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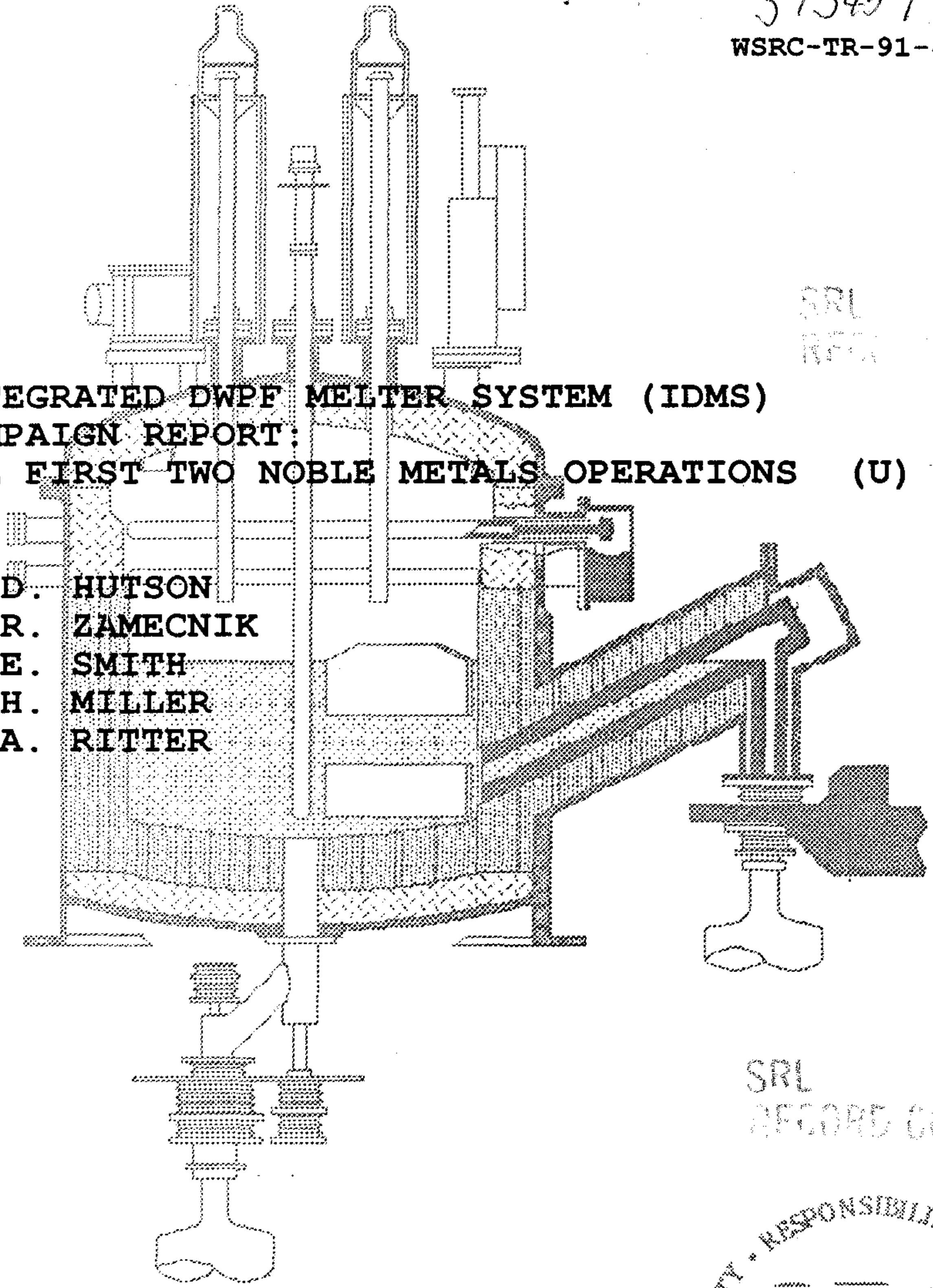

INTEGRATED DWPF MELTER SYSTEM (IDMS) CAMPAIGN REPORT: THE FIRST TWO NOBLE METALS OPERATIONS (U)

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ABSTRACT

The Integrated DWPF Melter System (IDMS) is designed and constructed to provide an engineering-scale representation of the DWPF melter and its associated feed preparation and off-gas systems. The facility is the first pilot-scale melter system capable of processing mercury, and flowsheet levels of halides and noble metals.

In order to characterize the processing of noble metals (Pd, Rh, Ru, and Ag) on a large scale, the IDMS will be operated batch-style for at least nine feed preparation cycles. The first two of these operations are complete. The major observation to date occurred during the second run when significant amounts of hydrogen were evolved during the feed preparation cycle. The runs were conducted between June 7, 1990 and March 8, 1991. This time period included nearly six months of "fix-up" time when forced air purges were installed on the SRAT MFT and other feed preparation vessels to allow continued noble metals experimentation.

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List of Acronyms

AA:	Atomic Absorption
ADS:	Analytical Development Section of SRL
CPC:	Chemical Processing Cell
DF:	Decontamination Factor
DWPF:	Defense Waste Processing Facility
DWPT:	Defense Waste Processing Technology Section of SRL
EES:	Equipment Engineering Section of SRL
FAVC:	Formic Acid Vent Condenser
HAN:	Hydroxylamine Nitrate
HEME:	High Efficiency Mist Eliminator
HEPA:	High Efficiency Particulate Air filter
HTRI:	Heat Transfer Research Institute
Bl1:	First IDMS Blended Sludge Run
BL2:	Second IDMS Blended Sludge Run
HLW:	High Level (Radioactive) Waste
HTC:	Heat Transfer Coefficient
IC:	Ion Chromatography
ICP:	Inductively Coupled Plasma
ICP-MS:	Inductively Coupled Plasma - Mass Spectrometry
IDMS:	Integrated DWPF Melter System
ISE:	Ion Selective Electrode
IXS:	Ion Exchange System
LEL:	Lower Explosive Limit
LC:	Liquid Chromatography
MFT:	Melter Feed Tank
MOC:	Minimum Oxidant for Combustion
MWWT:	Mercury Water Wash Tank
OGCT:	Off Gas Condensate Tank
PHA:	Precipitate Hydrolysis Aqueous
PHEF:	Precipitate Hydrolysis Experimental Facility
PNL:	Pacific Northwest Laboratory
PVVS:	Process Vessel Vent System
RSD:	Relative Standard Deviation
SAS:	Steam Atomized Scrubber
SCDHEC:	South Carolina Department of Health and Environmental Control
SME:	Slurry Mix Evaporator
SPC:	Salt Processing Cell
SRAT:	Sludge Receipt and Adjustment Tank
SRL:	Savannah River Laboratory
SRS:	Savannah River Site
TAC:	Total Aromatic Carbon
TC:	Total Carbon
WSRC:	Westinghouse Savannah River Company
WWPT:	Waste Water Pump Tank

1.0 Summary/Recommendations

The addition of noble metals to the feed simulations for DWPF represents the last step in the phased start-up of the Integrated DWPF Melter System (IDMS). The noble metals were introduced to determine the effects of these components on the glass melting behavior and specifically the effect on the melter electrical characteristics. The first two (of a planned nine) runs are completed.

These runs determined that formic acid destruction by noble metal catalysis results in much larger hydrogen evolution than was originally expected. Only a few ppm (by volume) of hydrogen in the feed preparation offgas system was expected but the second run produced hydrogen at a maximum rate of 0.17 pph (0.51 scfm) during the formic acid reflux. See Figures 5.2 and 6.1. While the first run did not indicate this quantity of hydrogen was produced the entire cycle was not monitored for hydrogen evolution. Based on subsequent laboratory scale (2 liter) and University of Georgia (0.2 liter) studies hydrogen evolution is inhibited by the presence of nitrite such that the hydrogen evolution rates are very low until all the nitrite is destroyed. The first run was not monitored for hydrogen after the nitrite was destroyed and for that reason hydrogen is thought to have been evolved at a rate larger than reported during the first run.

Due to a failure of the wastewater treatment facility (Ion Exchange) and the legal ramifications associated with the operation of a SCDHEC licensed facilities, wastewater was recycled to the IDMS SRAT. This action resulted in differences for the key batch parameters for the second run when compared to either the first batch or a DWPF reference batch. These differences include:

- the SRAT heel composition prior to the sludge transfer,
- the amount of formic acid addition (to account for the caustic content of the SRAT heel, and
- the rate of formic acid addition (when compared to the first run, the rate was scaled for the DWPF reference batch).

The excess caustic resulted in a fouled SRAT/SME steam coil twice during the run. The first time during formic acid addition, reflux and PHA addition. The 1/4 inch thick layer of sludge material which was removed during subsequent operations, but the coil was fouled a second time after the frit was added. Under these processing conditions the hydroxyl groups link together and form a gel. The gel incorporates the frit and when it contacts a hot surface, such as a steam coil, it drys to form a hard layer on the coil.

Since this can occur during DWPF operations (specifically during trim chemical addition to the SME) the following recommendation is made:

Recommendation #1: Delete the use of NaOH and KOH as trim chemicals. Sodium nitrate is recommended as a substutite for the caustic. Potassium nitrate is recommended as a substitute for the KOH.

The effect of a fouled coil on the hydrogen evolution rate during the second run is expected to be a minimum (see section 6.1.2). However, future IDMS runs will duplicate the effect of having a hot surface exposed to the bulk fluid.

The amount and rate of formic acid addition both play roles in nitrite destruction chemistry, especially kinetics. Both the increased amount and rate tend to increase the nitrite destruction rate, as observed in the second run, by increasing the initial acid concentration. These two parameters may account for the observed differences in the NOx evolution between the two runs but their direct role in hydrogen evolution is unclear and is being evaluated in both IDMS and laboratory scale runs.

In response to the hydrogen issue, studies are focusing on the role of these major components: the amount of noble metals, the amount of formate ion present, the amount of formic acid present, and the amount of iron contained in the sludge.

One melter operational problem was encountered during the run. The melter pouring problem is discussed in detail in section 5.3.9, but the exact cause of the problem (which has been corrected) is still not known. Investigation of the problem was hampered by inadequate baseline information as noted in the recommendation below.

Recommendation 2. Ensure that the normal pressure drop between the canister and the melter/bellows differential pressure instrument tap is recorded as baseline data. This data should be taken as a part of the first cold chemical melter operation.

For reference the baseline data collected during the IDMS start-up is contained in reference 4.

2.0 Campaign Overview

Slurry-fed ceramic melters are being developed worldwide to convert high-level nuclear waste to a durable borosilicate glass for permanent disposal. All of these high-level waste forms, including SRS waste, contain noble metals which are produced from U-235 fission.[1]

The noble metals are defined as silver, ruthenium, rhodium, and palladium. They are called noble because of their resistance to oxidation in contrast to the base metals that oxidize when heated in air. They are easily reduced and all occur naturally in elemental form. Silver and palladium can be reduced to elemental form by heat without a reducing agent. The ease of reduction and high densities of the noble metals suggest the possibility of accumulation on the floor of glass melters.[2]

All of the major production and research facilities worldwide have experienced operational problems which can be traced to noble metal precipitation caused by various processing problems, such as overly reducing conditions, and/or agglomeration problems due to high concentrations in the melter feed.

The Defense Waste Processing Facility (DWPF) has been designed to process about 3 lbs/day of noble metals, mainly ruthenium. Current information is insufficient to determine the final chemical form, and the effect of the noble metals components on the melter operation. All previous large scale melter tests have omitted, or have not had the reference levels of at least one of the following: noble metals in their anticipated chemical forms; potential alloying agents: lead, mercury, tellurium, selenium; or the expected reference concentrations of reducing and oxidizing agents. Previous melter runs with noble metals have not had electrodes similar in geometry to DWPF and have therefore not been able to model accurately the electrical response of the melter to noble metals deposition.

Recently, in studies conducted using the SRL Research Melter, up to 20% of the noble metals in the simulated DWPF melter feeds were found to settle on the melter floor. These feeds were very reducing and the small melter (8 inches in diameter) contained practically no natural convection.[3]

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 of DWPF capable of processing mercury and flowsheet levels of halides, sulfates, and noble metals.

In order to characterize the processing of noble metals it was planned to operate the IDMS batch-style for nine feed preparation cycles. During this campaign, the facility will be operated close to the DWPF flowsheet conditions for three sludge simulations: (1) Blend, (2) Purex (high iron, low viscosity) and (3) HM (high aluminum, high viscosity).

The primary objectives are as follows:

- Demonstrate the long term effects of noble metals on the operating performance of the melter.
- Determine the noble metals material balance around the SRAT, SRAT Condenser, and Mercury Water Wash Tank(MWWT).
- Determine the noble metals material balance around the melter system.
- Determine the effects of noble metals on mercury stripping and recovery.
- Investigate the noble metals catalysis of formic acid destruction.
- Determine the chemical form of the noble metals in the glass.
- Evaluate the effects of noble metals on off gas and off gas condensate composition.
- Evaluate the effects of mercury on noble metals agglomeration, characterizing agglomerate size distribution and composition.
- Determine the particle size of noble metals and /or noble metals alloys in the glass.

The first two runs are complete and are referred to as Blend 1(B11), and Blend 2 (B12), respectively. While not all of the objectives for the campaign have been addressed, it is important to provide interim reporting on several. The most important observation to date has been the higher than expected hydrogen evolution encountered during Blend 2.

3.0 System Description

A flowsheet of the IDMS Feed Preparation, Process Vessel Vent, Feed Delivery, Melter, Melter Off gas, and Ion Exchange Systems is shown in Figure 3.0.1. A brief description of each system is given below. A more detailed description of each system and its associated processes is given elsewhere.[4]

3.1 Feed Preparation System

The Feed Preparation System consists of a Sludge Receipt and Adjustment Tank/Slurry Mix Evaporator (SRAT/SME), a SRAT/SME Condenser, a Mercury Water Wash Tank (MWWT) and a Waste Water Pump Tank (WWPT). The feed preparation process steps in the SRAT/SME are:

1) sludge receipt,

2) trim chemical addition (e.g. noble metals and Hg),

3) formic acid addition to control glass redox, improve rheology and reduce mercury to metallic form,

4) refluxing to remove mercury by steam stripping, and then concentration by boiling,

5) PHA addition, concentration by boiling and, if necessary, further refluxing to remove mercury,

6) frit slurry addition, and

7) feed concentration.

3.2 Process Vessel Vent System

Primary containment of mercury and organic vapors in the Feed Preparation System is accomplished by maintaining all of the vessels under a vacuum using the Process Vessel Vent System (PVVS). The PVVS consists of the Formic Acid Vent Condenser (FAVC), a blower for routine use, a steam jet for backup and emergency use, a three inch diameter stack and a nitrogen supply system.

The PVVS serves every vessel containing mercury and organics in the IDMS except the Melter and the Off-Gas Condensate Tank (OGCT). The vessels it serves are the SRAT/SME, the MWWT, the WWPT and the Melter Feed Tank (MFT). Air bleeds are provided on all four tanks, with the air addition flow rate set to simulate the Design Basis air inleakage in the DWPF tanks. The overflow lines on each tank have water filled seal pots to prevent uncontrolled air inleakage into the tanks.

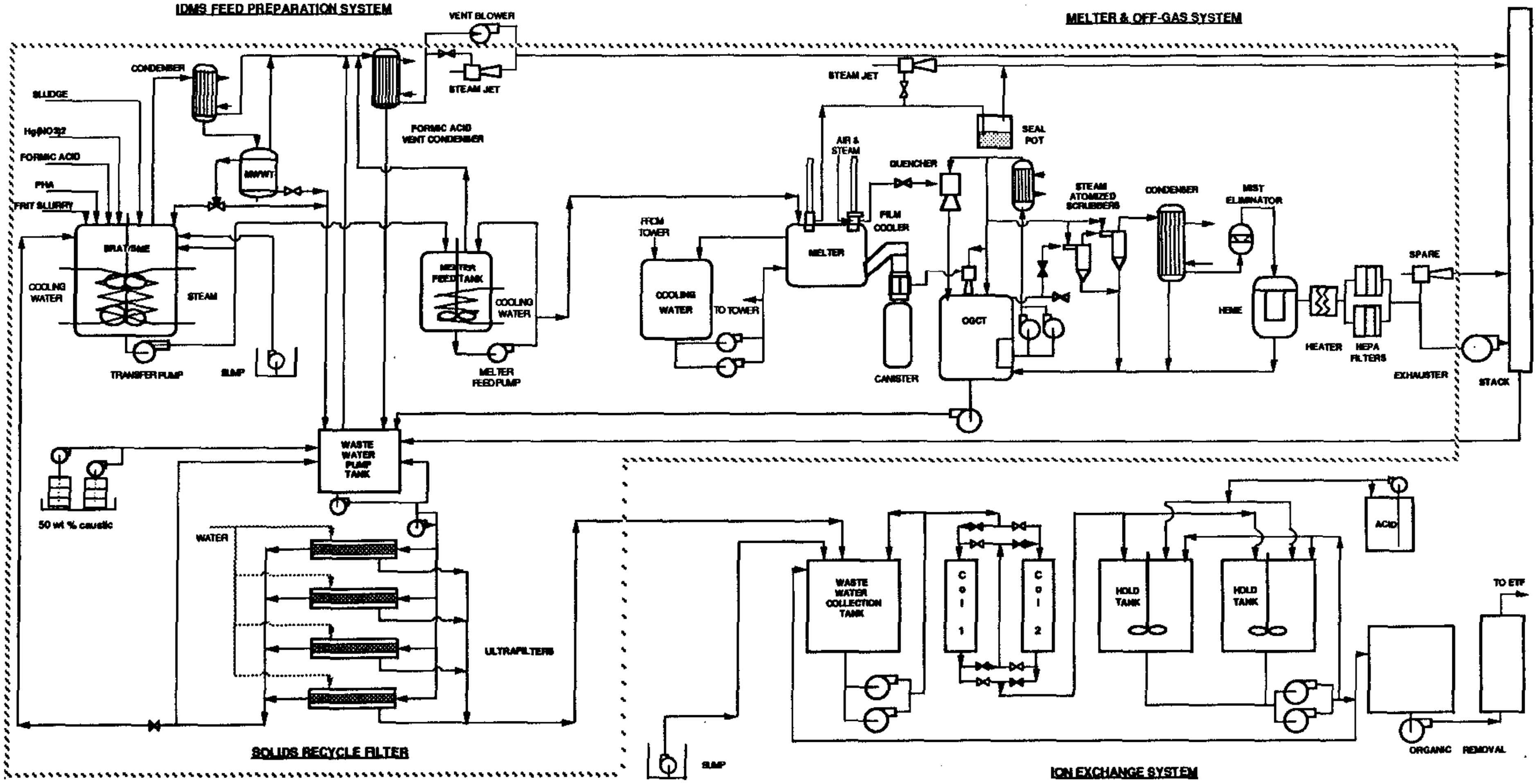

Figure 3.1 IDMS Overall Flowsheet

3.3 Feed Delivery System

The Feed Delivery System consists of the MFT and a recirculation feed system similar to that used in the DWPF. Feed prepared in the SRAT/SME is transferred to the MFT. The slurry is recirculated through a two inch line using a non-prototypic, disk pump. (This pump was changed just prior to the run from the previously used double diaphragm air operated pump.) The disk pump operates similarly in concept to a centrifugal pump except that the impeller (which consists of multiple flat disks instead of a vaned propeller) does not have close tolerances with the pump casing. This prevents excessive impeller and casing erosion by the abrasive slurry. The fluid next to disk is essentially stagnant which further reduces erosion to the disk and mechanical seal.

A restricting orifice located at the recycle line return nozzle to the MFT provides backpressure which forces the slurry through a strainer, a three-way valve and fifty feet of 1/4 inch ID piping to the melter feed tube. The feed tube extends through the melter lid past the lid heaters and discharges the slurry one foot above the melt pool. The flow rate is controlled by varying the pump speed. Process water is piped into the feed line through a three-way valve so that the feed line can be flushed back to either the melter or the strainer.

3.4 Melter

The IDMS melter is a refractory lined, cylindrical tank operated at a glass temperature of about 1150°C. It is used to remove water from the feed by evaporation, react the feed components and melt the solids to form a homogeneous glass pool that can be poured into steel canisters. The IDMS melter has a 24 inch inner diameter, which gives a melt pool surface area approximately 1/9 that of the DWPF melter. Since the melt rate is directly proportional to the surface area, the IDMS melter can be slurry-fed to produce glass at 25 lb/hr, as compared to 228 lb/hr for the DWPF melter.

3.5 Melter Off-Gas System

The melter off-gas consists of steam, non-condensible gases from sludge decomposition, air from inleakage and purges, mercury vapor, and particulate matter from entrainment and volatilization. The purposes of the off-gas system are to maintain a negative pressure in the melter plenum, 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. Even though there are no radionuclides present in the IDMS, all of the DWPF processing steps are incorporated into the IDMS to enable adequate evaluation of the processing efficiency, mechanical reliability, corrosion, and fouling of filters, demister pads and heat exchange surfaces. Unlike the DWPF, however, 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.

The melter off-gas is normally processed through the Primary Off-Gas System. This system consists of the following equipment: an Off-Gas Film Cooler (OGFC) to reduce deposits at the entrance to the Off-Gas System; a Film Cooler Brush to clean the Film Cooler; a Quencher (Ejector Venturi) to cool the off-gas and remove large particulate; an OGCT to separate the liquids and gases; a two-stage Steam Atomized Scrubber (SAS) and condenser to remove submicron particulates; a High Efficiency Mist Eliminator (HEME) to remove fine mists and particulates; a High Efficiency Particulate Air (HEPA) Filter with a preheater to further remove very fine particulates; and a blower with a steam jet back-up.

A bypass system, which is driven by a steam jet, is used on the melter vent line to the seal pot to insure a negative melter pressure when the primary system is not operating. It is also equipped with a brush to clean deposits from the section of the line adjacent to the melter.

A water driven spout jet pulls a vacuum on the melter pour spout to control glass pouring.

4.0 Raw Materials

Five raw materials were required for this campaign: simulated Blend type sludge, trim chemicals, Frit 202, formic acid, and Precipitate Hydrolysis Aqueous Product (PHA). The first four were purchased materials, whereas the PHA was supplied from the 1/5 scale Precipitate Hydrolysis Experimental Facility (PHEF).

4.1 Simulated Blend Sludge

The simulated sludge was purchased on AX-845275 according to "Specification - IDMS Sludge Slurry", Rev. 0, May 21, 1988. This specification provides the procedure for the vendor to produce four basic sludge types: Batch 1 (used during the PHA and Mercury campaigns in the IDMS), Blend, Purex and HM. For this campaign 3,000 gallons each of the latter three types were specified. The Blend type was used for the first two runs and was formulated to be the DWPF "reference" or design basis sludge.

The sludge was extensively sampled and characterized prior to the run[5]. Tables 4.1 and 4.2 reproduce Tables 8 and 9 from reference 5 and provide the average of the 64 analytical determinations (16 samples each analyzed in quadruplicate).

Even with this extensive sampling and analytical characterization it was difficult to confirm that the sludge was within the tolerances specified (see Table 4.3). The specification for five of the major components (concentrations greater than 1.5 wt%) was met. These are: iron, manganese, sodium (by AA determination, but not ICP), nickel, and chloride (by IC determination). The nitrite concentration was only slightly out of specification (10.7% vs 5% allowable) while the remaining species (aluminium, calcium, silicon, zirconium, sulfate and nitrate) were significantly out of specification. The hydroxide and carbonate were not compared to the specification since it is known that hydroxide will be converted to carbonate in the presence of CO_2 (from air).

The minor components ranged from -90 to +70% of the specification. Only cesium and magnesium were determined to be within the specification.

This essentially duplicates the experiences during the IDMS PHA campaign in which the confirmation of the minor sludge components was difficult. A recommendation to revise the sludge specification to include QA witnessing of the chemical additions and to require the vendors certificate of conformance to include completed procedures was made in that report[6]. Revision 1 of the feed simulates specifications for the DWPF[7] incorporated the change.

Table 4.1 Characterization of IDMS Blend Sludge

Elemental Analysis by ICP - Microwave Dissolution

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

Elemental Analysis by ICP - Na2O2 Fusion (wt%)

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

* indicates components which are most likely not present in the BLEND sludge. Measurements shown are the baseline value.

Table 4.2 Characterization of IDMS Blend Sludge

Ionic by IC

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

Ionic by ISE

Ion	Count	Mean	StDev	%RSD	Units
Cl	24	4307.136	1505.176	34.946	ppm
F	24	717.327	139.309	19.421	ppm

Carbon Analysis

Measurement	Count	Mean	StDev	%RSD	Units
TOC	65	148.008	85.428	57.718	mg/l
TIC	65	404.558	49.104	12.138	mg/l

Wet Chemistry

Measurement	Count	Mean	StDev	%RSD	Units
Solids	68	14.267	0.824	5.773	wt%
Density	68	1.093	0.030	2.790	g/ml
pH	68	11.313	0.061	0.536	
OH(received)	65	0.078	0.006	8.274	Molar
OH(filtered)	65	0.010	0.008	80.019	Molar

Elemental Analysis by AA - Microwave

Element	Count	Mean	StDev	%RSD	Units
Cs	64	0.006	0.007	122.284	wt%
K	64	0.341	0.078	22.814	wt%
Na	64	5.003	0.539	10.767	wt%
Si	63	2.114	0.798	37.752	wt%

Table 4.3 Sludge Composition vs Specification

Elemental by ICP

Element	Nominal[a] (wt%)	Error[a] (%)	Mean	St.Dev	% RSD	% Diff	Units
Al	5.82	5	6.863	0.292	4.254	-17.9	wt%
Ba	0.244	25	0.302	0.013	4.382	34.8	wt%
Ca	1.89	10	1.547	0.109	7.046	-18.2	wt%
Cr	0.22	25	0.048	0.036	76.071	-78.2	wt%
Cs[b]	0.008	25	0.006	0.007	122.284	-25.0	wt%
Cu	0.11	25	0.160	0.012	7.046	45.5	wt%
Fe	20.600	5	20.918	1.267	6.055	1.5	wt%
K[b]	0.298	25	0.341	0.078	22.014	14.4	wt%
Mg	0.183	25	0.141	0.027	19.054	-23.0	wt%
Mn	4.97	5	4.789	0.276	5.776	-3.7	wt%
Na	5.56	10	4.280	0.542	12.661	-23.0	wt%
Na[b]			5.003	0.539	10.767	-10.0	wt%
Nd	0.433	25	0.179	0.120	67.202	-58.6	wt%
Ni	1.98	10	1.873	0.114	6.060	-5.4	wt%
P	0.0411	25	0.069	0.010	14.838	67.9	wt%
Pb	0.265	25	0.435	0.037	8.581	70.6	wt%
Si	2.98	10	3.901	0.181	4.631	30.9	wt%
Si[b]			2.114	0.798	37.752	-29.0	wt%
Zn	0.173	25	0.332	0.017	5.257	91.9	wt%
Zr[e]	2.17	10	0.142	0.115	81.509	-93.5	wt%

Ionic by IC

Ion	Nominal[a,d]	Error[a] (%)	Mean	St.Dev	% RSD	% Diff	Units
SO4	1,025 mg/l	10	772	43.6	5.656	-24.7	mg/l
NO3	733 mg/l	10	1,362	41.8	3.073	-76.2	mg/l
NO2	12,165 mg/l	5	13,412	373.4	2.772	10.7	mg/l
Cl	1,025 mg/l	10	1,084	84	7.753	5.8	mg/l
Cl[c]			4,307	1,505.2	34.946	300	DPM
F	161 mg/l	10	845	298.1	35.269	360	mg/l
F[c]			717	139.3	19.421		ppm
Density			1.093	0.03	2.79		g/ml
pH			11.313	0.061	0.536		
Solids	15.4		14.270	0.824	5.773		wt%

(a) IDMS Sludge Slurry Specification
(b) by Atomic Adsorption (AA)
(c) by ISE
(d) corrected for density, total solids, and insoluble solids
(e) this studies indicated that Zr must be determined by the Na2O2 fusion methods not Aqua Regia as reported here

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Table 4.4 Characterization of PHA

Wet Chemistry

Measurement	Count	Mean	StDev	%RSD	Units
Total Solids	76	6.064	0.909	14.983	Wt%
Density	76	1.020	0.034	3.368	g/ml
pH	76	3.808	0.147	3.849	
Total Acid	75	0.128	0.026	20.233	Molar

Carbon Analysis

Measurement	Count	Mean	StDev	%RSD	Units
TOC	76	6514.947	221.885	3.406	mg/l
TIC	76	71.921	22.956	31.918	mg/l

Ionic by IC

Ion	Count	Mean	StDev	%RSD	Units
Formate	76	15675.053	694.084	4.428	mg/l
Nitrate	76	14856.263	909.240	6.120	mg/l
Sulfate	76	171.908	14.021	8.156	mg/l

Ionic by ISE

Ion	Count	Mean	StDev	%RSD	Units
Cl	20	97.384	22.088	22.682	ppm
F	20	4.474	0.133	2.972	ppm

Elemental Analysis by AA - Liquid (soluble fraction)

Element	Count	Mean	StDev	%RSD	Units
Cs	76	341.724	11.802	3.454	ppm
K	76	5290.250	390.088	7.374	ppm
Na	76	5356.711	802.591	14.983	ppm

Table 4.5 Characterization of the PHA

Elemental Analysis by ICP - Liquid

Element	Count	Mean (ppm)	StDev	%RSD
Ca	68	56.053	1.425	2.543
Cd	68	0.074	0.033	44.526 *
Co	68	0.082	0.043	52.828 *
Cu	68	292.840	9.416	3.215
Mg	68	19.559	0.459	2.348
Mn	68	99.115	2.953	2.979
Pb	68	1.321	0.444	33.585 *
Zn	68	6.648	0.204	3.064
Zr	68	0.036	0.031	87.556 *
Al	68	27.070	1.037	3.829
Ba	68	0.856	0.055	6.398
Fe	64	208.000	21.492	10.333
La	68	0.144	0.123	85.186 *
Li	68	0.383	0.071	18.572 *
Mo	68	0.066	0.024	36.749 *
Na	68	5163.941	161.030	3.118
Ni	68	30.013	0.800	2.665
Sn	68	0.185	0.099	53.492 *
Sr	68	0.954	0.032	3.320
V	68	0.031	0.036	116.122 *
B	68	1944.999	45.923	2.361
Cr	68	1.324	0.103	7.779
P	68	0.745	0.106	14.236
Si	68	31.935	3.628	11.361
Ce	64	0.460	0.504	109.684 *
Nd	68	4.874	0.930	19.076 *
Formate	76	15675.0	694.1	4.43
Nitrate	76	14856.3	909.2	6.12
Sulfate	76	171.9	14.02	8.16
pH	76	3.808	0.147	3.85
Total Acid	75	0.128 (M)	0.026	20.23
TOC	76	6514.95	221.9	3.41
TIC	76	71.92	22.9	31.92

* indicates components which are most likely not actually present in the PHA. Measurements shown are the baseline value.

4.2 Precipitate Hydrolysis Aqueous

The PHA was produced over several runs in the PHEF. It was extensively sampled and characterized prior to the run. Tables 4.4 and 4.5 reproduce the average compositions of the PHA presented in reference 5. All of the values appear to be consistent and reasonable when compared to the expected values.

4.3 Formic Acid

The formic acid used in the campaign was industrial grade at a concentration of 90 wt%. The formic acid was sampled and the concentration was verified prior to each batch.

4.4 Noble Metals and Other Trim Chemicals

The trim chemicals include: mercury, ruthenium, rhodium, palladium, silver, selenium, and tellurium. Table 4.6 contains the noble metals and mercury concentrations for the three sludge types to be used in this campaign and their additive form.

Table 4.6 Noble Metals and Mercury in Simulated Sludge

(wt% elemental dry basis)

Compound	Additive Form	Blend	Purex	HM
Ru	$RuNO(OH)_3 \cdot 2H_2O$	0.100	0.028	0.217
Rh	$Rh(NO_3)_3 \cdot H_2O$	0.018	0.008	0.038
Pd	$Pd(NO_3)_2 \cdot H_2O$	0.045	0.026	0.079
Ag	$AgNO_3$	0.014	0.014	0.014
Te	TeO_2	0.022	0.006	0.048
Se	SeO_2	0.002	0.001	0.004
Hg	$Hg(NO_3)_2 \cdot H_2O$	1.588	0.102	3.263

The Ru is purchased as $RuCl_3$ which is subsequently converted to a nitrosylruthenium (the anticipated form of the ruthenium in the waste tank farm). The procedure for this conversion is highlighted in Table 4.7[8] and was developed by R. M. Wallace and D. T. Hobbs of the Savannah River Laboratory. The procedure does not produce a pure nitrosylruthenium product but does result in a product which has undergone the same treatment steps as the actual waste.

The rhodium, palladium and silver were purchased as nitrate solutions to simulate the expected form in the separations facilities. While these materials undergo additional chemical treatment (neutralization) in the tank farm, it was judged that these materials would have similar melter and melter redox behavior (as compared to radioactive waste) if they were added to the IDMS

SRAT in the nitrate forms. Based on the second blend run this approach is being re-examined to also include SRAT hydrogen evolution potential.

Future laboratory scale runs will combine and co-precipitate all the noble metals and the mercury prior to the SRAT addition. This will require modification of the procedure highlighted in Table 4.7 to add the Pd, Rh, Ag and mercury between steps 12 and 13. The mixture will then be neutralized with excess caustic. This caustic mixture will be added to the SRAT. This preparation procedure will be compared to the current method of noble metals preparation procedure and recommendations for its use in IDMS will be made. The IDMS procedure will not be revised until this comparison is completed.

Selenium and tellurium are added to the SRAT as oxides. These materials were added since they are potential noble metals alloying agents which will enhance deposition on the melter floor. Recently these materials have also been shown to be catalyst poisons for the decomposition of formic acid; however, their effect in simulated and actual sludge is not yet known and is being investigated.

Mercury is added as mercuric nitrate. Upon addition to the alkaline sludge, the mercuric nitrate will react to form mercuric oxide (HgO), the anticipated form of mercury in SRS waste.

Table 4.7 Ruthenium Treatment Procedure[a]

Step	Description
1	Weigh out 1617 grams of $RuCl_3$
2	Add Ru to 6.5 liters of 1M HCl
3	Bring to boil and reflux
4	Weigh out 1613 grams of $NaNO_2$
5	Add to boiling mixture over 1 hr period
6	Cool to 80°C
7	Weigh out 2688 grams of $NaNO_2$
8	Add $NaNO_2$ to mixture over a 3 hr period
9	Measure 1143 mL of concentrated HNO_3
10	Add HNO_3 slowly
11	Bring to boil and reflux for four hours
12	Cool to 80°C
13	Add 5 liters of simulated sludge
14	Add 1292 grams of NaOH pellets while agitating
15	Cool to room temperature

[a] Amounts of Ru given are for Blend type sludge only

4.5 Frit 202

The frit for the runs was obtained from DWPF. The material was procured as part of the frit vendor qualification test program. Three vendors participated in the qualification tests which required each vendor to provide 20,000 pounds of Frit 202 to WSRC. SRL tests (including composition) performed on the frit resulted in the qualification of two vendors. These runs used the frit produced by APEC and shipped in four storage bins containing 5,000 pounds each. The frit composition contained in Table 4.8 is an excerpt from the qualification report[9].

Table 4.8 Frit-202 Composition Blend 1 & 2

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

Frit bin "W" was used for both runs
n/a = not available

5.0 Campaign Chronology

Section 5 provides the chronology of the two runs. Section 5.1 summarizes Blend 1. Section 5.2 summaries a failure of the wastewater treatment system, which lead to complications and uncertainty in the second run. Section 5.3 summarizes Blend 2.

5.1 Blend 1 Batch History

The processing of the first batch of melter feed containing noble metals began on 6/19/90 by transferring 1,678 pounds of solids of the Blend type sludge simulant from the Sludge Receipt Tank (SRT) to the IDMS SRAT/SME. Trim chemicals (mercury, noble metals and the alloying agents) were added and the sludge sampled. Formic acid (32 gallons at 0.22 gpm) was added on 6/20/90. Precipitate Hydrolysis Aqueous (PHA) product was transferred (1,983 gallons) to the SRAT in discrete batches and concentrated on 6/21 and 6/22. Frit 202 (2,765 pounds) was slurried with water and added to the SRAT on 6/23 and 6/24. The first of two major program delays was caused by the failure of an ultrafilter which became plugged during the SME cycle. The ultrafilter was replaced.

The final SME concentration was completed on 7/20 and 700 gallons transferred to the Melter Feed Tank (MFT). This feed was held in the MFT until 8/27/90 due to wastewater treatment problems. These problems and the run difficulties they caused are discussed in section 5.2. The run produced 2,809 lbs of glass.

5.1.1 Sludge Transfer and Trim Chemical Addition for Blend 1

The sludge was transferred into the SRAT on 6/19/90. Three discrete transfers of 364, 495 and 406 gallons were made with the sludge being concentrated after each addition. The SRAT contained a water heel (and residual SME material) from the third mercury run prior to the sludge transfer. The final sludge volume was 1,170 gallons at 19 wt% solids.

Trim Chemicals were then added to provide the elemental compositions provided in Table 4.6. Table 5.1 contains the actual amounts of trim chemicals added to the SRAT.

Table 5.1 Amount of Noble Metals and Mercury Added to the SRAT for Blend 1

(Amount of the Additive Form in grams unless otherwise noted)

Compound	Additive Form	Desired Amount	Actual Amount
Sludge		1735 lbs**	1678 lbs
Ru	$RuNO(OH)_3 \cdot 2H_2O$*	1617.0	1617.4
Rh	$Rh(NO_3)_3 \cdot H_2O$***	2871.0	2871.5
Pd	$Pd(NO_3)_2 \cdot H_2O$***	4037.0	4040.5
Ag	$AgNO_3$	174.0	173.9
Te	TeO_2	217.0	216.4
Se	SeO_2	22.0	21.9
Hg	$Hg(NO_3)_2 \cdot H_2O$	47.1 lbs	48.0 lbs

* Amount given is for the ruthenium conversion procedure and is grams $RuCl_3$

** 1735 pounds of sludge solids was the basis for the trim chemical addition

*** Amount given for Rh, and Pd, are grams of solution. The $Rh(NO_3)_3$ solution is 4.933 wt% Rh and the $Pd(NO_3)_2$ solution is 8.769 wt% Pd.

5.1.2 Formic Acid Addition

Thirty-two gallons of 90 wt% formic acid were added to the SRAT. The basis for the addition was the experimental technique developed by C. W. Hsu.[10] This technique accounts for acid required to:

- neutralize the hydroxide and carbonate,
- decompose the nitrous acid,
- reduce the Mn(IV) to Mn(II),
- reduce the Hg(II) to elemental mercury, and
- modify the sludge rheology.

Table 5.2 details the formic acid calculational bases for Blend 1.

The analysis of free hydroxide was conducted two ways: (1) on the sludge sample as is, and (2) on the sludge filtrate. The results were significantly different. The free hydroxide from the sludge sample (unfiltered) was 0.07 Molar, while the value from the filtrate was 0.0086 Molar. It was suspected that the difference was caused by the inclusion of carbonates in the free base titration of the unfiltered sample and therefore the smaller number was used. It was later proposed that the free hydroxide was being tied up by $Al(OH)_3$. Use of the larger value (0.07 M) would have increased the addition of formic acid by about 4 gallons.

Table 5.2 Formic Acid Calculational Bases for Blend 1

Reactant	Amount	Units	gr Moles Reactant	gr moles HCOOH
Hydroxide	0.00862	Molar	41.27	41.27
Carbonate	0.03398	Molar	162.72	325.45
Nitrite	13396.3	mg/l	1308.5	981.40
MnO_2	4.8	wt%	670.1	1005.2
$Ni(OH)_2$	1.88	wt%	245.6	147.4
HgO	28.08	Lb Hg	63.49	63.49
Total gram moles of HCOOH				2564.13
Total HCOOH Required @110%				2820.58
Total gallons of 90 wt% formic acid				31.49

During the coupled feed campaign (PHA 1-3), large spikes of nitric oxide (NO) were generated in the SRAT offgas during the formic acid addition/digestion step. The NO is the product of the formic acid reaction with corrosion inhibiting nitrites in the simulated sludge. The NO then reacted with oxygen from air inleakage in the SRAT vapor space and the Process Vessel Vent System (PVVS) to form nitrogen dioxide (NO_2). This exothermic reaction caused elevated temperatures in the PVVS and temperatures as high as 28°C at the vapor exit of the FAVC.

Violation of the high temperature interlock (20°C) during formic addition or reflux will stop the acid addition, shut off the steam, and turn on the cooling water to the SRAT vessel. To avoid this during the mercury campaign, the formic acid was added at half the nominal rate. This resulted in a more gradual evolution of gases and better control on the exothermic reaction. This same approach was used during Blend 1.

Figure 5.1 shows the NO_x and CO_2 evolution for Blend 1 along with the formic acid addition flowrate, steam flowrate and SRAT temperature.

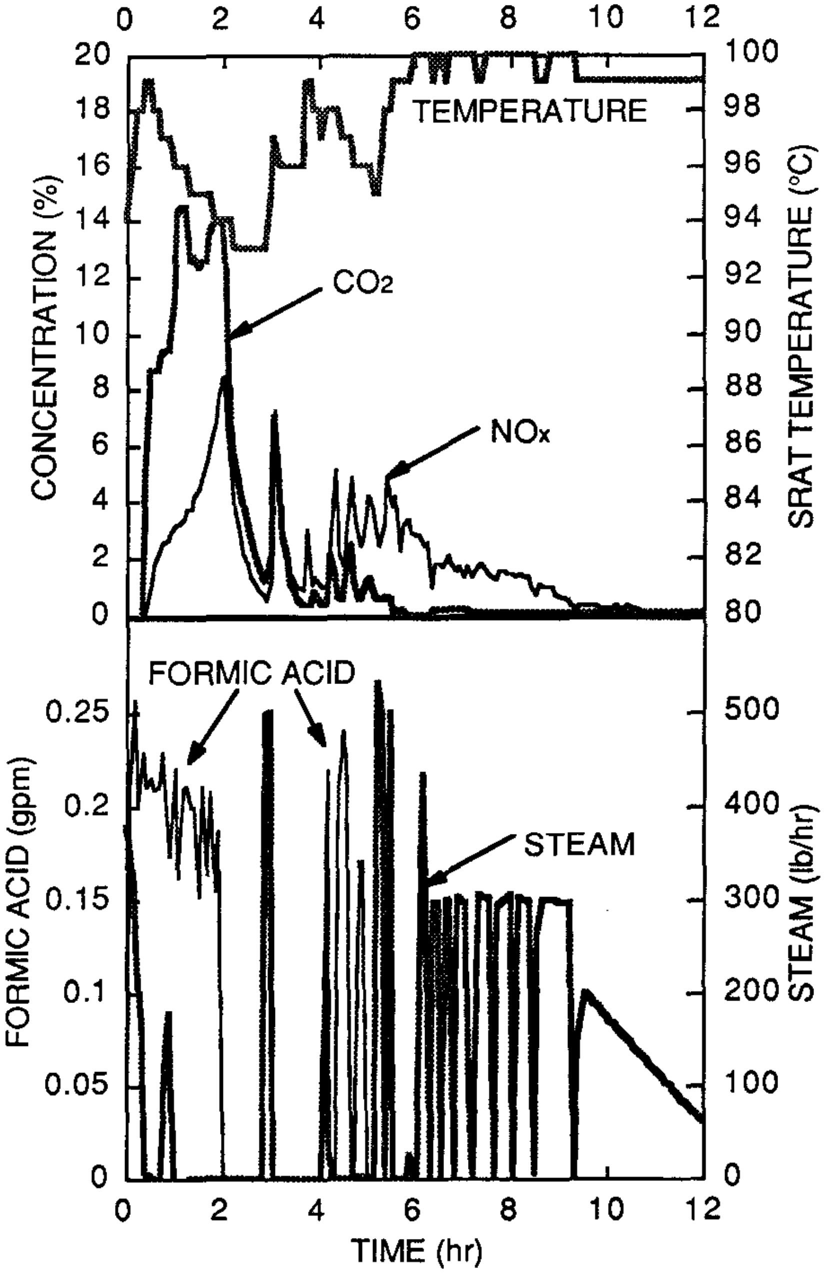

Figure 5.1 CO2 and NOx Evolution During Formic Acid Addition of Blend 1

The CO_2 evolution was typical with two peaks during the addition. The first peak was most likely a result of the neutralization of carbonates and the second from simultaneous decomposition of nitrite (which produces the single NO_x peak) and the reduction of manganese. The formic acid flow was stopped after 23.1 gallons (elapsed time = 2.0 hours) had been added. The remaining 9.9 gallons were added over the next three hour period, but the addition was erratic with many FAVC high exit temperature interlocks. Generally the CO_2 and NO_x evolution increased as the formic acid was added.

Boiling was established (elapsed time = 6 hours) and a typical NO_x peak (associated with the reduced NO_x solubility at an increased temperature and the steam stripping) occurred. Both the CO_2 and NO_x evolution decreased to essentially zero during the six hour reflux period.

Hydrogen was monitored during the formic acid addition and reflux period using a Gas Chromatograph (GC) at the FAVC exit. This was the first time on line hydrogen monitors were used during a DWPF feed preparation demonstration. The hydrogen concentration was about 100 ppm.

5.1.3 PHA Addition/Concentration for Blend 1

About 1,983 gallons (933 lbs PHA solids) were added in two discrete batches of 450 and 300 gallons each plus one continuous batch of the remaining material. The discrete batches were added at approximately 4-6 gpm. The continuous batch was added 2-3 gpm, while boiling the SRAT at an equivalent rate such that the level remained essentially constant. During the PHA concentrations and the subsequent SME cycle, significant foaming and solids carryover were observed. This was quite surprising since an antifoam agent was being added on a regular basis. Upon inspection of the antifoam agent, it was discovered that the material shelf life had expired. The material being used was approximately 1.5 years old verses the expected shelf life of 6 months. Fresh antifoam agent has been procured for subsequent IDMS demonstrations.

Hydrogen was monitored only during the first PHA addition. The hydrogen concentration never exceeded 200 ppm. Demands of the monitoring equipment prevented its use for the complete feed preparation cycle. The data did, however, agree with the small scale studies conducted by C. W. Hsu[11]. These studies indicated that for sludges containing high nitrite, mercury and noble metals the hydrogen concentrations should be around the 100 ppm level during formic acid addition and the first three hours of reflux. The PHA addition was not completed during the small scale studies and the complete six hour reflux period was not monitored.

5.1.4 SME Cycle for Blend 1

The "SME Cycle" of the SRAT/SME operation was started by making a 50 wt% frit-water slurry in the Frit Slurry Make-up Tank (FSMT). This frit slurry was prepared by adding 2,765 pounds of Frit-202 to 400 gallons of water. This material was then transferred to the SRAT/SME in two discrete batches. Additional water was added to the system to flush the FSMT of residual frit and to flush the transfer line to the SRAT/SME. The SRAT contents were then cooled and sampled.

Just prior to the last frit slurry addition the ultrafilter (a crossflow type filter used to remove entrained solids from the condensate prior to mercury removal) plugged. The ultrafilter was replaced and had minimal impact on operations other than a time delay.

Eight one-liter samples of the Blend 1 SME product were collected. An aliquot from each sample was then vitrified in Teflon™-coated crucibles. Each of the 8 resulting glasses were ground and enough sample taken from each to run all analyses in quadruplicate, producing 32 analytical results (8 sets of 4).

The composition of the resulting SME composition and the predicted glass product characteristics are discussed in reference 5 and summarized in Tables 5.3, 5.4 and 5.5.

5.1.5 Melter Operation for Blend 1

The slurry was transferred (700 of 1100 gallons) to the MFT on 7/20. However, due to the IXS processing problem (see section 5.2) the melter operation was delayed until 8/24. The new melter feed pump was installed prior to this run and operated for the first time. Also due to the IXS problem the remaining SRAT contents were emptied and temporarily stored in drums. Draining was difficult and only three drums (150 gallons) were filled.

Feeding was also difficult and the slurry was noted by the operators to be "very thick". The pH and yield stress of the slurry was checked and determined to be 7.24 and 78 Pascals, respectively. This pH was significantly higher (7.2 vs < 6.0) than the prior runs (except Hg#2 where caustic was added as a trim chemical) and the yield stress is about double the normal values.. This was originally suspected as the cause for the poor draining. However, following Blend 2 the SRAT was cleaned and a metal obstruction (a nut) was removed from the entrance to the SRAT bottom drain.

Feeding continued until the MFT level reached 18%. Glass production totaled only 2,800 pounds compared to the normal value of 4,500 to 5,000. After adjusting for the MFT volume it was concluded that a significant heel volume remained in the SRAT.

Table 5.3 Blend 1 SME Composition

Elemental Analysis by ICP - Microwave Dissolution

Element	Count	Mean(wt%)	StDev	%RSD
Ca	32	0.590	0.029	4.875
Cu	32	0.141	0.003	2.117
Mg	32	0.789	0.049	6.195
Mn	32	1.599	0.034	2.153
Pb	32	0.157	0.029	18.567
Zn	32	0.178	0.006	3.619
Zr	32	0.154	0.012	7.580
Fe	32	7.486	0.143	1.905
Na	32	6.766	0.334	4.931
Ni	32	0.619	0.014	2.293
Ti	32	0.087	0.002	1.945
Cr	32	0.106	0.006	6.053
P	32	0.020	0.007	37.769
Nd	32	0.210	0.040	18.966

Elemental Analysis by ICP - Peroxide Fusion (Acid Uptake)

Element	Count	Mean(Wt%)	StDev	%RSD
Nd	32	0.248	0.050	20.216
Mg	32	0.799	0.014	1.740
Al	32	2.379	0.045	1.883
Ba	32	0.089	0.002	2.734
Fe	32	7.144	0.157	2.201
Li	32	2.014	0.052	2.569
Ti	32	0.078	0.008	9.837
B	32	1.980	0.052	2.611
Si	32	24.197	0.455	1.881

Table 5.4 Blend 1 SME Composition

Wet Chemistry

Measurem't	Count	Mean	StDev	%RSD	Units
pH	32	7.321	0.057	0.775	
solids (tot)	32	33.263	0.579	1.741	wt%
solids (cal)	30	27.359	0.312	1.139	wt%
Density	29	1.163	0.028	2.379	g/ml

Carbon Analysis

Measurem't	Count	Mean	StDev	%RSD	Units
TIC	32	232.06	38.491	16.586	mg/l
TOC	32	6204.55	85.367	1.376	mg/l

Ionic Analysis by IC

Ion	Count	Mean	StDev	%RSD	Units
Formate	32	25678.4	682.5	2.658	mg/l
Nitrate	32	23856.9	3904.6	16.367	mg/l
Sulfate	32	797.4	114.7	14.387	mg/l

Elemental Analysis by AA - Microwave Dissolution

Element	Count	Mean	StDev	%RSD	Units
Cs	32	0.044	0.008	17.112	wt%
K	32	1.545	0.047	3.056	wt%
Na	32	6.649	0.248	3.732	wt%
Hg	31	56.277	1.120	1.991	ppm
Si	31	17.372	1.380	7.944	wt%

Ionic Analysis by ISE - Na2O2 fusion (Water Uptake)

Ion	Count	Mean	StDev	%RSD	Units
Cl	30	1420.93	357.449	25.156	ppm

Table 5.5 Glass Properties as Predicted From SME Samples

Glass Property	Specification	Property Model
Liquidus (°C)	< 1050	941
Viscosity (P)	<100, >20	88
Durability (kcal/mol)	> -7.0	-4.55
TiO_2 (wt%)	< 1.0	0.153
P_2O_5 (wt%)	< 3.0	0.048
Cr_2O_3 (wt%)	< 0.3	0.163
NaF (wt%)	< 1.0	n/d
NaCl (wt%)	< 1.0	n/d
SO4 (wt%)	< 0.4	n/d

Table 5.6 Actual vs Target SME Composition

Variable	Target	Actual	% Error
% Frit Oxides	64.0	64.55	0.96
% PHA Oxides	8.0	7.85	1.98
% Waste Oxides	28.0	27.60	1.42
Sludge Added	1678 lbs	1678 lbs	0.00
PHA Added	933 lbs*	933 lbs	0.00
Frit Added	2705 lbs*	2765 lbs	2.22
Liquidus (°C)	967	941	2.79
Viscosity (Poise)	82	88	8.54
Durability (kcal/mol)	-5.16	-4.55	11.06

* Target amounts determined after sludge transfer and adjusted for the actual transfer.

5.2 Wastewater Treatment Facility Failure

Condensate (from the feed preparation and melter operations) is collected in the Waste Water Pump Tank (WWPT) where the pH is adjusted to a minimum of 11.0 with caustic. This reduces corrosion and precipitates additional solids. The condensate is then filtered via a sintered metal crossflow filter designed to remove these particulates and colloids which are larger than 0.02 micron. The filtrate is then collected in the Waste Water Collection Tank (WWCT) which is a part of the IXS, a state permitted waste water treatment facility.

Once 1,000 gallons or more is collected in the WWCT the condensate is then processed through two columns in series containing GT-73 resin which adsorbs the mercury and other heavy metal compounds. The condensate is collected in one of two hold tanks and analyzed for mercury prior to being neutralized (pH= 6 to 9) with phosphoric acid.

While processing the condensate produced during the final SME concentration, the mercury discharge limit of 10 ppb could not be met. TNX operations personnel elected to change the resin. This was accomplished on 7/19 by using the the mercury contaminated water (6 ppm) contained in the WWCT to jet the resin into the columns.

The condensate was reprocessed (twice) but the discharge limit was not met either time. Following discussions with several SRL specialists the resin was changed again on 7/26. Fresh water was used to jet the resin since a possible cause of the problem was thought to have been the use of the contaminated water. Laboratory testing of the resins and the condensate also started.

The condensate was reprocessed through the new resin but again did not meet the discharge limit.

Laboratory Testing determined the cause of the problem to be the mercury coupled with iron in the condensate forming an insoluble compound which passes through the columns untreated by the resin. The source of the iron is not known for certain but it could have come from 1) a cooling water spill which had drained to the IDMS sump and was processed through the ultrafilters and the IXS, 2) TNX process water, which contains high concentrations of iron, 3) the post-precipitation of solids after filtration, precipitation of solids in this type environment is known to take up to 30 minutes, but the residence time provided by the IDMS WWPT and ultrafilter system can be less than 5 minutes.

Studies indicated that the insoluble particulates were removed by a 0.45 micron filter and after treatment with the GT-73 resin the mercury content was well below the 10 ppb discharge limit. Since the IDMS ultrafilters were designed to remove particulates 0.02 micron and larger, a proposal was made to recycle the wastewater to the IDMS SRAT where it would be evaporated and the condensate would be processed in a normal method. The proposal was presented to EPD personnel on August 3rd, and to SCDHEC on August 7th. The plan was approved by SCDHEC on August 14th.

The SME material had been transferred (700 of 1,100 gallons) to the MFT on 7/20 following the final concentration. The remaining material was drummed to make room for the wastewater rework and to prevent feed dilution. However, less than 200 gallons of feed could be drained (via the bottom drain). A significant heel of SME material remained in the SRAT.

Approximately 3,400 gallons of wastewater from the IXS WWCT and the two hold tanks was reprocessed through IDMS. The wastewater contained a high concentration of caustic (pH>11) and residual phosphate from previous hold tank neutralization steps. The non-volatile components were concentrated during this operation and an analysis of the SRAT heel (1,100 gallons) is provided in Table 5.7.

Comparison of Tables 5.3 and 5.7 indicates that the heel solids were essentially Blend 1 SME material and the soluble fraction contained significantly more phosphate and hydroxide than previous heels. The possible effects of these compounds on Blend 2 processing is discussed in Section 6.

Table 5.7 SRAT Heel Analysis Prior to Blend 2

Species	Dried Solids (wt%) Aqua Regia	Dried Solids (wt%) Na_2O_2	Filtrate (ppm)
Al	2.517	1.867	1.673
B	1.211	1.436	1986.8
Ba	0.102	0.075	0.136
Ca	0.584	0.341	4.511
Cu	0.157	0.108	0.568
Cr	0.016	0.064	0.421
Fe	7.946	5.824	0.219
K	1.103	-----	
Li	1.011	1.456	1547.3
Mg	0.465	0.602	0.610
Mn	1.695	1.249	0.043
Na	6.581	-----	11850.
Nd	0.348	0.193	1.726
Ni	0.656	0.465	0.478
P	0.221		194.2
Pb	0.169	0.091	1.441
Si	16.3		3058.8
Sn	0.006	0.009	1.026
Sr	0.044	0.029	0.150
Ti	0.056	0.075	0.160
Zn	0.161	0.087	2.360
SO4			816
PO4			618
OH			0.37 (molar)
pH			>11
HCOOH			11616
NO3			12817
NO2			0.5
TOC			2927
TIC			441

5.3 Blend 2 Run Summary

The processing of the second batch of melter feed containing noble metals began on 9/10/90 by transferring 1,655 pounds of Blend type sludge solids from the SRT to the IDMS SRAT/SME. Trim chemicals (48 pounds of dissolved mercuric nitrate and noble metals) were added after sludge transfer on 9/12/90. Formic acid (60 gallons at 0.37 gpm) was added on 9/12 and resulted in the evolution of hydrogen in quantities greater than expected. PHA (980 gallons) was added to the SRAT in discrete batches on 9/14 to 9/18.

Following the PHA addition a pause in the campaign was taken to analyze the hydrogen evolution and other data collected during Blend 2. The SRAT agitator was removed and the vessel inspected. Steam coil deposit samples were taken and analyzed. Also during the pause, a second failure of the Ion Exchange Waste water treatment facility occurred. This failure resulted in water accumulation in the IDMS sump, MFT and SRAT which was subsequently processed through the SRAT prior to additional operations.

On 12/3/90 an additional 350 gallons of PHA was added to the SRAT. This completed the SRAT operation cycle.

The frit-water slurry (1,770 pounds of frit in 400 gallons of water and 2 gallons of formic acid) was prepared on 12/6/90 and was transferred to the SRAT on 12/7 and 12/14/90.

Following the frit addition the water in the MFT was transferred to the SRAT and concentrated from 1/2/91 to 1/17/91. The SME product was then transferred to the MFT and melter feeding started on 2/12/91. Feeding continued until 3/8/91. Glass production totaled 4,368 pounds. One pouring problem was encountered during the run (see Section 5.3.5).

5.3.1 Sludge Transfer and Trim Chemical Addition

The sludge was transferred into the SRAT on 9/10/90. Three discrete transfers of 370, 400 and 484 gallons were made with the sludge being concentrated after each addition. The SRAT contained a water heel and a large SME heel from Blend 1 prior to the sludge transfer. The final sludge volume was 1,100 gallons at 30 wt% solids.

During the final concentration the SRAT steam coil Heat Transfer Coefficient (HTC) dropped steadily. The HTC (measured at boiling temperatures) averaged 100 BTU/Hr-Ft^2-°F during the first two concentration steps but following the third addition the HTC peaked at 80 BTU/Hr-Ft^2-°F and declined steadily to 40 BTU/Hr-Ft^2-°F. The fouling decreased the steam flow from 800 pph to less than 300 pph and raised the steam coil chest pressure to the supply temperature (110 psig).

Trim Chemicals were then added to provide the elemental compositions provided in Table 4.6. Table 5.8 contains the actual amounts of trim chemicals added to the SRAT for Blend 2.

Table 5.8 Amount of Noble Metals and Mercury Added to the SRAT for Blend 2

(Amount of the Additive Form in grams unless otherwise noted)

Compound	Additive Form	Desired Amount	Actual Amount
Sludge		1735 lbs**	1655 lbs
Ru	$RuNO(OH)_3 \cdot 2H_2O$*	1617.0	1617.0
Rh	$Rh(NO_3)_3 \cdot H_2O$***	2871.0	2871.9
Pd	$Pd(NO_3)_2 \cdot H_2O$***	4037.0	4037.0
Ag	$AgNO_3$	174.0	174.0
Te	TeO_2	217.0	217.0
Se	SeO_2	22.0	22.0
Hg	$Hg(NO_3)_2 \cdot H_2O$	47.1 lbs	47.6 lbs

* Amount given is for the ruthenium conversion procedure and is grams $RuCl_3$

** 1735 pounds was the basis for the trim chemical addition

*** Amount given for Rh, and Pd, are grams of solution. The $Rh(NO_3)_3$ solution is 4.933 wt% Rh and the $Pd(NO_3)_2$ solution is 8.769 wt% Pd.

5.3.2 Formic Acid Addition

Sixty gallons of 90 wt% formic acid were added to the alkaline sludge in the SRAT. As in Blend 1 the method developed by Hsu was used, but was modified to account for the phosphate and hydroxide contained in the heel. These two changes increased the amount of formic acid required by 23.8 gallons.

The analysis of hydroxide was conducted on the sludge sample as received since it was proposed that the hydroxide was tied up by $Al(OH)_3$. This larger value for the hydroxide increased the formic addition by 4.6 gallons. Table 5.9 contains the formic acid calculational bases for Blend 2.

The total formic addition for Blend 2 (60 gallons) was the largest addition made to date in an IDMS run. It was roughly twice the addition made for the same type sludge during Blend 1.

Table 5.9 Formic Acid Calculational Bases for Blend 2

Reactant	Amount	Units	gr Moles Reactant	gr moles HCOOH
Hydroxide	0.0800	Molar	383.0	383.0
Carbonate	0.0339	Molar	162.7	325.5
Nitrite	13396	mg/l	1308.5	981.4
MnO_2	4.8	wt% Mn	670.1	1005.2
$Ni(OH)_2$	1.88	wt% Ni	245.6	147.4
HgO	28.08	Lb Hg	63.5	63.5
Hydroxide *	0.37	Molar	1890.6	1890.6
phosphate *	600	mg/l	30.3	30.3
Total gram moles of HCOOH				4826.8
Total HCOOH Required @110%				5308.3
Total gallons of 90 wt% formic acid				59.2

* components contained in the SRAT heel

The Formic addition rate for Blend 2 was also increased back to the DWPF scaled flowrate of 0.4 gpm. To accomplish this the FAVC vapor exit temperature interlock was increased to 35°C. Annual mercury emissions were not increased above permissible amounts since the emission basis was 47 runs/year but the actual average is six runs/year. The 35°C was selected to allow 12 runs/year without exceeding the permissible levels.

Figure 5.2 shows the CO_2, NO_x, and H_2 evolution for Blend 2 along with the formic acid addition rate, steam flowrate, and SRAT temperature. As shown, the formic addition was started and a small CO_2 peak resulted. The acid addition was stopped after about 5.5 gallons had been added due to a leak in the metering pump. The pump was repaired and the addition was restarted approximately 3 hours into the cycle. The remaining formic acid was added essentially continuously over the next 3 hours, only two short interruptions were encountered. The formic acid flowrate was about 0.35 gpm.

As in Blend 1 the CO_2 evolution exhibited a double peak. The peak concentration was about twice the concentration of Blend 1 due to the higher addition rate. The NO_x peak (23%) occurred simultaneously with the second CO_2 peak. This peak was nearly 3X the size of the Blend 1 peak. At the conclusion of the addition both the CO_2 and NO_x declined rapidly.

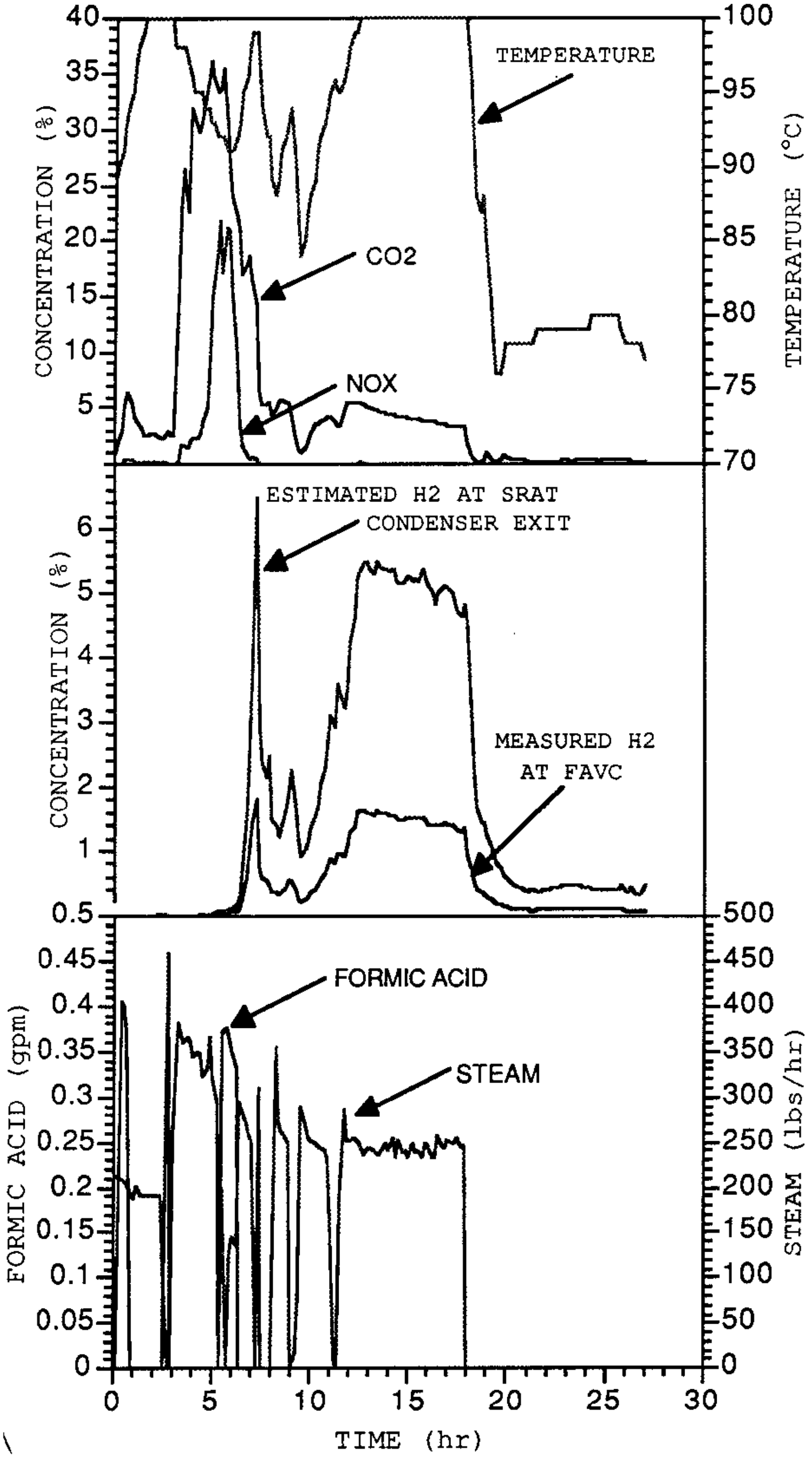

Figure 5.2 Hydrogen, CO2 and NOX Evolution During Formic Acid Addition of Blend 2

Hydrogen was noted to evolve during the formic acid addition as had occurred during Blend 1. The concentration was approximately 2X higher than Blend 1 (200 ppm), but still well below any flammability concerns (4.1 vol% or 41,000 ppm).

During the heat-up to boiling the hydrogen evolution increased rapidly. Fifteen minutes after the completion of the formic addition the hydrogen had increased to 0.3 vol%, a factor of 4.5X from the value fifteen minutes prior to the completion of the formic addition when the value was only 0.08%. The hydrogen continued to increase over the next 30 minutes to 1.5 vol%. The hydrogen concentration as reported above was measured at the FAVC vapor exit at 5 minute intervals. Since the air inleakage for the WWPT, MFT, and MWWT enters the vent system between the SRAT Condenser and the FAVC, the hydrogen concentration in the SRAT vapor space and the SRAT Condenser was higher than the measured concentration. During the Blend 2 formic addition and reflux the flowrates were such that the hydrogen concentration at the SRAT Condenser exit was approximately 4.3X the measured concentration. Figure 5.2 shows both the measured hydrogen profile and the estimated hydrogen profile at the SRAT Condenser exit.

Since the hydrogen concentration at the SRAT Condenser exit exceeded 4%, system operations were stopped by turning off the SRAT steam and initiating the cooling water. The hydrogen evolution was curtailed as the bulk temperature was reduced.

The IDMS facility has a nitrogen purge system which allows processing high concentrations of flammable materials. The nitrogen system is generally only used during the PHA addition and concentration cycle (benzene evolution periods), but was used for the remainder of Blend 2. The automatic interlocks for high oxygen concentrations were reduced from 8% to 3% (60% of 5%, the Minimum Oxidant Concentration [MOC] for hydrogen in air) to allow operations to resume.

Sludge samples were taken after the cooling water was initiated and indicated that the pH was 6.2 and the formate concentration was 42,000 ppm. The large formic acid addition had not produced excessively low pH's due to the formate buffer system.

The steam was restarted to the SRAT at about 9 hours into the cycle and the hydrogen evolution increased with increasing bulk temperature. The hydrogen peaked (1.6 vol % measured, 5.5 vol % estimated at the SRAT Condenser exit) with the onset of boiling. The SRAT was refluxed for 6 hours during which the hydrogen decreased to 1.4 vol % measured. The SRAT steam coil HTC was 26 BTU/Hr-Ft^2-°F during the reflux.

Samples of the SRAT were taken and analyzed for pH and formate. The values were 7.0 and 38,000 ppm respectively. Comparison to the samples taken immediately after formic addition indicated that the pH increased by 0.8 units and the formate decreased by 4000 ppm.

Following the reflux period the steam was turned off and the cooling water initiated. The hydrogen decreased to a steady value of 0.2 vol% (measured) with the SRAT temperature being maintained between 75 and 80°C.

5.3.3 PHA Addition/Concentration

In order to add the Precipitate Hydrolysis Aqueous (PHA) it was necessary to dewater the sludge. This was done on 9/13 during the 4-12 shift. Figure 5.3 shows the SRAT temperature and measured hydrogen concentration during the concentration and the PHA additions and dewatering steps which followed.

During the sludge dewatering the hydrogen concentration increased to 0.9 vol% and decreased (as during the formic reflux) to 0.75 vol%. The SRAT temperature was decreased to less than 75°C and held until the 4-12 shift of 9/14 when the first PHA addition was made.

During the day shift of 9/14 TOS maintainence confirmed that there was no blockage in the SRAT steam coil condensate line or steam trap. During a previous run the automatic block valve (which closes to hold the nitrogen purge gas but opens to allow steam flow) failed partially closed. This forces the steam coil chest pressure to increase and has the same effect on the HTC as fouling. Confirmation of no blockage suggested the SRAT steam coil had been fouled during the final sludge transfer and concentration (see Section 5.3.1).

The fouled steam coil limited the steam flowrate to about 300 pph, which corresponds to a continuous PHA addition rate of 0.6 gpm. This low flow can not be maintained and therefore forced the PHA additions to be discrete rather than continuous. Five PHA additions were made of 200,200,200,200 and 177 gallons respectively.

During the first PHA addition the hydrogen evolution was approximately half the pre-PHA addition sludge dewatering step (0.4 vs 0.8 vol%). This decline continued during the second PHA addition to 0.2 vol% and essentially remained constant at this value for additions 3, 4 and 5. The final PHA dewatering was completed on 9/18. The final SRAT cycle pH was 7.5.

5.3.4 SRAT Inspection and Coil Residue Analysis

Following the SRAT cycle a pause was taken in the run to analyze the hydrogen data and inspect the SRAT. Six drums of slurry were removed to expose the top three rows of the steam and cooling coils, and the agitator was removed. Coil deposit samples were obtained. These sample analysis are discussed in Section 6.3

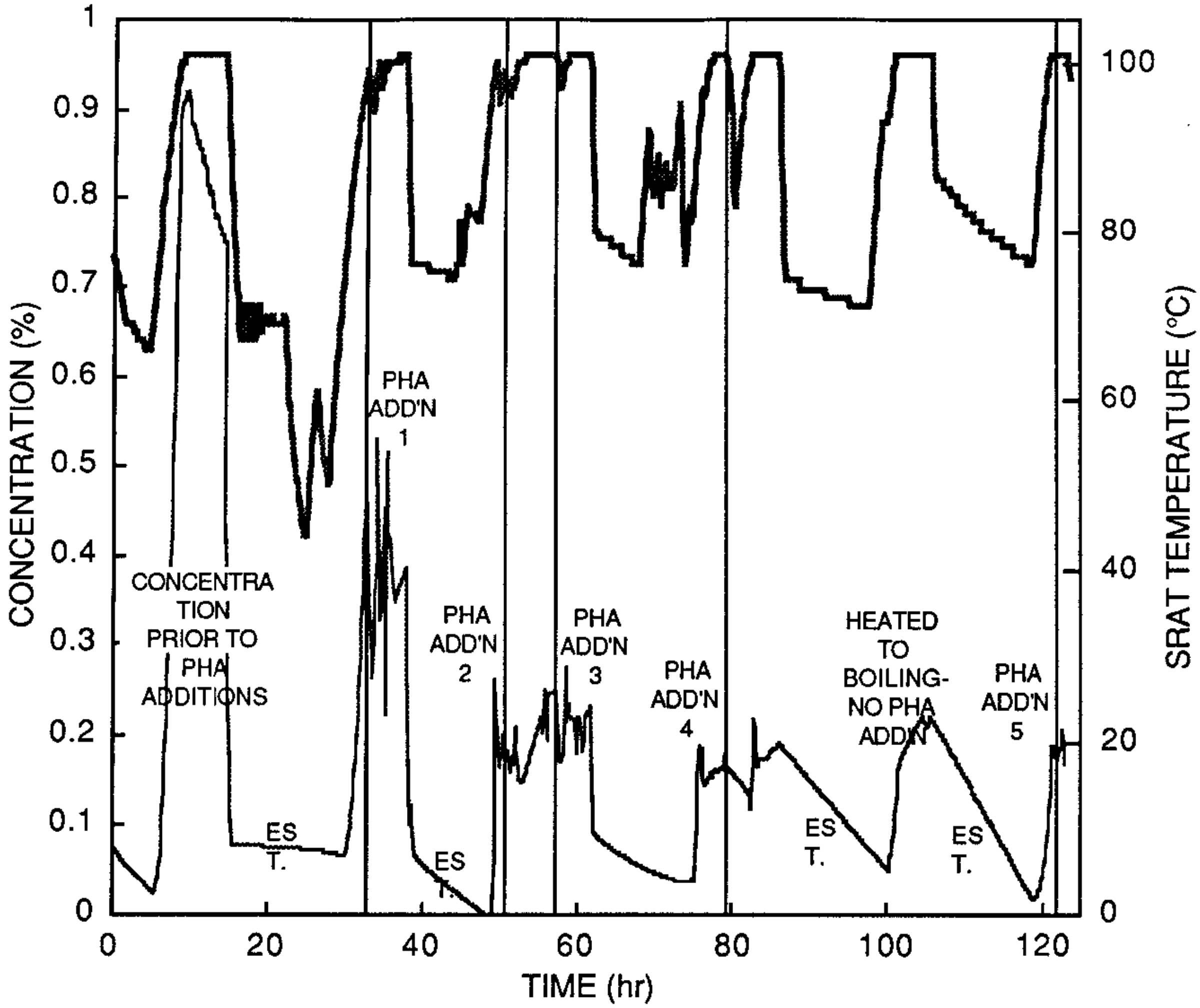

Figure 5.3 Hydrogen Evolution During PHA Additions of Bl 2

5.3.5 Sump Overflow and Second IXS Failure

On 10/15/90 a TOS operator inadvertently left the process water valve, used to fill the off gas condensate tank seal pot, partially open. The seal pot overflowed to the IDMS sump and over about a ten hour period filled the sump to the point of overflowing the inlet trench. The sump was pumped into the SRAT to reduce the level in the trench. The SRAT agitator was re-installed and the SRAT was heated to boiling and dewatered.

During this operation the SRAT steam coil HTC returned to the nominal values (100 $BTU/Hr-Ft^2-°F$). It is presumed that the deposits were thermally shocked as steam was introduced to the cold coil and resulted in the break-up of the deposits. This is similar to the technique used to remove deposits from U-tube evaporator coils.

Also during the dewatering step the IXS failed for the second time to meet the 10 ppb discharge limit. Investigation returned the same problem as had been experienced during the June failure. Mercury was complexed with iron forming an insoluble compound which was passing through the resin columns untreated.

Following the successful demonstration of the filtration technique in June, a design modification of the IXS to include a set of 0.2 micron filters before the columns (after the WWCT) was requested from SCDHEC. This permit revision had not been approved and requests by DWPT and TOS management for assistance from EPD personnel to expedite the revision were ineffective.

To provide the emergency overflow protection required, the sump level was reduced by filling the SRAT a second time and by filling the MFT.

The situation was worsened on 11/19 and 20 when poor communications between TOS Works Engineering and TOS Operations resulted in the overflowing of the Melter Cooling Water Tank (MCWT) which filled and overflowed the IDMS sump. About 300 gallons of mercury contaminated water (15 ppb) were discharged to an outfall not permitted for mercury.

With assistance from EPD, SCDHEC approved the IXS permit revision. The cartridge filters were installed on 11/23. No additional IXS failures have occurred since the installation of the filters.

Between 11/23 and 11/30 the water contained in the sump was processed through the SRAT, ultrafilters, and IXS. The SRAT material removed for inspection of the coils was returned to the SRAT and the material was dewatered.

5.3.6 Final PHA Addition for Blend 2

During the pause, chemical analysis of the SRAT product and data analysis by the Process Modeling and Control Group using the Product Composition and Control System software indicated the need for additional alkali. This alkali was provided by making a final PHA addition of 350 gallons on 12/3 and 12/4. This brought the total PHA addition to 1,327 gallons.

5.3.7 SME Cycle for Blend 2

The SME cycle for Blend 2 began on 12/6 when a mixture of 400 gallons of water, 2 gallons of formic acid and 1,770 pounds of Frit 202 was prepared in the FSMT.

The frit slurry was added to the SRAT in 3 discrete batches, one each on 12/6, 12/7, and 12/14. Throughout this period the SRAT was boiled to provide SRAT Condenser and FAVC Condenser performance data. The objective of this data was to confirm the HTRI computer code for condensation in the laminar flow region.

Also during this period the HTC for the SRAT steam coil declined indicating fouling had occurred a second time. The suspected cause was the addition of a binder (frit) to a highly concentrated caustic solution. Under these processing conditions the hydroxyl groups link together and form a gel. The gel incorporates the frit and when it contacts a hot surface, such as the steam coil, it drys to form a hard layer on the coil.

This is an important observation for the DWPF. Since the DWPF plans to use caustic as a SME trim chemical it is possible for this situation to occur.

Recommendation #1: Delete the use of NaOH and KOH as trim chemicals. Sodium Nitrate is recommended as a substitute for the caustic. Potassium Nitrate is recommended as a substitute for the KOH.

Following the frit addition the contents of the MFT (dilute MFT heel) were transferred back to the SRAT and concentrated. This operation occurred between 1/2/91 and 1/8/91. The SME product was ready to be transferred to the MFT (see Tables 5.10 and 5.11). However, the feed rheology was a concern since the pH was very high at >9.5. SME samples were taken and titrated in the laboratory. The room temperature titration indicated that 16 gallons of formic acid were required to reduce the pH to less than 7.0

The SRAT was heated to 90°C and 16 gallons of formic acid added. The pH decreased to only 8.5. The titration and addition process was repeated a second time using 13 gallons of formic acid. The pH again decreased only marginally, to 8.0. The titration was repeated a third time using an elevated temperature (90°C). The slurry was titrated to a pH of 6.0 but increased with time as the slurry was held at temperature. Little hydrogen was observed during the IDMS formic acid additions although formic/formate destruction was the presumed cause for the pH shift. Carbonate also increases during this period.

Following the second formic addition the rheology was determined to be below the limit of 100 Pascals.

Table 5.10 Blend 2 SME Composition

Elemental Analysis by ICP - Microwave Dissolution

Element	Count	Mean(wt%)
Ca	8	0.596
Cu	8	0.174
Mg	8	0.744
Mn	8	1.80
Pb	8	0.169
Zn	8	0.214
Zr	8	0.076
Fe	8	8.097
Na	8	6.928
Ni	8	0.709
Ti	8	0.090
Cr	8	0.128
P	8	0.108

Elemental Analysis by ICP - Peroxide Fusion (Acid Uptake)

Element	Count	Mean(Wt%)
Nd	8	0.377
Mg	8	0.761
Al	8	2.763
Ba	8	0.112
Fe	8	8.041
Li	8	1.811
Ti	8	0.090
B	8	1.949
Si	8	23.438

Elemental Analysis by AA - Microwave Dissolution

Element	Count	Mean(wt%)
Cs	8	0.04
K	8	1.543
Na	8	6.623

Table 5.11 Glass Properties as Predicted From SME Samples

Glass Property	Specification	Property Model
Liquidus (°C)	< 1050	1002
Viscosity (P)	<100, >20	89
Durability (kcal/mol)	> -7.0	-4.55
TiO_2 (wt%)	< 1.0	0.157
P_2O_5 (wt%)	< 3.0	0.258
Cr_2O_3 (wt%)	< 0.3	0.196
NaF (wt%)	< 1.0	n/d
NaCl (wt%)	< 1.0	n/d
SO4 (wt%)	< 0.4	n/d

5.3.8 Melter Operation for Blend 2

The Slurry was transferred to the MFT on 2/5/91. As noted above the slurry was thick and feeding was difficult. Feeding continued until 2/18/91. Glass production totaled 4,368 pounds.

Following the run, the SRAT was cleaned by pumping out the heel and flushing with water. (Later the SRAT was further cleaned with oxalic and nitric acids. These operations will be described in future reports.) The SRAT flush water was transferred to the MFT and vitrified. During the processing of this material a melter pouring problem was encountered.

5.3.9 Melter Pouring Problem

The low pour rate problem occurred on February 27th after about 770 pounds of feed from the SRAT heel had been fed into the melter. This was a large percent of the IDMS Melter capacity of 900 pounds of glass.

Initially three scenarios were postulated to explain the low pour rate - high glass viscosity due to the SRAT tank flushing, a riser throat block pluggage or failure, or a bellows vacuum line pluggage. The viscosity scenario was investigated first since pouring was possible at roughly twice the normal canister vacuum. MFT samples showed that the feed had a viscosity of 66 poise and a predicted liquidus of 1,047°C. The viscosity was well within the normal operating range of 20 to 100 poise, but the liquidus was near the upper acceptable limit of 1,050°C.

Due to the pouring problem there were concerns that the unheated riser entrance had been partially blocked due to the formation and accumulation (over the two year operational period) of spinels and/or acmite. This unheated riser entrance is a cold spot with temperatures below 900°C. It should be noted that the DWPF Melter does not have an unheated riser throat block, and therefore will not be as sensitive to spinel/acmite formation. Due to the higher liquidus of the current feed, calculations were done to determine how the liquidus of the feed could be reduced by about 20°C. Remediation of the feed was completed with the addition of 150 pounds of Frit 202 to the MFT.

Investigation of the third concern (that the vacuum pour line was plugged between the bellows and the vacuum sensor tap line) showed that the the pressure drop between the tap and the bellows was 7 inches of water. The pressure drop on this 12 inch long section of piping should have been near zero. This line was pressurized back into the bellows, but no deposits were observed to be discharged. The resulting pressure drop was lowered by only 1 inch of water. Due to the complexity of inspecting this line, it was decided to pour glass with the remediated feed.

Inspection of the last filled canister before the problem showed a large slug of glass that was thought to have been at the tip of the pour spout and which subsequently fell into the canister at the end of the pour. This buildup could have also contributed to the problem. After these actions were completed, pouring of the melter was achieved with normal canister vacuum.

Recommendation 2. Ensure that the normal pressure drop between the canister and the melter/bellows differential pressure instrument tap is recorded as baseline data. This data should be taken as a part of the first cold chemical melter operation.

6.0 Hydrogen Evolution

A small amount of hydrogen evolution was expected to be present in the SRAT off-gas due to metal catalyzed formic acid decomposition reactions. Formic acid can be decomposed into a variety of gaseous products including CO, CO_2, H_2O, and H_2, according to the following reactions:

$$HCOOH \longrightarrow H_2 + CO_2 \quad \text{Eq 6.1}$$

$$HCOOH \longrightarrow H_2O + CO \quad \text{Eq 6.2}$$

$$HCOOH + 1/2\ O_2 \longrightarrow H_2O + CO_2 \quad \text{Eq 6.3}$$

Laboratory scale studies conducted by Hsu[11] confirmed the presence of hydrogen when noble metals are present and also suggested that the concentration was low (especially when mercury is also present). During the first IDMS run containing noble metals the low concentration was thought to be confirmed. Hydrogen monitors (used during the formic acid addition, reflux and the first PHA addition) indicated the hydrogen concentration was about 200 ppm. However, during Blend 2 the hydrogen evolution was orders of magnitude higher.

After Blend 2, a task team was chartered to address the hydrogen evolution, since clearly an evolution rate which exceeds the lower explosive limit (for reference air inleakage rates) had been demonstrated. As the task team began their investigation many of the differences between the two blend runs were questioned as to their potential role in the increased hydrogen evolution. Section 6 discusses these differences, some observations about the runs and hydrogen formation in general, compares previous IDMS runs to Blend 2, and compares Blend 2 to the observations noted in the literature search which was completed by Hsu[12].

6.1 Blend 1 vs. Blend 2 Comparison

The key batch parameters for the two runs are outlined in Table 6.1. The major differences are:

- the SRAT heel composition prior to the sludge transfer,
- the amount of formic acid addition, and
- the rate of formic acid addition.

Table 6.1 Blend 1 / Blend 2 Operating Parameter Comparison

Parameter	Blend 1	Blend 2	Remarks
SRAT Heel	Primarily Water	SME Heel, IXS Water	
Sludge Solids (lbs)	1,678	1,655	
Trim Chemical Add Order	Noble Metals, Hg	Noble Metals, Hg	
Formic Addition (gal)	32	60	Required for Excess Caustic
Formic Add Rate (gpm)	0.22	0.37	Blend 2 is DWPF Scaled
SRAT Temperature During Formic Add (°C)	92 to 98	92 to 100	
Hydrogen Evolution During Formic Add. (ppm)	100	200	
Steam Flow During Reflux (pph)	300	250	
Hydrogen Evolution During Reflux (ppm vol)	100	16,000	
PHA Addition (gal)	1,983	980 + 350	
Addition Method	2 Discrete 1 Contin.	5 Discrete + 1 Discrete	
Hydrogen Evolution During PHA Add (ppm vol)	200	5,000	
Peak Hydrogen Evolution Rate (pph)	0.0005	0.17	

6.1.1 SRAT Heel Effects

The composition of the solid and aqueous fractions of the SRAT heel prior to Blend 2 are provided in Table 5.7. Comparison of Tables 5.3 (Blend 1 SME Composition) and 5.7 indicates that the heel solids were essentially Blend 1 SME material while the soluble fraction contained significantly more phosphate and hydroxide than previous heels.

Both phosphate and hydroxide were suspected to play a major role in the steam coil fouling which occurred during the final sludge addition and concentration step (Section 5.3.1). A phosphate balance was performed to determine if there had been an accumulation of phosphate on the steam coil (a reduction of phosphate from the bulk solution). Table 6.2 contains the bulk solution phosphate balance for the heel, following the sludge addition (after the fouling occurred), and after PHA was added.

The material balance indicates that the "missing" phosphate remained the same during the PHA addition but did increase slightly (0.8 pound) during the sludge addition. However, coil deposit samples did not confirm that phosphate had accumulated on the steam coil.

Table 6.2 Phosphate Balance for Blend 2

Amounts in pounds

	Prior Balance	New Transfer	Total[a] Expected	Total Analyzed	Missing
SRAT Heel	0.05	24.00[b]	24.05	16.89	7.16
After Sludge Addition	24.05	3.60[c]	27.65	19.71	7.94
SRAT Product	27.65	0.0	27.65	19.67	7.98

a Total Expected is the Sum of Prior Balance and New Transfers
b Assumes 3400 gallons of IXS Wastewater was returned to IDMS
c Analyzed amount in the Sludge Transfer.

Coil deposit samples (taken after the PHA addition) were analyzed by SEM, X-ray fluorescence, ICP-MS, and Liquid Chromatography (LC). The LC results indicated a small amount of phenol (only 0.03 wt%) with a smaller amount of nitrophenol also present. Diphenylamine and biphenyl were not detected.

SEM and X-ray fluorescence indicated the deposits were a sodium/calcium-silicate gel-like material. It was not enriched in sludge, frit, phosphate, nor noble metals.

The residual SME material in the heel contained noble metals. These are expected to be reduced to the elemental valance state and may have contributed to the higher hydrogen evolution. This "second run" effect will be investigated during future IDMS demonstrations containing noble metals. Current plans call for SRAT product to be retained from one run and to be returned to the vessel (prior to the addition of sludge) for the next run and compare the hydrogen evolution values. The presence of reduced noble metals in the bulk solution at the start of formic addition may lead to hydrogen evolution earlier in the cycle or higher evolution rates.

6.1.2 Hot Wall Effect

During Blend 1 the steam coil chest pressure was 30 to 40 psig. Saturated steam at this pressure results in a wall temperature of 135°C which is only slightly higher than the bulk fluid temperature. During Blend 2, the fouled coil resulted in an increased chest pressure to 100 psig and an increased wall temperature to 170°C. This increase in surface temperature has been postulated to result in an increased hydrogen evolution by increasing the decomposition reaction rates.

Figure 6.1 plots the hydrogen evolution data for Blend 2 (provided in Figure 5.2 as a function of elapsed time in the cycle) as a function of SRAT temperature as measured by the thermowell. The hydrogen evolution is shown to correlate logarithmically with the bulk temperature. If the hydrogen generation were a function of the coil surface temperature the correlation would not be valid.

Furthermore, coil deposits reduce the heat transfer by insulating the coil. The inner coil deposit surface temperature is approximately the same as the steam condensation temperature but the outer coil deposit surface temperature is reduced by the resistance to heat transfer provided by the deposit and approximates the bulk solution temperature. Therefore there is not a hot surface exposed to the bulk solution and the hot wall effect (which has occurred in at least one of the small scale laboratory experiments) is not likely for DWPF type equipment.

6.1.3 Nitrite Observation

As shown on Figure 6.1, the hydrogen evolution was extremely low during the formic acid addition step, while during this same period the SRAT temperature was elevated in the 90 to 100°C range. Only after the NO_x evolution decreased (the nitrite was destroyed) did the hydrogen evolution increase. This important observation is postulated as the key to understanding the differences in the measured hydrogen evolution rates between Blend 1 and Blend 2.

During Blend 2 the nitrite was completely destroyed during the formic acid addition step. The slurry sample taken after the aborted heat-up to boiling indicated zero remaining nitrite. This was vastly different from any other IDMS demonstration where after the 6 hour reflux period the residual nitrite ranged from 115 mg/l to 8,300 mg/l. During Blend 1 the nitrite remaining after the reflux was 1,700 mg/l and the nitrite was not destroyed until at least the second PHA addition and concentration. Therefore, the hydrogen monitoring during Blend 1 was not adequate to determine if significantly higher hydrogen evolution rates were experienced during the later processing steps.

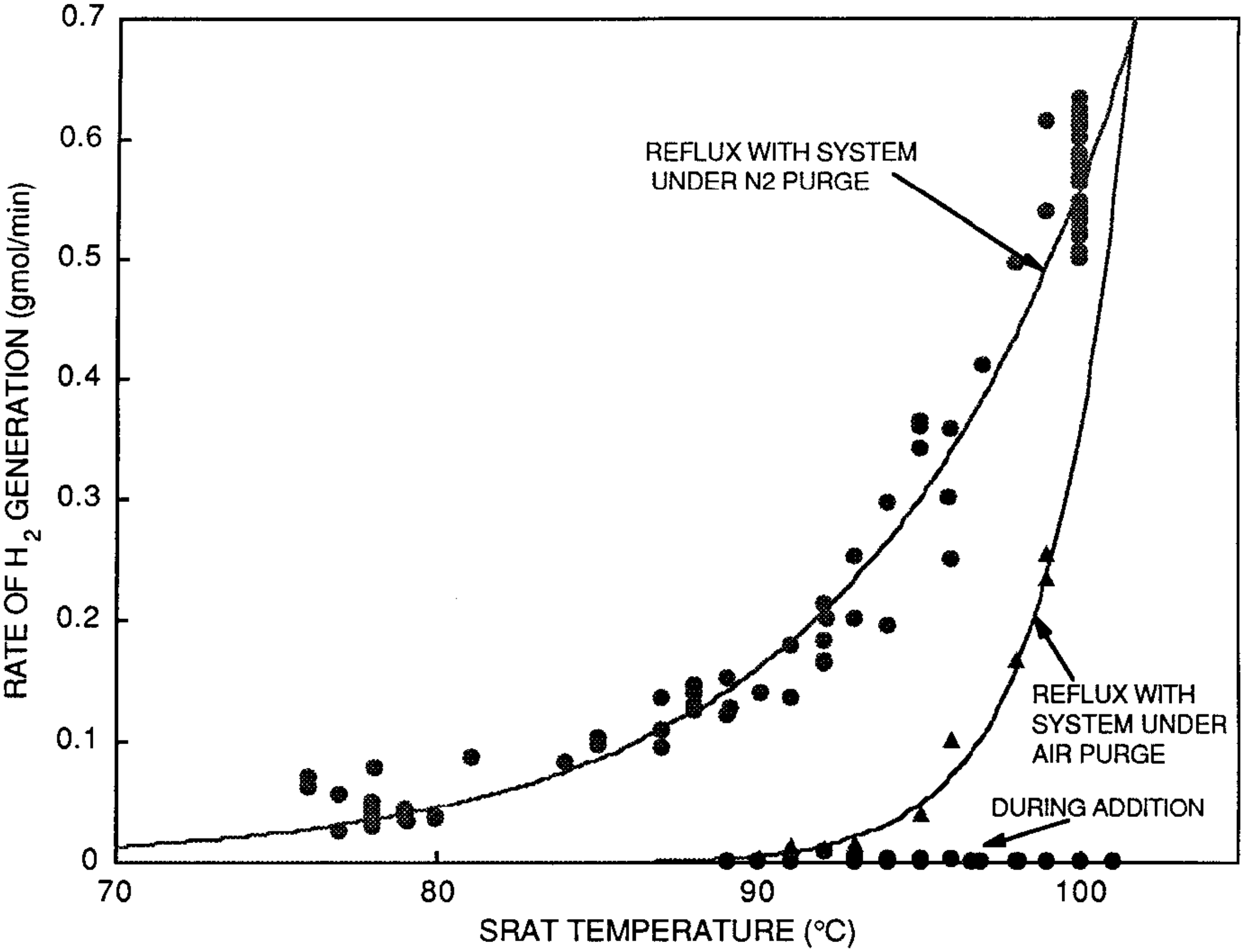

Figure 6.1 SRAT Temperature vs Hydrogen Generation Rate During the Formic Addition and Reflux of Blend 2

The nitrite observation has been validated by both researchers at SRL and the University of Georgia (under contract to study metal catalyzed formic acid destruction). The observation is best described as an induction period. Maintaining a minimum nitrite concentration (by controlling its destruction kinetics or by the addition of fresh nitrite) is postulated to maintain a nitrous acid concentration sufficient to inhibit hydrogen evolution. The inhibition mechanism is further postulated to be either 1) simple reaction preferences, i.e., the nitrite destruction kinetics are so fast as compared to the noble metal catalyzed formic destruction that the latter reaction does not have an opportunity to take place or 2) as long as there is nitrite present it will complex the noble metal ions such that the formate ion can not occupy the same site until all the nitrite is destroyed.

Another explanation for the delayed hydrogen evolution is the time required to reduce the noble metals to their elemental state, if the catalyst form is the elemental state. Table 6.2 contains the soluble percentage of each noble metal species during each phase of the feed preparation cycle. The data suggest that palladium is reduced before ruthenium and rhodium (as predicted by the EMF series) and that all the noble metals were over 80% reduced at the end of the formic acid addition.

Table 6.3 Solubility of Noble Metals During Blend 2.

Element	Before Formic	After Addition	After Reflux	After PHA
Ag	0.2	2.2	0.4	0.2
Pd	53.6	0.2	2.1	1.2
Rh	84.0	18.7	2.0	2.0
Ru	21.1	23.0	2.4	1.1
Ca	0.2	58.7	70.6	28.4
Mn	0.0	42.5	12.8	0.3
Sr	0.1	26.0	26.6	13.9
Ni	0.0	5.1	0.3	0.0

soluble amounts as a percentage of the total

Table 6.2 also contains the soluble amount of the other elements of interest. The Ca, Mn, and Sr are all solubilized as expected, but they become insoluble again as the pH increases above 7.0.

Additional work is planned in IDMS to confirm when the reduction of the noble metals occurs.

6.1.4 Amount and Rate of Formic Addition

The amount and rate of formic acid addition both play roles in nitrite destruction chemistry, especially kinetics. Both the increased amount and rate tend to increase the nitrite destruction rate, as observed in Blend 2, by increasing the initial acid concentration. These two parameters may account for the observed differences in the NOx evolution but their direct role in hydrogen evolution is unclear and is being evaluated in both IDMS and laboratory scale runs.

6.1.5 Effect of Diluent Composition on Hydrogen Evolution

Figure 6.1 also leads to a potentially important observation with respect to the diluent composition. This figure contains three curves showing the relationship between bulk temperature and hydrogen evolution, one for the formic acid addition, a second for the heat-up to boiling using the air purge (this heat-up was aborted at about 98-99°C), and a third for the heat-up to boiling and reflux using the nitrogen purge. Clearly, the hydrogen production is higher when the nitrogen purge is used. The maximum hydrogen evolution rate with the nitrogen purge is 0.64 gmol/min (0.17 pph). When the data for the air purge is extrapolated by 2°C to the boiling temperature the maximum hydrogen evolution is estimated to be 0.35 gmol/min (0.09 pph). This difference is a factor of nearly two.

This observation has been noted by the studies conducted at the University of Georgia (UGA) where tests conducted using a system of 88% formic acid which excluded oxygen resulted in higher hydrogen evolution rates. UGA results also indicated oxidation of formic acid to carbon dioxide and water can be Rh(III) catalyzed and can be a dominent reaction under certain conditions. Aeration of the liquid phase may be desirable to minimize hydrogen evolution.

It should also be pointed out that the time period in which the air purge was used is also the initial hydrogen evolution stage. During bench scale runs and recent IDMS runs with noble metals as the final amount of nitrite is destroyed the hydrogen evolution gradually increases while at the boiling temperature. The increase normally takes 1-2 hrs. This observation may be a function of the initial hydrogen stages and not be a true function of the diluent gas composition as suggested.

6.2 Comparison of Blend 2 and Prior IDMS Runs

There are several important parameters which must be considered when comparing IDMS batch operations. These include: the amount of sludge solids, the composition of the sludge solids (especially the nitrite and carbonate since these effect the off gas composition directly), the amount of formic acid addition, and the rate of formic acid addition (since the latter two also effect the reaction kinetics as discussed in Section 6.1.4). Table 6.4 provides a comparison of these parameters.

The run which is most like Blend 2 with respect to the amount and rate of formic acid addition is PHA 1. The two runs have similar nitrite destruction kinetics as evidenced by similar residual nitrite (Table 6.5), only 115 mg/l remained after the reflux of PHA 1 and none after the addition in Blend 2. However, the off gas evolution data for PHA 1 is not available (the on-line instrumentation installation was not completed until PHA 2 such that direct comparisons of PHA 1 and Blend 2 cannot be made.

Table 6.4 Key Parameter Summary of IDMS Coupled Feed Runs

Run	Sludge Solids (lbs)/(wt%)	Formic Addition (Gal)/(gpm)	Reflux Steam (pph)	PHA Amount (Gal)/(lb Solids)
PHA 1	1762 / 20	48 / 0.42	300	2000 / 950
PHA 2	1762 / 20	36 / 0.42	500	2000 / 950
PHA 3	1762 / 20	10+20+10/ 0.30	600	2000 / 950
HG 1	1762 / 15	40 / 0.20	500	2000 / 950
HG 2	1867 / 28	38 / 0.20	300	2000 / 950
HG 3	1762 / 27	35 / 0.20	500	2800 /1330
Bl 1	1678 / 19	32 / 0.22	250	1983 / 933
Bl 2	1655 / 30	60 / 0.4	300	980+350 / 470+170

10+20+10 indicates three discrete additions of 10, 20, & 10 gal each

PHA 2 is the second best choice with respect to the formic acid addition since all the others were either completed at 1) reduced addition rates or 2) intentionally broken into discrete additions. Both PHA 2 and Blend 2 also had essentially continuous formic acid additions.

Figure 6.2 compares directly the formic acid addition and reflux cycle during PHA 2 and Blend 2. Both runs exhibited a double CO_2 peak (the peaks are more distinct in PHA 2) with the NO_x evolution peaking simultaneously with the second CO_2 peak. The CO_2 peak appears to be less during PHA 2; however, the CO_2 monitor maximum concentration was 25 vol % during PHA 2 and material balance estimates made at the time of the run indicated that the peak may have been as high as 40%[6]. The NO_x peak for Blend 2 was over twice the height of PHA 2. The NO_x declined much more rapidly during Blend 2 and reached the analyzer low detection limit just after the formic acid addition was completed. The NO_x evolution of Blend 2 did not exhibit the long slow decline over the six hour reflux period which was typical of PHA 2. As indicated in Table 6.4, PHA 2 had 485 mg/l of residual nitrite at the end of the reflux step, as compared to zero at the end of formic addition during Blend 2.

During the coupled feed runs an increase in nitrate was noted to occur. This is partly due to the stripping of NO_x in the SRAT Condenser and the return of nitric acid to the SRAT (see reference 6 for details) and may be partly due to disproportionation of nitrous acid. Runs which start with low concentrations of nitrate exhibit this behavior (e.g., PHA 1, PHA 2, PHA 3, Hg 1, and Blend 1 all start with less than 3,000 mg/l of nitrate and all increase in

Table 6.5 Summary of IDMS Runs Anion Concentrations

IDMS Run	Nitrite	Nitrate	Formate	pH	$COOH^-/NO3^-$
Initial Sludge (plus any Heel)					
PHA1	15000	2000	0	11.5	
PHA2	14500	2150	0	11.7	
PHA3	15300	2200	0	11.7	
HG1	11200	3000	0	10.9	
HG2	17000	13200	12800	8.8	
HG3	NA	NA	NA	NA	
BL1	15000	1800	5500	9.0	
BL2	12000	12500	7800	NA	
Formated sludge (after Reflux)					
PHA1	115	11000	51000	4.3	4.6
PHA2	485	11000	32800	5.8	3.0
PHA3	250	9000	42000	5.1	4.7
HG1	225	7600	21000	NA	2.8
HG2	2880	19800	42700	NA	2.2
HG3	8300[a]	12600[a]	44000[a]	6.5	3.5
BL1	1800	14700	26000	7.3	1.8
BL2	0	12300	38000	7.1	3.1
SRAT Product					
PHA1	0	NA	69000	4.2	NA
PHA2	0	45000	62000	4.7	1.4
PHA3	0	56000	90000	4.2	1.6
HG1	0	31300	43600	4.7	1.4
HG2	0	NA	NA	NA	NA
HG3	0	46500	91500	6.5	2.0
BL1	0	24500	26000	7.0	
BL2	0	25000	37000	7.5	1.5
Unconc'd SME					
PHA1	0	NA	NA	NA	NA
PHA2	0	54000	61500	5.7	1.1
PHA3	0	32000	98000	4.7	3.1
HG1	0	39700	48600	4.5	1.2
HG2	0	30200	47200	6.7	1.6
HG3	0	46800	90000	6.2	1.9
BL1	0	24594	25963	7.3	1.1
Conc'd SME					
PHA1	NA	NA	NA	NA	NA
PHA2	0	55000	61500	5.7	1.1
PHA3	0	48000	61000	4.7	1.3
HG1	0	NA	NA	NA	NA
HG2	0	38000	61000	9.7*	1.6
HG3	0	NA	NA	NA	NA
BL1	NA	NA	NA	NA	NA
BL2	0	23565	32450	8.6	1.4

* Measured after NaOH was added as a trim chemical

NA Not Available

a Formic Added at boiling

nitrate by about 4,000 to 12,000 mg/l). Run Hg 2 which started with 13,200 mg/l of nitrite also increased in nitrate by about 3,600 mg/l during the reflux period, but Blend 2 which started with 12,500 mg/l nitrite ended the reflux period with essentially the same amount of nitrate. Formic acid denitration reactions may have taken place to reduce the nitrate in the SRAT to below their original values.

Carbon and nitrogen balances for all the IDMS coupled feed runs (for which off gas concentration data exits) are presented in Tables 6.6 and 6.7. The material balances are based on analysis of the sludge for nitrite, nitrate, ammonium, formate, Total Carbon (TC), and Total Inorganic Carbon (TIC) and of concentrations in the off gas of carbon dioxide and nitrogen oxides (NO and NO_2). Carbon dioxide was measured directly whereas NO_x was measured after a 750:1 dilution with nitrogen since the range of the analyzer was only 200 ppm NO_2.

The carbon balances were performed in two ways. The TC analysis of the sludge was used for one method, while the second used the formate and TIC determination. CO_2 evolution was determined for both methods by integrating the concentration multiplied by the flowrate over time.

With the exception of HG-1, the best carbon balance uses the formate and TIC determination. Generally, the carbon expected to remain in the SRAT after the formic acid reflux (initial sludge analysis + formic acid carbon - CO_2 carbon) was no more than 20% higher than the amount which was determined to be there analytically. The best overall carbon balance, were for PHA 2 and Blend 2 where the percent differences were less than 2%.

The nitrogen balance closure was determined in a similar manner. The initial sludge nitrogen (nitrate and nitrite) less the nitrogen evolved as NO_x is compared to the amount of nitrogen remaining (nitrate, nitrite, and ammonium) in the SRAT as determined analytically. The nitrogen expected to remain in the SRAT was generally 40% higher than the analytically determined amount. This suggests that either 1) the NO_x evolution rates were biased low (due to the dilution probe or the analyzer) or 2) another nitrogen species was being evolved.

Future IDMS runs will have the ability to determine both CO_2 and NO_x via two new independent methods and the ability to determine N_2O. Both CO_2 and NO will be determined by a Gas Chromatograph (GC) and CO_2, NO AND NO_x by a Mass Spectrometer (MS). The GC will also monitor for N_2O. These measurements should improve both the carbon and nitrogen balances.

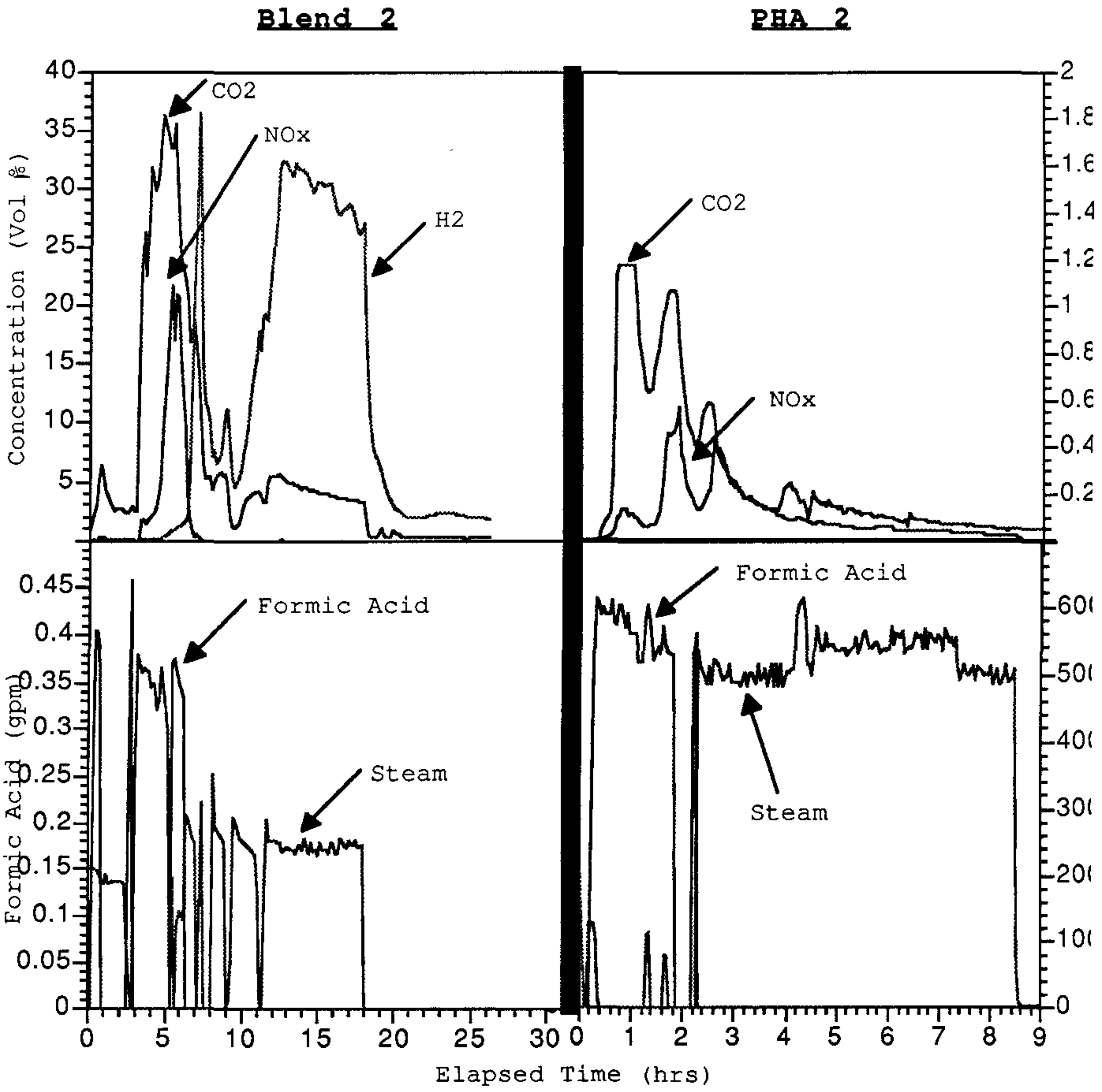

Figure 6.2 Comparison of PHA 2 and Blend 2

Table 6.6 Summary of IDMS Runs Carbon Balance

Carbon amounts in Lb-moles

	PHA 2	PHA 3	HG 1	HG 2	Bl 1	Bl 2
Carbon by Formate and Total Inorganic Carbon Analysis						
Sludge	0.50	1.00	0.57	3.18	2.04	2.53
Formic Acid	7.40	7.73	7.83	7.47	7.43	11.74
Total Carbon (by sum)	7.90	8.73	8.40	10.65	9.47	14.27
CO_2 Evolved	1.91	2.74	1.01	1.63	0.86	3.57
Carbon Left (by diff)	5.99	5.99	7.39	9.02	8.61	10.70
Carbon Left (analytical)	5.91	4.70	4.98	8.06	7.45	10.73
% Difference	-1.3	-21.5	-32.6	-10.6	-13.5	0.28
Carbon by Total Carbon Analysis						
Sludge	0.70	1.44	0.72	2.94	2.06	2.65
Formic Acid	7.40	7.73	7.83	7.47	7.43	11.74
Total Carbon (by sum)	8.10	9.17	8.55	10.41	9.49	14.39
CO_2 Evolved	1.91	2.74	1.01	1.63	0.86	3.57
Carbon Left (by diff)	6.19	6.43	7.04	8.78	8.63	10.82
Carbon Left (analytical)	4.80	4.97	5.70	6.12	5.97	9.56
% Difference	-22.4	-27.4	-19.0	-30.3	-30.8	-11.6

Table 6.7 Summary of IDMS Runs Nitrogen Balance

Nitrogen amounts in Lb-moles

	PHA 2	PHA 3	Hg 1	Hg 2	Bl 1	Bl 2
Sludge	3.11	2.46	2.793	5.518	5.627	5.107
NO_x Evolved	0.83	0.47	0.550	0.765	0.768	0.763
Nitrogen Left (by diff)	2.28	1.99	2.243	4.753	4.859	4.344
Nitrogen Left analytical)	1.37	1.12	1.270	3.187	3.803	2.542
% Difference	-39.9	-43.7	-44.4	-32.9	-21.7	-41.5

6.3 Literature Search

Metal catalyzed decomposition of gaseous formic acid to produce hydrogen has been studied extensively as evidenced by the inclusion of this topic in most text books dealing with the heterogeneous catalysis.[13] However, the same is not true for the decomposition of aqueous formic acid, where comparably little work has been conducted.

Ruthven and Upadhye[14], studied palladium catalyzed decomposition of aqueous formic acid in 0.05 to 0.9 molar solutions, showed that 1) no other gaseous products were detected other than CO_2 and H_2, 2)the heat of adsorption was comparable to that found in the vapor studies, 3) the catalyst was continuously deactivated during the course of the reaction as a result of the adsorption of the hydrogen product and 4) activation energies for the palladium catalyst with varying surface areas ranged from 5 to 10 cal/gmol.

Hill and Winterbottom[15] investigated a system which is more applicable to the treatment of HLW. They studied the palladium catalyzed decomposition of aqueous formic acid/sodium formate solutions in various concentrations. Their studies indicated a small but possibly significant dependence of the rate of hydrogen evolution on the pH of solution, where the optimum rate was observed in the range of 3.8 to 6.5. Activation energies ranged from 21 to 42 KJ/mol (5 to 10 kcal/gmol) , where the higher values occurred at the extremes of the composition range.

Both of these studies reported similar dependence of the formic acid/formate ion concentration on the reaction rate. Ruthven and Upadhye reported a square root dependence of the formic acid concentration, whereas Hill and Winterbottom reported a dependence ranging from 0.33 to 1.07 depending on whether formic acid or formate ion was the predominate species.

Pacific Northwest Laboratory (PNL) reported the evolution of hydrogen gas (about 3 vol%) during the formic acid treatment of a simulated Hanford type waste that contained noble metals.[16]

6.3.1 Blend 2 Compared to the Literature

The data from Blend 2 agrees with the observations contained in the references sited above. As indicated by the studies of Ruthven and Upadhye, the decomposition of formic acid into hydrogen and carbon dioxide was postulated to be the only reaction to occur during the DWPF feed preparation cycle. During the latter stages of Blend 2 formic acid reflux, the hydrogen evolution was accompanied by an equal molar carbon dioxide evolution. During the same period carbon monoxide was not observed. Reaction 6.2 is therefore not considered for further discussion.

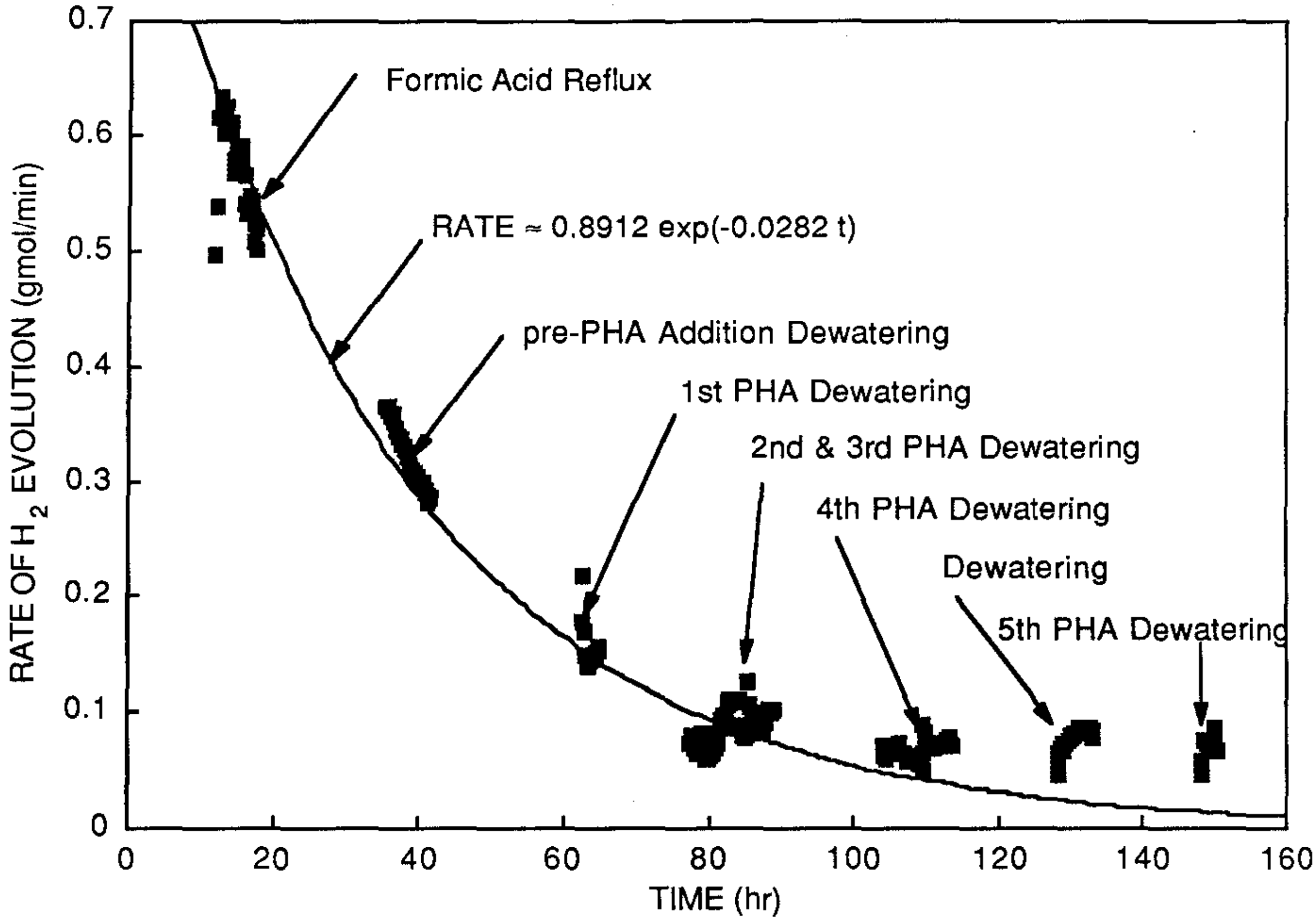

Figure 6.3 Hydrogen Evolution vs Time During the Formic Acid Addition, Reflux, pre-PHA, and 5 PHA Addition Concentrations

As shown in Figure 6.3 the catalyst appears to be deactivating with time. The hydrogen evolution rate correlates well versus a first order decay function as was the case with the Ruthven and Upadhye studies. It should be noted that during the SRAT cycle the pH was also increasing (from 6.2 to 7.5). This also agrees with the observations of Hill and Winterbottom.

The activation energies calculated for the various steps are provided in Table 6.8 and Figures 6.4 and 6.5. These show similar trends to the Hill and Winterbottom studies, with the highest concentration of formic acid corresponding to the highest activation energy. However, the activation energies calculated from the IDMS data are about 2-4X higher than the literature values for heterogeneous palladium catalysis.

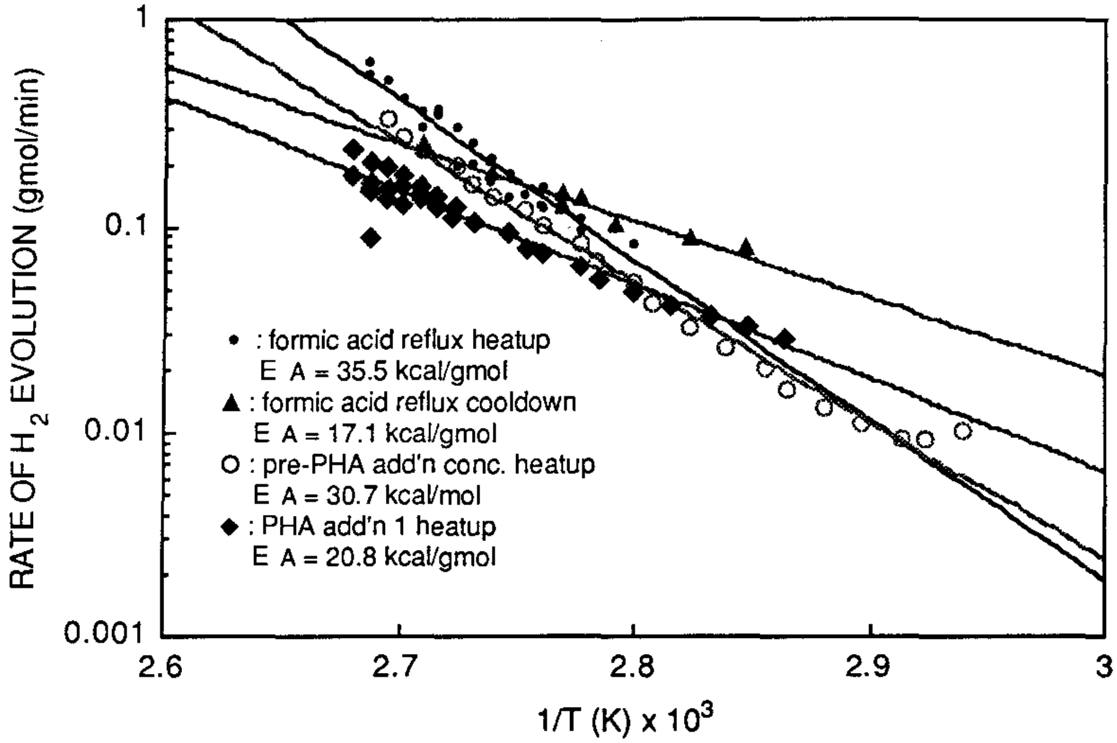

Figure 6.4 Activation Energy Plot for the Separate Steps of Blend 2

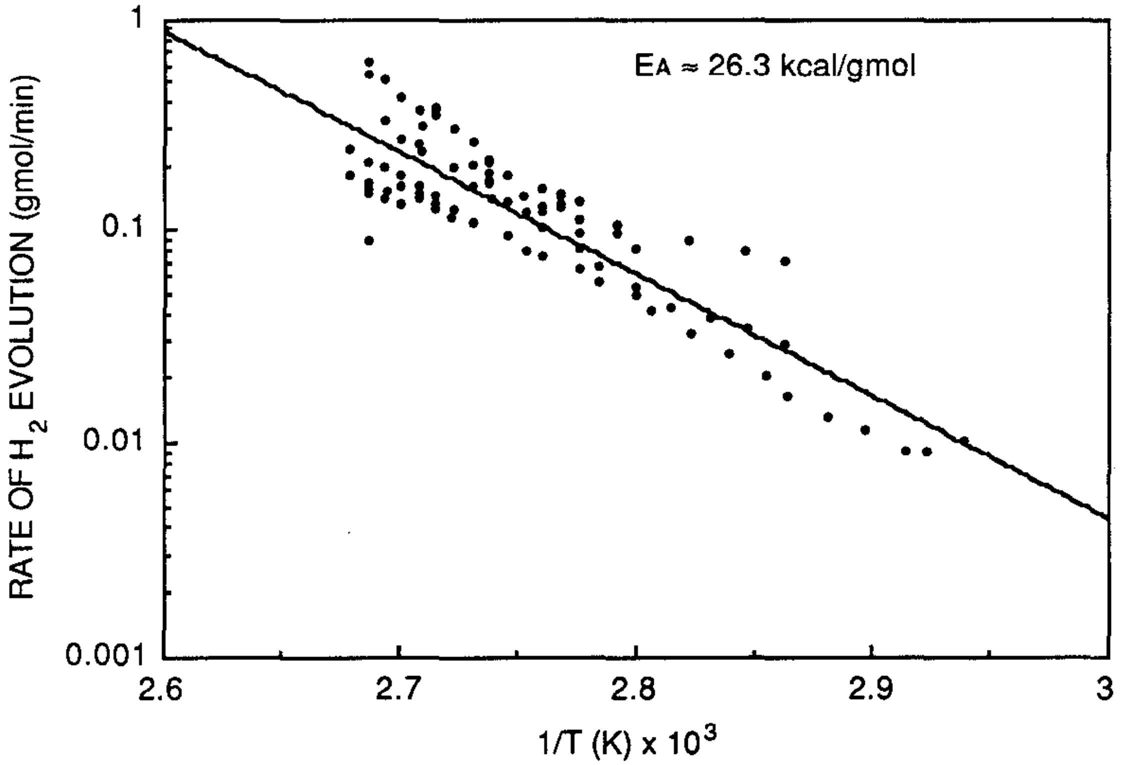

Figure 6.5 Combined Activation Energy Plot for Blend 2

Table 6.8 Summary of the Activation Energies

Study	Activation Energy (kcal/gmol)
IDMS Formic Reflux Heat-up	35.5
IDMS pre-PHA Addition #1 Heat-up	30.7
IDMS PHA Addition #1 Heat-up	20.8
IDMS Overall	26.3
Ruthven & Upadhye	5 to 10
Hill and Winterbottom	5 to 10

7.0 Noble Metals Behavior in the Glass Melter

Significant progress can be reported on four of the objectives.

7.1 Long Term Operating Effects on the Melter

To determine the long term operating effects of noble metals on the melter, electrical power usage of the melter electrodes and the resistance of the glass were monitored during feeding and idling periods of the Blend campaign. Table 7.1 summarizes these basic values. The total power remained constant during these two runs.

Table 7.1 Electrical Characteristics of the IDMS Melter During the Blend Campaign

Measurement	Mercury Feeding	Mercury Idling	Blend 1 Feeding	Blend 1 Idling	Blend 2 Feeding	Blend 2 Idling
A-B Electrodes kW (1359WT)	16	12	11	15	10	9
C-D Electrodes kW (1372WT)	15	21	22	21	23	26
A-B Electrode Amps (1357WT)	360	290	290	350	290	280
C-D Electrode Amps (1370WT)	330	420	420	440	480	510
A-B Elect. AC Volts (1358WT)	48	42	42	43	37	33
C-D Elect. AC Volts (1371WT)	41	46	46	43	45	45
A-B Elect. DC mV (1356WT)	-9	-9	-9	-9	-9	-9
C-D Elect. DC mV (1369WT)	-9	-9	-9	-9	-9	-9
A-B Resistance Ohms (1360WT)	0.13	0.13	0.14	0.11	0.14	0.11
C-D Resistance Ohms (1373WT)	0.12	0.11	0.10	0.10	0.09	0.09

Another potentially important electrical characteristic is the A-B/C-D resistance ratio. Usage of this ratio normalizes any changes in the glass pool resistivity due to changes in the composition and temperature of the glass. An increase in this ratio would indicate a relative decrease in the lower glass pool resistance versus the upper glass pool and may indicate if accumulation of noble metals is occurring. Figure 7.1 provides a comparison of this ratio during the Mercury and Blend runs.

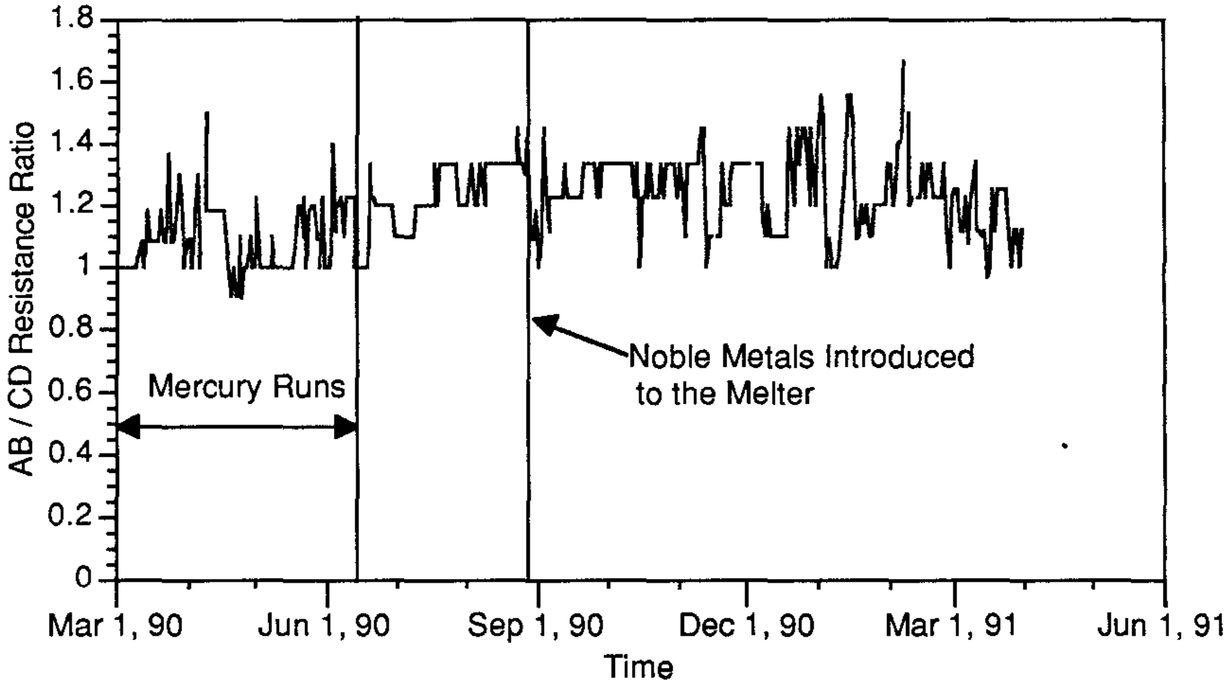

Figure 7.1 IDMS Melter Electrode Resistance Ratio Comparison for the Mercury and Blend Campaign

The ratio stayed relatively constant (varying from 1.0 to 1.2) during the entire mercury campaign. The ratio tended to drift upwards during the time periods between the campaigns, but remained at this level for most of the time after the introduction of noble metals. The ratio tended to slip back down to values similar to the mercury campaign after Blend 2 melter feeding was completed on 3/1/90.

The electrical characteristics were not severely impacted by the initial introduction of noble metals into the feed. However it should be noted that less than 40 pounds of noble metals have been processed by the melter. The electrical characteristic will be monitored throughout the noble metals campaign.

7.2 Noble Metals Chemical Form and Particle Size in the Glass Product

During Research Melter (774-A Laboratory) tests conducted in 1988, approximately 5 to 20% of the noble metals introduced settled to the bottom of the melter as particles up to 0.5mm in diameter. The particles were rounded Ru, RuTe, RuO2 and Ru/Pd/Rh/Te alloys[17]. The overly reducing melt ($Fe^{++}/Fe^{+++} > 0.5$) was postulated to have increased the deposition. These results were in direct contrast to the other noble metals experiences worldwide where large crystalline structures of RuO_2 were deposited on the bottom of the melter. The results reported below are the first chemical form and particle size determinations made on SRS simulated waste which contains the proper balance of reducing and oxidizing agents and potential alloying agents.

7.2.1 Canister Glass

Glass samples from both Blend runs were analyzed via a Scanning Electron Microscope (SEM). Several glass samples taken directly from poured canisters were examined. The glass from Blend 1 contained both individual and clustered ruthenium "needles" (RuO_2 crystals). The needles were usually not more than 5 microns long. The ruthenium crystal was also quite frequently associated with Fe/Mn/Cr/Ni spinel crystallization. None of the other noble metals (Pd, Rh, and Ag) were found in the Blend 1 glass.

Analysis of glass poured from Blend 2 also showed individual ruthenium needles about 5 microns long and ruthenium/spinel clusters of about 20 microns. These samples also contained spinel growth which had been nucleated by an apparent ruthenium/rhodium aggregate. Palladium/rhodium and palladium/ruthenium aggregates were also evident. These aggregates are present as spherical "nuggets" of about 2 microns. No silver was detected in the Blend 2 glass; however, silver is compositionally the smallest of the noble metals and it is expected to be somewhat soluble in the glass form.

7.2.2 Melter Bottom Glass

Glass samples were taken directly from the melter. About 2 months after the feeding of Blend 1 slurry, a sample was taken of the melter "bottom" (actually at about 1-2 inches above the floor). The sample revealed no evidence of the presence of any noble metals or crystal formation.

A second sample was taken at the end of the Blend 2 run (approximately five months after noble metals were first introduced to the melter). This sample revealed ruthenium needles approximately 5-15 microns long which were present, for the most part, in 20-40 micron clusters. There was no evidence of any Pd, Rh, Ag, Se, or Te accumulation.

7.2.3 Melter Cold Cap

During the feeding of Blend 2 slurry, a dip sample of the melter "cold cap" region was taken. SEM analysis of these partially vitrified samples revealed ruthenium needles of up to 20 microns long present in 20-50 micron clusters. The samples also contained scattered one micron silver iodide salts, ruthenium sulfates and/or sulfides, palladium 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 amalgamation and/or agglomeration of these species. The SEM micrographs indicated the noble metal species (especially Pd) were preferentially located on the surface of vitrified "gas bubbles". This indicates that the frothing which takes place as a result of vitrification offgases may promote the growth of noble metal nodules.

7.2 Noble Metals effects on Heat Transfer Coefficients

The Heat Transfer Coefficients (HTC's) of the IDMS process heat exchange equipment are tracked to provide an indication of the performance of the equipment and evidence of fouling. The HTC's are monitored continuously for the life of the facility. The IDMS monitors the HTC's for seven exchangers: (1) the SRAT/SME steam coil, (2) the SRAT/SME cooling coil, (3) the SRAT/SME Condenser, (4) the Formic Acid Vent Condenser (FAVC), (5) the Melter Feed Tank (MFT) cooling coil, (6) the Off Gas Condensate Cooler, and (7) the Off Gas Condenser. The heat transfer coefficients have been reported for prior runs[4,6,18]. These HTC's are listed in Table 7.2 along with the coefficients from Blend 1 and 2.

7.3 Melt Rate

The design melt rate for the IDMS Melter is 8.0 Lbs/Hr-Ft^2 of melter surface area. This requires an average glass production rate of 25 lbs/hr as compared to 228 lbs/hr for the DWPF Melter. The melt rate was estimated using a calculation which incorporates the slurry feed rate as follows:

$$M = 8.34 \bullet Q \bullet p \bullet C / A$$

where M = melt rate in Lb/hr-Ft^2
Q = slurry feed rate in gal/hr
C = wet calcine ratio
A = the melter surface area in Ft^2

The Blend 1 melt rate was not determined due to the erratic feed rate. The melt rate for Blend 2 was 6.5 Lbs/Hr-Ft^2. The lower than target rate was due to lower than normal solids content of the melter feed (37 vs 45 wt%) and not because of the introduction of noble metals to the melter.

Table 7.2 IDMS Heat Transfer Coefficients (HTC's)

	SRAT/SME Steam Coil	SRAT/SME Cooling Coil	SRAT/SME Condenser	FAVC	Off-Gas Condenser
Design	120	60	185	6.5	24
Water Runs	113	147	175	--	--
PHA Runs	115	157	120	5	--
Hg-1	100	180	70	5	30
Hg-2	200	160	100	5	18
Hg-3	80	140	100	5	15
Blend 1	90	N/A	105	8	15
Blend 2	40 *	140		6	20

* fouled condition during the formic acid reflux, but returned to nominal values during part of the campaign and then became fouled again after the frit addition.

8.0 Quality Assurance

This part of the task was completed in accordance with "DWPT Task Plan - IDMS Noble Metals Studies" [19].

This part of the task was controlled in accordance with "Task QA Plan - IDMS Noble Metals Studies" [20].

A records package will be assembled for this work when the entire task is complete.

Laboratory Notebooks currently in use include WSRC-NB-90-207 and WSRC-NB-90-163.

9.0 Acknowledgements

The completion of these runs involved the cooperation and effort of many persons and organizations located not only at TNX but across the site. These organizations include TOS Operations, TOS Projects and Works Engineering, Analytical Development Section and the DWPT Analytical Laboratory. We thank them for their services.

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