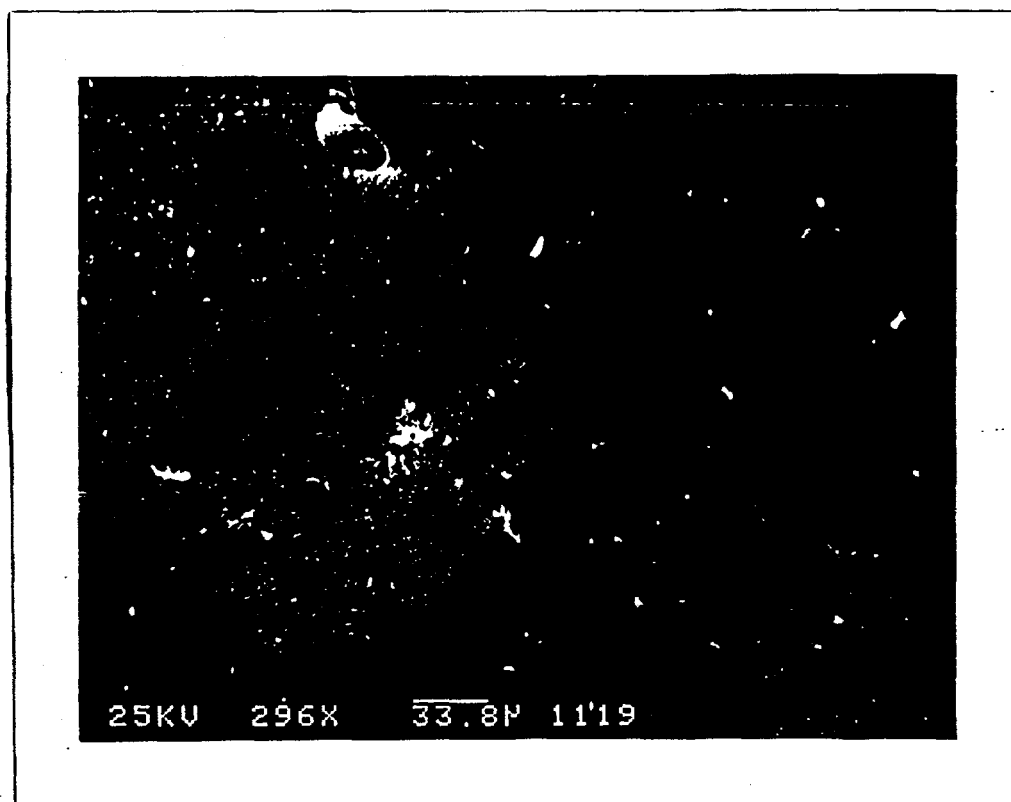


Figure 13. SEM Micrograph of IDMS Melter Cold Cap Sample (I-COLD-3690)

5.1.3 In the Melter Offgas Deposits / Offgas Condensate

The formation of deposits in the melter offgas line has been a problem common to all slurry-fed melters. These deposits have normally been composed of alkali-rich chlorides, sulfates, borates, and fluorides with entrained Fe_2O_3 , spinels, and frit particles. The melter offgas deposit samples obtained from the IDMS melter were composed of these same components and have also contained trace quantities of RuO_2 , $(\text{Ru,Rh})\text{O}_2$, and Ru/Rh/Te mixtures (and some entrained Cd compounds during the NCAW processing). [22,24] While the formation of RuO_4 , a toxic gas, is possible in very oxidizing conditions, most of the Ru exiting the melter was the result of entrainment rather than volatility as the RuO_2 in the melter offgas deposits were most often associated with entrained spinel crystals.

Analysis of the soluble fraction of the melter offgas condensate revealed very low concentrations of the noble metals. However, analysis of the insoluble solids present in the offgas condensate showed the solids to contain RuO_2 crystals, spinels, and insoluble silver halide (AgI , AgCl) salts. However, the amount of the noble metals exiting the melter through the offgas line is small and should not significantly affect the overall mass balance of any of the elements.

5.1.4 In the Canistered Glass Product

The canistered glass products of several IDMS campaigns have been examined by SEM/EDX. Ruthenium was the most frequently observed of the platinum metals in the glass product. The ruthenium was present as both individual and clustered acicular (needlelike) RuO_2 crystals (See Figure 14) which were usually $< 10 \mu\text{m}$. [22,24,25]

The RuO_2 was also quite often associated with $(\text{Ni,Mn})\text{Fe}_2\text{O}_4$ and $(\text{Ni,Mn})\text{Cr}_2\text{O}_4$ spinels. It had been previously shown that RuO_2 will serve as a seed for the heterogeneous nucleation of these spinels. [27] The SEM/EDX analysis of the IDMS glass also revealed spinel growth which had been nucleated by aggregates of $(\text{Ru,Rh})\text{O}_2$, Ru/Rh , Ru/Pd , and Rh/Pd . Upon further analysis via Transmission Electron Microscopy (TEM), it was found that the Ru and Rh oxides not only act as nucleating agents for the formation of the spinel structure but the Ru and Rh have also substituted with other spinel components (See Figure 15) to become part of the spinel structure itself.

Palladium, as Pd and Pd/Te, was also occasionally found in the canistered glass product. The silver is completely dissolved within the glass matrix.

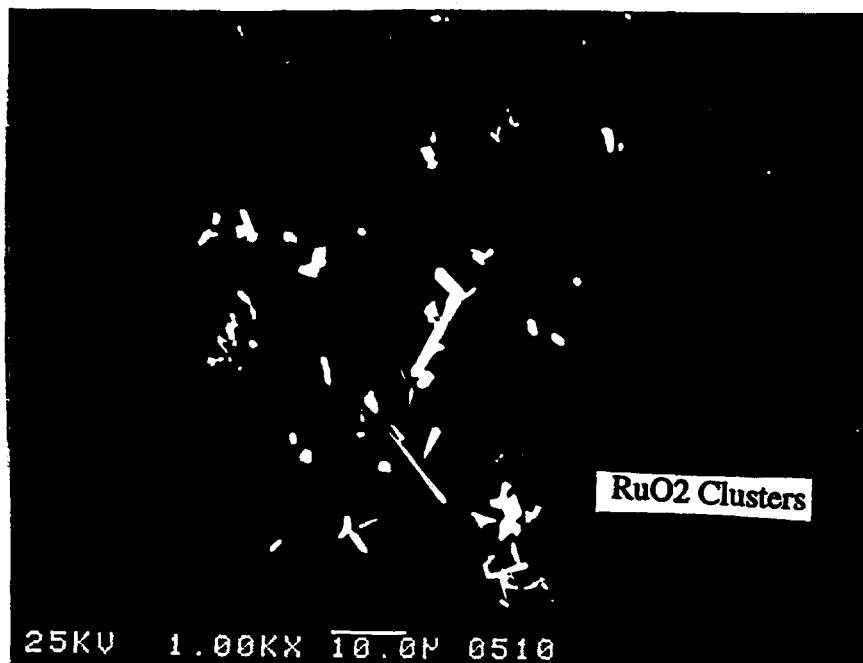


Figure 14. SEM Micrograph of IDMS Canistered Glass Product (H-GLAS-0264)

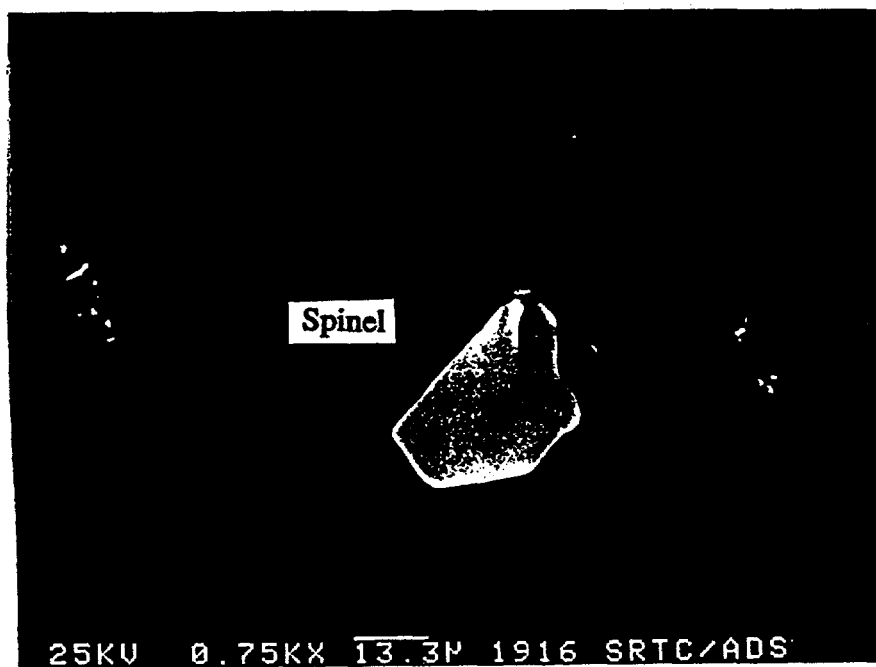


Figure 15. SEM Micrograph of IDMS Canistered Glass Product (H-GLAS-0446)

5.1.5 In the Melter Floor Samples

Since the introduction of noble metals in the IDMS melter, samples of the melter floor have been taken on a regular basis. The samples are taken using a "grain thief" type sampling device. The samples are normally taken through the feed tube port but have also been taken from the borescope port (See Figure 16).

About 2 months after feeding the initial noble metal doped slurry, a sample was taken of the melter floor (actually at about 1-2 inches above the floor). The sample revealed no evidence of the presence of any noble metals or crystalline material. Another sample of the melter floor (again at about 1-2 inches) was taken approximately 5 months after the initial floor sample. This sample showed very scattered RuO_2 needles approximately 5 to 15 μm long. These needles were present, for the most part, in 20 to 40 μm clusters. There was no evidence of any deposition of Pd, Rh, Ag, Se, Te or any of their compounds.

Approximately 13 months after the introduction of the noble metals, a third melter floor sample was taken. The sampler was modified so that samples could be taken to within 1/2-inch of the melter floor. This sample revealed a significant increase in the amount of RuO_2 from the earlier samples (Figure 17). There was also evidence of a small amount of Pd deposition. The sample was, however, relatively free of spinel accumulation.

Since there was a considerable increase in the amount of deposited RuO_2 , the frequency of melter floor sampling was increased and another sample was taken at 15 months into noble metal operations. This sample (I-MELT-4790) was just before the start of the feeding of the first batch of NCAW feed slurry. Micrographs of this sample revealed a dense layer of melt insolubles, mainly RuO_2 and $(\text{Ni}, \text{Mn})(\text{Fe}, \text{Cr})$ spinels (Figure 18). This sample also revealed the first evidence of Rh deposition on the melter floor (Figure 19). On sampling of this material, it was noted that there was an obvious layer on the melter floor that was much more viscous than the bulk glass. This viscous layer (of approximately 1-2 inches) has been obvious in every melter floor sample taken thereafter.

Another sample was then taken at 16.5 months into processing which was during the feeding of the HWVP1 melter feed slurry. This sample (H-MELT-0330, shown in Figure 20) again revealed significant RuO_2 and spinel accumulation and also individual metallic Pd. After the completion of the feeding of the HWVP1 melter feed, a sample was again taken of the melter floor (17 months). This sample, (H-MELT-0329) as before, revealed dense RuO_2 /spinel accumulation and scattered Rh accumulation.

A melter floor sample was taken after completion of the feeding of the HWVP2 material (19 months). This sample (I-MELT-4804) was chemically analyzed but not examined by the microscope. The chemical analysis (Table 8) revealed that the Ru, Rh, and spinel components (Cr, Mn, and Fe) had all decreased. This suggested that the noble metals and

spinel may have been "flushed" out of the melter or possibly rearranged on the melter floor. [22]

Figures 21 and 22 show plots of the concentrations of Cr, Ni (Figure 21) and Ru (Figure 22) during Hanford glass production (HWVP1 and HWVP2). One can see in Figure 21 that there is an abrupt increase in Ni and Cr (spinel components) between HWVP1 and HWVP2. This, along with SEM analysis and chemical analysis of melter floor (center) samples gives further support to the theory that the spinels were moved from the melter center to the outer edge and flushed out with the glass. However, although the RuO₂, it seems, was also moved from the center to the outside edge, it was not flushed. The concentration of Ru in the glass product decreased with the idling time between HWVP1 and HWVP2, thereby indicating settling of RuO₂ from the bulk melt and an increase in the concentration of RuO₂ on the melter floor. This apparent spinel flushing is not possibly advantageous with respect to increasing the lifetime of the melter. Since the spinels are not highly conductive, compared to the noble metal compounds, they may behave as insulators and increase the overall resistivity of the deposited material.

Another sample (I-MELT-5219) was taken at 19.5 months and is shown in Figures 23 - 25. This sample was the first taken through the borescope port. The sampling point was just at the face the bottom electrode which is closest to the riser throat entrance (see Figure 16). The SEM examination revealed that, like I-MELT-4804, there was much less of an accumulation of spinels than in previous samples. Chemical analysis confirmed that the spinel components (Cr, Fe, etc.) were indeed lower than previous samples. However, the concentration of ruthenium was much higher (9 wt%) than in previous samples. This further confirmed that the spinels had been "flushed" out while the RuO₂ was merely swept from the center of the melter to the outside of the melter floor. Figure 23 shows the normal RuO₂ clusters, Rh-nucleated Cr/Ni/Fe spinel, and an elongated formation of ruthenium disulfide, RuS₂, a compound which decomposes at temperatures > 1000°C. Figure 24 shows a relatively large mass of metallic palladium. Figure 25 reveals the presence of rhodium in this sample. The presence of RuS₂ in this sample was quite surprising. Since this compound decomposes at temperatures > 1000°C [4], one can assume that the temperatures at the outside portion of the melter may have been <1000°C despite the fact that the bulk glass temperature was held at 1100 - 1150 °C.

Another floor sample (I-MELT-5242) was then taken from the center of the melter (feed tube port) at 20 months. This sample, shown in Figure 26, revealed large masses of deposited material, mainly RuO₂ and spinels.

The next sample (I-MELT-5270) was taken from the borescope port of the melter at 21 months. This sample showed a dense accumulation of noble metals and spinels and again confirmed the presence of RuS₂. The analysis of this sample, as shown in Table 8,

confirmed the increase in spinel components (especially Cr). Representative micrographs are shown in Figure 27.

Table 8 shows the amounts (in wt%) of selected components in each melter floor sample (analyses by ICP-AES/Sodium Peroxide Fusion-HCl uptake). These results suggest a non-uniform layer of noble metals (mainly RuO₂) and Ni/Fe/Cr spinel on the melter floor. The samples analyses which have been shaded are those which have been taken from the borescope port. Analysis of these samples have consistently revealed a higher concentration of Ru as compared to the samples taken from center of the melter. This suggests that the convective currents in the melter tend to "push" the RuO₂, spinels and other melt insolubles from the center of the melter (where they enter) to the outside edges. Also, these convective currents may not be the same during periods of idling since an extreme temperature gradient (the cold cap) is no longer present. This may help to explain the apparent flushing of crystalline spinels from the melter.

The accumulation of RuO₂ and Rh/Pd/Te is consistent with what has been demonstrated in waste vitrification simulations in Germany. [28] However, in melter floor samples taken from a research melter in Karlsruhe, Germany, the RuO₂ needles were much more acicular and perfectly formed. The RuO₂ crystalline growth in SRS, Hanford, and West Valley [16] glasses and cold cap samples appear to be inhibited by the glass itself. This may be explained by the fact that glass beads are used as the primary glass forming additive in German tests while tests conducted in the IDMS facility and the West Valley SFCM used a finely ground glass frit and batch chemicals. It has been suggested that RuO₂ crystals are initially formed in the melter cold cap via Ostwald ripening. Ostwald ripening may occur when a large number of crystallites differing in size are present and is characterized by simultaneous growth and dissolution of crystals in order to minimize surface free energy. The "large" voids are present between the glass beads of the German slurry feed allowing unhindered growth of the RuO₂ crystals in the cold cap. Alternatively, the frits used in US melters soften at lower temperatures than the German glass beads and eliminate the voids in the cold cap thus hindering the growth of the RuO₂ crystals.

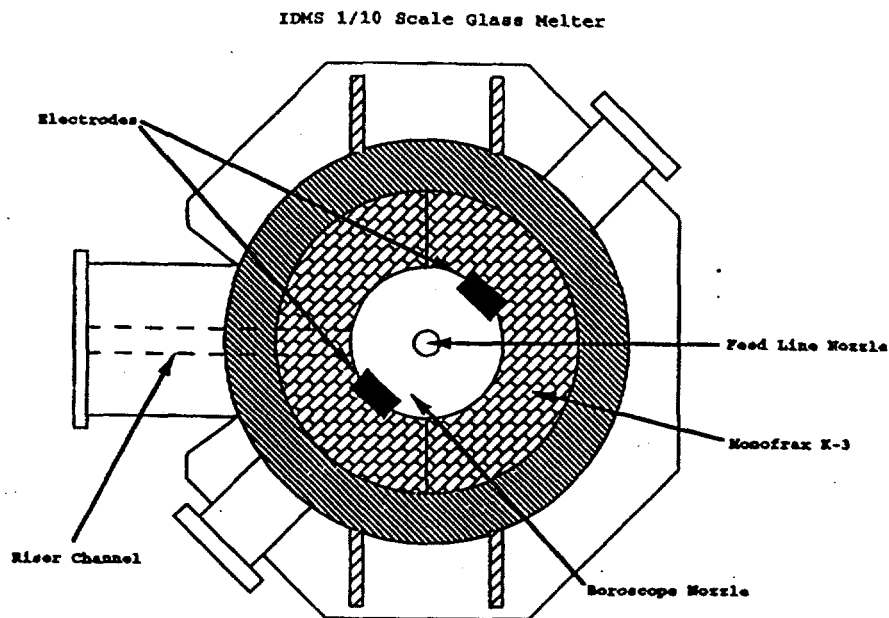


Figure 16. Top View of IDMS Melter Showing Points of Melter Floor Sampling

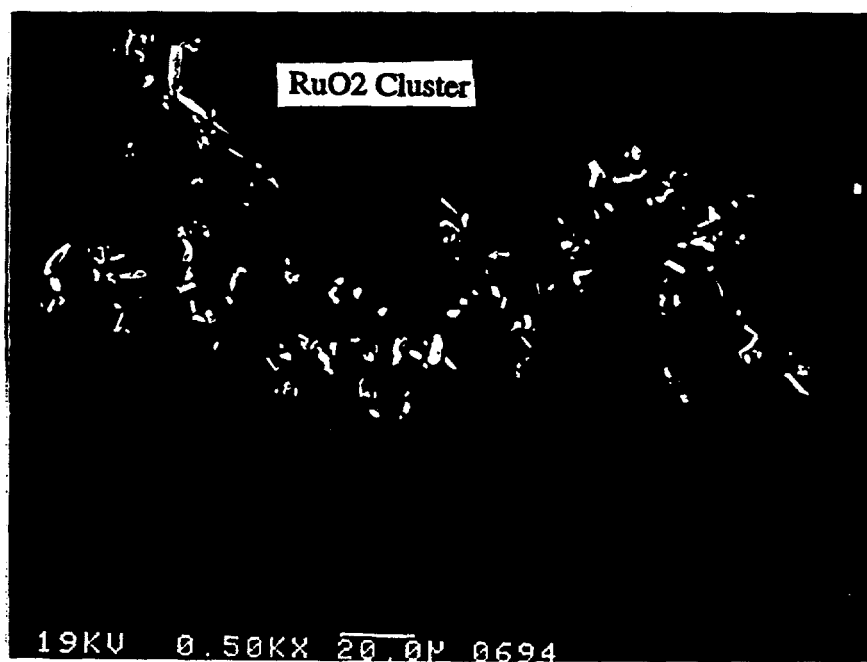


Figure 17. IDMS Melter Floor Sample (I-MELT-4312) taken 8/23/91

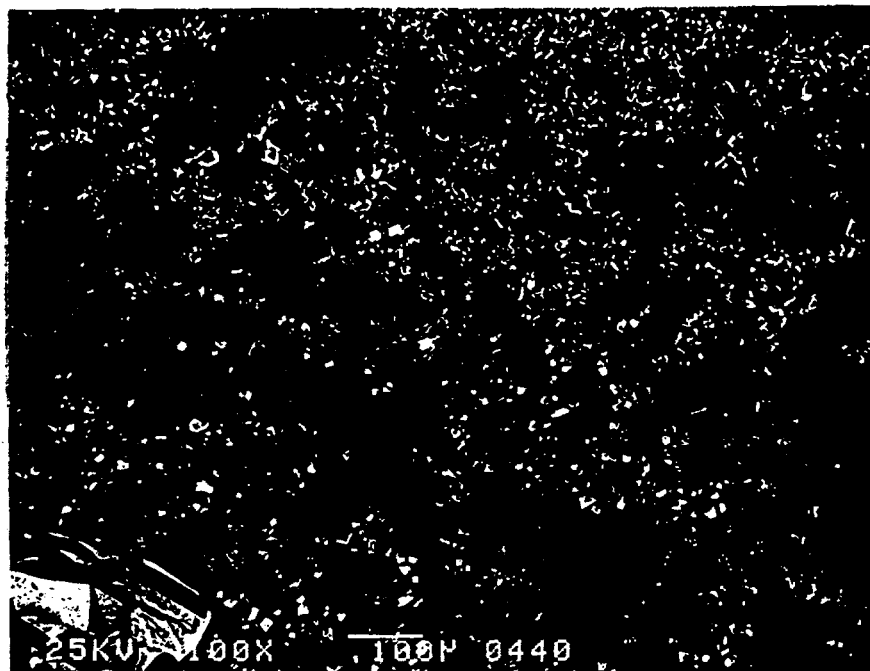


Figure 18. IDMS Melter Floor Sample (I-MELT-4790) taken 10/15/91

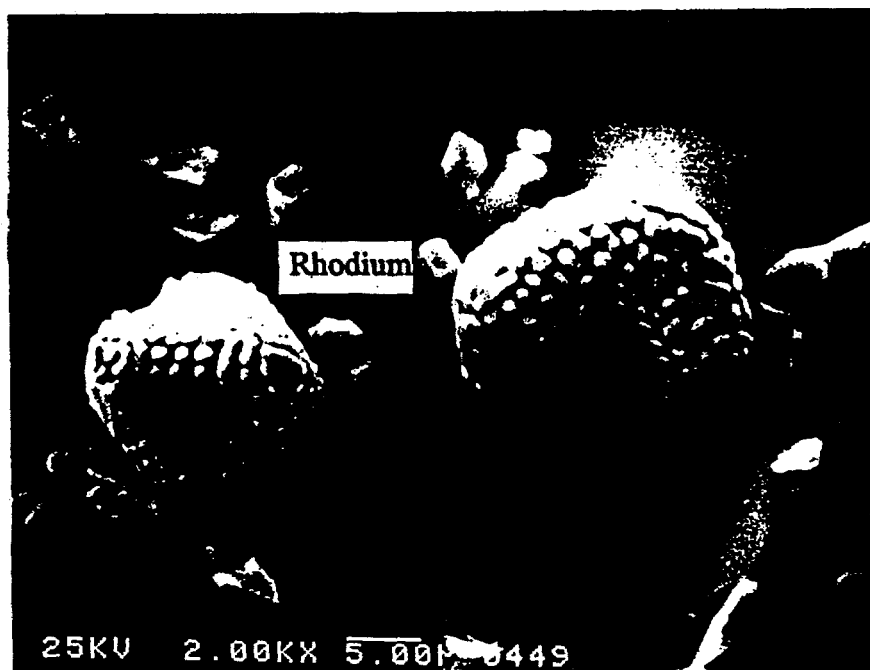


Figure 19. IDMS Melter Floor Sample (I-MELT-4790) taken 10/15/91

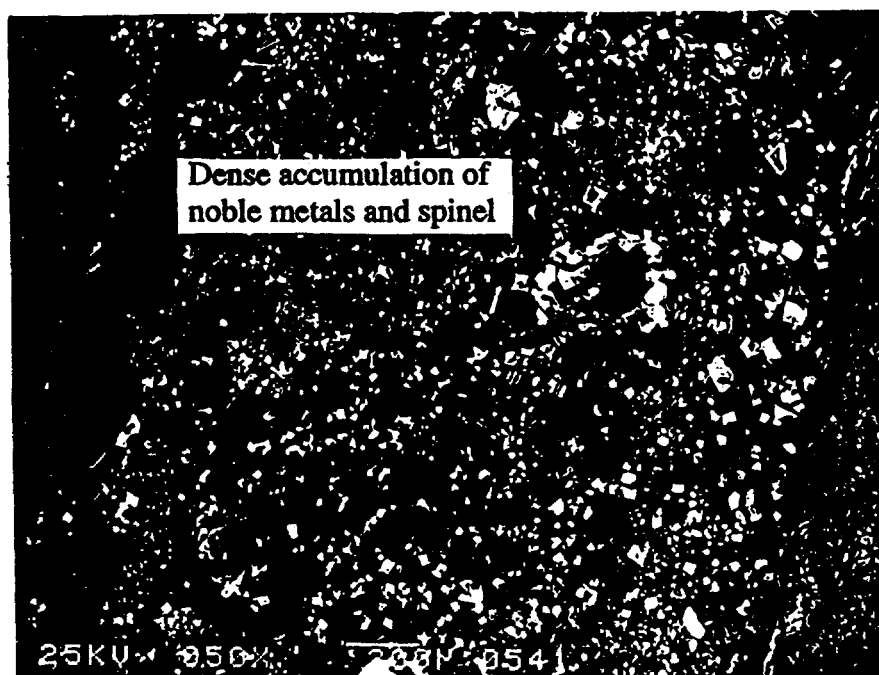


Figure 20. IDMS Melter Floor Sample (H-MELT-0330) taken 12/4/91

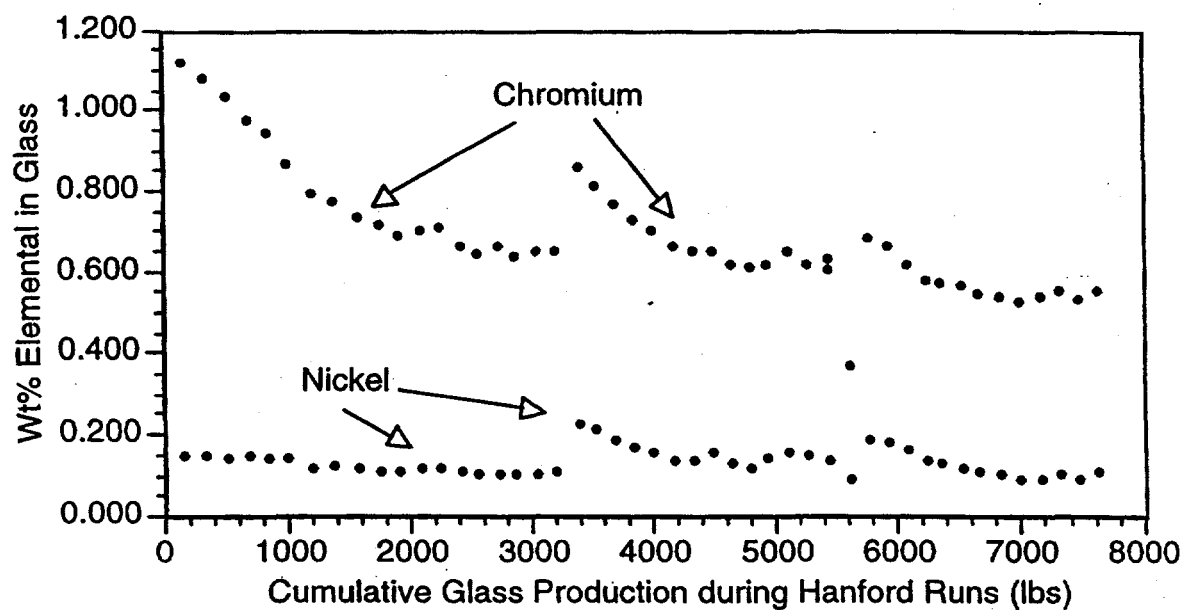


Figure 21. Spinel Components (Cr and Ni) in Canistered Glass during Hanford Runs

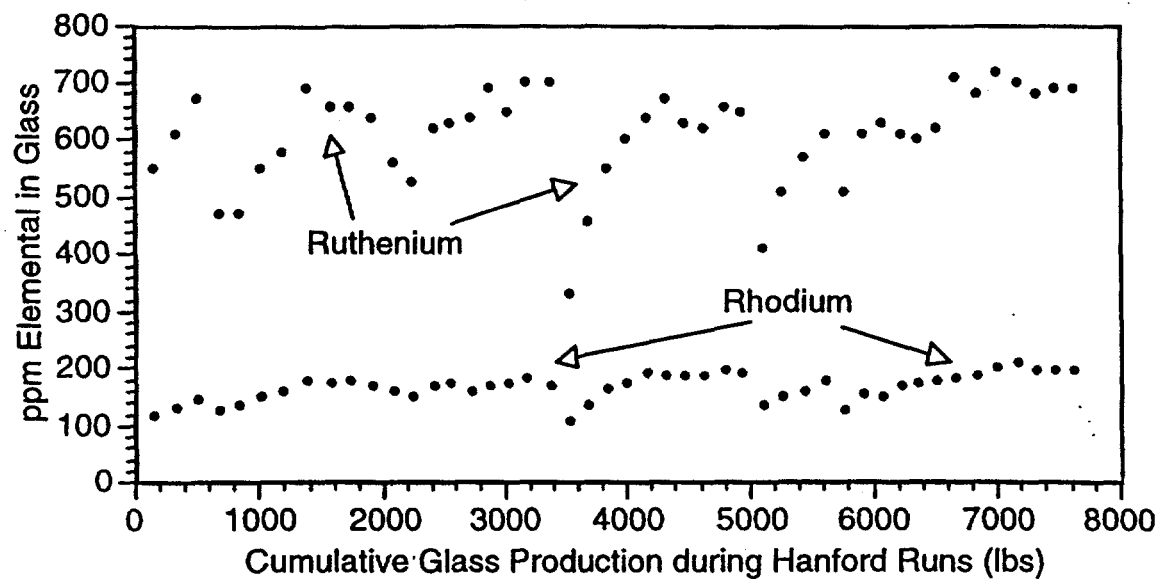


Figure 22. Ruthenium in Canistered Glass during Hanford Runs

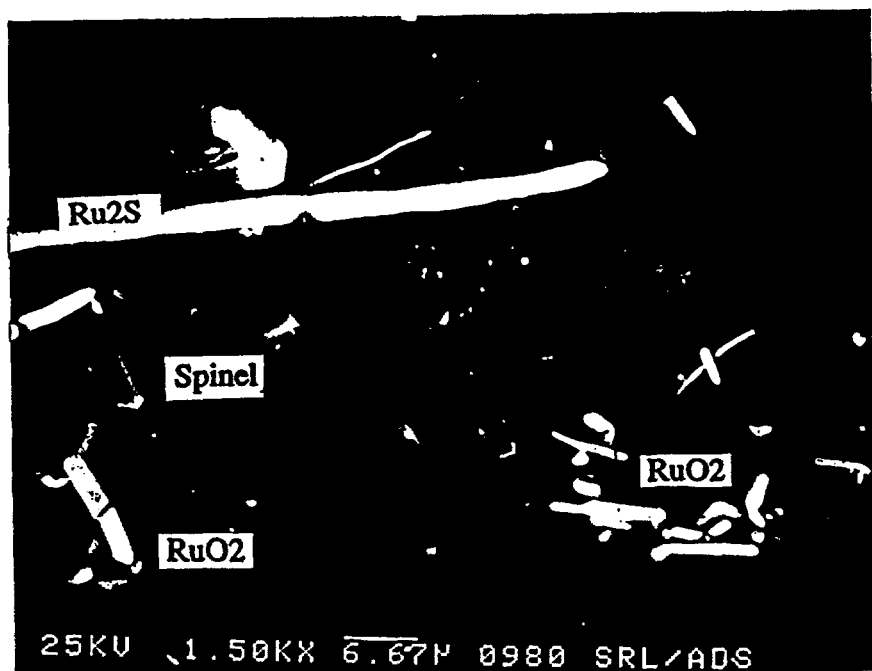


Figure 23. IDMS Melter Floor Sample (I-MELT-5219) taken 3/6/92

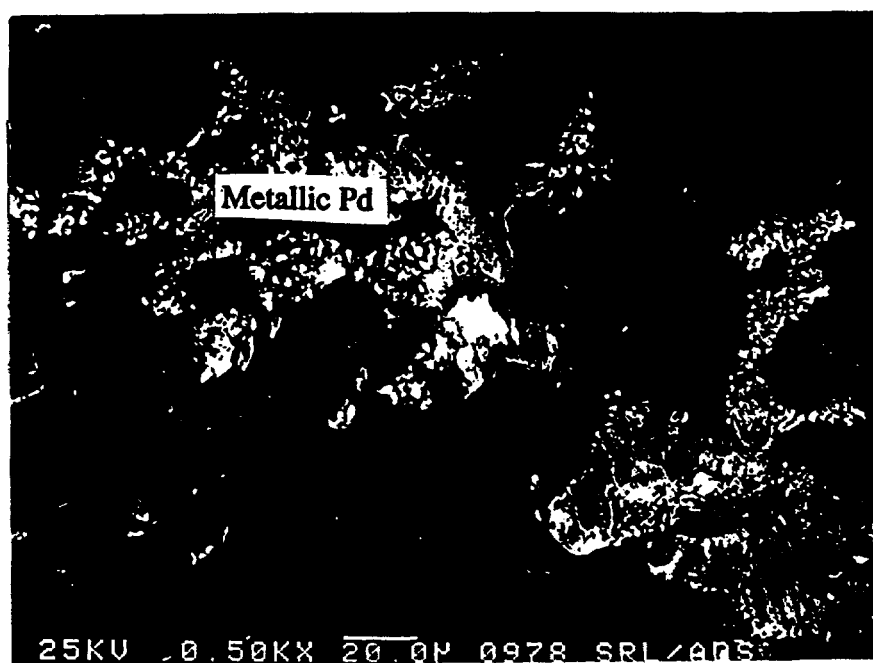


Figure 24. IDMS Melter Floor Sample (I-MELT-5219) taken 3/6/92



Figure 25. IDMS Melter Floor Sample (I-MELT-5219) taken 3/27/92

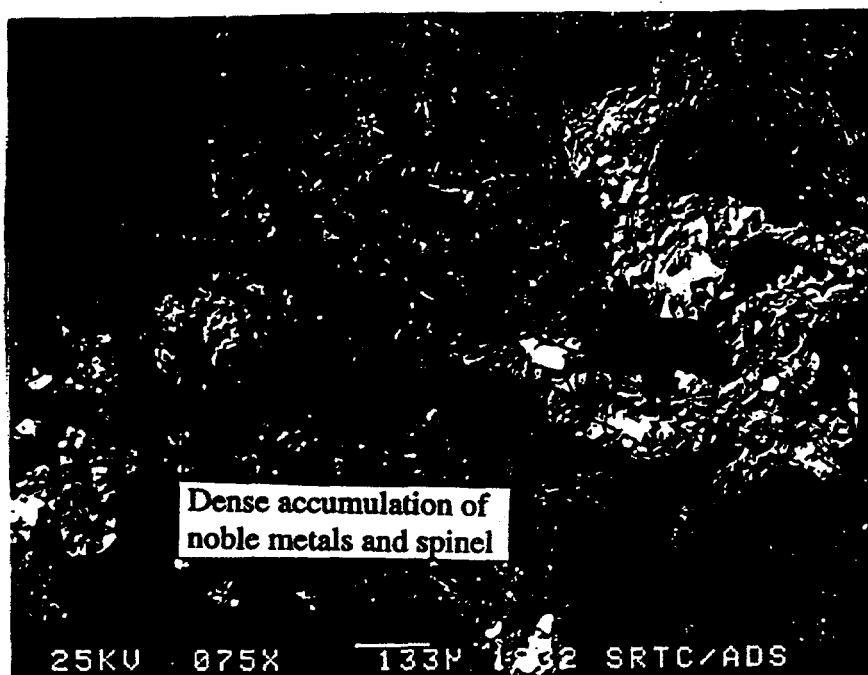


Figure 26. IDMS Melter Floor Sample (I-MELT-5242) taken 3/27/92

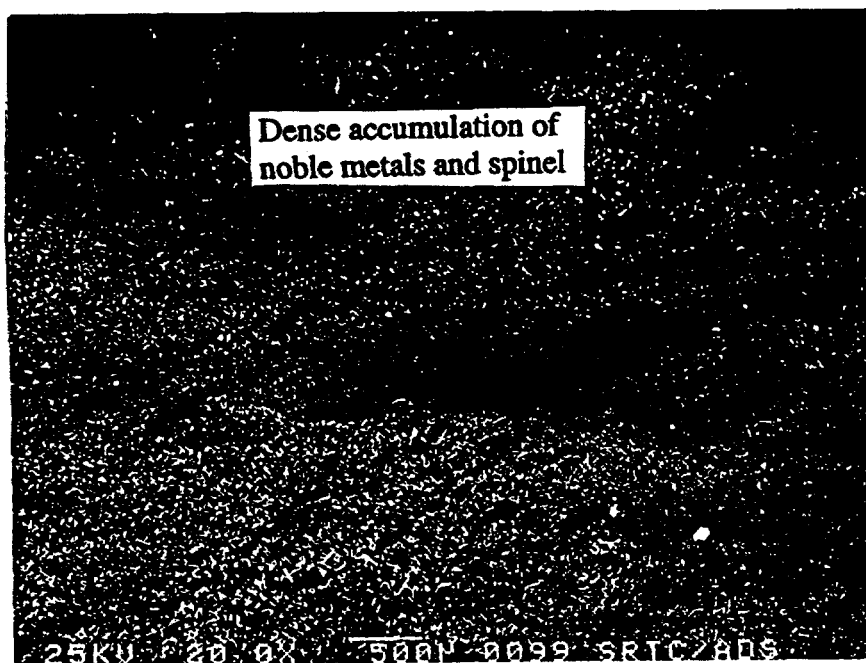


Figure 27. IDMS Melter Floor Sample (I-MELT-5270) taken 4/20/92

	I-MELT- 3701	I-MELT- 4313	I-MELT- 4790	H-MELT- 0330	H-MELT- 0329	I-MELT- 4804	I-MELT- 5242	H-MELT- 5710	I-MELT- 6670	H-MELT- 7220	I-MELT- 8228A	H-MELT- 8228B	I-FED- 928/94
Ag	275/91	8/23/91	10/15/91	12/4/91	12/18/91	2/18/92	3/27/92	5/20/92	10/29/92	12/2/92	9/28/94	9/28/94	9/28/94
WT %		0.005	<0.01	<0.01	0.017	0.030		<0.01	0.030	<0.01	<0.018	<0.021	<0.021
Al	2.700		2.858	2.884	1.350	1.200	1.430	2.630	1.440	0.230	1.580	1.290	1.290
B	2.090		1.876	2.220	2.545	3.420	3.510	2.560	2.030	0.190	2.340	1.850	1.850
Ba	0.110		0.123	0.095	0.059	0.050	0.050	0.130	0.070	0.050	0.064	0.052	0.052
Ca	0.540		0.897	0.601	0.372	0.330		0.530	0.530	0.530	0.424	0.538	0.538
Cd			<0.01	0.196	0.440								
Ce			<0.01	<0.01	0.025	0.510		1.840	0.250	0.220	0.499	0.458	0.458
Cr	0.100		0.816	3.193	3.404				0.059	0.020	<0.54E-2	<0.53E-2	<0.53E-2
Cs	0.010		0.060	0.030	0.060	0.060		0.060	0.246	0.260	0.144	0.184	0.184
Cu	0.140		0.184	0.181	0.129				6.400	0.260	5.990	4.670	4.670
Fe	8.140		8.890	11.080	9.006	4.350	4.390	5.210	2.006	0.260	1.420	1.810	1.810
K	1.659		1.821	1.245	0.523					0.260			
La			<0.01	<0.01	<0.01	1.940	2.310	1.950	2.110	0.260	2.180	1.660	1.660
Li	2.050		1.836	1.853	1.797				1.000	0.260	0.963	0.763	0.763
Mg	0.810		0.759	0.753	0.349	0.160		0.750	1.180	0.260	0.858	1.140	1.140
Mn	1.650		2.447	2.521	1.229	0.430		0.250		0.260			
Mo			<0.01	0.032	0.054	4.800		5.330	6.160	0.260	5.600	7.220	7.220
Na	7.387		6.744	5.457	4.361			5.330	0.300	0.260	<0.030	<0.030	<0.030
Nd	<0.05		0.127	0.448	0.838	0.740	0.980	0.710	0.840	0.260	1.010	1.330	1.330
Ni	0.630		1.812	1.212	1.065	0.610		1.160	0.030	0.260	<0.51	0.053	0.053
P	<0.05		0.021	0.020	0.030			0.530	0.120	0.260	0.077	0.097	0.097
Pb	0.090		0.222	0.201	0.157			0.158	0.330	0.260	<0.136	<0.136	<0.136
Pd		0.034	0.065	0.023	<0.01	1.010		<0.01		0.260	0.373	1.410	1.410
Rh		0.007	0.405	0.029	0.302	0.930		0.210	0.460	0.260	4.220	15.600	15.600
Ru	<0.01	0.019	4.682	0.418	6.202	7.330	5.530	1.160	4.730	0.260			
Se			0.017	0.010	<0.01				15.450	0.260	23.800	18.400	18.400
Si	27.870		17.800	16.000	14.900	19.900	15.230	17.100		0.260			
Sn			0.016	0.026	0.024				0.010	0.260	0.009	0.011	0.011
Sr	0.050		0.048	0.032	0.027	0.030		0.030		0.260			
Te			<0.01	<0.01	<0.01				0.160	0.260	0.091		

NOTE: Shaded samples taken from borescope port, non-shaded samples taken from feed port (center of melter).

5.2 Noble Metals Material Balance

5.2.1 Analytical Measurements

In order to complete a meaningful material balance of the noble metals in the melter system (*i.e.* in order to determine the extent of deposition), accurate analytical measures of the noble metals must be made in the glass product and melter feed slurry. This has proven to be a very challenging task. Several methods have been used to determine the concentration of noble metals in the melter feed slurry and glass. These have included:

- ICP-AES (Aqua Regia Dissolution)
- ICP-AES (Na_2O_2 Fusion/HCl Dissolution)
- ICP-AES (Microwave Acid Dissolution)
- ICP-MS (Aqua Regia Dissolution)
- XRF (X-Ray Florescence)

While ICP-AES and ICP-MS are both excellent analytical tools, their effectiveness is highly dependent upon the type of sample preparation used. The aqua regia and microwave acid procedures proved to be ineffective in the dissolution of the noble metals (especially RuO_2), and spinels. The sodium peroxide fusion procedure is a very aggressive method and proved to be adequate for getting all components into solution. The results of the ICP-AES (Na_2O_2 /HCl prep) determinations agreed quite well with those obtained by XRF. However, with both of these analyses, one must carefully analyze a matrix-matched noble metal blank along with the samples of interest. The blank results are then used to correct the raw results from the process samples.

A contract was established with an outside analytical laboratory (Monarch Analytical Laboratories, Inc.). Monarch measured the Ru, Rh, and Pd by ICP-AES for glass samples from glass from every canister filled during the noble metals runs. The analytical solutions were prepared by dissolving the glass matrix in aqua regia and separating the Ru, Rh, and Pd by carrier precipitation with copper as the insoluble sulfides. The separated sulfides were then fused with sodium peroxide in zirconium crucibles and dissolved in hydrochloric acid. The resulting solution contained all of the platinum metals but was free of the matrix elements. The solution for tellurium analysis was prepared similarly with excess selenium being used as precipitating agent. Plots of the Monarch analyses versus production time are given in Figures 28 - 30. When one examines the analyses plotted versus production time, it is obvious that the noble metal concentrations increase with continuous feeding, approaching the target concentration. However, the concentration decreased significantly during periods of idling (non-feeding time periods).

5.2.2 Material Balances

Plots of the cumulative amount of noble metals fed to the melter and the cumulative amount exiting the melter with the glass versus glass production are shown in Figures 31 - 33 (amount of the metals fed to melter based on melter feed analyses). Figure 31a shows that approximately 35% of the ruthenium fed to the melter is retained in the melter as deposits on the melter floor. Similarly, Figure 31b shows that approximately 21% of the rhodium fed to the melter is retained. Figure 32a suggests that palladium is fully removed from the melter. However, melter floor samples prove that this is not the case. However, except in a few samples, the Pd found on the melter floor has been present as very small (1 μ m) particles and very dispersed. This, along with other analytical measurements, suggest that <10% of the Pd fed to the melter is retained in the melter. Figures 32b and 33a show mass balance calculations for tellurium and selenium. Since these compounds are quite frequently found alloyed with palladium, one would expect that they would be retained in the melter in a similar extent as Pd. This is the case with Te (at 15% retained). However, the Monarch analyses suggested that 43% of the Se which was fed to the melter was retained within the melter. This is not likely. This is more likely a result of the difficulty to analytically measure this compound (especially in the <25 ppm range). Figure 33b shows that, as expected, no silver is retained in the melter as the silver is readily incorporated into the borosilicate glass. No silver or silver compounds have ever been found on the melter floor.

Since the Monarch measurements provide the most extensive analytical data, they have been presented here. However, several analytical methods have been used to measure the noble metals in glass; and, while the analyses may not always agree on the absolute amount of Ru, Rh, etc. in a sample, with each analytical method the tendency is for the noble metals to be retained in the melter in the following relative amounts: Ru > Rh >> Pd > Ag.

5.2.3 Discharge Efficiency

The discharge efficiency of each of the noble metals, Se, and Te are shown in Figures 34 - 36. The discharge efficiency is defined as:

$$\text{Discharge Efficiency (\%)} = \frac{\text{Amount of NM exiting the melter}}{\text{Amount of NM fed to the melter}} \times 100$$

NOTE: "Amount of NM fed to melter" based on IDMS Melter Feed Tank analyses.

The discharge efficiencies of Rh, Pd, and Ag, at times, exceed 100%. This can be explained by the fact that these measurements were made when the concentrations of the noble metals, etc. were at "Blend" levels. These lower concentrations are more difficult to measure and are thus more subject to error. Additionally, this calculation assumes that the noble metals in the glass are homogeneously distributed within the glass and therefore may be another source of error.

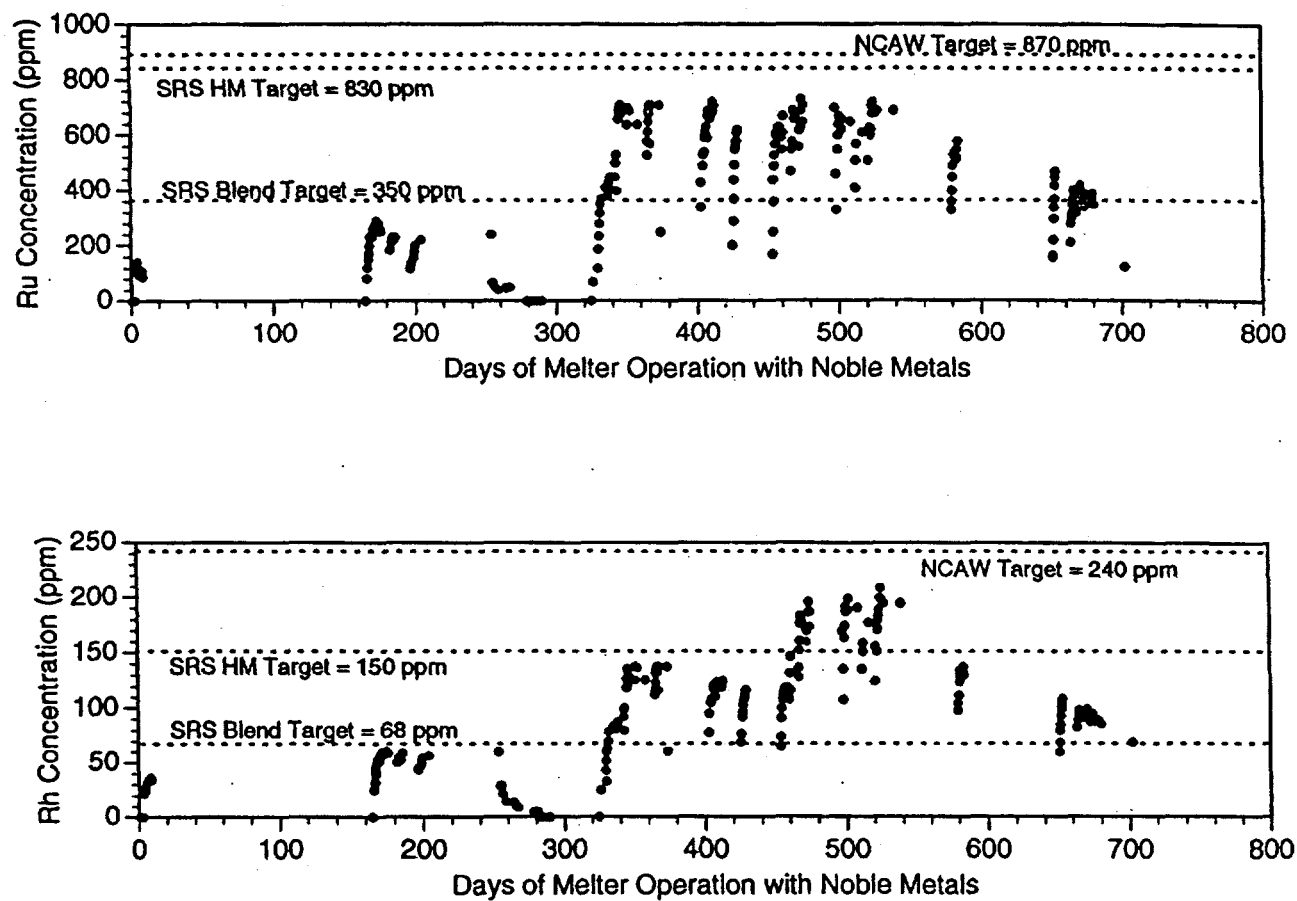


Figure 28. Ru and Rh Analyses with Glass Production

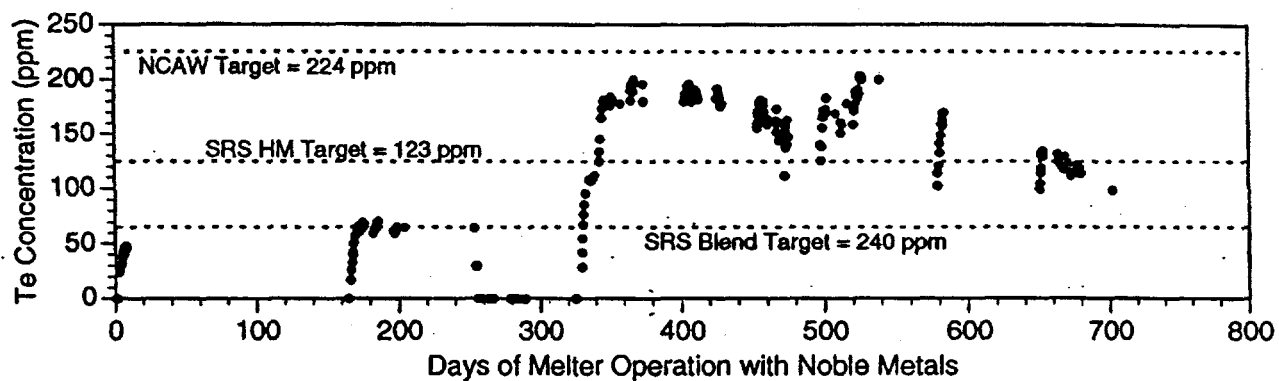
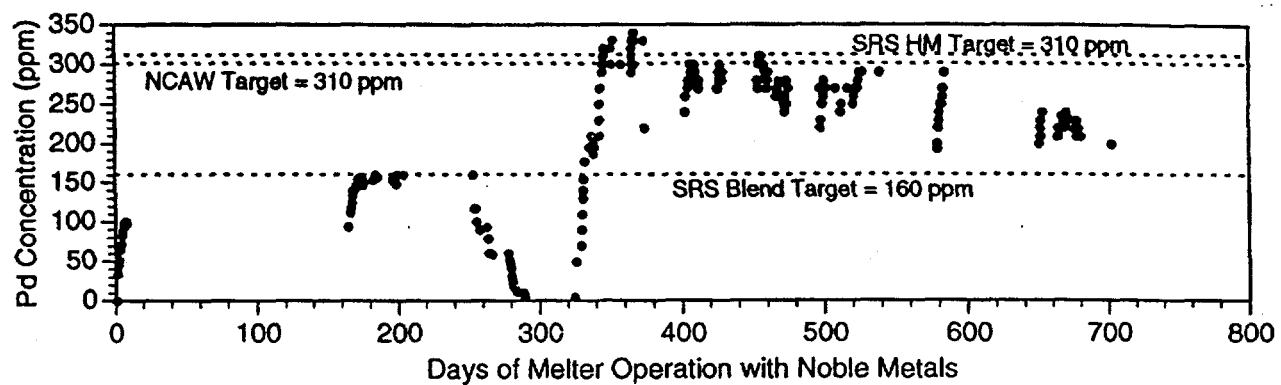


Figure 29. Pd and Te Analyses with Glass Production

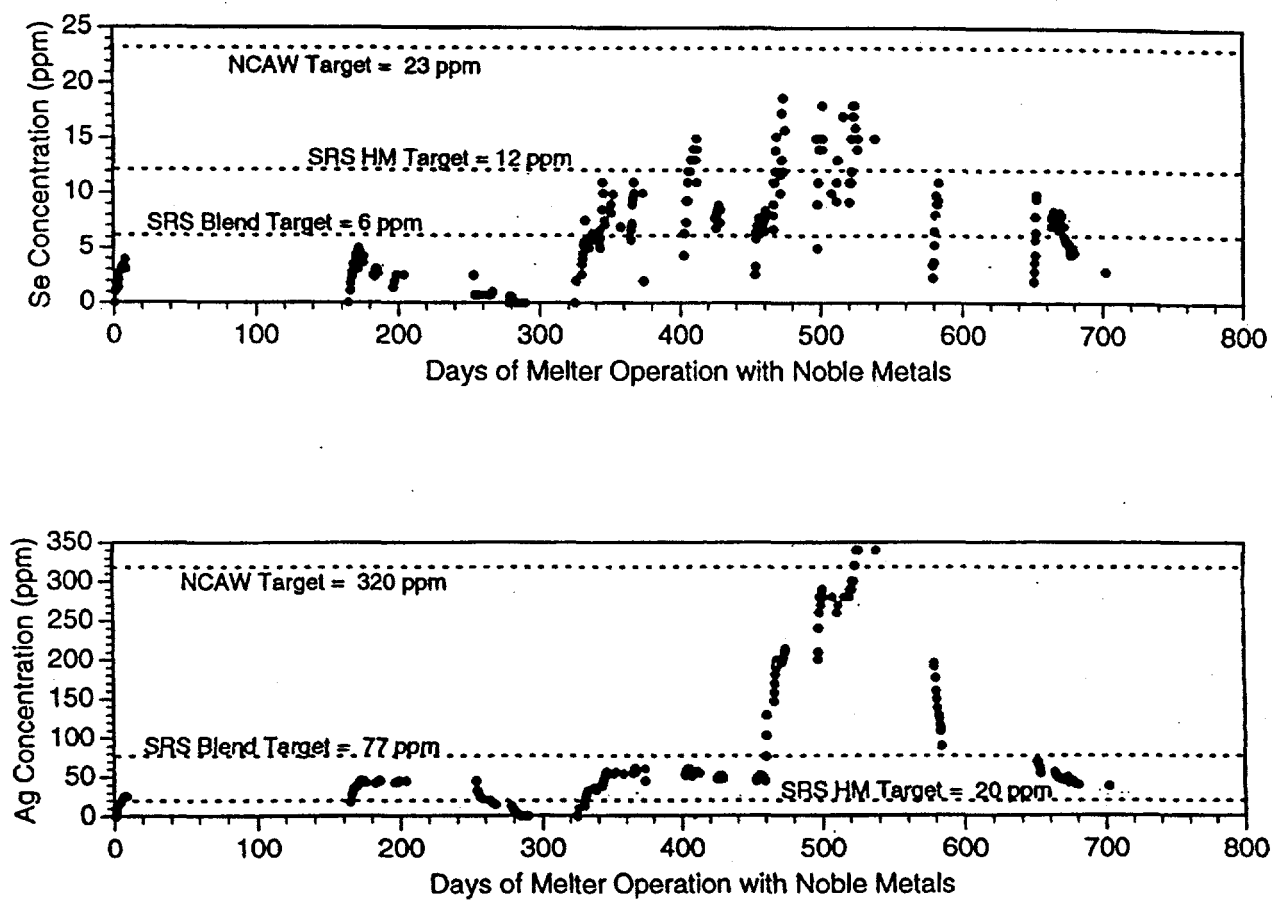


Figure 30. Se and Ag Analyses with Glass Production

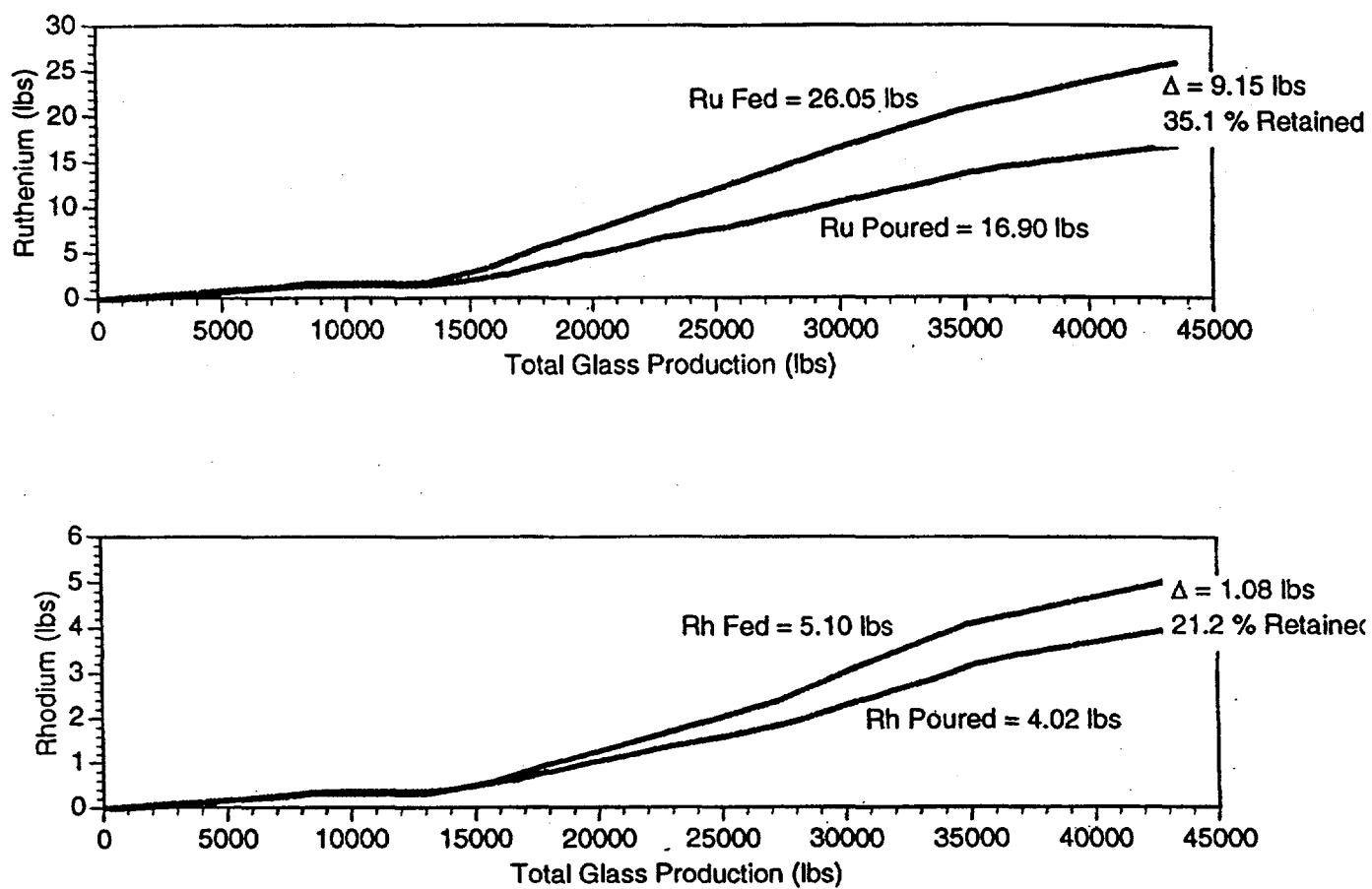


Figure 31. Ru and Rh Overall Material Balance

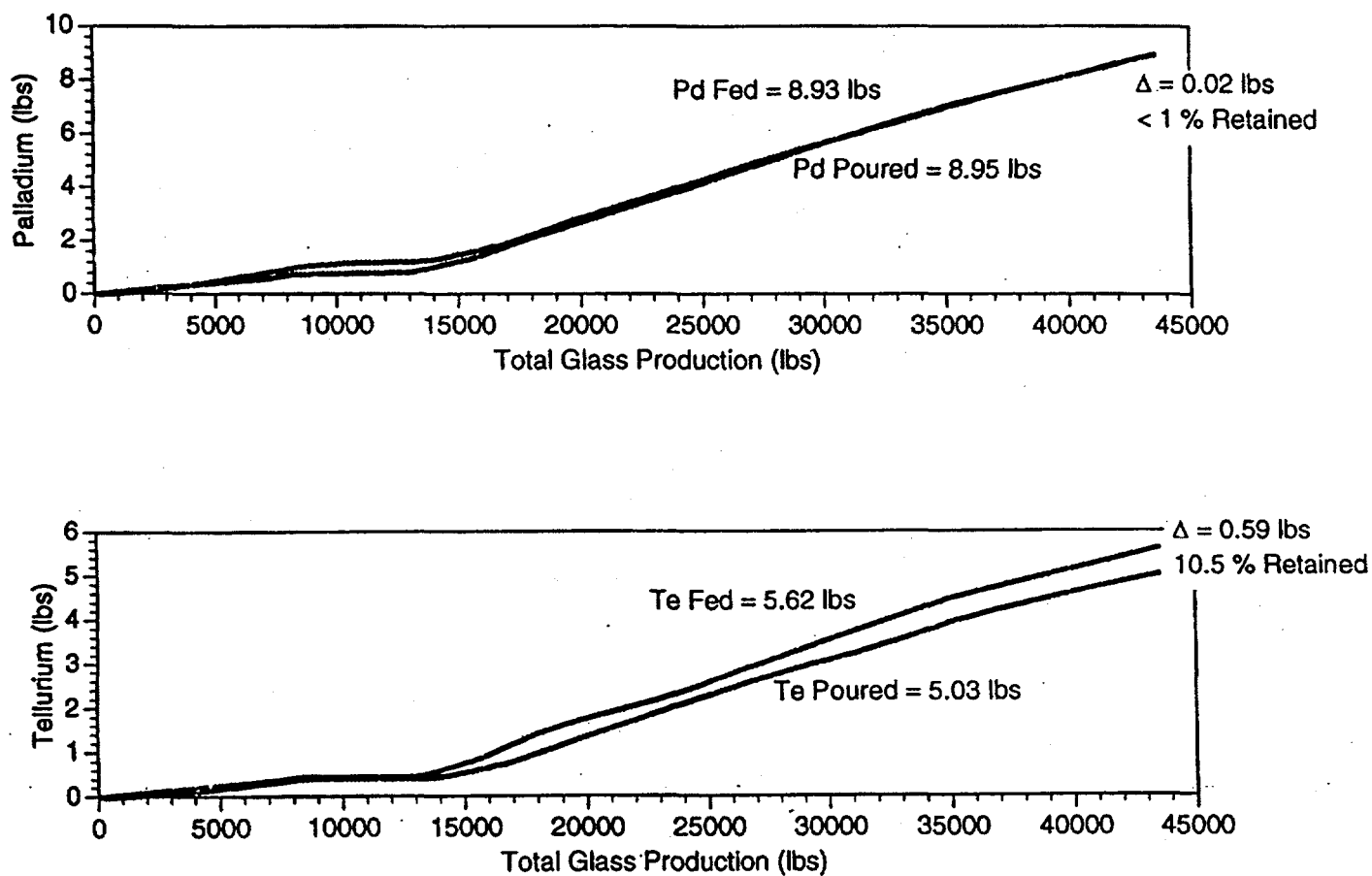


Figure 32. Pd and Te Overall Material Balance

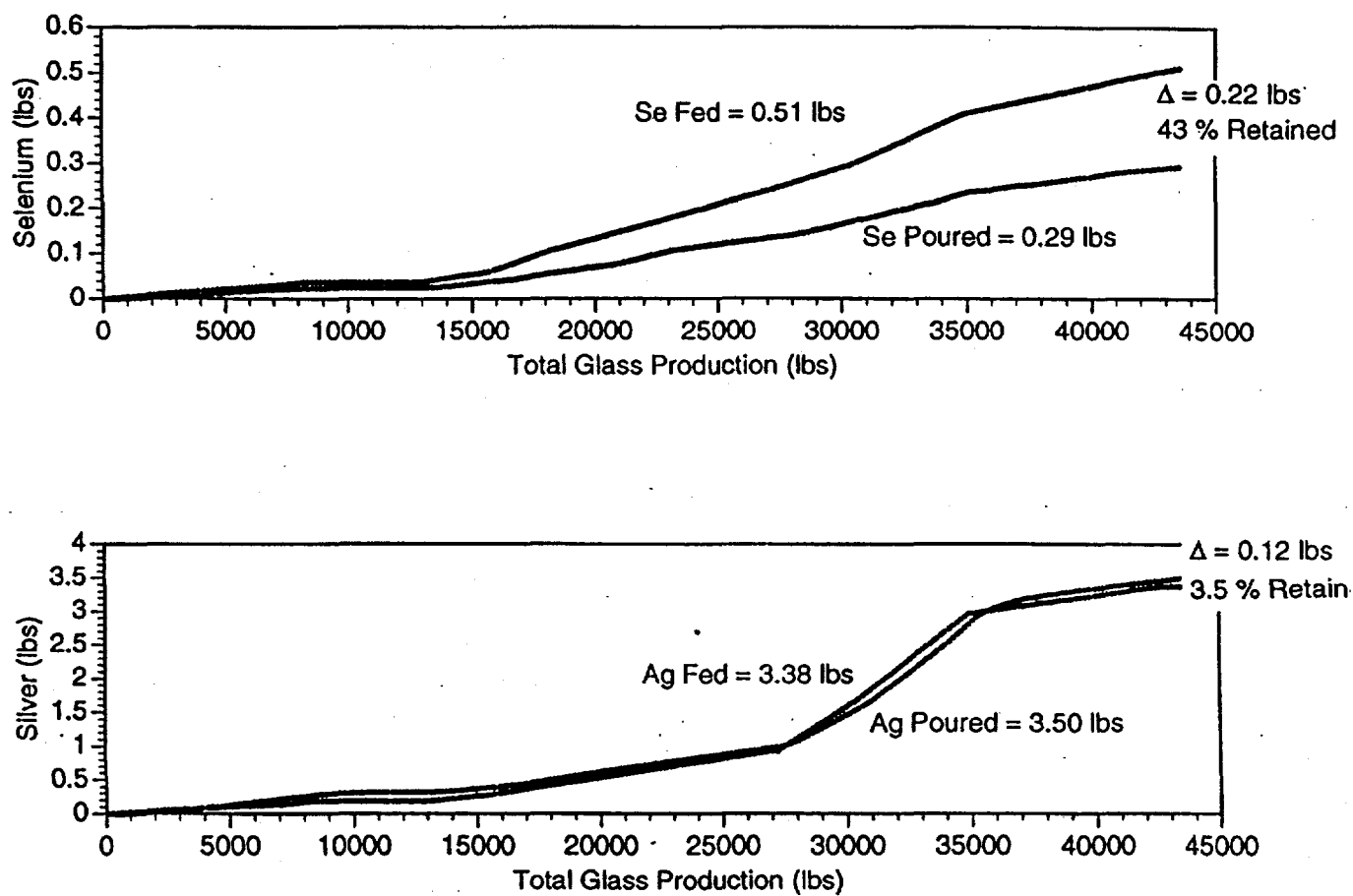


Figure 33. Se and Ag Overall Material Balance

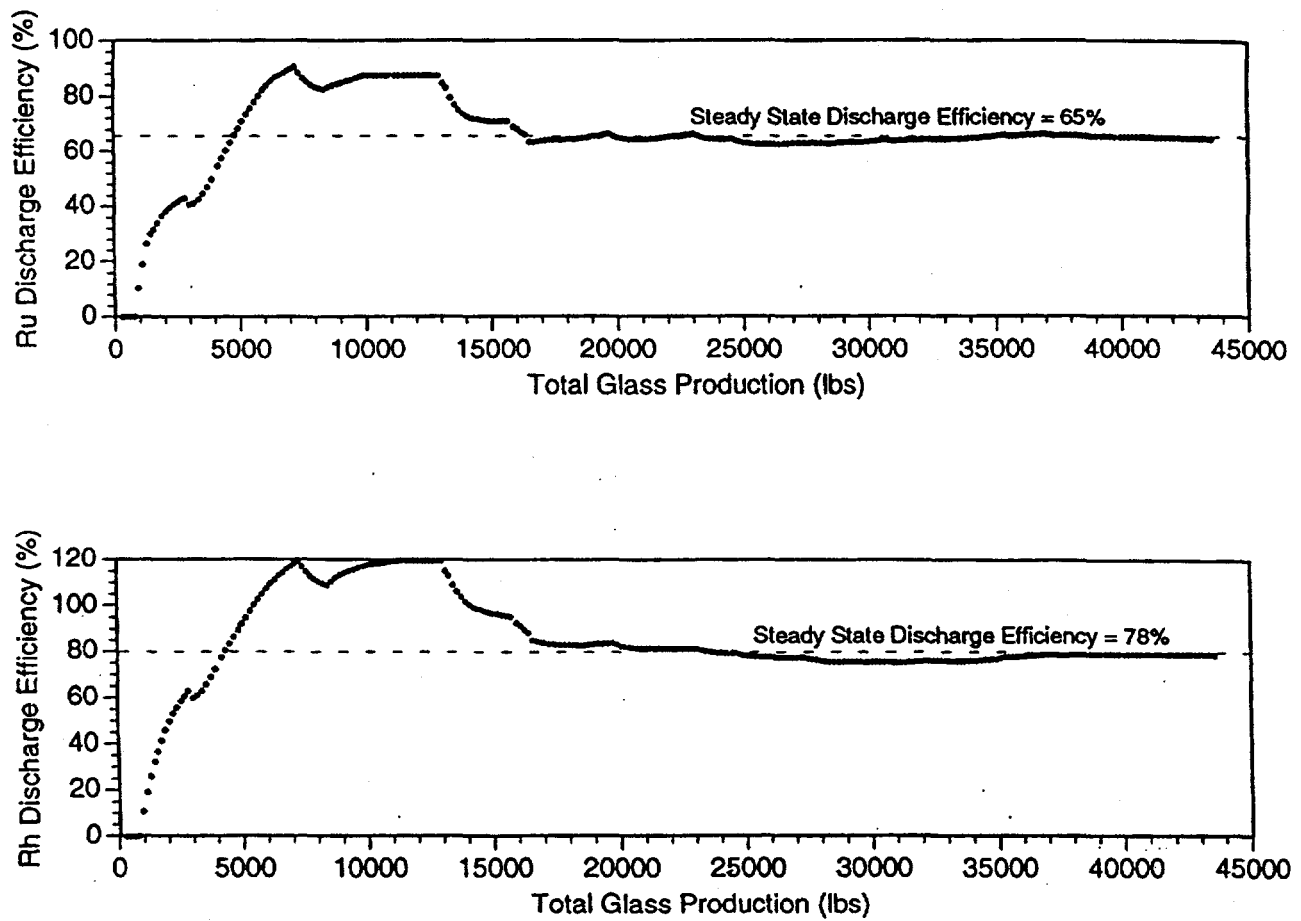
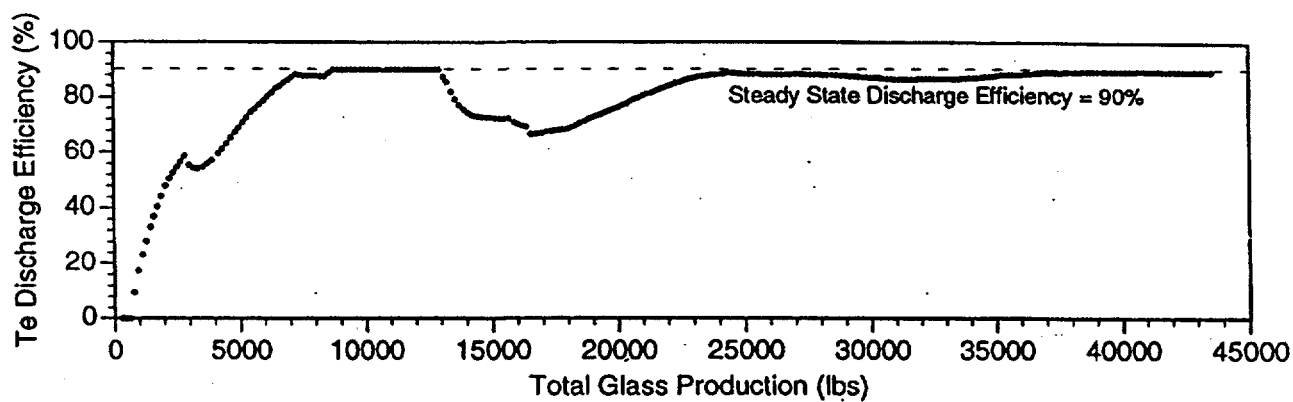
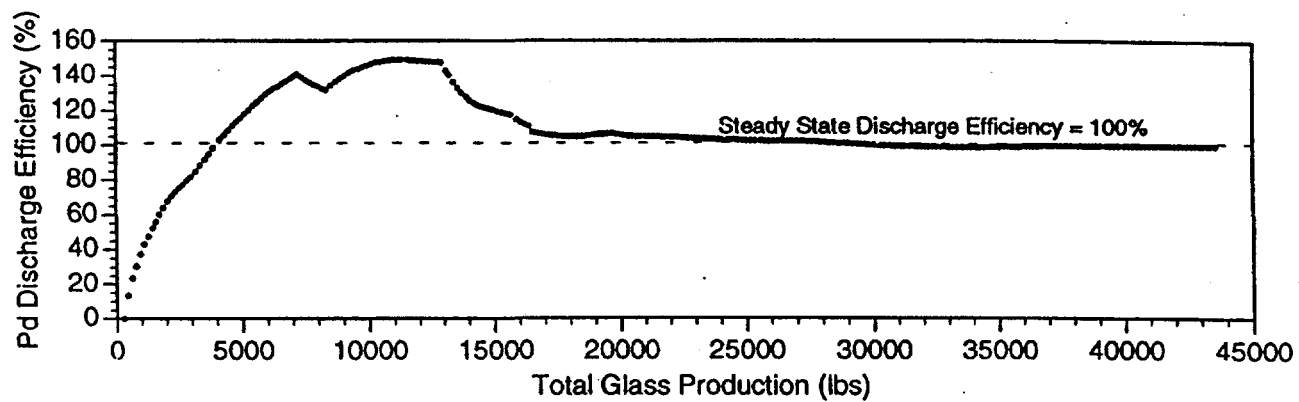


Figure 34. Ru and Rh Discharge Efficiency



INFORMATION ONLY

Figure 35. Pd and Te Discharge Efficiency

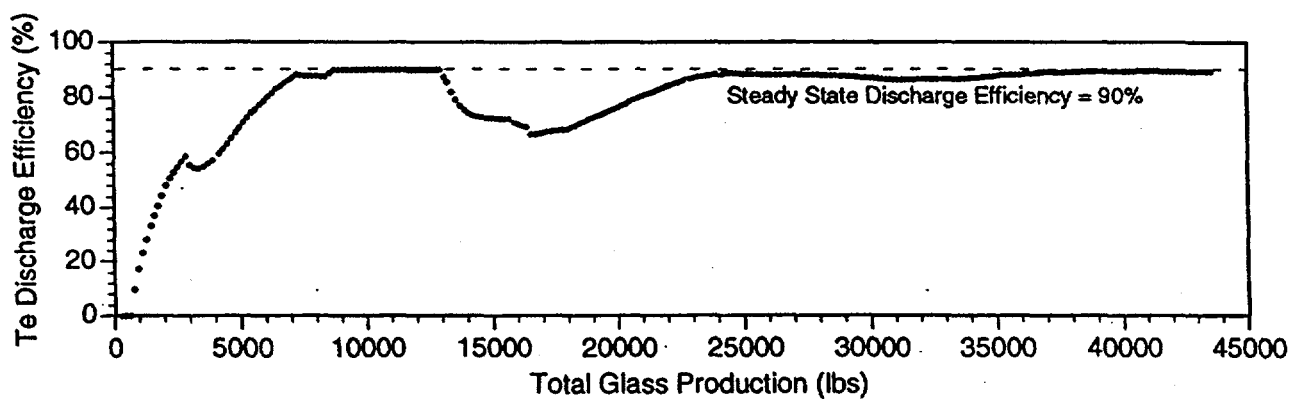
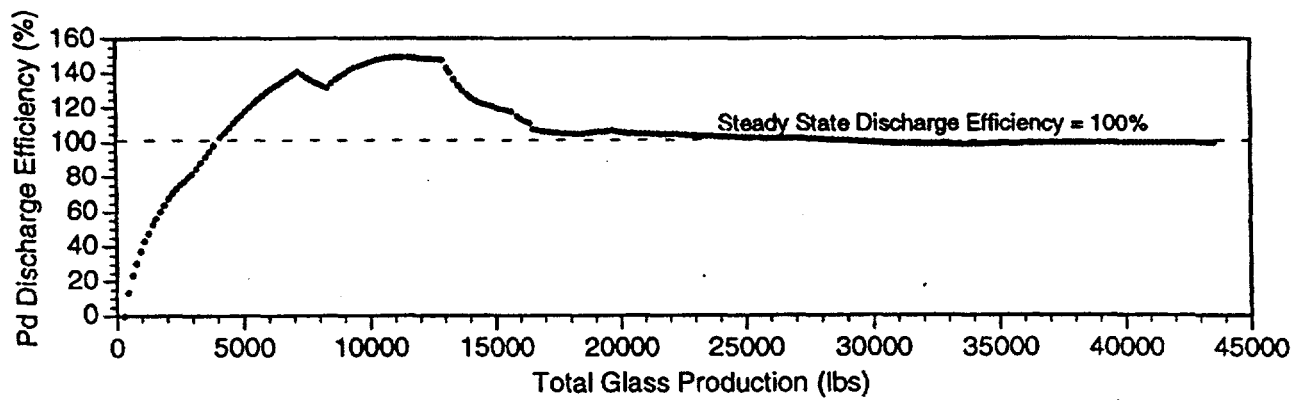


Figure 36. Se and Ag Discharge Efficiency

5.3 The Effects of Idling and Natural Convection

5.3.1 The Effects of Idling in the IDMS Melter

Figure 37 shows a plot of cumulative glass production in the IDMS versus operating time from 8/90 to 8/92. This Figure distinguishes between periods of feeding (glass production) and non-feeding (idling). During this two year period, the IDMS melter was fed for 2900 of 17561 hours. This corresponds to an on-line efficiency of approximately 17% (or was idled for 83% of the time).

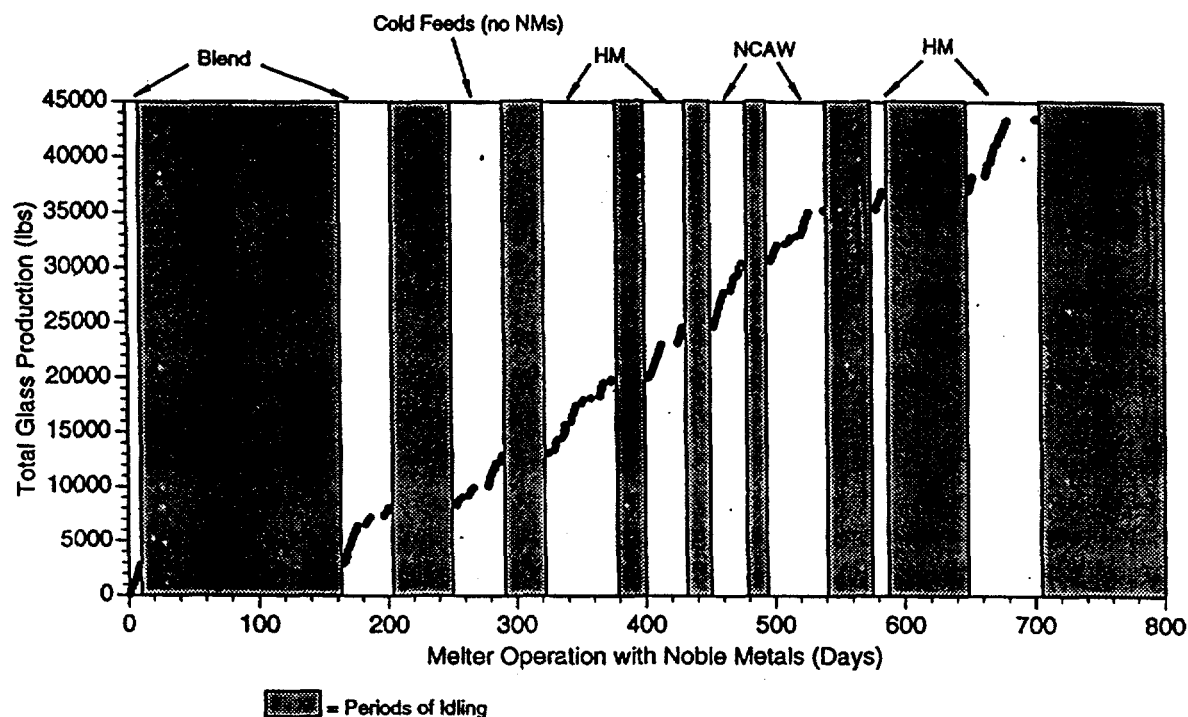


Figure 37. IDMS Cumulative Glass Production

There are several things that contributed to this seemingly large idling time:

- the measurement of hydrogen as a feed preparation offgas product caused a 21 week delay in the operation while safety analyses and facility upgrades were completed.[19]
- the noble metal catalyzed decomposition of formic acid resulted in a corresponding increase in the waste simulant pH and the release of ammonia gas, another safety concern.[29]
- the relatively high pH of the melter feed slurries containing noble metals were much more difficult to process because of degraded rheological properties.

- normal downtime associated with Research and Development activities (evaluation and reporting of data). etc.

It was not known to what extent idling would affect the settling of the melt insolubles in the melter. The Germans had noted that changes in the electrical resistivity in the glass pool were especially obvious during extended periods of idling. It has been suggested that the convective currents that are present during slurry feeding are sufficient to keep the noble metal particles suspended. The suspended noble metals then exit the melter as inclusions in the glass product. However, during periods of idling these convective currents are relatively minor which may allow the particles to settle to the melter floor.^[13] In Figures 28 - 30, one can see that the concentrations of the noble metals (esp. Ru and Rh) decreased significantly during periods of idling and sharply increases, toward the target concentration, during periods of continuous feeding. This indicates that most all of the deposition takes place during periods of idling.

The settling of the noble metals, spinels, etc. has been hypothesized to be similar to a typical sedimentation/thickening of a flocculation. Flocculations tend to be complicated structures (as are the melt insolubles) which initially settle in either free or hindered settling. The usual settling equations apply in principle; however, it is not practical to quantitatively apply the settling laws directly because the diameter and shape of a floc is not readily determined.

The changes in concentration of Ru during periods of idling were determined from the Monarch Analytical data. These concentrations (as $Ru(t)/Ru(0)$) are plotted versus idling time in Figure 38a. One can see that this data follows the same general trend as the hypothetical sedimentation relationship illustrated in Figure 38b. Thus one can generalize that initially the relative concentration varies linearly until the critical point (C in Figure 38b) is reached, and then the rate of change of concentration decreases rapidly until the ultimate concentration is reached. This data then suggests that the Ru is present in the melt as particles which will and will not easily settle. This ultimate concentration represents the amount of Ru in the melt that will not easily settle.

From the data in Figure 38a, the critical settling point seems to be reached between 10 and 20 days of idle time. Therefore, the data taken before 20 days was used to generate a least-squares relationship for relative Ru concentration versus idle time for the IDMS melter. This relationship is shown in Figure 38c. From this information, the linear region is described by:

$$\frac{[Ru]_t}{[Ru]_0} = 0.9814 - 0.04713 t \quad \text{where } t \text{ is idle time in days}$$

The transition region cannot be described well and thus no regression relationship is provided. However, the ultimate relative concentration appears to be between 0.25 and 0.30

indicating that approximately 25 to 30% of the Ru in the melter is of a size or shape that does not settle easily.

5.3.2 The Effects of Concentration

As shown, idling of the melter (periods of non-feeding) severely influences the settling of the noble metals and other glass insolubles to the melter floor. However, the greatest increase in the amount of material on the melter floor occurred in the time period just after the noble metal concentrations in the melter feed were increased from "Blend" levels to "HM" levels even though the idling time between runs was relatively short. The longest period of idling occurred between the feeding of BL1 and BL2 feed materials. However, during this time, only a small amount of material settled to the melter floor.

In the Research Scale Melter (RSM) studies at PNNL, the results suggested that there was a significant nonlinear increase in the amount of noble metal compounds deposited on the melter floor with a 2-fold increase in the nominal noble metal content of the NCAW melter feed simulant. This resulted in a 9-fold increase in the fraction settling.^[11]

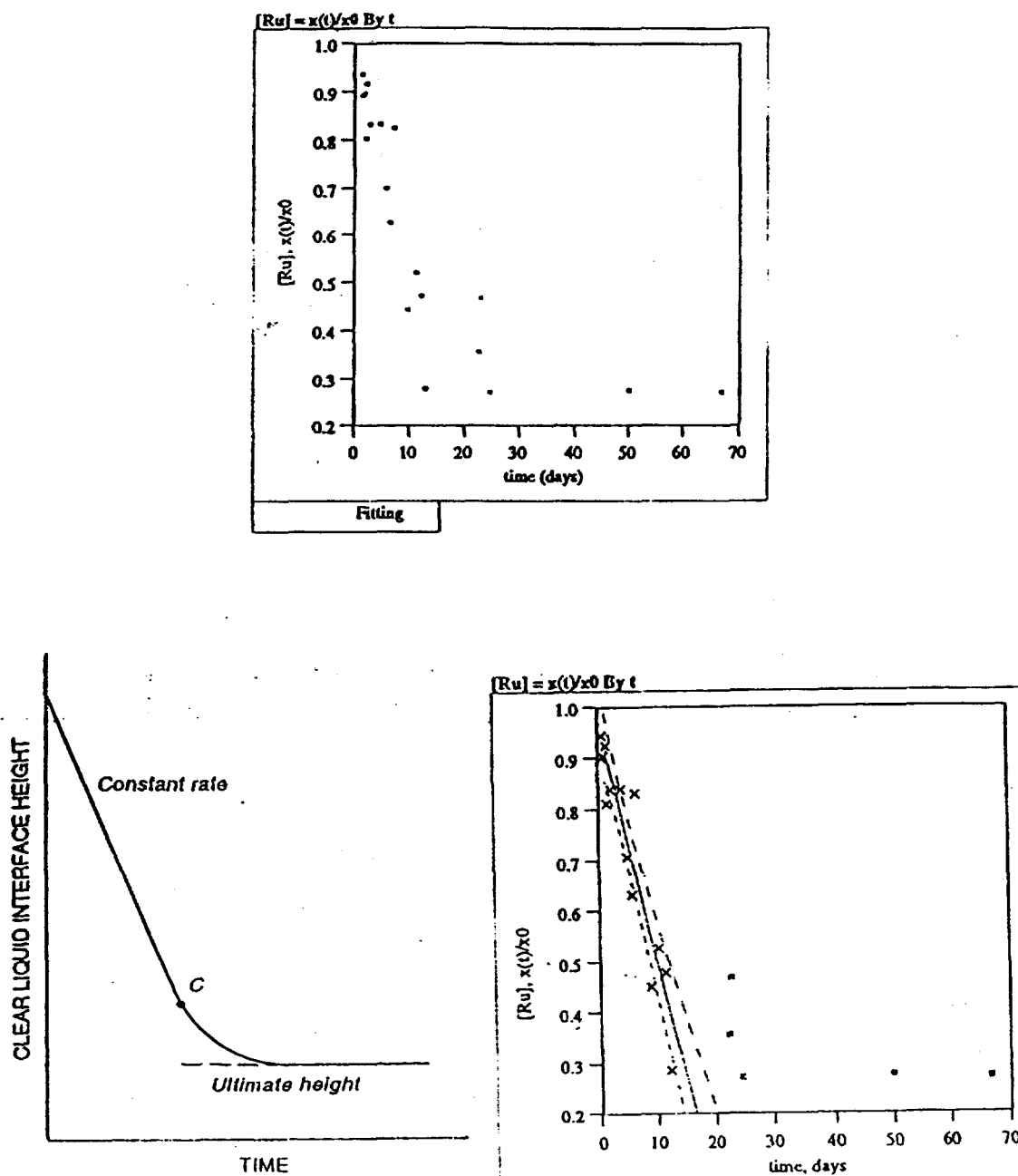


Figure 38. (a) Ruthenium Concentration In IDMS Glass Versus Idling Time, (b) Hypothetical Sedimentation Curve, (c) Linear Relationship between Ru Concentration and Idling Time

6.0 Results of the Post IDMS Melter Shutdown Floor Sampling

After the IDMS melter was shutdown, samples of the material at the bottom of the melter were taken and analyzed. [31] High concentrations of spinel (27 to 66 wt%) were found in these samples. In addition, the samples were also highly enriched in Ru and varied from 0.16 to 7.74 wt%. The range of Rh was 0.026 to 1.21 wt%, and the range of Pd was 0.031 to 0.17 wt%. The Ru present was RuO₂. Due to how the samples were taken, it was not possible to quantify the amount of noble metals that had remained in the melter. Table 9 gives the noble metals concentrations of these floor samples.

Table 9. Wt% Concentration of Spinel and Noble Metals (Ru, Rh, and Pd) from IDMS Floor Samples

Sample ID	ADS NUMBER	TREVORITE Wt%	Ru Wt%	Rh Wt%	PD Wt%
BLOB-1	58577	42	0.33	0.078	0.068
BLOB-2	58579	66	1.12	0.026	0.062
BLOB-3	58580	33	5.37	0.069	0.041
BLOB-4	58581	29	7.74	1.21	0.066
BLOB-5	58582	27	5.66	1.00	0.160
BLOB-6	58583	51	1.19	0.210	0.083
BLOB-7	58584	48	0.16	0.062	0.075
BLOB-8	58585	27	0.41	0.130	0.031
BLOB-9	58586	36	1.60	0.39	0.14
BLOB-10	58587	44	1.7	0.410	0.170

7.0 Effects of Noble Metal Deposition on the Melter

7.1 Effects on the Melter Operation

The electrical characteristics of the IDMS melter are constantly monitored in an effort to judge the effects of the deposition of glass insoluble components. Initially the resistance of the lower melt pool was used as an indication of the accumulation of a conductive layer on the melter floor. However, this measurement is not entirely effective in determining the extent of accumulation of deposits in that each glass composition has a different electrical resistance at a given temperature. Therefore the ratio of the upper melt pool resistance to that of the lower melt pool was monitored as the indication of conductive material on the

melter floor. In using this measure, any changes in resistance due to differences in glass temperature or composition are normalized. A rise in this ratio would suggest an increase in the amount of conductive material on the melter floor. The resistance of the glass is calculated as follows:

$$\text{Resis}_{AB} = \frac{\text{Voltage}_{AB}}{\text{Current}_{AB}}$$

and

$$\text{Resis}_{CD} = \frac{\text{Voltage}_{CD}}{\text{Current}_{CD}}$$

so that

$$\text{Resistance Ratio} = \frac{\text{Resis}_{AB}}{\text{Resis}_{CD}}$$

where AB = upper electrodes and CD = lower electrodes

Figures 39 - 45 show various operating parameters of the melter. Figure 39 shows the upper and lower currents of the electrodes. Figure 40 shows the corresponding melt resistivities (as calculated using the above equations). The dotted lines indicated the initial (before the introduction of noble metals) values. Figure 41 shows the upper-to-lower resistance ratio. Again, the dotted line indicates the initial value of the ratio. One can see that the ratio is stable, oscillating from 1.1 to 1.3 until approximately 550 days of operation. The ratio then begins to increase dramatically and has continued upward to 2.3 - 2.5. It is interesting to note that the quick increase in the resistance ratio corresponded to a time when melter floor samples revealed a significant increase in the amount of material on the melter floor. Appendix B [32] gives a statistical analysis of the effects of noble metals on the IDMS melter upper-to-lower resistance ratio from for all the noble metals runs from Blend-1 to HWVP-2. (total of 17,620 grams of noble metals added). The conclusion of the analysis was that there was a statistically significant (95% confidence level) increase in this ratio as the addition of noble metals was continued in the melter. Figure 42 shows the upper melt temperature and the upper electrode pair current requirement while Figure 43 shows the upper melt temperature with the glass pool resistivity. Figure 44, similarly, shows the lower glass pool temperature and the lower electrode pair current requirement while Figure 45 shows the lower glass pool temperature with the lower glass pool resistivity. One can see that the resistivity of the lower glass pool has decreased, increasing the current requirement to the point that a current limit (set at 600 amps) prevented the melter from being operated in the desired temperature range (1100 - 1150°C). The current limit has now been increased and a current of 650 amps was required to maintain the lower glass pool at approximately 1070°C (glass required to be above liquidus temperature limit set at 1050°C. This current exceeded the design current density (6.1 amps/in² versus the design value of 5.0 amps/in²), however it was not deemed to place the lower electrodes at any risk.

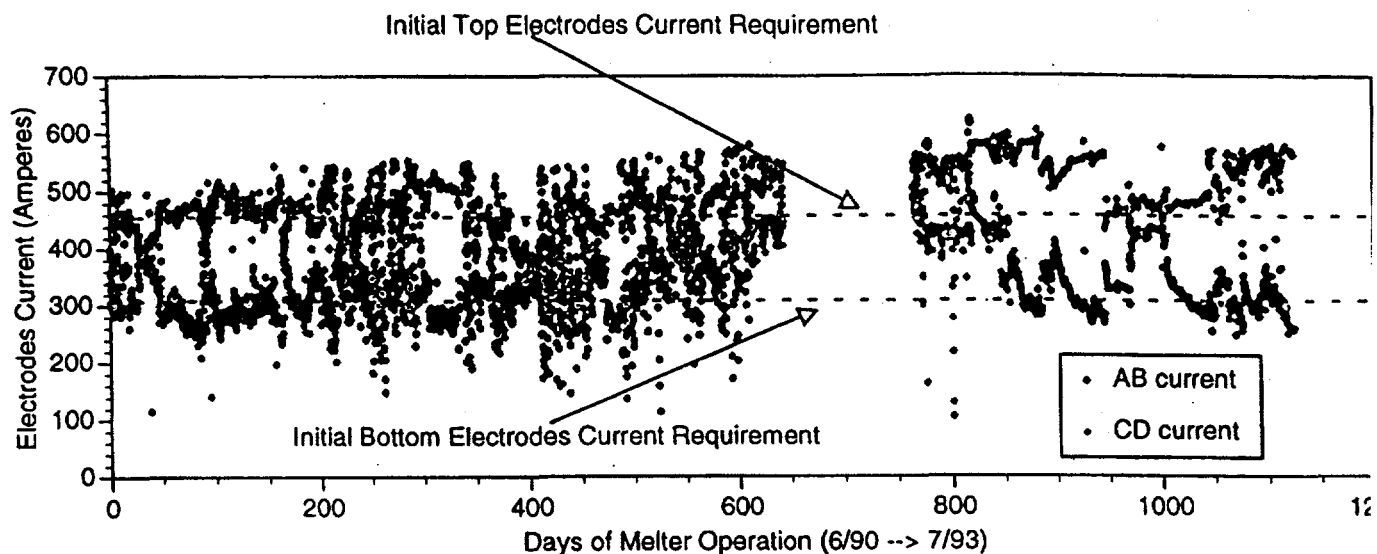


Figure 39. IDMS Melter Upper and Lower Electrode Currents (Amperes)

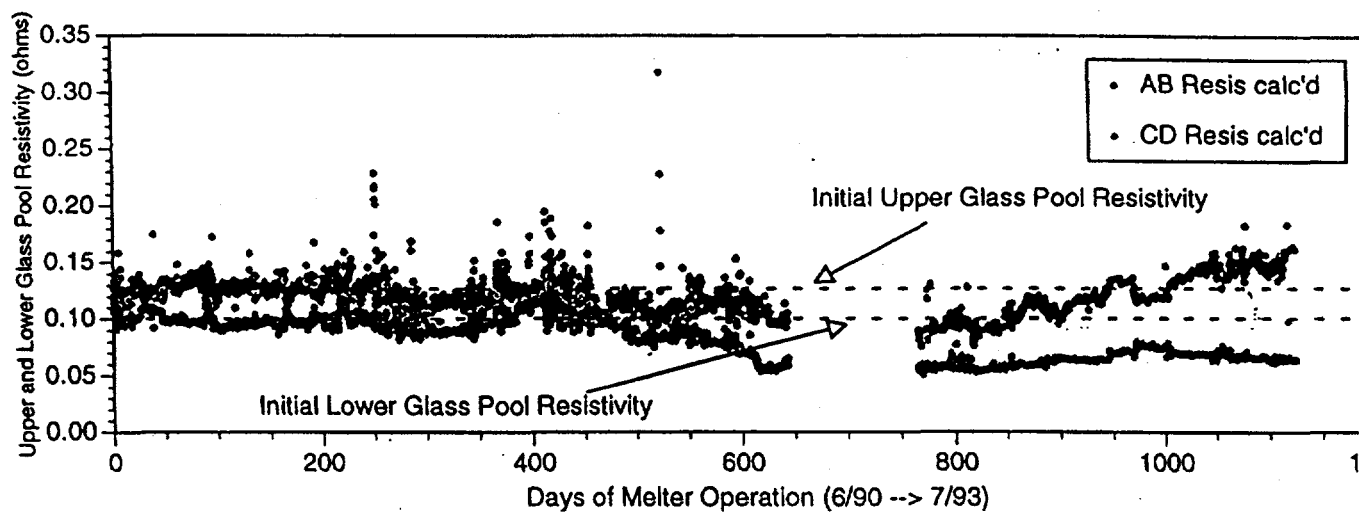


Figure 40. IDMS Melter Upper and Lower Melter Resistivities (Ohms)

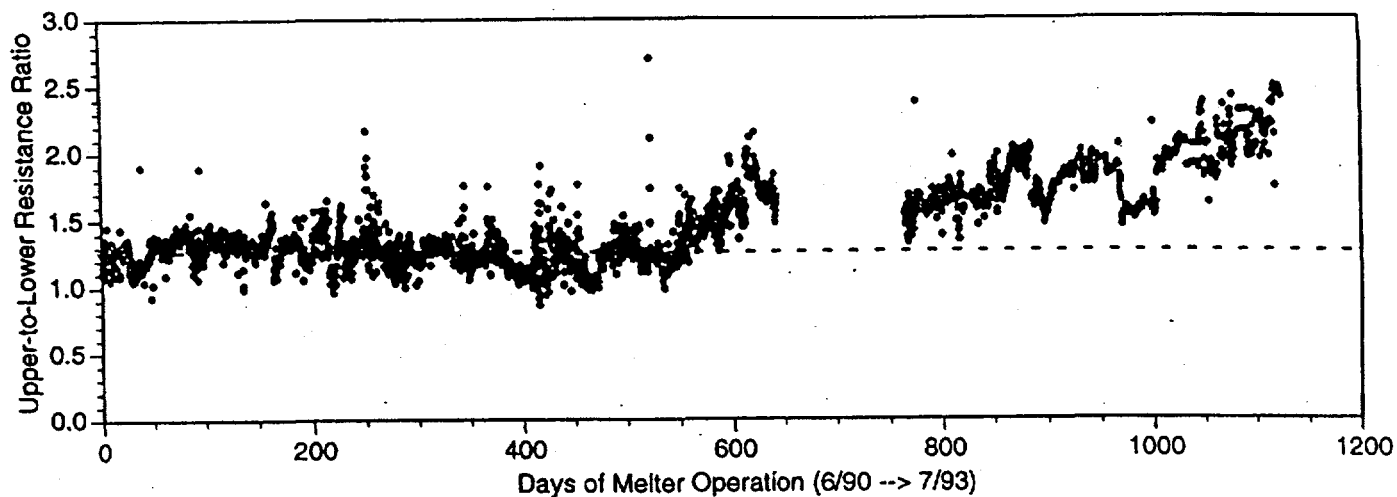


Figure 41. IDMS Upper-to-Lower Resistivity Ratio

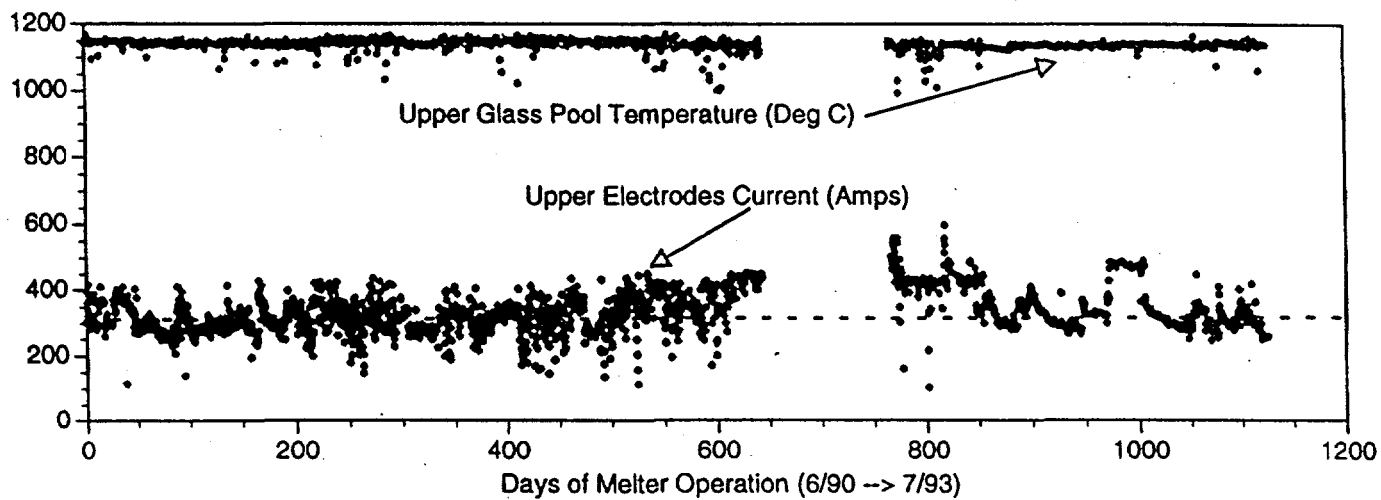


Figure 42. IDMS Melter Upper Melt Pool Temperature ($^{\circ}\text{C}$) and Upper Electrode Current

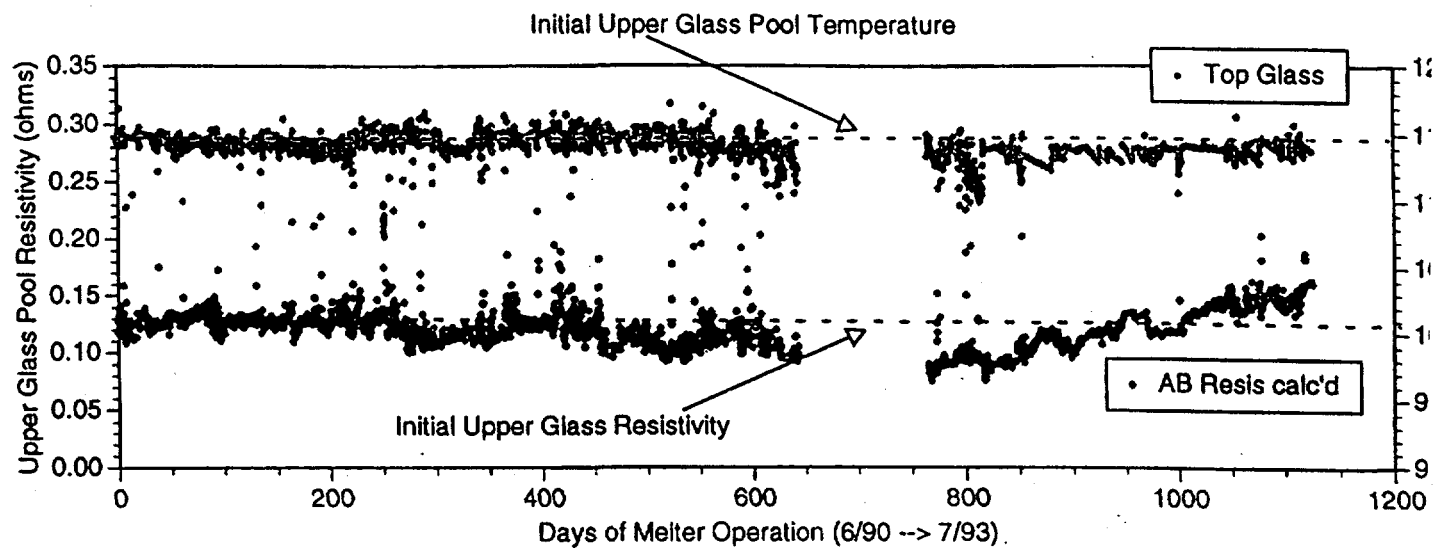


Figure 43. IDMS Melter Upper Melt Pool Temperature ($^{\circ}\text{C}$) and Upper Melter Pool Resistivity (Ohms)

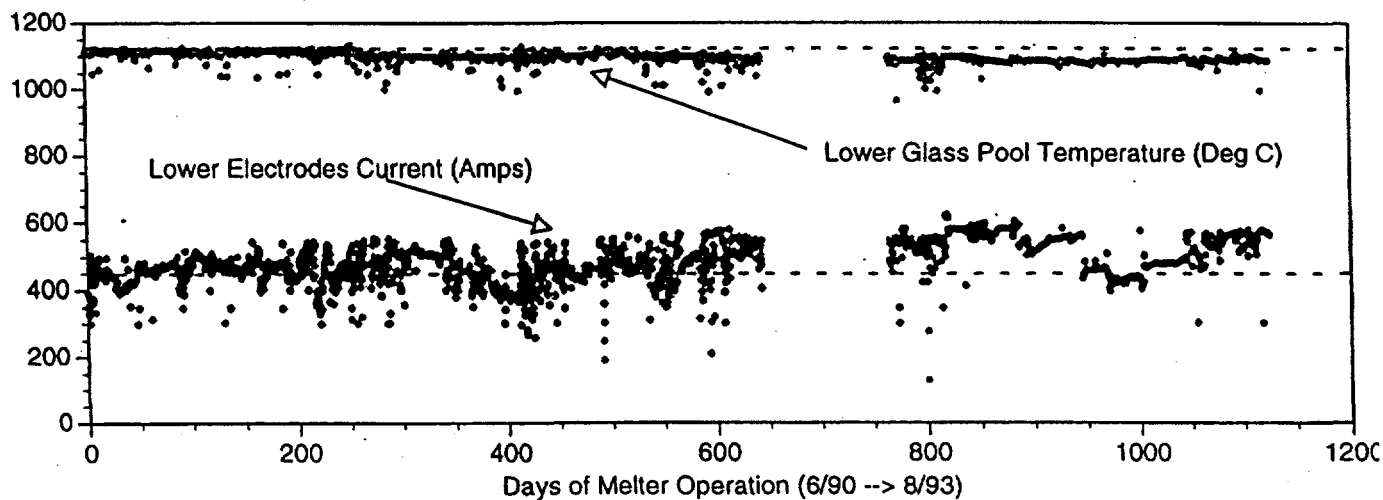


Figure 44. IDMS Melter Lower Melt Pool ($^{\circ}\text{C}$) and Lower Electrode Current

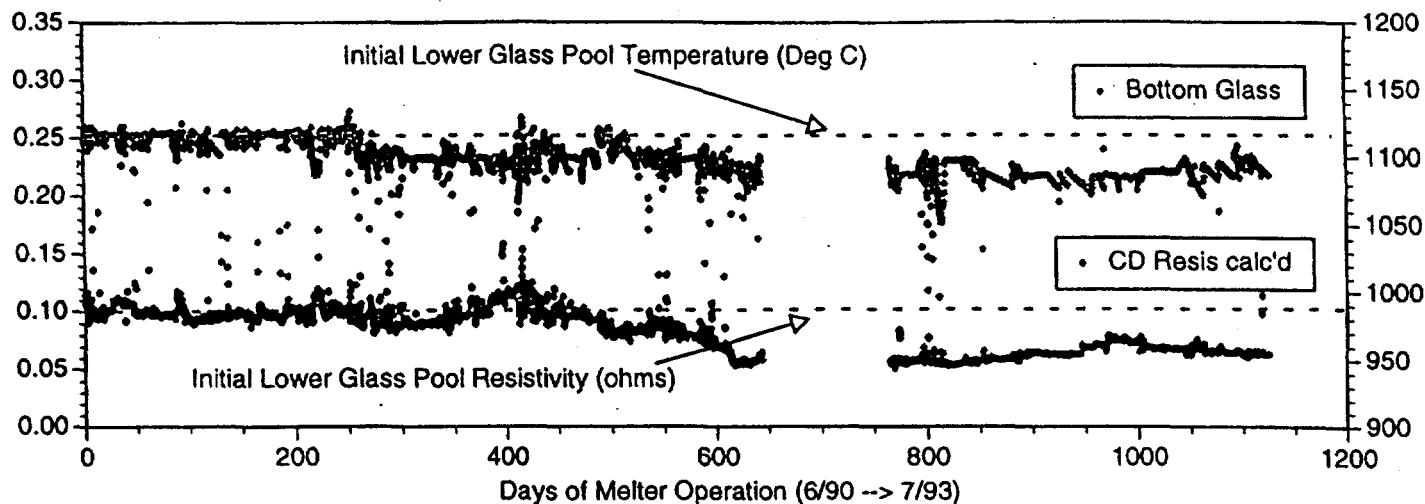


Figure 45. IDMS Melter Lower Melt Pool Temperature ($^{\circ}\text{C}$) and Lower Melter Pool Resistivity (Ohms)

7.2 Results of the Melter Inspection

Approximately two inches of material was lost from the bottom face of the lower electrodes, and the electrodes were very rounded in this area. Mechanisms considered for this are all associated with noble metals deposits; 1) low viscosity glass at hot spot near the junction of the electrodes and the glass could have accelerated wear, 2) high electrical current densities could have accelerated oxidation and electrochemical attack of the electrodes, 3) alloying of the electrodes at the surface with the noble metals Se or Te could have adversely affected the Inconel's ability to develop a passive corrosion inhibiting surface layer, and 4) localized overheating could have caused localized electrode melting.

The upper electrodes faces were also heavily worn, especially at the ends. The extent of the attack was proportionally higher in this melter than in other SRTC melter that had operated for comparable times. The electrodes were still functional.

The most likely cause of the high attack at the bottom of the electrodes is a combination of mechanisms 1 and 2. The general wear pattern is consistent with attack in regions of high current density, which adversely affects electrochemical corrosion rates. High current densities can also be expected to produce local high temperature regions, especially in

normally stagnant areas such as under the bottom electrodes. There was no direct indication of electrode melting which has been seen in smaller melters and which generally produces a melter short.

Noble metal alloying and enhanced corrosion is unlikely to have been an effect since the thermowell was examined in detail and this mechanism was not observed. However, it is possible that the combination of noble metals and the electrical currents at the electrode faces resulted in such an effect. Detailed metallurgical examination of the electrode would be necessary to determine the actual mechanism.

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8.0 Implications for the DWPF Melter Operation

Since the IDMS melter continued to operate in spite of damage, it is difficult to predict the maximum lifetime of the DWPF melter based on the operational experience of the IDMS melter. However, assuming the DWPF melter will withstand the same conditions to which the IDMS melter has been exposed, estimates of the minimum lifetime have been made.

There are several caveats which should be considered when interpreting these estimations. Firstly, the IDMS melter was subjected to numerous idling periods in excess of 20 days. As stated above, approximately 70% of the noble metals in the melter will settle to the floor during this short idling period.

IDMS Production

1 IDMS glass with HM or NCAW Noble Metals	40,300 lbs
2- IDMS glass with Blend Noble Metals	8,346 lbs
3- Max IDMS glass capacity	1,063 lbs
4- Number of melter HM turnovers (1 / 3)	38 turnovers
5- Number of melter Blend turnovers (2 / 3)	8 turnovers

Equivalent DWPF Production

6- Max DWPF glass capacity	13,136 lbs
7- 38 DWPF Melter turnovers (6 x 38 turnovers)	499,168 lbs
8- DWPF Melter turnovers (6 x 8 turnovers)	105,088 lbs
9- DWPF 100% production rate	228 lbs/hr
10- Target minimum nominal operating time, 2 years @ 70%	511 days
11- Nominal melter turnovers in 511 days	213 turnovers

Equivalent DWPF HM Operating Time

12- Hm sludge Ru content	0.217 wt%
13- Equivalent HM operating time ((7 / 9)/24 hrs per day)	91 days

Equivalent DWPF Blend Operating Time

14- Blend sludge Ru content	0.100 wt%
15- Equivalent Blend operating time ((8 / 9)/24 hrs per day)	19 days

Equivalent Combined Blend Operating Time

16- Equivalent combined Blend operating time (13 + 15)	110 days
--	----------

Equivalent Combined Tank 51 Operating Time

17- Tank 51 Ru content ^[30]	0.005 wt%
18- Equiv. Tank 51 operating time (((12 x 13)+(14 x 15))/17)	4,329 days

NOTE: bold numbers in calculations shown [as given in ()'s] show line items used

Recommendation: Based on IDMS data, the settling of the noble metals appears to be much less during periods of feeding and pouring. This impact, however, may be less in the DWPF Melter due to its larger inner diameter. Therefore, the DWPF should avoid periods of idling when operating with melter feeds containing noble metals. A few extended outages appear preferable to several short period outages; thus when outages must be scheduled, for maintenance, etc., all necessary work should be completed within the extended outage in order to avoid short term outages later.

Secondly, this estimation assumes that the noble metals settle linearly with concentration. This is most likely not the case. In tests conducted at PNNL, it was observed that the settling of the noble metals increased nonlinearly with a 2-fold increase in the noble metal content over the nominal NCAW levels. Therefore, the amount of noble metals settling to the floor while feeding "Blend" melter feed will be much higher than that seen with the existing Tank 51 batch 1a sludge. Still more rapid changes can be expected if HM sludge noble metal concentrations are fed to the DWPF.

The first DWPF melter has not experienced any operational problems associated with noble metals deposition to date. However, because of uncertainties in the blending of Tank Farm wastes, it is difficult to predict a minimum lifetime for subsequent sludge batches.

Recommendation: Tank Farm blending strategies should consider the content of the noble metals in the respective waste tanks. The wastes could be blended such that the noble metal contents are evenly distributed and have a content no greater than that predicted for "Blend-type" sludge (Ru about 0.1 wt% of the dried sludge solids to the DWPF). This is advantageous not only in the maximization of the DWPF melter life but also in the minimizing of hydrogen production the Chemical Processing Cell (CPC). Alternatively, delaying operations with high concentrations of noble metals (HM sludge) to outlying years until possible modifications can be made to subsequent DWPF melters to make them less susceptible to noble metals deposition problems could be done as well.

An inspection of the IDMS melter after shutdown showed that the bottom electrodes had sustained appreciable damage on their lower portions. The Inconel 690® drain valve and pipe also had extensive corrosion. This damage was probably due to a high current density caused by noble metals partially shorting out the melter.

Recommendation: The bottom electrodes of the IDMS melter should be removed from the melter and characterized for change in dimensions and mode of metallurgical attack. Samples previously removed from the bottom of the melter should be measured for viscosity and electrical conductivity. Any deposits remaining under the electrodes should be removed for physical characterization (viscosity, electrical conductivity) and chemical composition.

The ratio of upper-to-lower glass pool resistance has proved to be an effective measure in indicating the accumulation of noble metals on the floor of the IDMS melter. This ratio continue to rise during the noble metals runs, thereby showing that the bottom electrode circuit resistance was being lowered. This implied that a conductive layer of material (noble metals) was forming on the melter bottom. The post shutdown inspection of the melter showed this was indeed the case.

Recommendation: The DWPF should monitor this ratio as an indication of a conductive accumulation on the DWPF melter floor. The individual circuit resistances should also be routinely monitored and trended with time. When feeds with higher noble metals concentrations are used estimates of noble metals settling should be trended. When noble metals accumulations approach 1-2 kg/ft of melter bottom, electrical disruption and electrode attack may occur.

Although there is an obvious trend of international vitrification facilities to move toward sloped bottom melters, this is not necessarily a viable alternative for the DWPF should problems occur. Firstly, the technical time and capital invested in the melt cell does not easily allow radical changes in the present melter design. A sloped bottom melter would require a redesign of the drain valve. Fortunately, melter design and testing in Germany and Japan has proceeded to include reliable drain valves that can function with noble metals. Other facilities have moved to sloped bottom melters. The smallest deviation from existing DWPF design and operating practice which appears technically feasible is a combination of 1) a bottom drain assembly of the German or Japanese type, which have been demonstrated to work with noble metals, 2) mechanical removal of melter bottom deposits after melter draining and cooling, and 3) raising and reshaping the bottom electrodes to minimize local current densities.

One modification to the DWPF melter which could be accommodated is the raising of the lower electrodes. It is not known what effect this would have on the operation of the melter with or without a conductive bottom layer. Mathematical models, however, do exist which can be used to predict the effects of such as modification.

Recommendation: Finite element mathematical models should be used to predict the effects of a modified electrode configuration in the DWPF melter.

The West Valley Demonstration melter is designed to be less susceptible to noble metals than the DWPF (which was designed in 1983). The WVDP modifications appear to have been partially successful, yet two-thirds of the electrical resistance in the WVDP melter circuits have been lost after one year of operation with noble metals concentrations comparable to SRS HM waste. WVDP is actively following the electrical response of its melter.

Recommendation: DWPF and SRTC should actively participate in the work at WVDP concerning the electrical response of the WVDP melter, as well as follow their approach to dealing with these issues, which includes the following activities:

- trending of historical operating data;
- updating a computer model for use as a tool in predicting future melter performance, including power needs;
- remote sampling of deposits;
- remote probing the deposits to determine their location and depth; and
- developing remote tools to dislodge deposits of noble metals in situ and performing associated mockups, as applicable.

Acknowledgments

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APPENDIX:
(A) MONARCH ANALYTICAL DATA
&
(B) STATISTICAL ANALYSIS OF IDMS UPPER/LOWER ELECTRODE
RESISTANCES OVER TIME

APPENDIX A

Glass ID	Glass Poured (lbs)	Total Glass Poured	Ru (ppm)	Pd (ppm)	Rh (ppm)	Te (ppm)	Se (ppm)	Ag (ppm)	Total Ru Poured (gms)	Total Pd Poured (gms)	Total Rh Poured (gms)	Total Te Poured (gms)	Total Se Poured (gms)	Total Ag Poured (gms)
3444	128	128	0	0	0	0	0	0	0	0	0	0	0	0
3446	144	272	0	0	0	0	1	6	0	0	0	0	0	0
3458	160	432	0	34	0	0	1.2	8	0	2	0	0	0	1
3461	175	607	0	44	0	0	1.8	11	0	6	0	0	0	2
3471	183	770	0	52	0	24	2.2	14	0	10	0	2	0	3
3477	166	936	110	64	22	28	1.4	16	8	15	2	4	1	4
....	164	1100	125	68	24	30	2.1	17	18	20	3	6	1	5
3488	165	1265	141	72	26	32	2.8	18	28	25	5	9	1	7
3494	166	1431	105	82	30	38	2.9	21	36	31	8	11	1	8
3499	125	1556	96	89	32	42	3.1	23	42	36	9	14	1	10
3502	157	1713	108	91	32	40	3.3	23	49	43	12	17	2	11
3508	164	1877	116	95	33	44	3.3	25	58	50	14	20	2	13
3511	167	2044	105	99	34	47	3.2	25	66	57	17	23	2	15
3516	154	2198	104	101	35	45	3.4	26	73	64	19	27	2	17
3522	155	2353	108	100	34	44	3.2	25	81	71	22	30	3	19
3527	156	2509	102	100	36	44	3.4	26	88	79	24	33	3	20
3534	145	2654	110	100	36	48	3.9	25	95	85	27	36	3	22
3540	155	2809	88	97	34	46	3	25	101	92	29	39	3	24
3504	161	2970	0	94	0	0	0	18	101	99	29	39	3	25
Per Batch Addition Values														
Per MFI Sample Values														
Total glass poured (kg)	1348.38													
Total Ru poured (gm)	101	Discharge eff (Ru)	14.8	Ru added (gm)	683.15	Discharge eff (Ru)	39.0	Ru added (gm)	260					
Total Pd poured (gm)	99	Discharge eff (Pd)	27.9	Pd added (gm)	354	Discharge eff (Pd)	76.0	Pd added (gm)	130					
Total Rh poured (gm)	29	Discharge eff (Rh)	20.4	Rh added (gm)	141.6	Discharge eff (Rh)	57.9	Rh added (gm)	50					
Total Te poured (gm)	39	Discharge eff (Te)		Te added (gm)		Discharge eff (Te)	54.0	Te added (gm)	70					
Total Se poured (gm)	3	Discharge eff (Se)		Se added (gm)		Discharge eff (Se)	46.0	Se added (gm)	7					
Total Ag poured (gm)	25	Discharge eff (Ag)	22.7	Ag added (gm)	110.5	Discharge eff (Ag)	83.8	Ag added (gm)	30					

BLD 2 SPREAD-NM.WKS

Glass ID	Glass Poured (lbs)	Total Glass Poured	Ru (ppm)	Pd (ppm)	Rh (ppm)	Te (ppm)	Se (ppm)	Ag (ppm)	Total Ru Poured (gms)	Total Pd Poured (gms)	Total Rh Poured (gms)	Total Te Poured (gms)	Total Se Poured (gms)	Total Ag Poured (gms)
3607	184	184	83	112	25	17	1.1	27	7	9	2	1	0	2
3610	183	367	122	118	32	26	1.8	30	17	19	5	4	0	5
3613	183	550	150	125	39	33	2.3	34	30	30	8	6	0	8
3616	168	718	171	133	43	40	2.8	36	43	40	11	9	1	10
3619	176	894	199	135	47	42	2.5	37	58	50	15	13	1	13
3623	259	1153	230	140	51	50	3.5	37	86	67	21	19	1	18
3626	164	1317	230	140	53	51	3.2	38	103	77	25	22	1	20
3630	172	1489	230	143	51	57	3.6	38	121	89	29	27	2	23
3636	177	1666	240	142	53	59	3.9	41	140	100	33	32	2	27
3641	166	1832	260	147	57	62	4.4	42	159	111	38	36	2	30
3644	143	1975	260	146	57	64	3.9	43	176	120	41	40	3	33
3650	161	2136	270	154	59	66	4.5	45	196	132	46	45	3	36
3655	167	2303	270	152	60	65	4.5	45	217	143	50	50	3	39
3658	168	2471	260	156	60	67	5	46	236	155	55	55	4	43
3661	155	2626	290	155	60	61	4.8	46	257	166	59	60	4	46
3664	173	2799	260	157	60	64	4.1	45	277	178	64	65	4	50
3667	167	2966	280	155	61	64	4.1	45	298	190	68	69	5	53
3670	156	3122	260	152	59	70	4	44	317	201	72	74	5	56
3673	163	3285	260	146	58	69	3.6	43	336	212	77	80	5	59
3677	168	3453	250	149	59	69	4.2	43	355	223	81	85	5	63
3682	161	3614	186	153	51	60	2.5	42	369	234	85	89	6	66
3685	166	3780	210	156	56	65	2.4	43	385	246	89	94	6	69
3691	165	3945	230	160	54	64	3	44	402	258	93	99	6	72
3695	136	4081	220	156	53	70	3	45	415	268	96	103	6	75
3698	144	4225	230	157	59	71	2.7	46	430	278	100	108	6	78
3706	161	4386	121	154	44	62	1.4	43	439	289	104	112	7	81
3710	181	4567	139	152	46	60	1.9	43	451	302	107	117	7	85
3712	150	4717	157	148	48	66	2.5	44	461	312	111	122	7	88
....	150	4867	180	160	51	65	2.5	45	474	323	114	126	7	91
....	164	5031	200	160	55	65	2.5	45	489	335	118	131	7	94
....	174	5205	220	160	57	65	2.5	45	506	347	123	136	7	98
....	171	5376	240	160	60	65	2.5	45	525	360	127	141	8	101
Per MFT Sample Values														
Total glass poured (kg)	2440.70													
Total Ru poured (gm)	525		Discharge eff (Ru)	76.8		Ru added (gm)	683.15		Discharge eff (Ru)	65.6		Ru added (gm)	800	
Total Pd poured (gm)	360		Discharge eff (Pd)	101.6		Pd added (gm)	354		Discharge eff (Pd)	97.2		Pd added (gm)	370	
Total Rh poured (gm)	127		Discharge eff (Rh)	89.9		Rh added (gm)	141.6		Discharge eff (Rh)	74.9		Rh added (gm)	170	
Total Te poured (gm)	141		Discharge eff (Te)			Te added (gm)			Discharge eff (Te)	74.3		Te added (gm)	190	
Total Se poured (gm)	8		Discharge eff (Se)			Se added (gm)			Discharge eff (Se)	50.6		Se added (gm)	15	
Total Ag poured (gm)	101		Discharge eff (Ag)	91.6		Ag added (gm)	110.5		Discharge eff (Ag)	92.0		Ag added (gm)	110	

HM2 NM SPREAD WKS

Glass ID	Glass Poured (lbs)	Total Glass Poured	Ru (ppm)	Pd (ppm)	Rh (ppm)	Te (ppm)	Se (ppm)	Ag (ppm)	Total Ru Poured (gms)	Total Pd Poured (gms)	Total Rh Poured (gms)	Total Te Poured (gms)	Total Se Poured (gms)	Total Ag Poured (gms)
3951B	127	127	68	49	25	0	2	10	4	3	1	0	0	1
3965B	172	299	120	70	33	29	2.6	13	13	8	4	2	0	2
3964	166	465	188	90	43	42	3.5	17	27	15	7	5	1	3
***	162	627	234	110	52	55	4	20	45	23	11	9	1	4
3979B	177	804	280	130	60	68	4.5	24	67	34	16	15	1	6
3996	148	952	320	140	63	77	5.3	26	89	43	20	20	2	8
3993	162	1114	350	154	70	86	5.6	29	114	54	25	26	2	10
4099B	109	1223	370	177	79	96	7.5	32	133	63	29	31	2	12
4098B	157	1380	410	195	84	108	5	34	162	77	35	39	3	14
4106B	156	1536	380	195	81	107	6.2	35	189	91	41	46	3	17
4113B	160	1696	410	210	86	108	6	36	219	106	47	54	4	19
4119B	162	1858	400	192	83	110	6.3	36	248	120	53	62	4	22
4120B	176	2034	430	199	86	108	5.8	35	282	136	60	71	5	25
4126B	176	2210	430	200	88	110	6	35	317	152	67	80	5	27
4130	174	2384	450	195	87	112	6	34	352	167	74	89	5	30
4132B	177	2561	410	186	83	111	6.3	33	385	182	81	98	6	33
4155	237	2798	450	210	92	125	5.4	38	434	205	91	111	7	37
4164	151	2949	500	230	99	134	6.6	43	468	221	97	120	7	40

HM3 SPREAD NM .WKS

Glass ID	Glass Poured (lbs)	Total Glass Poured	Ru (ppm)	Pd (ppm)	Rh (ppm)	Te (ppm)	Se (ppm)	Ag (ppm)	Total Ru Poured (gms)	Total Pd Poured (gms)	Total Rh Poured (gms)	Total Te Poured (gms)	Total Se Poured (gms)	Total Ag Poured (gms)
....	151	151	400	250	80	125	5	40	27	17	5	9	0	3
....	164	315	530	270	100	145	6	45	67	37	13	19	1	6
4186	153	468	660	290	119	165	8.5	50	113	57	21	31	1	10
4194	146	614	690	300	127	173	11	53	158	77	30	42	2	13
4199	150	764	690	310	126	173	10	54	205	98	38	54	3	17
4207	176	940	710	300	121	180	10	54	262	122	48	68	4	21
4214	156	1096	710	320	136	181	7.1	57	312	145	57	81	4	25
....	146	1242	675	310	131	179	7.5	55	357	166	66	93	5	29
4234	168	1410	640	300	126	176	8.2	54	406	188	76	107	5	33
4239	170	1580	700	320	138	184	9	54	460	213	86	121	6	37
4284	172	1752	690	330	137	182	9.9	56	514	239	97	135	7	41
4309	168	1920	640	300	126	178	6.9	54	563	262	107	149	7	46
4344	160	2080	530	290	113	181	5.8	55	601	283	115	162	8	50
4347	158	2238	580	300	118	190	6.6	56	643	304	123	175	8	54
....	50	2288	615	310	124	192	7	57	667	311	126	180	8	56
....	168	2456	650	320	132	194	7	58	706	336	136	194	9	59
4364	158	2614	690	330	135	196	7.2	60	756	359	146	209	9	64
4369	143	2757	680	330	133	196	9	61	800	381	155	221	10	68
4374	160	2917	710	340	138	197	9.5	61	852	406	165	236	11	72
4383	142	3059	570	300	117	189	9.6	56	888	425	172	248	11	76
4388	98	3157	710	340	134	200	11	60	920	440	178	257	12	78
4393	140	3297	710	330	138	196	10	59	965	461	187	269	12	82
....	169	3466	710	330	138	196	10	60	1020	486	198	284	13	87
NOTE: 1ST TWO CANS POURED HAD NO SAMPLE - BASED ON HM2 WHICH WAS JUST BEFORE THIS RUN														
Total glass poured (kg) 1573.56														
Per Batch Addition Numbers														
Per MFT Sample Values														
Total Ru poured (gm)	1,020	Discharge eff (Ru)	67.5	Ru added (gm)	1511	Discharge eff (Ru)	64.9	Ru added (gm)	1570					
Total Pd poured (gm)	486	Discharge eff (Pd)	91.1	Pd added (gm)	534	Discharge eff (Pd)	97.3	Pd added (gm)	500					
Total Rh poured (gm)	198	Discharge eff (Rh)	76.9	Rh added (gm)	257	Discharge eff (Rh)	76.0	Rh added (gm)	260					
Total Te poured (gm)	284	Discharge eff (Te)		Te added (gm)		Discharge eff (Te)	81.2	Te added (gm)	350					
Total Se poured (gm)	13	Discharge eff (Se)		Se added (gm)	95	Discharge eff (Se)	48.5	Se added (gm)	27					
Total Ag poured (gm)	87	Discharge eff (Ag)	91.1	Ag added (gm)		Discharge eff (Ag)	96.2	Ag added (gm)	90					

PX1 SPREAD-NM.WKS

Glass ID	Glass Poured (lbs)	Total Glass Poured	Ru (ppm)	Pd (ppm)	Rh (ppm)	Te (ppm)	Se (ppm)	Ag (ppm)	Total Ru Poured (gms)	Total Pd Poured (gms)	Total Rh Poured (gms)	Total Te Poured (gms)	Total Se Poured (gms)	Total Ag Poured (gms)
4603	159	159	200	270	69	183	7.7	48	14	19	5	13	1	3
4610	165	324	200	270	77	192	6.8	48	36	40	11	28	1	7
4618	167	491	370	290	92	183	7.7	48	64	62	11	41	2	11
4625	144	635	440	280	97	188	8.2	51	93	80	24	54	2	14
....	168	803	495	290	103	185	8.4	50	131	102	32	68	3	18
4637	147	950	550	300	108	183	8.6	50	167	122	39	80	3	21
4643	148	1098	560	290	111	178	8.9	50	205	142	47	92	4	25
4648	146	1244	580	280	111	176	8.7	51	244	160	54	104	5	28
4655	162	1406	610	290	117	176	7.3	51	288	181	62	117	5	32
4662	142	1548	620	290	117	178	8.5	48	328	199	70	128	6	35
4683	138	1686	170	280	65	156	2.6	48	339	234	74	138	6	38
4686	140	1826	250	270	74	160	3.3	45	355	255	79	148	6	41
4693	162	1988	350	280	91	168	5.9	47	381	255	85	160	6	44
4703	163	2151	440	300	100	171	6.4	48	414	277	93	173	7	48
4709	178	2329	490	300	108	178	6.5	50	454	301	102	187	7	52
4719	212	2541	530	310	111	177	7	51	505	331	112	205	8	57
4725	176	2717	570	310	115	174	7	52	550	356	121	218	9	61
4730	170	2887	600	310	118	181	6.3	52	596	380	131	232	9	65
4735	187	3074	610	310	119	179	7.7	52	648	406	141	248	10	69
4741	179	3253	600	300	118	173	6.3	50	697	430	150	262	10	73
4744	183	3436	630	300	119	180	7.2	51	749	455	160	277	11	77
4754	172	3608	620	300	120	176	7.2	50	798	479	170	290	12	81
4759	173	3781	630	290	117	171	6.9	47	847	502	179	304	12	85
4766	188	3969	600	290	114	166	7.8	46	898	526	188	318	13	89
4772	179	4148	590	280	110	161	7.4	46	946	549	197	331	13	93
4777	84	4232	590	270	108	163	7.1	45	969	559	202	337	14	94
Per Batch Addition Values														
Total glass poured (kg)	1921.33								Per MFT Sample Values					
Total Ru poured (gm)	969		Discharge eff (Ru)	64.1		Ru added (gm)	1511		Discharge eff (Ru)	54.7	Ru added (gm)	1770		
Total Pd poured (gm)	559		Discharge eff (Pd)	104.8		Pd added (gm)	534		Discharge eff (Pd)	98.1	Pd added (gm)	570		
Total Rh poured (gm)	202		Discharge eff (Rh)	78.4		Rh added (gm)	257		Discharge eff (Rh)	65.0	Rh added (gm)	310		
Total Te poured (gm)	337		Discharge eff (Te)			Te added (gm)			Discharge eff (Te)	91.1	Te added (gm)	370		
Total Se poured (gm)	14		Discharge eff (Se)			Se added (gm)			Discharge eff (Se)	46.9	Se added (gm)	29		
Total Ag poured (gm)	94		Discharge eff (Ag)	99.4		Ag added (gm)	95		Discharge eff (Ag)	78.7	Ag added (gm)	120		

PX2 SPREAD-NM.WKS

Glass ID	Glass Poured (lbs)	Total Glass Poured	Ru (ppm)	Pd (ppm)	Rh (ppm)	Te (ppm)	Se (ppm)	Ag (ppm)	Total Ru Poured (gms)	Total Pd Poured (gms)	Total Rh Poured (gms)	Total Te Poured (gms)	Total Se Poured (gms)	Total Ag Poured (gms)
....	174	174	250	220	61	180	2	45	20	17	5	14	0	4
4454	162	336	340	240	78	180	4.3	52	45	35	11	27	0	7
4459	158	494	430	260	95	186	6.3	57	76	54	17	41	1	11
4469	161	655	490	270	105	186	7.3	60	111	73	25	55	1	16
4473	147	802	530	280	109	194	9.3	59	147	92	32	67	2	20
4483	172	974	540	280	109	196	9.3	60	189	114	41	83	3	24
4492	176	1150	590	300	118	196	11	56	236	138	50	98	4	29
....	169	1319	610	300	120	190	12	53	283	161	59	113	5	33
4505	160	1479	630	290	122	183	12	51	329	182	68	126	5	37
4508	181	1660	590	280	111	180	12	51	377	205	77	141	6	41
4511	162	1822	670	290	123	186	13	53	426	226	86	156	7	45
4518	145	1967	690	290	124	187	13	55	472	245	95	167	8	48
4526	169	2136	660	300	121	191	13	55	522	268	104	182	9	53
4535	163	2299	680	290	121	190	13	57	573	290	113	196	10	57
4540	152	2451	690	280	122	191	14	56	620	309	121	209	11	61
....	156	2607	690	280	120	190	14	56	669	329	130	222	12	65
4552	169	2776	680	280	119	187	13	56	721	351	139	237	13	69
4560	154	2930	720	270	123	188	14	57	772	369	148	250	14	73
4564	124	3054	690	270	119	185	15	55	811	385	154	260	15	76
4571	154	3208	710	270	123	182	11	55	860	404	163	273	16	80
4578	136	3344	710	280	125	184	14	55	904	421	171	284	17	83
Per MFT Sample Values														
Total glass poured (kg)	1518.18													
Total Ru poured (gm)	904		Discharge eff (Ru)	59.8		Ru added (gm)	1511.4		Discharge eff (Ru)	66.5	Ru added (gm)	1360		
Total Pd poured (gm)	421		Discharge eff (Pd)	78.8		Pd added (gm)	533.9		Discharge eff (Pd)	95.6	Pd added (gm)	440		
Total Rh poured (gm)	171		Discharge eff (Rh)	66.4		Rh added (gm)	256.8		Discharge eff (Rh)	77.5	Rh added (gm)	220		
Total Te poured (gm)	284		Discharge eff (Te)			Te added (gm)			Discharge eff (Te)	129.3	Te added (gm)	220		
Total Se poured (gm)	17		Discharge eff (Se)			Se added (gm)			Discharge eff (Se)	72.4	Se added (gm)	23		
Total Ag poured (gm)	83		Discharge eff (Ag)	87.4		Ag added (gm)	95.3		Discharge eff (Ag)	92.6	Ag added (gm)	90		

HANFORD SPREAD-NALWS

Class ID	Glass Poured (lbs)	Total Glass Poured	Ru (ppm)	Pd (ppm)	Rh (ppm)	Te (ppm)	Se (ppm)	Ag (ppm)	Total Ru Poured (gms)	Total Pd Poured (gms)	Total Rh Poured (gms)	Total Te Poured (gms)	Total Se Poured (gms)	Total Ag Poured (gms)
114	169	169	550	270	117	159	6.5	76	42	21	9	12	0	6
***	168	337	610	280	132	162	7.5	103	89	42	19	25	1	14
130	170	507	670	290	147	164	8.4	129	140	64	30	37	2	24
134	179	686	470	260	129	160	6.7	147	179	86	41	50	2	36
139	155	841	470	260	137	163	8	158	212	104	51	62	3	47
144	175	1016	550	270	153	152	9	169	255	125	63	74	4	60
150	179	1195	580	280	161	173	11	181	303	146	76	88	4	75
156	195	1390	690	270	177	162	11	191	364	170	91	102	5	92
162	193	1583	690	280	184	144	13.9	189	424	195	108	115	7	108
244	167	1750	660	270	178	161	12	200	474	215	121	127	8	123
246	172	1922	670	270	179	144	15.2	200	526	236	135	138	9	139
250	175	2097	560	250	160	152	10	196	571	256	148	150	10	155
254	150	2247	670	260	173	112	11.7	196	613	274	160	158	10	168
260	178	2425	670	240	170	158	12	200	663	293	173	171	11	184
265	135	2560	630	250	173	153	13	200	702	309	184	180	12	196
278	174	2734	690	260	187	138	17.3	203	756	329	199	191	13	212
275	137	2871	730	280	196	140	18.7	209	802	347	211	200	15	225
288	165	3036	650	250	174	163	12	210	850	365	224	212	16	241
293	158	3194	710	270	188	147	15.8	214	901	385	237	222	17	257
***	196	3390	700	270	170	140	15	200	964	409	252	235	18	274
Per Batch Addition Values														
Total Glass poured (kg)														
1539.06														
Per MFT Sample Values														
Total Ru poured (gm)	964	Discharge eff (Ru)	1866.9	Ru added (gm)	68.3	Discharge eff (Ru)	68.3	Ru added (gm)	1390	Discharge eff (Ru)	68.3	Ru added (gm)	68.3	Ru added (gm)
Total Pd poured (gm)	499	Discharge eff (Pd)	643.1	Pd added (gm)	80.9	Discharge eff (Pd)	80.9	Pd added (gm)	460	Discharge eff (Pd)	80.9	Pd added (gm)	80.9	Pd added (gm)
Total Rh poured (gm)	252	Discharge eff (Rh)	517.1	Rh added (gm)	70.1	Discharge eff (Rh)	70.1	Rh added (gm)	360	Discharge eff (Rh)	70.1	Rh added (gm)	70.1	Rh added (gm)
Total Te poured (gm)	235	Discharge eff (Te)		Te added (gm)	81.0	Discharge eff (Te)	81.0	Te added (gm)	290	Discharge eff (Te)	81.0	Te added (gm)	81.0	Te added (gm)
Total Se poured (gm)	18	Discharge eff (Se)		Se added (gm)	66.6	Discharge eff (Se)	66.6	Se added (gm)	27	Discharge eff (Se)	66.6	Se added (gm)	66.6	Se added (gm)
Total Ag poured (gm)	274	Discharge eff (Ag)	684.7	Ag added (gm)	76.2	Discharge eff (Ag)	76.2	Ag added (gm)	360	Discharge eff (Ag)	76.2	Ag added (gm)	76.2	Ag added (gm)

Glass ID	Glass Poured (lbs)	Total Glass Poured	Ru (ppm)	Pd (ppm)	Rh (ppm)	Te (ppm)	Se (ppm)	Ag (ppm)	Total Ru Poured (gms)	Total Pd Poured (gms)	Total Rh Poured (gms)	Total Te Poured (gms)	Total Se Poured (gms)	Total Ag Poured (gms)
312	153	153	330	220	108	126	5	210	23	15	8	9	0	15
309	149	302	460	230	136	139	9	240	54	31	17	18	1	31
324	149	451	550	250	164	156	11	260	91	48	28	29	2	48
335	166	617	600	250	175	166	14	280	136	67	41	41	3	70
347	166	783	640	280	192	172	14	270	185	88	55	54	4	90
350	162	945	670	260	188	166	15	280	234	107	69	66	5	110
353	154	1099	630	270	189	173	14	290	278	126	82	78	6	131
359	152	1251	620	270	189	170	15	280	321	144	96	90	7	150
362	159	1410	660	270	199	183	18	280	368	164	110	103	8	170
377	140	1550	650	270	191	169	10	280	410	181	122	114	9	188
374	176	1726	410	240	136	151	9.3	260	443	200	133	126	10	209
385	146	1872	510	240	152	161	11	270	476	216	143	137	10	227
388	172	2044	570	250	159	159	13	270	521	236	155	149	11	248
393	181	2225	610	270	178	178	17	280	571	258	170	164	13	271
406	147	2372	510	250	125	159	9.2	280	605	274	178	175	13	290
411	155	2527	610	260	156	172	11	290	648	293	189	187	14	310
422	162	2689	630	270	152	172	11	290	694	313	201	199	15	331
429	158	2847	610	270	171	178	11	290	738	332	213	212	16	352
432	116	2963	600	270	173	189	12	300	770	346	222	222	16	368
437	167	3130	620	270	180	185	15	300	817	367	236	236	18	391
447	140	3270	710	270	184	184	17	300	862	384	247	248	19	410
450	181	3451	680	270	189	183	18	300	918	406	263	263	20	434
460	161	3612	720	280	200	191	17	320	970	426	277	277	21	458
467	167	3779	700	290	209	187	18	320	1023	448	293	291	23	482
479	158	3937	680	290	198	203	16	340	1072	469	307	305	24	506
....	147	4084	690	290	195	200	15	340	1118	489	320	319	25	529
492	150	4234	690	290	195	203	14	340	1165	508	334	333	26	552
....	157	4391	690	290	195	200	15	340	1214	529	348	347	27	576
....	170	4561	690	290	195	200	15	340	1268	551	363	362	28	603
Per Batch Addition Values														
Per MFT Sample Values														
Total glass poured (kg)	2070.69													
Total Ru poured (gm)	1268	Discharge eff (Ru)	67.9	Ru added (gm)	1866.9				Discharge eff (Ru)	73.7	Ru added (gm)	1720		
Total Pd poured (gm)	551	Discharge eff (Pd)	85.7	Pd added (gm)	643.1				Discharge eff (Pd)	96.7	Pd added (gm)	570		
Total Rh poured (gm)	363	Discharge eff (Rh)	70.1	Rh added (gm)	517.1				Discharge eff (Rh)	84.3	Rh added (gm)	430		
Total Te poured (gm)	362	Discharge eff (Te)		Te added (gm)					Discharge eff (Te)	92.9	Te added (gm)	390		
Total Se poured (gm)	28	Discharge eff (Se)		Se added (gm)					Discharge eff (Se)	54.9	Se added (gm)	51		
Total Ag poured (gm)	603	Discharge eff (Ag)	88.0	Ag added (gm)	684.7				Discharge eff (Ag)	103.9	Ag added (gm)	580		

HM4 SPREAD - NM.WKS

Glass ID	Glass Poured (lbs)	Total Glass Poured	Ru (ppm)	Pd (ppm)	Rh (ppm)	Te (ppm)	Se (ppm)	Ag (ppm)	Total Ru Poured (gms)	Total Pd Poured (gms)	Total Rh Poured (gms)	Total Te Poured (gms)	Total Se Poured (gms)	Total Ag Poured (gms)
5277	150	150	330	193	98	103	2.3	196	22	13	7	7	0	13
5278	145	295	360	200	105	114	3.4	191	46	26	14	15	0	26
5275	147	442	400	220	112	121	3.7	177	73	41	21	23	1	38
5279	145	587	450	230	124	133	5.3	160	102	56	29	31	1	48
***	147	734	490	240	130	141	6.5	150	135	72	38	41	1	58
5245	157	891	530	250	135	149	8	139	173	90	48	51	2	68
5251	144	1035	540	250	134	159	9.8	129	208	106	56	62	3	77
5254	150	1185	510	250	130	157	9	125	243	123	65	72	3	85
***	157	1342	515	260	130	160	9	117	280	142	74	84	4	93
5262	126	1468	520	270	131	163	9	109	309	157	82	93	4	100
5267	113	1581	550	270	138	169	9.4	111	338	171	89	102	5	105
5272	146	1727	580	290	132	170	11	90	376	190	98	113	6	111
***	125	1852	160	200	60	100	2	70	385	202	101	119	6	115
5637	137	1989	166	210	69	105	2.9	70	396	215	105	125	6	120
5645	138	2127	220	220	80	114	3.7	68	409	229	110	132	6	124
5653	144	2271	300	210	86	118	4.4	69	429	242	116	140	6	128
5658	128	2399	340	230	93	119	5.8	65	449	256	121	147	7	132
5667	117	2516	370	230	99	130	6.4	64	468	268	127	154	7	136
5669	128	2644	420	230	102	133	7.9	63	493	281	133	162	8	139
5673	164	2808	450	240	107	135	9.5	61	526	299	141	172	8	144
5676	150	2958	470	240	109	130	9.9	55	558	315	148	181	9	148
***	105	3063	470	240	109	130	9.9	55	581	327	153	187	9	150
5752	163	3226	210	210	83	132	7	56	596	342	159	197	10	154

PX3 SPREAD NM.WKS

Glass ID	Glass Poured (lbs)	Total Glass Poured	Ru (ppm)	Pd (ppm)	Rh (ppm)	Te (ppm)	Se (ppm)	Ag (ppm)	Total Ru	Total Pd	Total Rh	Total Te	Total Se	Total Ag
5756	163	163	280	210	90	125	7.7	54	21	16	7	9	1	4
5759	145	308	300	220	90	125	8	51	40	30	13	17	1	7
5765	117	425	320	210	90	126	8	52	57	41	17	24	2	10
5768	160	585	350	220	93	129	7.4	50	83	57	24	34	2	14
5775	208	793	370	220	98	123	7.9	51	118	78	33	45	3	19
5778	167	960	400	220	94	122	8.4	49	148	95	41	54	3	22
...	181	1141	360	235	92	120	8.1	48	178	114	48	64	4	26
5789	171	1312	320	230	91	118	7.8	47	203	132	55	73	5	30
5792	234	1546	340	220	92	119	6.7	47	239	155	65	86	5	35
5799	170	1716	340	230	94	130	7.5	47	265	173	72	96	6	38
5803	162	1878	360	230	92	118	7.2	47	291	190	79	105	7	42
5806	156	2034	390	230	94	122	7.8	48	319	206	86	113	7	45
5811	162	2196	410	230	98	122	8.3	48	349	223	93	122	8	49
5814	161	2357	410	240	99	125	7.6	46	379	241	100	132	8	52
...	160	2517	415	235	99	122	7.8	46	409	258	107	140	9	56
5823	164	2681	420	230	99	119	8	47	441	275	115	149	9	59
5829	168	2849	340	230	88	117	7	50	467	292	121	158	10	63
5839	153	3002	340	230	90	112	6.1	46	490	308	128	166	10	66
5842	164	3166	350	230	91	113	6.1	43	516	325	134	174	11	69
5846	167	3333	370	230	93	115	5.8	45	544	343	141	183	11	73
5849	174	3507	390	220	95	113	5.6	44	575	360	149	192	12	76
5853	164	3671	360	220	88	119	5.6	43	602	377	155	201	12	79
5858	167	3838	360	220	89	117	5.2	45	629	393	162	210	13	83
5862	160	3998	350	230	89	122	5.2	44	655	410	169	219	13	86
5865	158	4156	360	210	88	120	4.8	43	680	425	175	227	13	89
5871	162	4318	370	230	90	117	4.4	42	708	442	182	236	14	92
5876	160	4478	370	220	89	114	4.4	41	734	458	188	244	14	95
5879	166	4644	370	220	88	118	4.7	41	762	475	195	253	14	98
5884	152	4796	390	210	89	119	5.1	41	789	489	201	261	15	101
6324	152	4948	350	210	86	114	4.6	40	813	504	207	269	15	104
6329	160	5108	126	200	69	99	2.9	38	823	518	212	276	15	107
Per Batch Addition Values														
Per MFT Sample Values														
Total glass poured (kg)	2319.03													
Total Ru poured (gm)	823		Discharge eff (Ru)	54.4		Ru added (gm)	1511.4		Discharge eff (Ru)	59.2			Ru added (gm)	1390
Total Pd poured (gm)	518		Discharge eff (Pd)	97.0		Pd added (gm)	533.9		Discharge eff (Pd)	105.7			Pd added (gm)	490
Total Rh poured (gm)	212		Discharge eff (Rh)	82.5		Rh added (gm)	256.8		Discharge eff (Rh)	81.4			Rh added (gm)	260
Total Te poured (gm)	276		Discharge eff (Te)			Te added (gm)			Discharge eff (Te)	92.1			Te added (gm)	300
Total Se poured (gm)	15		Discharge eff (Se)			Se added (gm)			Discharge eff (Se)	58.1			Se added (gm)	26
Total Ag poured (gm)	107		Discharge eff (Ag)	111.8		Ag added (gm)	95.3		Discharge eff (Ag)	96.9			Ag added (gm)	110

NOTE: NO MFT NOBLE METALS ANALYSES WERE AVAILABLE. THEREFORE THE ALTERNATIVE DISCHARGE EFFICIENCY VALU OTHER RUN SPREADSHEETS COULD NOT BE DETERMINED.

Appendix B

Statistical Analysis of The Effect of Noble-Metal Fission-Product Deposition on Electrical Shorting As Indicated by the Electrode Impedance Ratio of Waste-Glass Melter

INTRODUCTION

Melters are being developed for the conversion of high-level radioactive waste to borosilicate glass for permanent disposal. Operation of waste-glass melter treating simulated and actual commercial power reactor wastes indicated that noble-metal fission-product accumulation on melter floors can lead to distortion of electric heating patterns. This may decrease melter life, since any loss of electrical resistance from the formation of conductive phases reduces the power available for the melting process. Changes in melter geometry have been developed in Japan and Germany to reduce this effect. The two existing melter for the U.S. Department Energy's Defense Waste Processing Facility were designed in 1982, before this effect was known or characterized. Pilot scale tests are being conducted in the Integrated DWPF Melter System (IDMS) to determine if the effect is significant for U.S. defense wastes, and if the effect can be diagnosed and corrected without significant damage or changes to the melter design.

LITERATURE REVIEW

Platinum group metals are produced by irradiation in nuclear reactors. The solubility of these metals is low in glass even at 1150 °C [1]. The Japanese Power and Nuclear Fuel Development Corporation produced 3.5 tonnes of simulated waste-glass containing 0.74% RuO₂, 0.11% Rh, 0.30% Pd, and 0.02% Ag [2]. At the end of the test, the electrical field in the melter was distorted to the point where glass processing could not continue. The deposits were a mixture of RuO₂, and alloys of Pd/Te and Ru/Rh. Similar results were reported in tests in Europe [3,4]. The concentration ratios of the Japanese to U.S. feeds are typical of the difference in concentrations between commercial reprocessing wastes and defense wastes (Ru 18:1, Rh 14:1, Pd 1500:1, and Ag 3:1) [5].

These results suggested that the DWPF melter could experience significant distortion of power from the bottom electrode pair after about 150 melter throughputs, or about 1.5 years of continuous operation. Physical modeling of melter electrical patterns was evaluated for typical U.S. waste-glass [5]. See Figure 1. It was concluded that major melter design changes should not be necessary, provided that minor alterations in melter electrode design and monitoring of electrical characteristics could provide protection from shorting if noble metals accumulate [5].

METHODS

The IDMS melter is one-ninth (1/9) the capacity of the existing DWPF production melter, with two pairs of electrodes, similar to the DWPF electrode geometry. Over a period of two and one-half years 17,620 grams of noble metals have been fed to the IDMS melter, at concentrations typical of U.S. defense wastes. During this period the voltage and electrical currents necessary to maintain operating temperatures were recorded twice daily. Impedances were calculated by dividing the voltage (volts, 60 cycle AC) by current (amps). The calculated impedance of the top electrode pair was divided by the corresponding impedance of the bottom pair in an attempt to minimize effects caused by temperature and melt composition variations, as recommended by Reference 5. Missing data points and some conditions with temporary high resistances were not evaluated. Figure 2 indicates the electrode impedances and the corresponding ratios for the 906 useable data points.

RESULTS

A least squares regression of the overall data was calculated and is plotted in Figure 2. The test results were divided into three subsets to determine if the correlation coefficient could be improved. The two major subsets consisted of data from 1,180 to 11,560 grams of noble metals fed (B), and from 11,560 to 17,620 grams fed (C). The average and standard deviation of the impedance ratio was calculated for each

of these two subsets, and for the final cluster of data (D). The least squares regressions were calculated for each of the subsets, and are plotted for the two major subsets (B & C) in Figure 3. Statistical results are summarized in Table I, and hypothesis tested in Table II below.

TABLE I
RESULTS OF STATISTICAL ANALYSES OF IMPEDANCE RATIOS

DATA SET	GRAMS TO MELTER	RATIO		N	MEAN		REGRESSION	
		AVE.	S. DEV.		LCL	UCL	β_1	STD. ERROR OF β_1
A	1,180-17,620	1.247	0.1811	906	1.24	1.26	1.283E-5	9.820E-7
B	1,180-11,560	1.199	0.1438	733	1.19	1.21	-1.512E-6	1.270E-6
C	11,560-17,620	1.353	0.2077	284	1.33	1.38	5.520E-5	4.456E-6
D	14,590-17,620	1.414	0.2158	193	1.38	1.44	8.186E-5	9.597E-6

N = number of data points: Some values are shared between data subsets, e.g. at 11,560 grams. Pooled Std. Dev. of 1,180 to 11,560 and 11,560 to 17,620 subsets is 0.1641, with greater than 240 degrees of freedom.

LCL = Lower Confidence Limit of Mean, at 95% confidence level.

UCL = Upper Confidence Limit of Mean, at 95% confidence level.

β_1 = Regression Coefficient for slope of Impedance Ratio vs. Grams Noble Metals.

T.S.: $t = (\text{Average of data} - \text{Mean of population}) / (\text{std. dev.} / \text{square root}(\text{number of samples}))$

$t = \beta_1 / \text{std. error of } \beta_1$

TABLE II
HYPOTHESIS TESTING OF IMPEDANCE RATIOS

NULL HYPO.	RESEARCH HYPO.	$t_{0.05}$	$t_{\text{CALCULATED}}$	CONCLUSION
$\bar{X}_B - \bar{X}_C = 0$	$\bar{X}_B < \bar{X}_C$	1.645	-11.47	$\bar{X}_B < \bar{X}_C$
$\beta_{1A} = 0$	$\beta_{1A} > 0$	1.645	13.07	$\beta_{1A} > 0$
$\beta_{1B} = 0$	$\beta_{1B} > 0$	1.645	-1.19	$\beta_{1B} = 0$
$\beta_{1C} = 0$	$\beta_{1C} > 0$	1.645	12.39	$\beta_{1C} > 0$
$\beta_{1D} = 0$	$\beta_{1D} > 0$	1.658	8.53	$\beta_{1D} > 0$

DISCUSSION

The overall effect was an increase in the impedance ratio as the test progressed. This is proven by use of the t-statistic to examine the difference of the averages of data sets A and C, and is significant at the 95% confidence level. This is further demonstrated by the t-statistic of the standard error of β_1 of data set A (overall data), which proves that the overall data has a positive slope. No significant shift occurred in the impedance ratio between 1,180 and 11,560 grams of noble metals added to the 1/9 scale melter, since the calculated t-statistic is less than the critical value for this portion of the test. The impedance ratios increased significantly at the 95% confidence level for the two final sets of the test data (C and D) since the t-statistic of each β_1 is less than the critical value.

Significant electrical shifts have been measured in a 1/9 scale version of the DWPF melter after feeding of 17,620 grams of noble metals as simulated fission products. No statistically significant shift in melter power occurred during the first 11,560 grams of noble metals fed to the melter. Pilot scale tests confirm the earlier physical modeling, and conclude that the effect will be detectable and quantifiable before damage to the bottom electrodes occurs.

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FIGURE 2

Electrical Impedance of IDMS Electrodes vs. Noble Metals Fed to Melter

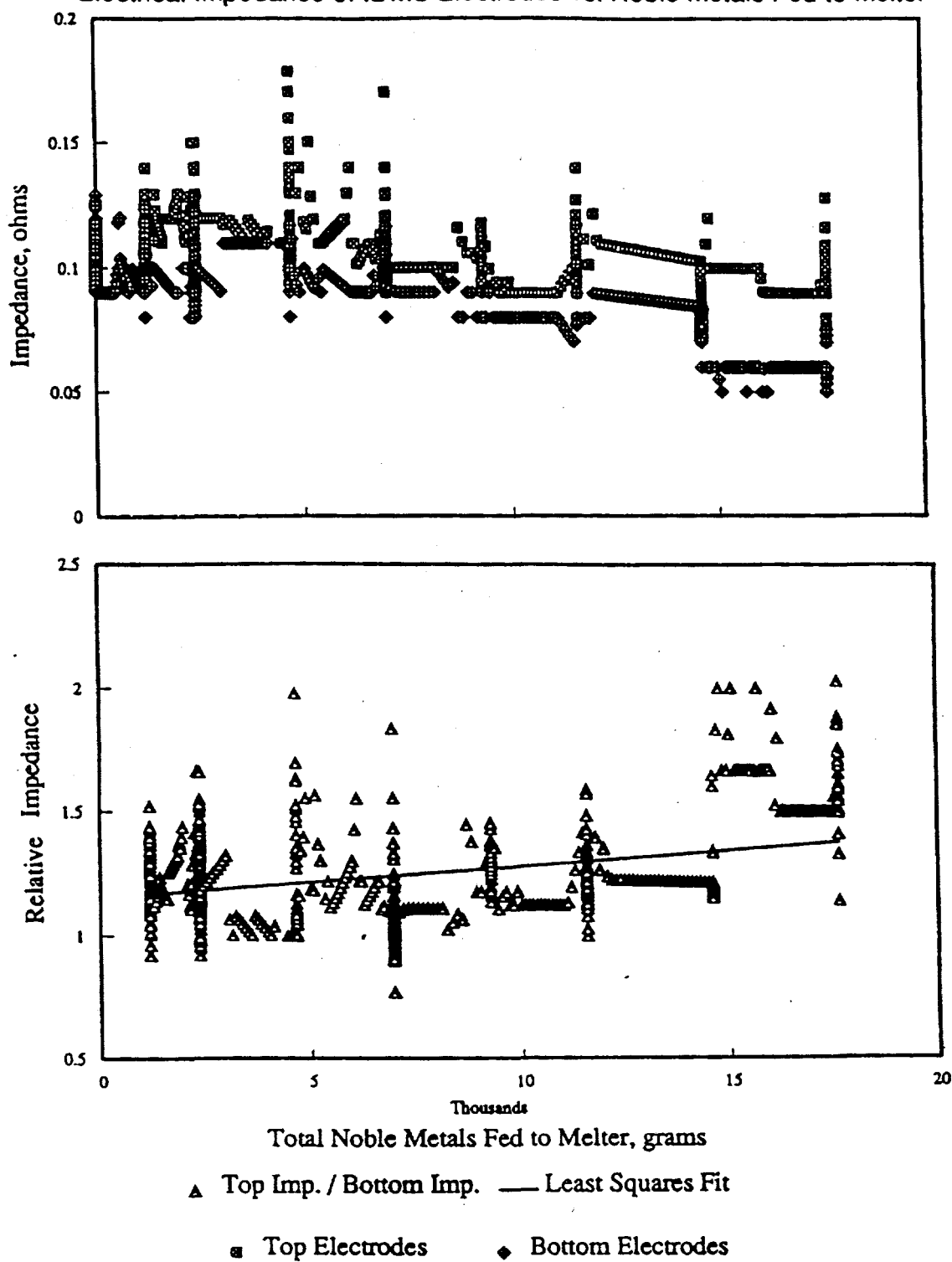
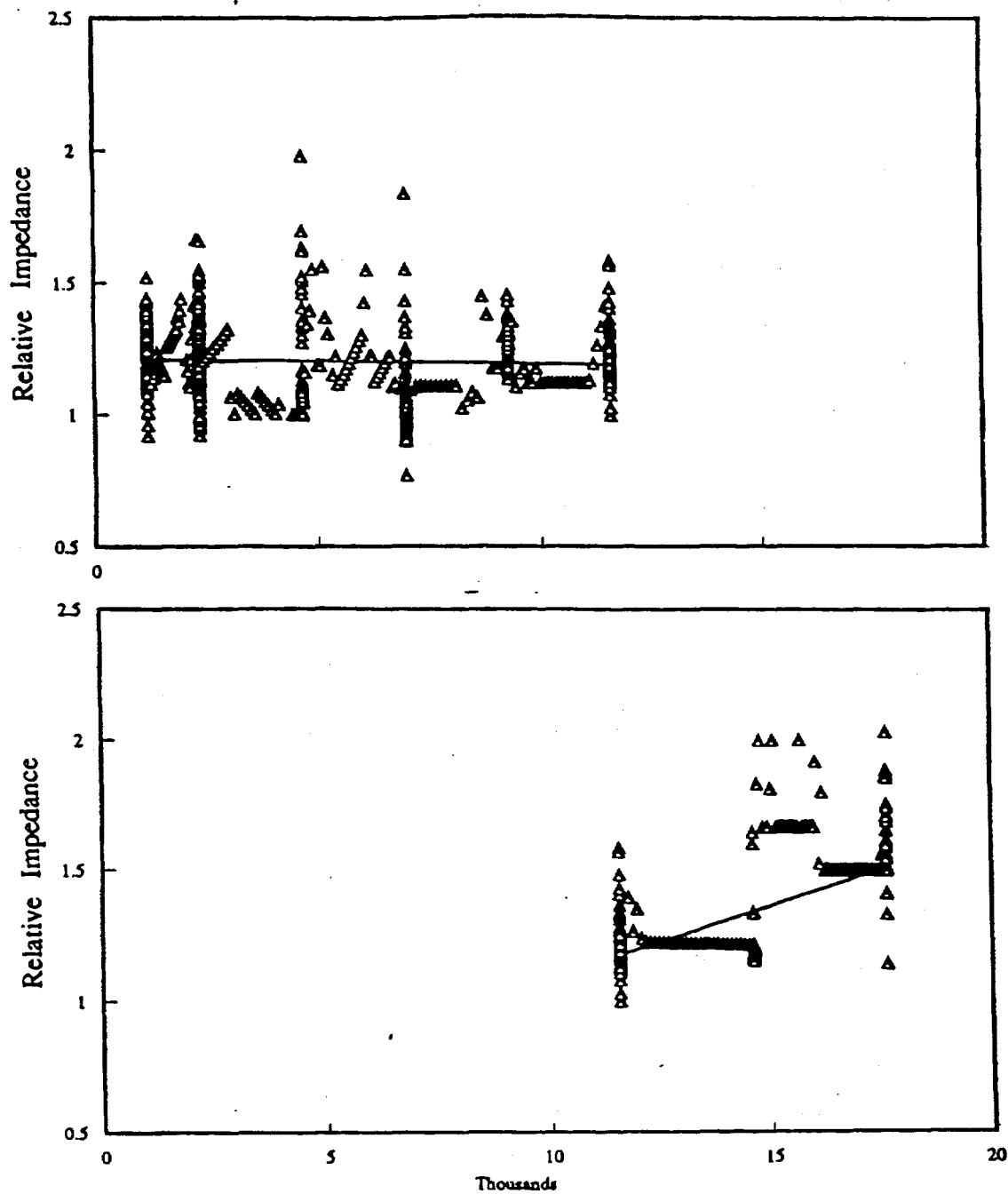


FIGURE 3

Electrical Impedance of IDMS Electrodes vs. Noble Metals Fed to Melter



△ Top Imp. / Bottom Imp. — Least Squares Fit

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