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Preliminary Evaluation of Noble Metal Behavior
in the Hanford Waste Vitrification Plant
Reference Glass, HW-39**

**R. W. Geldart
S. O. Bates
S. J. Jette**

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

**Pacific Northwest National Laboratory
Operated for the U.S. Department of Energy
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Richland, Washington 99352

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SUMMARY

The precipitation and aggregation of ruthenium (Ru), rhodium (Rh) and palladium (Pd) in the Hanford Waste Vitrification Plant (HWVP) low chromium reference glass HW-39 were investigated to determine if there is a potential for formation of a noble metal sludge in the HWVP ceramic melter. Significant noble metal accumulations on the floor of the melter will result in the electrical shorting of the electrodes and premature failure of the melter. The purpose of this study was to obtain preliminary information on the characteristics of noble metals in a simulated HWVP glass. Following a preliminary literature review to obtain information concerning the noble metals behavior, a number of variability studies were initiated. The effects of glass redox conditions, melt temperature, melting time and noble metal concentration on the phase characteristics of these noble metals were examined in crucible melt tests. Ferrous/ferric ratios (Fe^{+2}/Fe^{+3}) ranging from 0.0 to 0.65 were used as a measure of glass redox conditions. Melt temperatures of 940°C, 1100°C and 1170°C were studied. Noble metal concentrations ranged from the HWVP reference level of 0.26 wt% to the level observed in the sludge layer of the PAMELA melter of the Federal Republic of Germany (FRG), 11 wt%. Melting times studied were 2.4, 24, and 240 hours. One crucible melt test was designed to provide some indication of noble metal behavior under cold cap conditions present in large-scale ceramic melters.

In the crucible tests, agglomeration and settling of the noble metal precipitates were functions of temperature, time, noble metal concentrations and glass redox conditions. Increasing temperature increased the particulate settling rate and decreased the size and number of particles observed. As time proceeded, particulate size increased and particles settled to the bottom of the crucible. The only effect observed when the concentration of noble metals was increased was an increase in the amount of particulate matter. The redox conditions of the glass and the type of reducing agent affected both the quantity and type of particulate. The crucible melts revealed that

gas bubbles may act as nucleating sites for Ru and aid in their transport to the glass surface. Ruthenium and Rh acted as nucleating agents and were often present in large agglomerates of spinel.

Noble metals behavior was also studied in a liquid-fed minimelter (LFMM). The target ferrous/ferric ratios for glass produced by the minimelter ranged between 0.03 and 0.3, levels representative of those expected in the large-scale HWVP melters. The ferrous/ferric ratios of the output glass from the LFMM ranged from 0.18 to 0.51. The LFMM target redox values could not be obtained because of interference with undetermined reduction reactions in the minimelter. Thus, the redox conditions observed in the minimelter were not representative of those expected in large-scale HWVP melters. Oxidation of chrome from Inconel in the LFMM crucible appears to have contributed to unexpectedly high redox values. The oxidation caused many large high-chrome spinel in the output glass from each minimelter experiment. Submicron particles high in Ru were also present in each output sample. Small Pd particles were also observed in the output glass but were not as common as the Ru particles.

A core of the glass in the minimelter crucible was obtained following approximately 4 to 5 minimelter turnovers to study the settling behavior of the noble metals. The core sample of glass from the minimelter crucible revealed metallic nodules as large as 0.5 cm in diameter near the base of the crucible. Analysis of one of the nodules indicated that it is an alloy of Ru, Rh, and Pd with some Te, Cu, Ni, Fe, and Mo present. Many of the nodules accumulated near the end of an Inconel thermowell, indicating possible catalysis by the Inconel.

The majority of the particulates observed in the crucible melts were under 10 μm in diameter. Studies have shown that settling of particles under 10 μm is insignificant in large-scale ceramic melters. Large (5 mm) nodules were observed in the LFMM tests. These nodules may be a result of large amounts of chromium observed in the minimelter, and may not be representative of actual HWVP melter conditions. However, the presence of the nodules suggests that

further work is needed to study the noble metals behavior under conditions representative of those in the large-scale joule-heated HWVP melters.

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1.0 INTRODUCTION

At melter operating temperatures (approximately 1150°C), noble metals (Ru, Rh, and Pd) are only slightly soluble in borosilicate nuclear waste glasses. The solubility of Ru has been observed to be less than 0.001 wt% in borosilicate melts.¹ The presence of noble metals in nuclear waste glasses has also been observed in large-scale vitrification plants in the Federal Republic of Germany (FRG) and Japan. In the case of the FRG PAMELA melter, the noble metal phases caused a viscous, conductive sludge to accumulate at the bottom of the melter. The sludge caused short-circuiting of the lower melter electrodes and failure of the bottom drain of the melter.² The Hanford Waste Vitrification Plant (HWVP) reference glass composition (HW-39) for pretreated neutralized current acid waste (NCAW) has approximately the same concentration of total noble metals as is found in the glass processed in the FRG PAMELA melter. Therefore, conditions similar to those observed in PAMELA could occur in the HWVP melter.

This study was initiated to determine if there is a potential for the formation of a noble metal sludge in the HWVP melter. Extensive accumulation of noble metals in the HWVP melter will impact both melter design and operation.

Because of the high cost of the noble metals (\$34/liter of simulated NCAW/HW-39 melter feed), only small amounts of Ru have been included in previous nonradioactive engineering- and pilot-scale melter tests. Noble metals have also been included in some laboratory-scale testing for HWVP reference glass development. Particles of Pd metal and RuO₂ crystals have been observed in previous laboratory melts.

The effects of glass redox conditions, noble metal concentrations, temperature and time were studied using both crucible glass melts and the liquid-fed minimelter (LFMM). Crucible glass melts were used to characterize the precipitation, agglomeration, and settling behavior of the noble metals. The LFMM was used to study noble metal precipitation in a small-scale continuous

feed process designed to partially simulate the conditions of the larger-scale ceramic melters. Testing was performed by the Waste Form Development subtask (V110202). Results of this study will support closure of the HWVP Technology Plan, issue 2.1.1, "Reference Glass Development."

2.0 OBSERVATIONS AND CONCLUSIONS

The following observations were made during the noble metals behavior study:

Crucible Studies

Based on the crucible melt tests, the following observations were made regarding the effects of temperature, time, noble metal concentrations, and redox environment on noble metal precipitation.

- Noble metal phases observed in the crucible study included Fe-Cr-Ni spinel with varying amounts of Ru, Rh and Pd. Metallic-appearing nodules of Pd, Ru, and Rh and various combinations of all three noble metals were observed in some of the melts. Many of these nodules often had traces of Cu, Fe, Ni, and Cr. Palladium was observed to alloy with Te in some cases. Besides the metallic-like nodules, some noble metal oxides (RuO_2 and RhO_2) were observed by x-ray diffraction.
- In the temperature range planned for HWVP melter operation, temperature played a role in the agglomeration and settling behavior of the predominant iron-spinel crystals. Although agglomerations of the crystals increased in both size and number as the temperature decreased, individual crystal sizes did not vary over the temperature range examined.
- Both the settling and agglomeration behavior of the noble metal phases were observed to vary with time. The size of the spinel crystals in the agglomerates increased with time. As time increased, Pd was transported to the surface of the crucible. The mechanism for this transport was not determined.

- The only effect observed when the concentration of noble metals was increased was an increase in the quantity of the noble metal particulate throughout the melt.
- For redox conditions expected in the HWVP melters, redox conditions affected both the quantity and type of particulate observed. Glasses with ferrous/ferric ratios of 0.0 and 0.03 displayed large quantities of spinel crystals that contained small quantities of Ru, Rh and Pd. No spinel crystals were observed at ferrous/ferric ratios of 0.27. At this ferrous/ferric ratio, each of the noble metals agglomerated in high-purity particulates, with little mixing of elements. These high-purity noble metal agglomerates were not observed at the lower ferrous/ferric ratios.
- When sugar was used to obtain a glass with a ferrous/ferric ratio of 0.65, spinel crystals were observed. However, spinel crystals were no longer observed at a ferrous/ferric ratio above 0.27 when formic acid was used as a reducing agent.
- The cold cap sample from a crucible melt did not reveal any excessive formation of noble metals in the cold cap.
- Ru was observed (possibly as RuO_2) to adhere to bubbles present in the glass melt. These bubbles act as a transport mechanism to bring the Ru to the surface of the melt where it was observed to accumulate. Pd also accumulated at the surface of the crucible melts. These observations are consistent with observations made by the Japanese.³ The wetting and surface tension properties of the noble metals and the glass may be responsible for the accumulation.
- Ru and Rh phases acted as nucleating agents for other particulates. They were often present in large agglomerates of spinel and other noble metal particulates.

LFMM Studies

The following observations were made from the LFMM experiments.

- Large noble metal nodules were observed in the LFMM. Some of the high Ru, Pd, and Rh noble metal nodules were as large as 0.5 cm in diameter. Many of the nodules accumulated near the end of an Inconel thermowell, indicating possible catalysis by the Inconel.
- The glass redox state of the minimelter output glass could not be controlled satisfactorily by sugar addition presumably because of the corrosion of the Inconel. Thus, the LFMM conditions are not fully representative of those expected in the large-scale HWVP melters.
- High-chrome spinel crystals in agglomeration sizes up to 100 μm were abundant in the output glass of each minimelter test. These spinels were the result of corrosion of the Inconel vessel. Although particulates containing Ru and Pd were observed in the output glass, these particulate were usually under 1 μm in diameter.

Based on the above observations, the following conclusions can be made:

Crucible Testing

- A wide variety of noble metal phases may form at conditions expected in the HWVP melter using the reference level HWVP low-chromium glass compositions. These phases included a variety of iron-chrome-noble metal spinel phases, metallic-like nodules which included various combinations of Ru, Rh and Pd and agglomerates of submicron ruthenium crystals. The exact form of the ruthenium is unknown. All the phases have the potential to settle in stagnant glass melts.

- The crucible tests indicate that noble metal concentrations, temperature, time, glass redox conditions and type of reducing agent may all affect noble metal behavior under HWVP melter operating conditions.
- Based on crucible testing, there is the potential for formation of noble metal sludges in the HWVP melter. Further testing in engineer- and pilot-scale melters is needed to assess the sludge formation potential.

LFMM Studies

- The LFMM results were affected by the corrosion of the Inconel vessel.
- Noble metal concentrations in the reference level HWVP low-chrome glass were sufficient to cause precipitation of noble metals in the LFMM. Although the conditions in the LFMM are only partially representative of those in the large-scale HWVP melter, these results indicate that the potential exists for precipitation of noble metals to occur in the HWVP melter.

3.0 RECOMMENDATIONS

Based on the work conducted and the above conclusions, the following recommendations were made.

- Further studies should be conducted to better determine the effects of the type of reducing agent and the glass redox environment on noble metal behavior.
- Quantitative settling and agglomeration rates must be determined for the conditions expected in the HWVP melter. This information will be needed when examining alternative melter designs such as a sloped bottom ceramic melter.
- Testing should be conducted in prototype joule-heated melters to evaluate noble metal behavior under conditions representative of large-scale HWVP glass melters using HWVP feed.

4.0 LITERATURE REVIEW

A literature review concerning the behavior of noble metals in borosilicate nuclear waste glasses was conducted prior to laboratory testing. Little published material was found concerning the behavior of noble metals in borosilicate glasses. Much of the information regarding the noble metal precipitates was reported in unpublished documents provided by FRG and Japanese sources.

Ruthenium, rhodium, and palladium have often been observed in precipitates in nuclear waste glasses. The behavior of Ru in the borosilicate glass SRL-131 was investigated.¹ The study revealed that for a wide range of Ru dopants, redox additives, times, and melt temperatures, less than 0.001 wt% of Ru could be dissolved in the borosilicate glass. Ruthenium solubility was also investigated for sodium silicate and phosphate glasses.^{4,5} Ruthenium solubility increased with increasing Na₂O/SiO₂ ratios and rising temperatures. However, Ru solubility limits for silicate glasses were still only 100 to 2000 ppm. Ruthenium, rhodium and palladium have been observed by many to precipitate in borosilicate waste glasses.^{3,6-12} X-ray diffraction analysis has been used to identify many of the forms of the noble metal precipitates. Ruthenium dioxide was identified as a common form for the Ru.³ Rhodium has been observed in both metallic and oxide forms. The other noble metal that is of interest is Pd. Metallic Pd has been observed to alloy with both Rh and Te.

Convection currents in the melter are expected to suspend many of the small noble metal particulates in the glass melt. Another suspension mechanism that has been observed in glass melts is a result of gas bubbles. Some authors have observed that gas bubbles can transport a large fraction of the noble metals to the surface of glasses even though the densities of both the metallic and oxide forms of the noble metals are higher than that of the glass.³ Once at the surface, the surface tension of the glass apparently prevents the resettling of the noble metals to the bottom of the melt.³

The metallic-like conductivity of RuO_2 is another property of interest. Conductivity is of particular importance because RuO_2 has been observed in sludges in both Japanese and FRG glass melters,^{2,13} Noble metal precipitation has been shown to form conductive sludges in the bottom of the large-scale melters in Japan and Germany.^{2,13} The noble metal compositions of the waste glasses used by the Japanese and Germans, and those of the HWVP glass, HW-39; the West Valley glass, WV205; and the Savannah River Glass, SRL-165, are given in Table 1. The concentrations of Ru, Pd, and Rh observed are comparable for all of the glasses. This similarity indicates that the HWVP melter, as well as the Savannah River and West Valley melters, may experience noble metal precipitation similar to that observed by the Germans and Japanese.

The Japanese have examined new melter designs to resuspend precipitated noble metals in the glass melt using sparging techniques.¹⁴ Others have sought to separate the noble metals from the glasses for commercial use.¹⁵ The noble metal precipitation remains a significant world-wide problem for both defense and commercial nuclear waste vitrification.

Table 1. Comparison of Noble Metals in Familiar Glasses

Glass Oxide (wt%)	HWVP HW-39	DWPF SRL-165	WVDP WV-205	PAMELA LEWC	PNC
<u>RuO₂</u>	<u>0.15</u>	<u>0.13</u>	<u>0.08</u>	<u>0.15</u>	<u>0.74</u>
PdO	0.05	0.05	0.01	0.03	0.35
Rh ₂ O ₃	<u>0.05</u>	<u>0.02</u>	<u>0.01</u>	<u>0.09</u>	<u>0.14</u>
Totals	0.25	0.20	0.10	0.27	1.23

* The PAMELA LEWC composition was calculated assuming a 11 wt% waste loading in the glass. The waste composition was obtained in reference 11.

*The PNC glass composition was obtained from reference 13.

5.0 TECHNICAL APPROACH

The behavior of noble metals was studied using two different melt processes. These processes were crucible melts and the LFMM. The following is a description of the objectives and technical approach used in the study. The glass composition used for all testing was the HWVP reference glass, HW-39 incorporating the 1984, low-chrome version of the pretreated neutralized current acid waste (NCAW'84). The oxide compositions of the waste and resulting glass are presented in Table 2. The formulation used to make the waste slurry feed is shown in Table 3. Crucible melts provide an inexpensive and effective way to observe precipitation of noble metals. Temperature, glass redox conditions, noble metal concentrations and time are easily varied without the considerable time and effort needed for an actual large-scale melter run. Crucible melts have benefits in their simplicity but can not incorporate the dynamics of a continuously-fed system. The LFMM was used to provide a more representative comparison to large-scale melters. Operation of the LFMM was limited to studying glass redox conditions and time-related agglomeration.

5.1 CRUCIBLE MELT TESTS

The furnace and a typical crucible used for crucible melts are shown in Figure 1. The melt was begun by placing the crucible in the hot furnace and bringing the crucible to the required operating temperature. The melt temperature was measured by placing a type-K thermocouple at the base of the crucible. Fifty ml of a simulated slurry were poured into the crucible in 3 aliquots over a 30-minute period. The Ru, Rh and Pd were added to the feed as the oxides, RuO₂, Rh₂O₃ and PdO. Their average particle sizes were measured to be approximately 15 μm , 5 μm and 2 μm , respectively. After the feeding period was completed, the glass was stirred and allowed to melt for an additional 30 minutes. The crucible was then removed from the melt furnace and transferred to an annealing oven. The glass was annealed at 500°C and oven-cooled over night to ambient conditions.

Table 2. Composition of the HWVP NCAW'84 (Low Chrome) Reference Waste, Substituted Waste, and Glass (HW-39) at a 25 wt% Oxides Waste Loading.

OXIDE	NORMALIZED WASTE WT% OXIDE	SUBSTITUTED WASTE WT% OXIDE	SUBSTITUTED WASTE NOR. WT% OXIDE	SUBSTITUTED WASTE NOR. NO TOC	HW-39 FRIT WT% OXIDE	HW-39 GLASS WT% OXIDE
SiO2	3.89	3.89	3.12	3.14	67.25	51.22
B2O3	0.01	0.01	0.01	0.01	12.75	9.56
Na2O	11.1	11.1	11.2	11.3	18.25	18.52
Li2O	0.00	0.0	0.0	0.0	5.00	3.75
CaO	0.31	0.31	0.31	0.31	3.75	2.89
MgO	0.25	0.35	0.35	0.35	1.00	0.84
Fe2O3	46.3	46.3	46.9	47.2		11.79
ZrO2	2.5	2.5	2.5	2.5		0.63
Al2O3	17.9	17.9	18.1	18.2		4.58
NiO	2.47	2.47	2.50	2.52		0.63
La2O3	2.29	2.29	2.31	2.33		0.58
TOC	0.62	0.62	0.62	-		0.00
Nd2O3	1.79	2.07	2.09	2.11		0.53
SO3	1.54	1.54	1.56	1.57		0.39
F	1.24	1.24	1.25	1.26		0.31
MoO3	1.24	1.24	1.25	1.26		0.31
U3O8	0.62	SUB Nd	SUB Nd	SUB Nd		
CeO2	0.62	0.62	0.62	0.63		0.16
Cs2O	0.62	0.62	0.62	0.63		0.16
CuO	0.62	0.62	0.62	0.63		0.16
MnO2	0.62	0.62	0.62	0.63		0.16
RuO2	0.62	0.62	0.62	0.63		0.16
Cr2O3	0.56	0.56	0.56	0.57		0.14
BaO	0.43	0.43	0.44	0.44		0.11
Pr6O11	0.37	0.37	0.37	0.38		0.09
SrO	0.37	0.37	0.37	0.38		0.09
Tc2O7	0.37	DEL	DEL	DEL		
PdO	0.19	0.19	0.19	0.19		0.05
Rb2O	0.25	0.25	0.25	0.25		0.08
Rh2O3	0.19	0.19	0.19	0.19		0.05
Sr2O3	0.19	0.19	0.19	0.19		0.05
Y2O3	0.19	0.19	0.19	0.19		0.05
BeO	0.06	SUB Mg	SUB Mg	SUB Mg		
NpO2	0.12	DEL	DEL	DEL		
TeO2	0.12	DEL	DEL	DEL		
K2O	0.00	DEL	DEL	DEL		
PbO2	0.00	DEL	DEL	DEL		
SeO2	0.03		DEL	DEL		
Am2O3	0.02	DEL	DEL	DEL		
CdO	0.02	DEL	DEL	DEL		
Eu2O3	0.02	SUB Nd	SUB Nd	SUB Nd		
P2O5	0.02	DEL	DEL	DEL		
PuO2	0.02	DEL	DEL	DEL		
SnO2	0.02	DEL	DEL	DEL		
Ag2O	0.01	DEL	DEL	DEL		
Gd2O3	0.01	DEL	DEL	DEL		
Nb2O5	0.01	DEL	DEL	DEL		
Pm2O3	0.01	SUB Nd	SUB Nd	SUB Nd		
Ta2O5	0.01	DEL	DEL	DEL		
TiO2	0.01	DEL	DEL	DEL		
	100.0	98.869	100.0	100.0	100.0	100.0

Table 3. Compositions of HWVP Low-chrome Reference Level Waste Slurry.

<u>Compound</u>	<u>g Compound/L</u>
Al(OH) ₃	125.67
BaSO ₄	3.03
CaF ₂	1.95
Ce(OH) ₃	3.15
Cr(OH) ₃	3.48
CsNO ₃	3.93
Cu(OH) ₂	3.48
Fe(OH) ₃	1203.3
LaF ₃	6.69
La(OH) ₃	5.73
Mg(OH) ₂	2.28
Mn(OH) ₂	2.90
Na ₂ MoO ₄	8.07
Na ₂ C ₂ O ₄	15.87
NaF	5.04
NaI	2.10
NaNO ₃	34.17
NaOH	26.25
Na ₂ SO ₄	10.74
NdF ₃	1.8
Nd(OH) ₃	9.9
Ni(OH) ₂	14.07
PdO	0.87
Pr(OH) ₃	1.92
Rb ₂ CO ₃	1.34
Rh ₂ O ₃	0.87
RuO ₂	2.85
SiO ₂	14.16
Sm(OH) ₃	0.99
Sr(OH) ₂	4.39
TeO ₂	0.43
Y(OH) ₃	1.05
Zr(OH) ₄	14.58

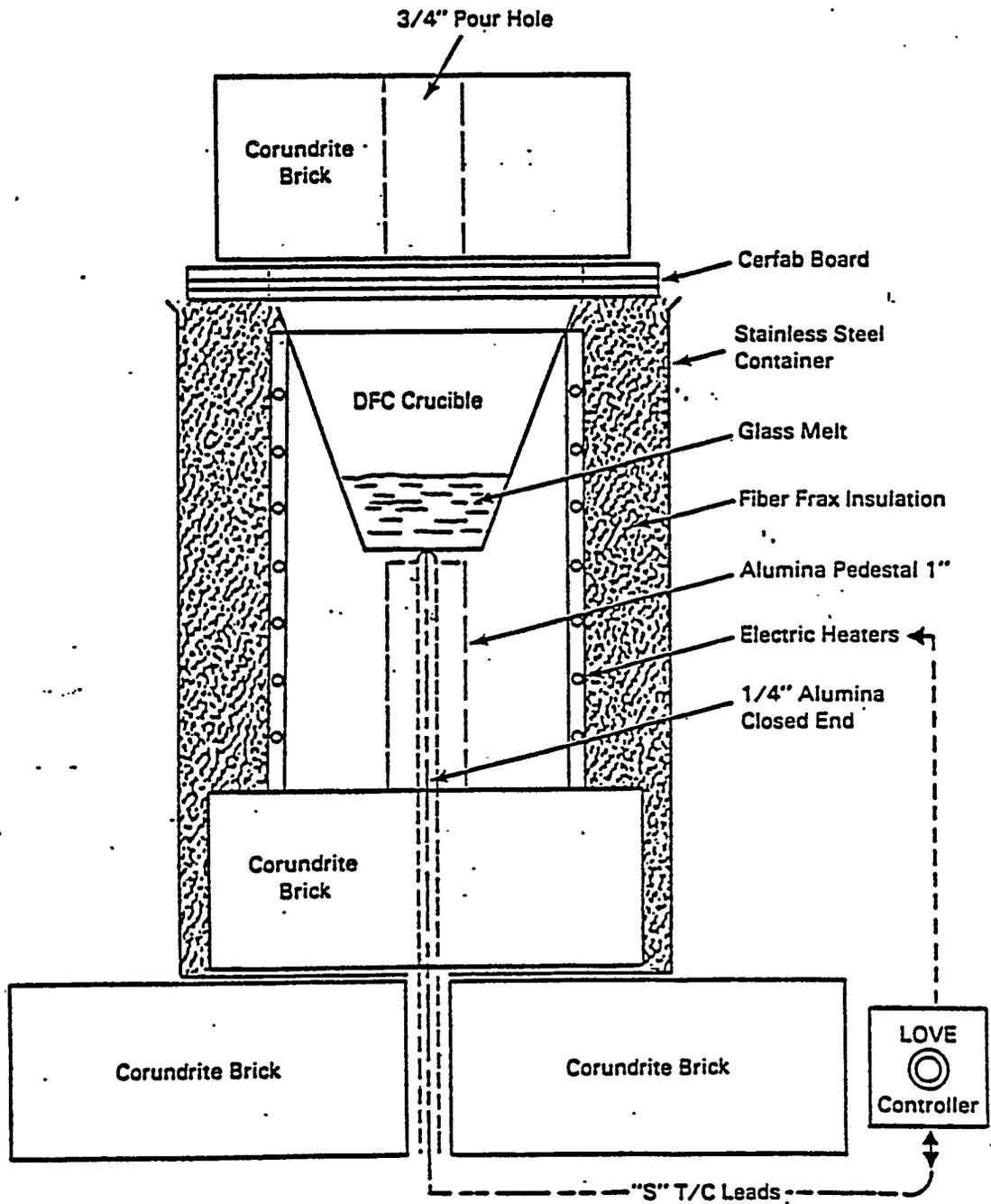


Figure 1. Schematic of experimental apparatus used in the crucible variability studies.

5.1.1 Analysis of Particulate

The glass depth in each crucible was approximately 8 to 10 mm. Thin sections of the annealed glass were cut along the axial length of the crucible as shown in Figure 2. Sections were polished and then analyzed by scanning electron spectroscopy (SEM/EDAX). A sample of the glass produced in the crucible was crushed and powdered in an agate disc mill and used to determine the glass redox and composition. Inductively coupled plasma mass spectroscopy (ICP) and x-ray fluorescence were used to analyze the glass compositions.

5.2 LFMM MELTS

Several different LFMM experiments were performed, using the LFMM apparatus shown in Figures 3 and 4. Each experiment used a simulated feed slurry to obtain the reference level HW-39 low-chrome glass composition shown in Table 2. The Ru, Rh and Pd were added to the feed as the oxides, RuO₂, Rh₂O₃ and PdO. Their average particle sizes were measured to be approximately 15 μm, 5 μm and 2 μm, respectively. The redox conditions for each glass were adjusted by adding sugar as a reducing agent to the reference level formed feed. Preliminary crucible melts were used to determine sugar additions necessary to achieve glass redox ratios between 0.03 and 0.3. The range of the slurry feed rate was 180 ml/h to 300 ml/h. The steady state glass depth in the LFMM crucible was approximately 10 cm. The bottom temperature of the LFMM crucible fluctuated from 1095°C to 1150°C, and the temperature at the top of the melt from 660°C to 1030°C, depending upon the proximity of the cold cap to the thermowell. LFMM output glasses were analyzed by x-ray fluorescence, SEM/EDAX, and ICP. A glass core was drilled in the glass remaining in the LFMM following completion of the LFMM experiments.

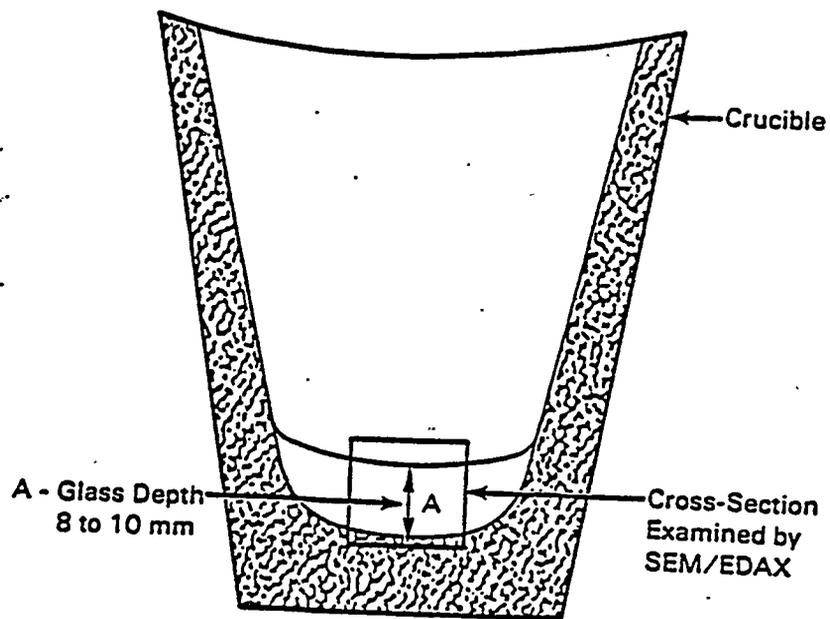


Figure 2. Cross-section of DFC crucible showing glass area analyzed by SEM/EDAX.

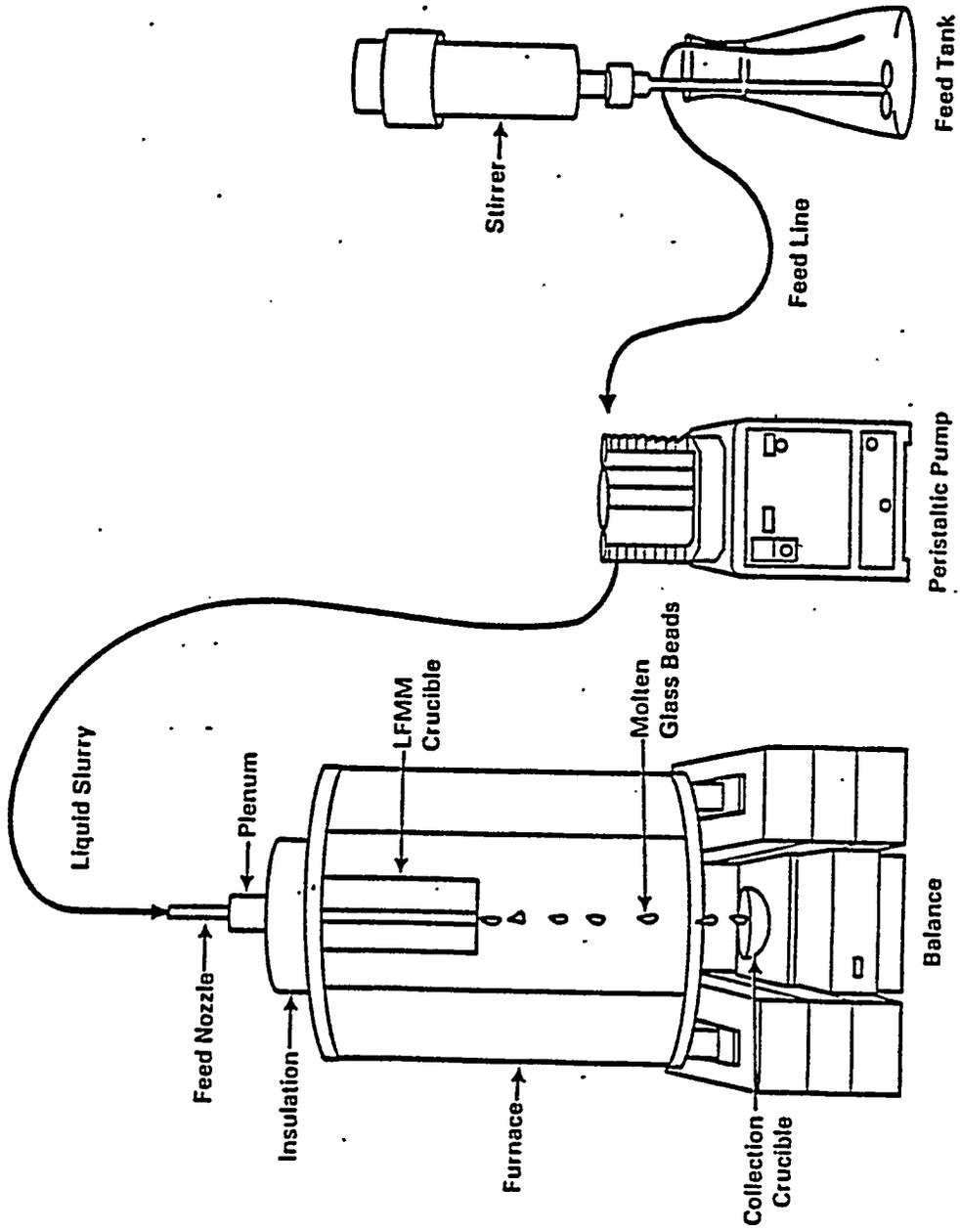


Figure 3. Schematic of experimental apparatus used in LFM studies.

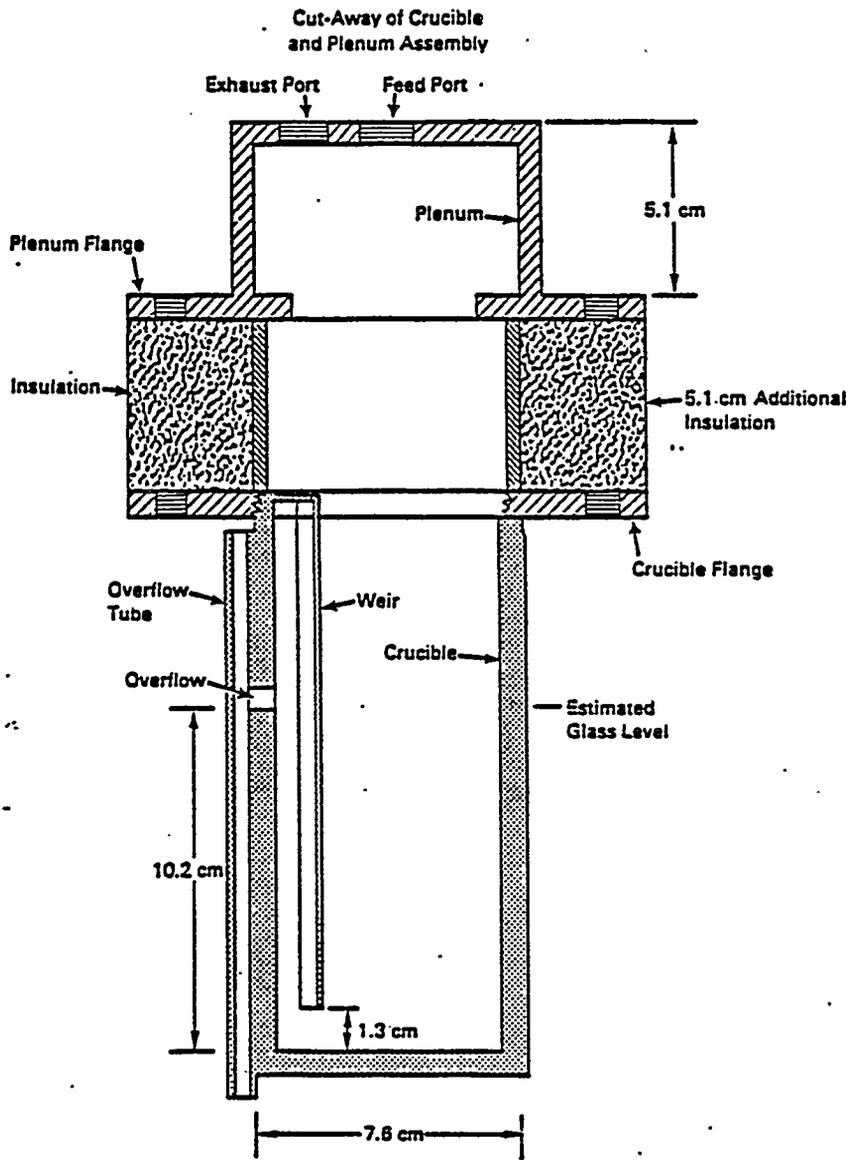


Figure 4. Cross-section of Inconel crucible in LFMM.

6.0 RESULTS AND DISCUSSION

This section includes a discussion of the results and observations from the crucible tests and the LFMM experiments. A summary of the observations from the crucible tests is given in Table 4.

6.1. CRUCIBLE TEMPERATURE VARIATION STUDY

The temperature study included three glasses with the reference composition given in Table 2. The glasses were all formed to the same level to achieve a reference ferrous/ferric ratio of 0.03. The three glasses were melted at temperatures of 940°C, 1100°C, and 1170°C for the standard 30-minute melting period.

6.1.1 Glass Temperature of 940°C

At this temperature, many particulates were observed, and consisted mainly of Fe-Cr-Ni spinel type crystals. Although the particles at the top and bottom of this crucible were very similar in composition, their sizes and appearances differed greatly. A SEM analysis showed that the majority of the crystals tended to be of a Fe-Cr-Ni spinel type, although the spinel in the top of the crucible varied from the spinel found in the bottom of the crucible. The crystals in the top had diameters ranging from 5 to 25 μm ; those at the base of the crucible were much smaller, having diameters ranging from 1 to 5 μm . The crystals at the base of the crucible appeared to have a high luster not seen in the spinel at the top of the crucible. Ru and Rh were present in the spinel in both the bottom and top parts of the crucible.

Table 4. Summary of Crucible Variability Studies

Variable	Range	Crucible Temperature	Time	Ferrous/Ferric Ratio	Noble Metal Oxide Core (wt%)	Effect
Temperature (°C)	940, 1100, 1170°C	NA	0 hrs	0.03	0.26	Size and number of agglomerates of spinel crystals containing noble metals increased as temperature decreased. Settling is more evident at higher temperatures.
Time (hrs)	2.4, 2.7, 240 hrs	1100°C	NA	0.03	0.26	As time increased spinel crystal sizes increased. Settling of spinel crystals was observed at 2.4 hours. Pd was transported to crucible surface as time increased.
Ferrous/Ferric	0.0, 0.03, 0.27, 0.65	1100°C	0 hrs	NA	0.26	As ferrous/ferric ratio increased the number of spinel crystals decreased. When formic acid was the reducing agent no spinel were observed at a ferrous/ferric ratio of 0.27. Spinel were still present at a ferrous/ferric ratio of 0.65 when sugar was the reducing agent.
Noble Metal Oxide Concentration (wt%)	0.26, 2, 11	1100°C	0 hrs	0.03	NA	Amount of noble metal phases increased as noble metal concentrations increased.
Cold Cap Study	NA	1100°C	0 hrs	0.03	0.26	Cold cap contained La and Zr precipitates not seen in the bottom of the crucible. No precipitation of noble metals was observed in the cold caps.

6.1.2 Glass Temperature of 1100°C

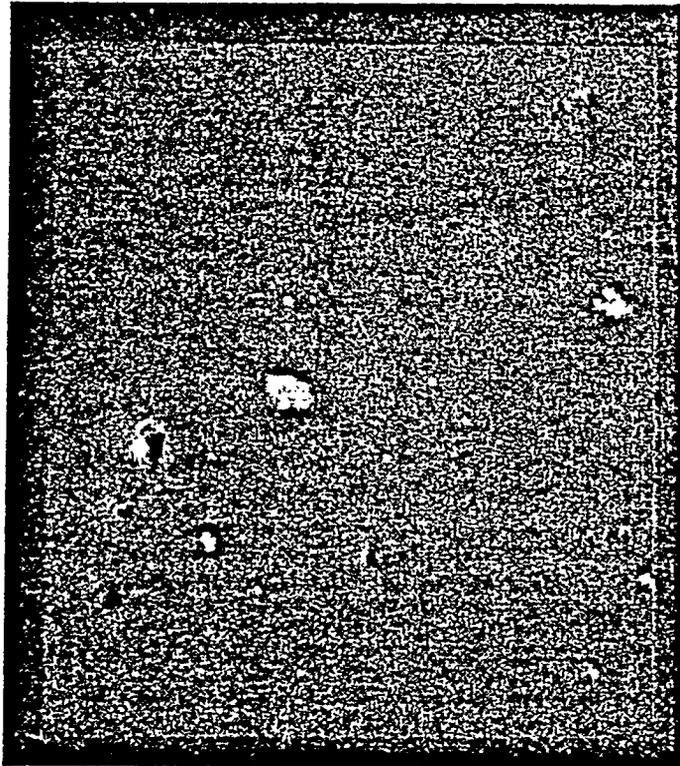
Iron-chrome-nickel spinel crystals were predominant in this glass. Some settling of the crystals had occurred at this time. Crystals in both the top or bottom of the crucible were in the range of 1 to 3 μm , although in the bottom of the crucible agglomerations of these spinel type crystals ranged from 10 to 20 μm . Many of the spinel crystals at the base of the crucible exhibited high levels of Rh and Pd. Some non-spinel particles at the top were a high-Ru-concentration phase.

6.1.3 Glass Temperature of 1170°C

Figures 5 and 6 show that at 1170°C there was a significant visual gradient in crystal density in the glass. The individual 2- to 4- μm crystals at the bottom of the crucible were spinel-type crystals with low amounts of Ru. The particles at the top of the crucible were noncrystalline agglomerations ranging in size from 1 to 5 μm . These agglomerations contained high levels of Ru. Rhodium and Pd were not observed in this glass. This result indicates Rh and Pd may have precipitated out at the higher temperatures or consolidated into larger nodules that were not bisected by the glass cross section.

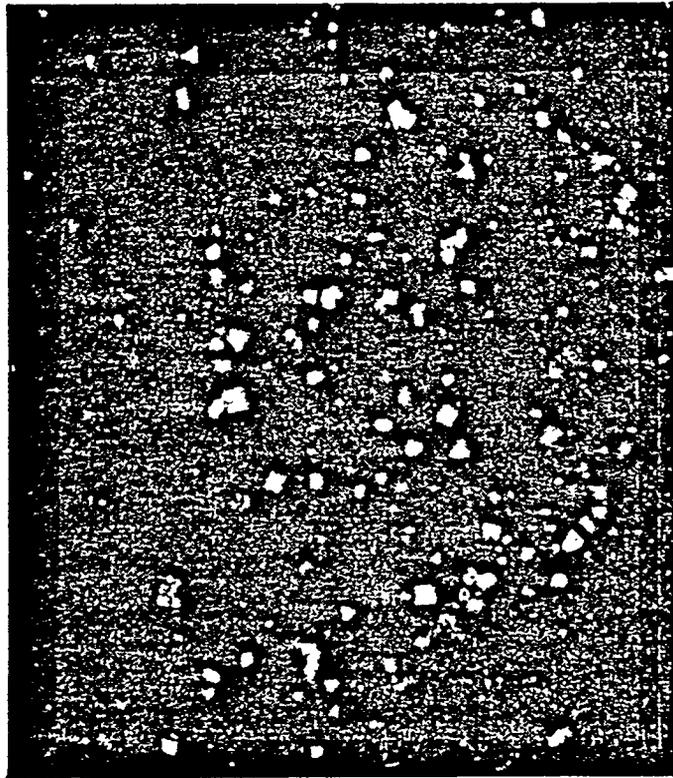
6.1.4 Temperature Variation Summary

The precipitate particles for all three temperatures were primarily the spinel type phases. For each temperature, the spinel crystals were typically 1 to 5 μm , although as the temperature decreased, more of the larger agglomerates with sizes up to 20 μm appeared. Phases which contained submicron crystals with high concentrations of Ru appeared at all three temperatures, usually in small agglomerations (1 to 3 μm). Many of the particles with higher Ru concentrations appeared in the tops of the crucibles. Rhodium and Pd were present as part of the spinel crystals at 1100°C, although they were not observed at the 1170°C glass. They may have precipitated out or consolidated



10 μ m
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Figure 5. SEM micrograph of top of crucible. Melt was conducted at 1170°C for the standard 30-minute melting period at a ferrous/ferric ratio of 0.03. Concentration of noble metals is 0.26 wt%. Figure shows scattered spinel crystals at top of melt.



10 μ m
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Figure 6. SEM micrograph of bottom of crucible. Melt was conducted at 1170°C for the standard 30-minute melting period at a ferrous/ferric ratio of 0.03. Concentration of noble metals is 0.26 wt%. Figure shows a large quantity of spinel crystals when compared to Figure 5.

into larger nodules that were not bisected by the cross section of the glass which was examined.

6.2. CRUCIBLE TIME VARIATION STUDY

The time study included melts held at 1100°C for 2.4, 24, and 240 hours beyond the standard 30-minute melt period. The feed used to make the glasses had the reference level oxide composition given in Table 2. The glasses were all formatted to the same level to achieve a reference ferrous/ferric ratio of 0.03 in the glass. The melt temperature was maintained at a temperature of 1100°C. Observations at the three times are discussed below.

6.2.1 Observations After 2.4 Hours

At 2.4 hours, significant settling of the larger particulate matter was observed. The particulates in both the top and bottom of the crucible were mainly of the spinel type. The spinel crystals in the top were small ($< 2\mu\text{m}$) and scattered; crystals in the bottom were more abundant and present in larger (2 to 5 μm) agglomerations. Noble metals were present in both the top and bottom of the crucible. Phases high in Ru and containing some Rh appeared in the top of the crucible; phases in the bottom of the crucible exhibited high levels of Rh and Pd and contained little or no Ru.

6.2.2 Observations After of 24 Hours

Figure 7 shows that at the end of 24 hours only scattered agglomerates remain at the top of the crucible. Although some of these agglomerates were as large as 10 μm , they consisted of crystals with diameters of 0.5 to 2 μm . Most of the agglomerates contained very high levels of Ru. Spinel-type crystals, 1 to 5 μm in diameter, were the predominant crystal form in the bottom of the crucible and were more abundant than in the top of the crucible. Individual spinel crystals in the bottom of the crucible were larger and more defined than those in the top of the crucible. Many of the spinel crystals

present in the bottom of the crucible contained some Ru and Rh with some particles having very high Ru levels. No Pd was observed in the crystals examined.

6.2.3 Observations After 240 Hours

At the completion of 240 hours the crystals at the bottom of the crucible were very large (10 to 20 μm), although some small particles (1 to 3 μm) were still present. Those at the top were approximately the same size as those at the bottom of the crucible, although there were somewhat fewer crystals. Many of the spinel crystals in both the top and bottom of the crucible contained small amounts of Ru and Rh. As was observed in the 24-hour melt, no signs of the Pd were immediately observed in the crucible section examined. However, a film that was visible on the surface of the melt was examined. As Figure 8 shows, the film consisted of two areas. The shiny area, which is well over 400 μm in length, consisted almost entirely of Pd with some traces of Cu and Fe in it. The other area consisted of a high-iron spinel phase that contained a moderate quantity of Rh.

6.2.4 Time Variation Summary

The time study showed that settling and agglomeration of the noble metals and spinel phases can be observed after only 2 to 3 hours. Many particles containing high concentrations of Ru were observed in both the 2.4 hour and 24 hour melt glasses. Rh on the other hand appeared in both the top and bottom of the crucible melts for all melting times, mainly as part of the spinel crystals. After only 24 hours it was clear that Pd was not visible in the main mass of glass in the crucible. A more detailed investigation of the 240 hour glass revealed that Pd was accumulating at the surface of the melt, along with considerable quantities of spinel crystals. Similar observations concerning noble metals were made by the Japanese.³ The mechanism that causes Pd and spinel to accumulate at the top of the melt is not known at this time.

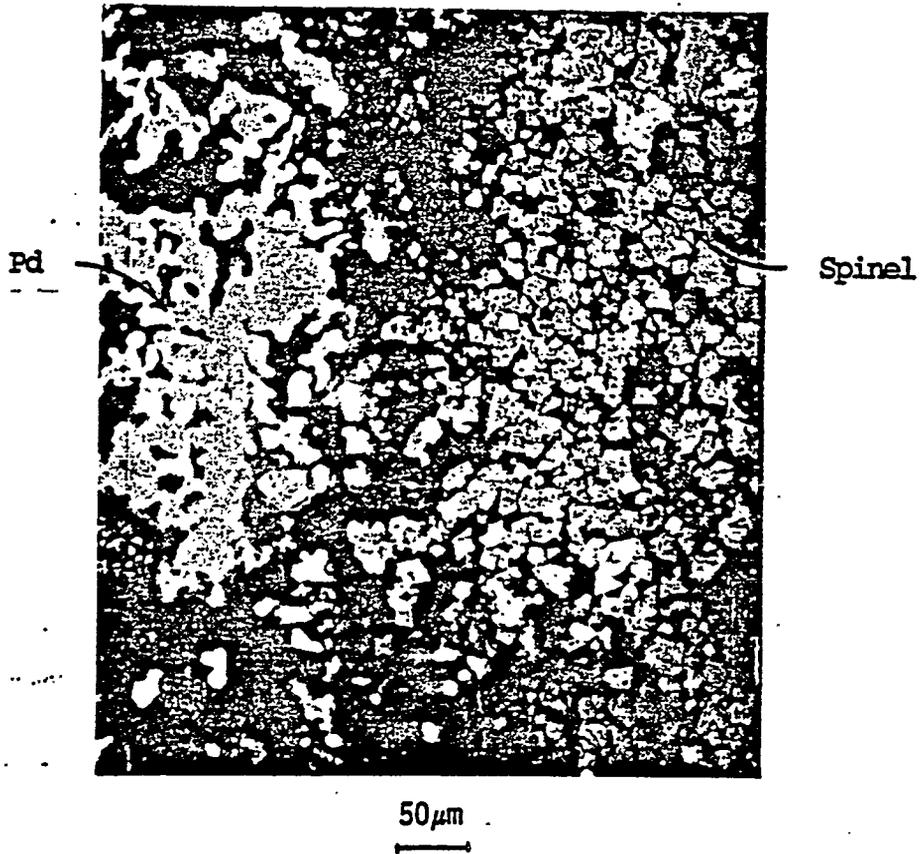


Figure 8. SEM micrograph of film observed at glass surface. Melt was conducted at 1100°C for 240 hours at a ferrous/ferric ratio of 0.03. Concentration of noble metals is 0.26 wt%. Figure shows metallic Pd film and spinel agglomeration at the surface of the melt.

6.3. CRUCIBLE CONCENTRATION VARIATION STUDY

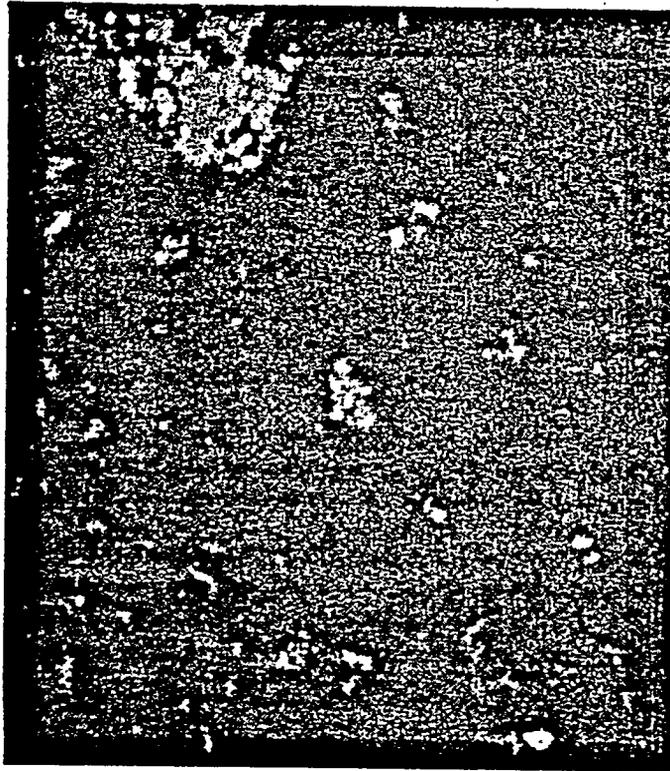
The concentration variability study included glasses at three different noble metal concentration levels. The glass mixture consisted of two fractions. One fraction contained the reference composition given in Table 2. The other fraction was a mixture of RuO₂, Rh₂O₃, PdO, and TeO₂. This noble metal oxide mixture had noble metal ratios identical to those of the reference glass. The first glass contained the reference level of noble metals, 0.29 wt% noble metal oxides. The other two glasses contained 2 wt% and 11 wt% noble metal oxides, respectively. The 11 wt% noble metal oxide was chosen as an upper limit because it was the noble metal concentration of the sludge deposited in the PAMELA melter,² although the sludge in the PAMELA melter consisted primarily of RuO₂.

6.3.1 Reference Glass (0.29% Noble Metal Oxide)

The most common crystals observed were spinel. A considerable difference in the quantity of crystals existed between the top and bottom portions of the crucible. Most of the crystals in both the top and bottom of the crucible were in the range of 1 to 3 μm , although in the bottom of the crucible agglomerations of these spinel type crystals ranged from 10 to 20 μm . Noble metals appeared both in the top and bottom of the crucible. High levels of Ru were exhibited in a Ru phase near the top of the crucible. Many of the particles at the base of the crucible exhibited high levels of both Rh and Pd.

6.3.2 Concentration of 2 wt% Noble Metal Oxide

Figures 9 and 10 show that the top and bottom of the crucible contained a vast quantity of particulate. Particles ranged from sub-micron sizes to agglomerates that were over 30 μm in size. Many shiny spherical particles were found to be Rh-Pd mixtures with small amounts of iron and other trace elements. Another type of spherical particulate that was observed consisted



10 μ m
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Figure 9. SEM micrograph of top of crucible. Melt was conducted at 1100°C for the standard 30-minute melting period at a ferrous/ferric ratio of 0.03. Concentration of noble metals is 2 wt%. Figure shows variety of noble metal phases.



10 μ m
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Figure 10. SEM micrograph of bottom of crucible. Melt was conducted at 1100°C for the standard 30-minute melting period at a ferrous/ferric ratio of 0.03. Concentration of noble metals is 2 wt%. Figure shows variety of noble metal phases.

of a Pd-Te mixture with trace levels of Fe. Other agglomerates consisted of highly concentrated Ru with small quantities of Fe, Ni, and Cr. The spinel crystals contained considerable quantities of Rh. Individual crystal sizes were usually sub-micron in size, although agglomerations of these small crystals were often over 20 μm in size.

6.3.3 Concentration of 11 wt% Noble Metal Oxides

The glass with 11 wt% noble metal oxides showed particulate types and sizes similar to those of the glass with 2 wt% noble metal oxides. Large quantities of high-Rh submicron spinel crystals were present. Some of the agglomerates of these submicron crystals were close to 200 μm in size. Spheres with high levels of Rh and Pd were evident. Some agglomerates (45 μm) of Ru were also observed. Feature 1 of Figure 11 shows a Ru-Rh particle with a shape commonly observed in the 11 wt% glass but not observed in the 2 wt% glass. The results of an EDAX analysis of this glass are shown in Figure 12.

6.3.4 Concentration Variation Summary

The quantity and variety of noble metal particulate increased at high noble metal concentrations. Spinel crystals were still evident at the high noble metal concentrations. The spinel crystals were submicron in size and contained high concentrations of Rh. Although the spinel crystals were small, agglomerates of the crystals were as large as 200 μm in diameter. Large metallic-like spheres of Rh and Pd were common, as were as some particles that were mixtures of Pd and Te. X-ray diffraction analysis indicated that some type of noble metal oxide (RuO_2 or RhO_2) was present.

6.4. CRUCIBLE REDOX VARIABILITY STUDY

The redox variability study was conducted at four different ferrous/ferric levels. Two of the ferrous/ferric ratios, 0.03 and 0.27, were achieved by adding formic acid to the unformatted feed slurry. The unformatted slurry

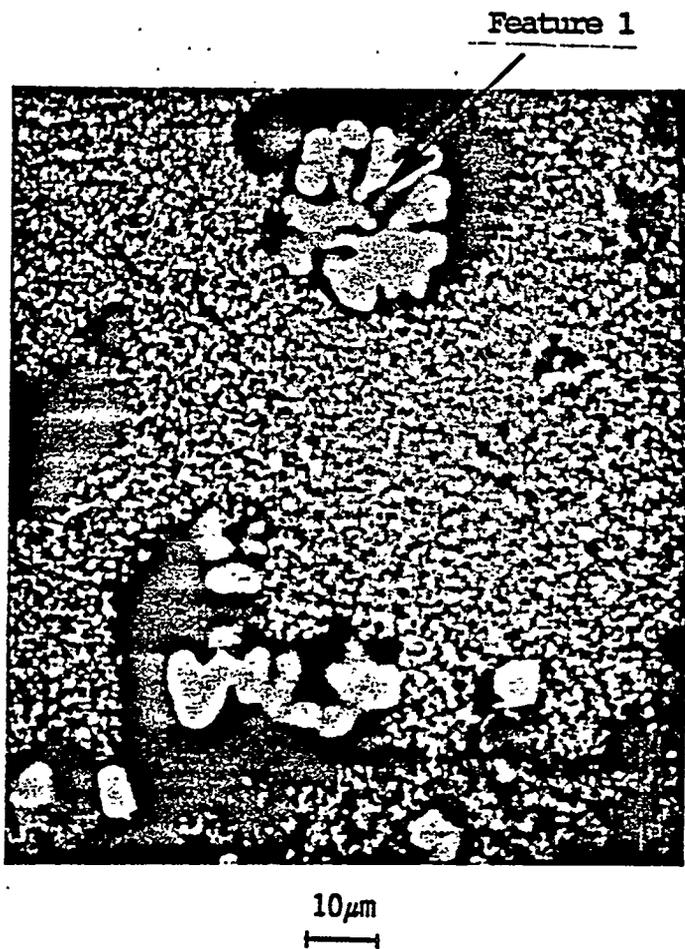


Figure 11. SEM micrograph of bottom of crucible. Melt was conducted at 1100°C for the standard 30-minute melting period at ferrous/ferric ratio of 0.03. Concentration of noble metals is 11 wt%. Feature 1 shows a noble metal shape not seen in the 2 wt% melt.

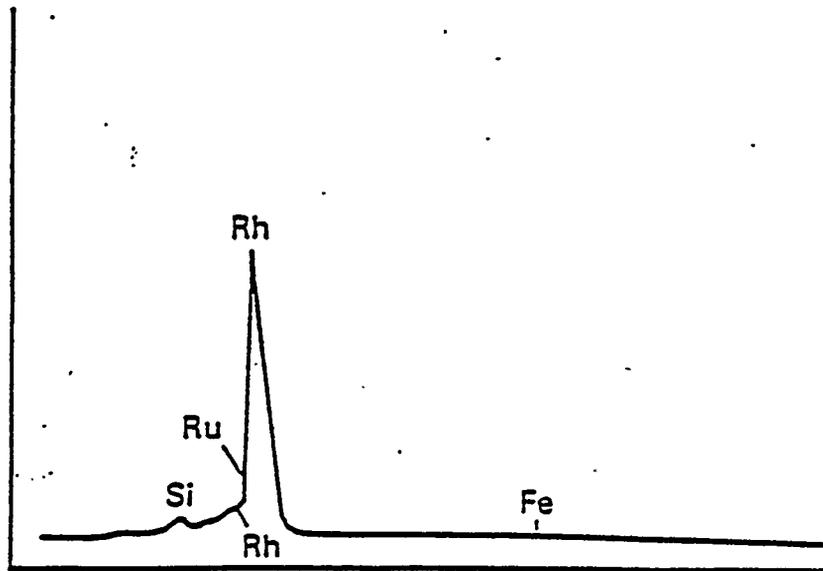


Figure 12. EDAX analysis of feature 1 in Figure 11 showing qualitative elemental analysis of the nodule.

resulted in a glass with a ferrous/ferric ratio of 0.0. A fourth ferrous/ferric ratio, 0.65, was obtained by using sugar as the reducing agent.

6.4.1 Ferrous/Ferric Ratio of 0.0

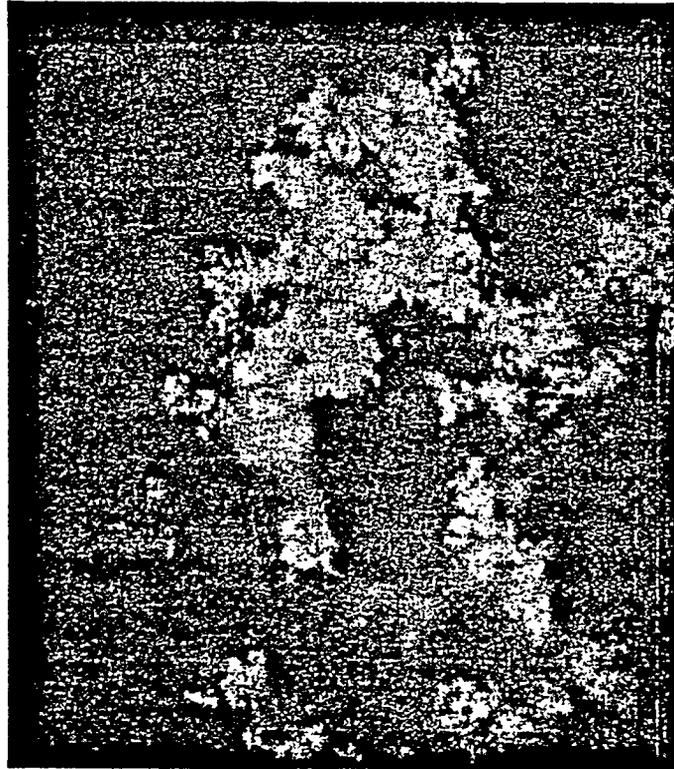
This glass was not formed. The spinel-type crystals that were predominant in the bottom of the crucible contained moderate amounts of all three noble metals, Ru, Rh and Pd. Spinel crystals ranged from 1 to 4 μm and had formed some small agglomerates. The particulate size in the top of the crucible was also 1 to 4 μm . The particles were spinel crystals and small agglomerates (4 μm) of a phase having a high Ru content.

6.4.2 Ferrous/Ferric Ratio of 0.03

Particulate of 1 to 10 μm were present in both the top and bottom of the crucible for glass with a redox ratio of 0.03. The larger particles such as the crystalline agglomeration shown in Figure 13 were mainly Ru with some Fe and Ni present. There were fewer particles in the top of the crucible than were observed in the 0.0 ratio glass. Neither Rh nor Pd were observed in the particles examined.

6.4.3 Ferrous/Ferric Ratio of 0.27

Unlike the more-oxidized glasses, the glass with a ferrous/ferric ratio of 0.27 contained no visible spinel crystals. Only a small quantity of particulate, ranging in size from 2 to 10 μm existed in this glass. Closer examination of each of the observed particles revealed that the particles contained very high noble metal concentrations. Particles included relatively pure Ru, Rh, and Pd. Very little mixing of the metals was observed in any of the particles.



1 μ m
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Figure 13. SEM micrograph of high-concentration Ru particle seen at bottom of crucible. Melt was conducted at 1100°C for the standard 30-minute melting period at a ferrous/ferric ratio of 0.03. Concentration of noble metals is 0.26 wt%.

6.4.4 Ferrous/Ferric Ratio of 0.65

The fourth glass, having a redox ratio of 0.65, began with the reference formate level and was then further reduced by addition of sugar. A small quantity of spinel type crystals existed in both the top and bottom of this crucible. These particles had sizes ranging from 0.5 to 2 μm , although some agglomerations up to 10 μm were visible. Only trace amounts of noble metals were present in these crystals. A detailed examination of the surface of the melt revealed that large quantities of particles with high Ru concentrations were present around surface bubbles and just below the melt surface. Large quantities of spinel crystals were also observed along the surface of the melt. The spinel contained moderate levels of Ru and Rh, although some particles near the bubble surface were almost pure Ru (possibly RuO_2 crystals). This high level of Ru near bubble surfaces was also noted by the Japanese.³ SEM/EDAX studies revealed that spinels in contact with the air were rich in iron, and only trace amounts of Ru and Rh were visible.

6.4.5 Redox Variation Summary

The number of crystals appeared to decrease with increasing ferrous/ferric ratios. The type of particulate seen was observed to be a function of both the glass redox conditions and the reducing agent. When formic acid was the reducing agent, spinel crystals disappeared at higher redox ratios. However, the spinel crystals still appeared when sugar was used as a reducing agent. It was observed that Ru and Rh may be present as part of a spinel phase near the surface of the glass. Furthermore, bubbles acted as nucleating sites for the Ru when sugar was used as a reducing agent.

6.5. CRUCIBLE COLD CAP STUDY

The cold cap kinetics seen in the large-scale melters was partially simulated using a glass of reference composition and redox levels. After

allowing the glass to melt at 1100°C, the reference HWVP feed was rapidly fed to the crucible and the glass was annealed to preserve the cold cap.

Major differences were noted in the glass near the top of the crucible compared to that near the bottom of the crucible. The top of the crucible contained many large (10 to 20 μm) unmelted particles high in La, Zr, or Fe; those at the bottom of the melt were mainly small spinel type crystals (1 to 3 μm) with traces of Ru, although some particles high in Pd and Cu were also observed. There was no indication that more noble metal particulate or spinel phases were forming in the cold cap compared with what had been observed in the glass.

6.6 REDOX VARIATION STUDY IN THE LFMM

The LFMM was used to study the effect of the redox environment in the LFMM on noble metal precipitation. Sugar was added to an already formatted HW-39 feed slurry. The feed which consisted of the waste shown in Table 3 and the frit given in Table 2 was mixed to obtain the glass composition given in Table 2. Four runs, approximately 8 hours each, covered a sugar addition range of 0 to 6 g of sugar/L of slurry to obtain target ferrous/ferric ratios of 0.03 to 0.3. The actual ferrous/ferric ratios ranged between 0.18 to 0.51, presumably to unknown redox reactions within the melt. The sugar was added to make the glass more reducing. X-ray fluorescence and ICP were used to analyze both the feed and output glasses from each run. The following observations were made.

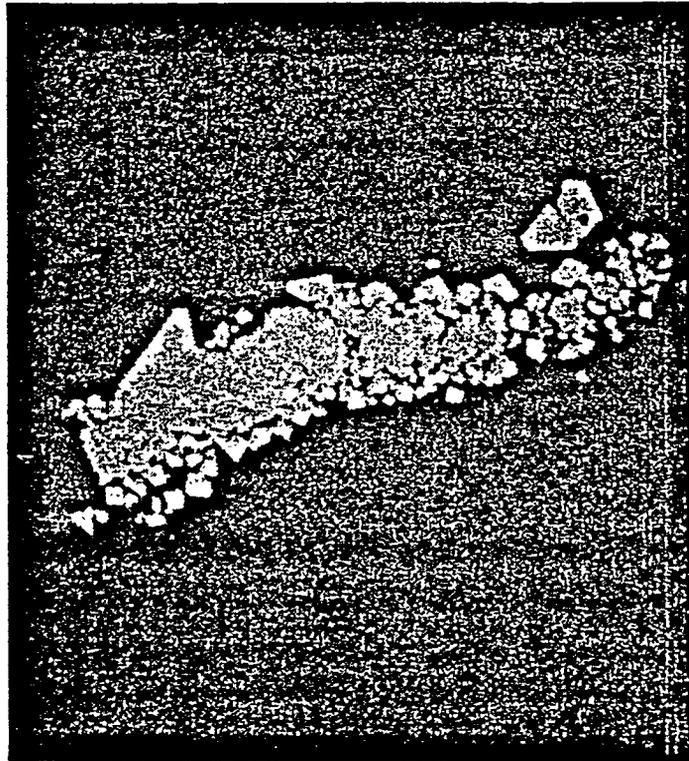
At the end of the fourth run, the crucible temperature was maintained at 1000°C for three days. Following this time period, the glass was allowed to cool to 400°C to anneal the glass. A core of glass was then removed from the minimelter for analysis.

6.6.1 0 Grams Sugar/L

A 7-hour melt was conducted in the LFMM without sugar in the feed slurry. SEM analyses of output glass samples were performed at the beginning and end of the 7-hour melt. The ferrous/ferric ratios of the output glass fluctuated between 0.24 and 0.51, much higher than the expected value of 0.03. Figure 14 shows a high-chrome spinel particle that was present in the output glass. These high-chrome spinel particles existed in large agglomerates of 10 to 100 μm . An SEM analysis revealed no obvious noble metal particulates. Some high-chrome spinel crystals 1 to 5 μm in diameter were still present at the end of the run. Many submicron noble metal particles were observed. Rh was also present in the spinel. Although Pd particulate was not observed in the glass output from this run, small amounts of Pd (19.1 ppm) were found when an x-ray fluorescence analysis of the output glass was performed. This level is very low compared to the target composition of over 400 ppm of Pd, indicating that most of the Pd was accumulating in the LFMM.

6.6.2 6 Gram Sugar/L

After approximately two crucible turnovers (16 hours) of the low redox feed, a high-sugar feed with 6 g of sugar/L of slurry was fed to the melter. The ferrous/ferric ratios of the output glass fluctuated between 0.36 and 0.48, which compare with the expected value of 0.3. The spinel observed ranged from 1 to 50 μm . Some submicron particles of Ru were observed. After 8 hours of feeding (1 turnover), larger agglomerates were apparent. These high-chrome spinels ranged from 5 to 150 μm in size. At the end of the run, submicron Ru particles were still present. A new type of particulate, a Pd-Te alloy with some Ru was observed at this time.



10 μ m
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Figure 14. SEM micrograph of output glass from LFMM showing high-chrome spinel particulate. Feed had 0 grams/liter of sugar. The sample was taken after 7 hours of minimelter operation.

6.6.3 3.5 Gram Sugar/L

Following the run at 6 g sugar/L, the feed was switched to a slurry containing 3.5 g of sugar/L. At the end of this run, agglomerates of high-chrome spinel were still evident and ranged in size from 5 to 50 μm . Submicron particles of Ru-spinel were also still evident. Like the other runs, the ferrous/ferric ratios of the output glass, which ranged from 0.18 to 0.47 were much higher than the target value of 0.15.

6.7 RESULTS OF LFMM CORE DRILL

The glass core that was removed after the LFMM runs consisted of two sections. The majority of the core was removed in a single sample from the top of the melt. This section included most of the glass in the top of the melter. The bottom of the melt was also cut away from the Inconel crucible. Figure 15 is a photograph of the upper portion of the core. Examination of the core revealed a large metallic nodule, approximately 0.5 cm in diameter. This nodule was analyzed by x-ray fluorescence and found to contain Ru, Rh, and Pd with some Te, Cu, Fe, Mo, and Ni present. Many more nodules were also present at the base of the melt, particularly in the area designated feature I in Figure 16. A close-up of this area is shown in Figure 17. This area was the location of the end of an Inconel thermowell that may have catalyzed the precipitation of the noble metals. Oxidation of the chrome in the thermowell is a possible mechanism for reduction of the noble metals. Although the target composition for Cr_2O_3 in the glass was only 0.14 wt%, the composition in the minimelter output glass ranged from 0.3 to 0.6 wt%, indicating that corrosion products from the Inconel crucible may be present in the glass. The corrosion mechanism is also suggested by the high ferrous/ferric ratios present in the output glasses examined which ranged from 0.18 to 0.51.

Each of the tests at the three sugar levels resulted in the formation of high-chrome spinels as the predominant form of particulate in the output

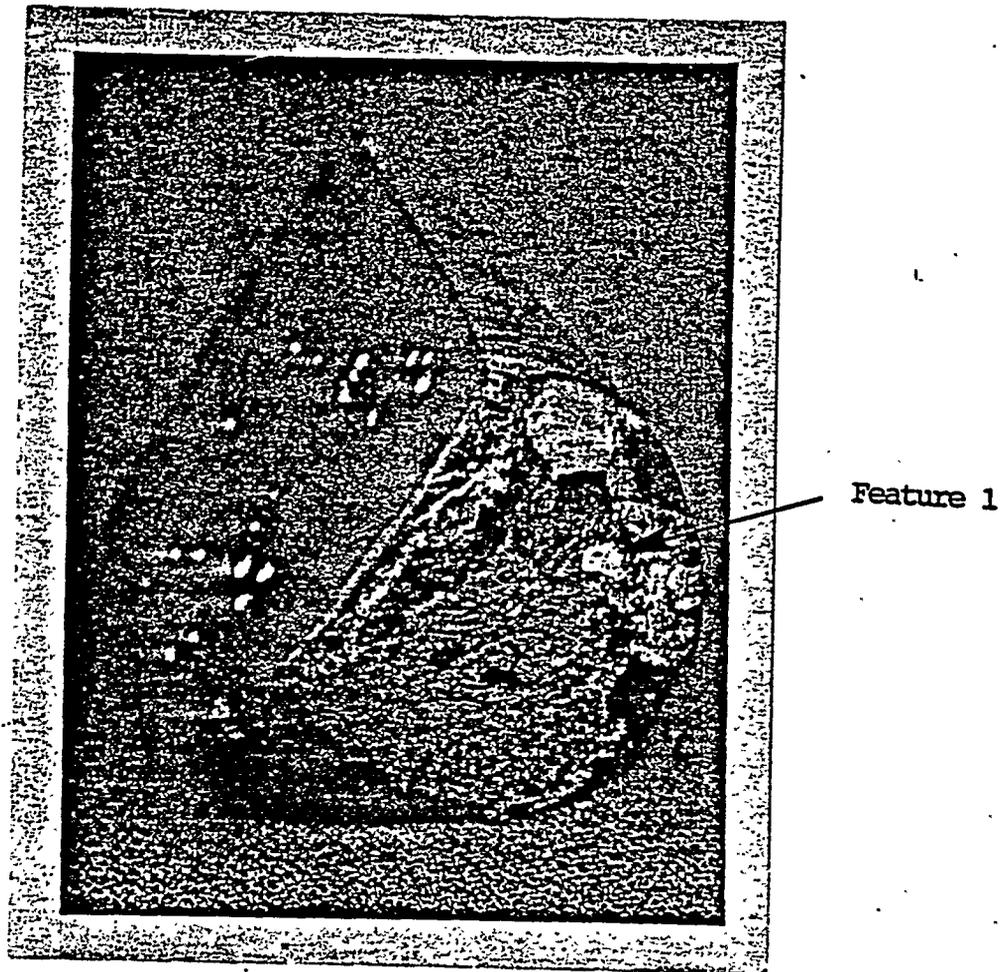


Figure 15. Glass core sample from LFMM. Feature 1 is a metallic nodule high in Ru, Rh and Pd.

Area 1

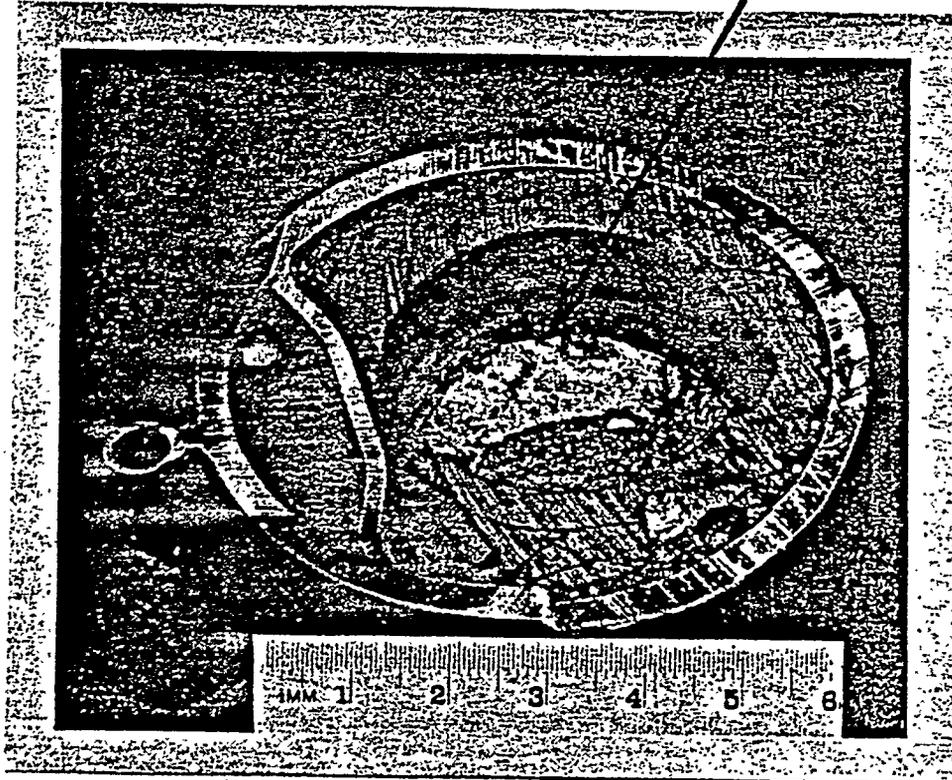


Figure 16. Bottom of inconel crucible. Area 1 shows region exhibiting a large number of metallic nodules.

Metallic Nodule

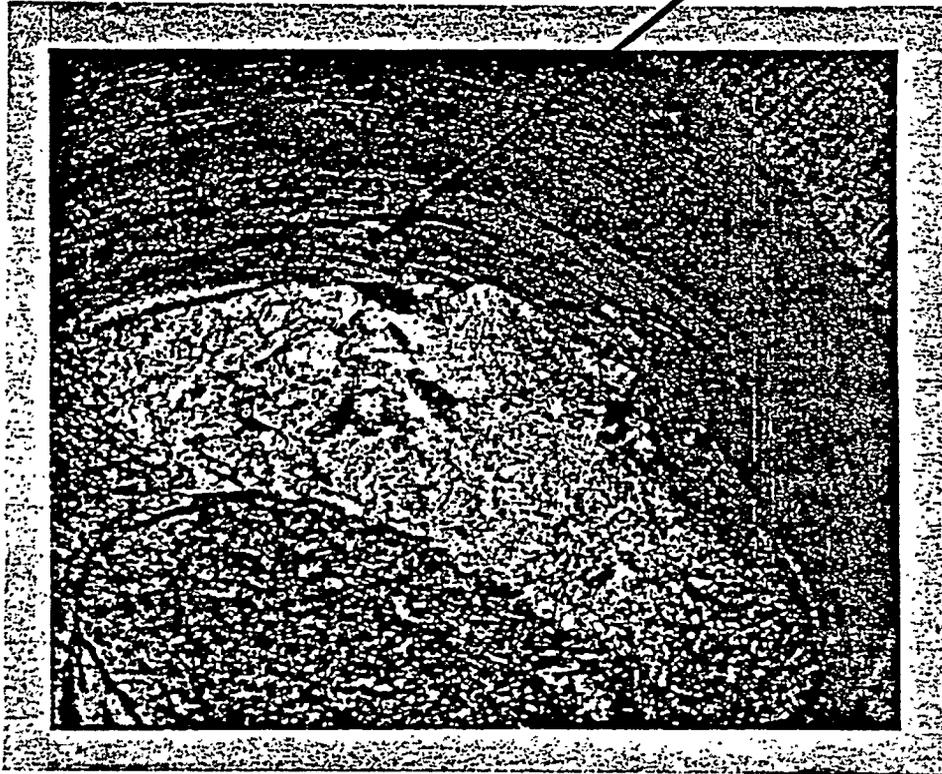


Figure 17. Close-up of nodule-rich area shown in Figure 16.

glasses. Although some submicron noble metal particles were present, the sugar addition appeared to have little effect on their type and size. For glasses with these sugar levels, analysis of the crucible glass melts indicated that the ferrous/ferric ratios of the output glasses would range from 0.0 to 0.3. However, the ferrous/ferric ratios ranged from 0.18 to 0.51. The high levels of chrome in the spinel indicate that oxidation of the Inconel crucible may further reduce the glass in the minimelter.

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