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by

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PILOT SCALE PROCESSING OF SIMULATED SAVANNAH RIVER SITE HIGH LEVEL RADIOACTIVE WASTE

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ABSTRACT

The Savannah River Laboratory operates the Integrated DWPF Melter System (IDMS), which is a pilot-scale test facility used in support of the start-up and operation of the U. S. Department of Energy's Defense Waste Processing Facility (DWPF). Specifically, the IDMS is used in the evaluation of the DWPF melter and its associated feed preparation and offgas treatment systems. This article provides a general overview of some of the test work which has been conducted in the IDMS facility. The chemistry associated with the chemical treatment of the sludge (via formic acid adjustment) is discussed. Operating experiences with simulated sludge containing high levels of nitrite, mercury, and noble metals are summarized.

INTRODUCTION

The Defense Waste Processing Facility (DWPF) at the Savannah River Site (SRS) will be the United States' first facility to process High-Level radioactive Waste (HLW). The waste will undergo chemical and physical treatment before being vitrified into a durable borosilicate glass. The resulting waste glass product will then be permanently stored in an off-site geologic repository. The original HLW is a highly acidic nitric acid solution. However, the HLW is stored in an alkaline form, at a pH of approximately 12, to inhibit corrosion of the carbon steel waste tanks. The waste is stored as both a sludge and a salt containing supernate. This supernate contains most of the radioactive cesium, some residual strontium and plutonium, and occupies 90% of the volume of the waste tanks. The sludge occupies the remaining volume, but contains 95% of the total radioactivity. In order to introduce the HLW to the glass melter and to meet glass processability and quality requirements, chemical treatment of the waste prior to vitrification is required.

The volume of the supernate will be reduced by precipitation of the cesium (via the addition of sodium tetraphenylborate) and adsorption of the residual strontium and plutonium (via the addition of sodium titanate). The resulting mixture will be filtered to concentrate the radioactive solids to about 10 wt%, while the decontaminated saltcake will be disposed of as low level waste. The concentrate will be further processed in the DWPF Salt Processing Cell by hydrolysis of the cesium tetraphenylborate (via formic acid) to benzene. The benzene will be vaporized and condensed, leaving behind the aqueous product (Precipitate Hydrolysis Aqueous or PHA) containing the high level radioactive species.

The sludge will first be washed in the tank farm to remove excess aluminum and caustic. Nitrite (approximately 0.06 to 0.30 M) will then be added to the washed sludge as a corrosion inhibitor.

The washed, inhibited sludge will be transferred to a reaction vessel (Sludge Receipt Adjustment Tank, or SRAT) in the DWPF Chemical Processing Cell (CPC). Following formic acid adjustment, the PHA will be blended with the sludge. After PHA addition, the material will be transferred to the Slurry Mix Evaporator (SME) where a borosilicate glass frit will be added to produce the feed for the melter. The melter will be continuously fed and the glass product poured into stainless steel canisters for ultimate burial. In each feed batch, sludge, PHA, and frit are blended in order to meet product processabiltiy and acceptability criteria.

The HLW also contains mercury from the use of mercuric nitrate as a catalyst during nitric acid dissolution of spent fuel rods. Since mercury and mercury compounds decompose at temperatures much less than 1150°C (the operating temperature of the DWPF melter), any mercury present in the melter feed will exit with the melter offgas. Recovery of mercury from the melter offgas would be difficult. Furthermore, mercuric halides are very corrosive, especially at elevated temperatures. Therefore, the

DWPF plans to remove most of the mercury prior to feeding the melter by reducing it to the elemental state with formic acid and subsequently removing it by steam stripping in the SRAT.

The Savannah River Laboratory (SRL) operates two engineering-scale demonstration facilities in support of the start-up and operation of the DWPF. The Precipitate Hydrolysis Experimental Facility (PHEF) is a one-fifth scale pilot facility used to evaluate the Precipitate Hydrolysis Process. The Integrated DWPF Melter System (IDMS) is operated for the evaluation of the DWPF melter and its associated feed preparation and offgas treatment systems. The IDMS feed preparation system is one-fifth scale, whereas the melter system is one-ninth scale.[1]

This article provides a general overview of the some of the work which has been conducted in the IDMS facility. A general description of the facility is provided along with a description of the chemistry associated with the chemical treatment of the sludge (via formic acid adjustment). Operating experiences with simulated sludge containing mercury, high levels of nitrite, and noble metals are summarized.

IDMS FACILITY DESCRIPTION

The IDMS feed preparation system, shown in Figure 1, is where all chemical adjustment of the sludge takes place. This system consists of the SRAT/SME, SRAT/SME Condenser, Mercury Water Wash Tank (MWWT), and the Formic Acid Vent Condenser (FAVC). The SRAT/SME is a single vessel in the IDMS facility that acts as both the SRAT and SME vessels in the DWPF. This vessel will be referred to by the operating mode that it is duplicating, *i. e.*, either as the SRAT or the SME. The SRAT/SME is equipped with steam and cooling water coils, and is agitated. Air is bled into the vessel through a side port to simulate the expected air inleakage of the DWPF.

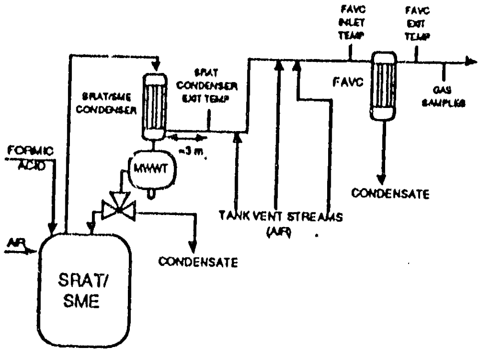

Figure 1. IDMS Feed Preparation System.

The SRAT/SME Condenser operates with process water at 25 to 50 deg C. The condensate from this condenser passes through the MWWT and then either back to the SRAT/SME during total reflux or to a condensate tank during concentration. The MWWT is a decanter which is designed to collect stripped elemental mercury in a sump for subsequent removal from the process.

The non-condensible offgases, after leaving the SRAT/SME Condenser, pass through the FAVC, which is a chilled water condenser designed to reduce the dew point to 10 deg C. Prior to entering the FAVC, vent streams from several other tanks enter the offgas system. The flowrates of these streams also simulate the air inleakages expected in the DWPF.

The IDMS melter system, shown in Figure 2, is comprised of the Melter (Figure 3), Melter Feed Tank (MFT), and the Melter Offgas System. The IDMS melter is a refractory lined, cylindrical tank operated at a glass temperature of about 1150 deg C. It removes water from the feed by evaporation, reacts the feed components, and melts the solids to form a homogeneous glass pool that can be poured into steel canisters.

The melter offgas consists of steam, non-condensible gases from sludge decomposition, air from inleakage and purges, mercury vapor, and particulate matter from entrainment and volatilization. The purpose of the off-gas system is to maintain a negative pressure in the melter plenum, provide adequate air for combustion in the plenum, treat the offgases to remove condensibles, particulates, and radionuclides, and provide the vacuum required to initiate and control the pouring of glass. Even though there are no radionuclides present in the IDMS feed, all of the DWPF processing equipment is incorporated into the IDMS to enable evaluation of process parameters, equipment reliability, and equipment performance. Moreover, most of the equipment is constructed of prototypic materials so that corrosion can be evaluated.

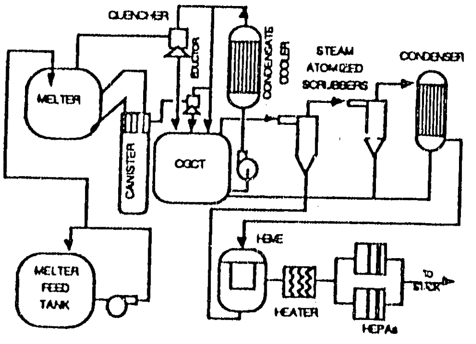

Figure 2. IDMS Melter System.

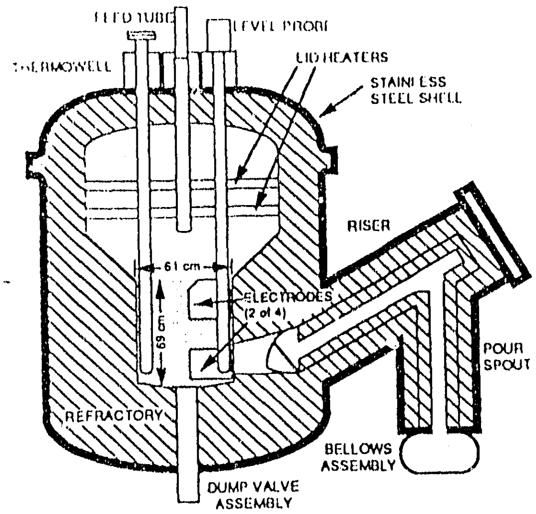

Figure 3. IDMS Melter.

The IDMS has a backup offgas system which vents offgases directly to the atmosphere if the primary system is inoperative. In the DWPF, the backup offgas system is a completely redundant system with all of the components of the primary system.

BATCH 1 OPERATIONS[3]

The Batch 1 Operations provided the first DWPF-prototypic operation in the IDMS facility. It was the first operation in which all three feed components (sludge, PHA, and frit) were used in the preparation of the melter feed. The objectives were to document the system material balances, characterize the chemistry of the formic acid addition phase, demonstrate mercury processing on a large scale, and document baseline equipment performance.

Six runs were performed with a sludge material which was prepared as a representation of the first batch of radioactive material to be processed in the DWPF. This sludge type is referred to as "Batch 1". Its nominal composition is shown in Table 1.[2] The first three runs did not contain mercury, while the last three contained mercury at a concentration of 1.2 wt% (dry basis).

Feed Preparation

Sludge, PHA, and frit must be blended to provide a melter feed which meets numerous processability and acceptability criteria. In the formic acid adjustment step, approximately 3,800 liters of simulated alkaline sludge were treated with 140 to 150 liters of 90 wt% formic acid. The resulting acidic sludge was then blended with approximately 7,600 liters (at 4 to 5 wt% solids) of the PHA. Approximately 1,360 kg of a borosilicate glass frit was then added to this "blended sludge". The resulting product of this blending is the melter feed. Before being fed to the melter, the composition of this material was verified analytically to ensure that it meets processability and glass durability requirements.

Table 1.
Nominal Batch 1 Sludge Composition

Cation	Wt %	Cation	Wt %	Anion	Wt%
Al	6.56	Mn	4.68	$SO_4^{=}$	0.665
Ba	0.163	Na	5.68	$PO_4^{\equiv}$	0.092
Ca	2.16	Nd	0.249	$CO_3^{=}$	2.92
Cr	0.179	Ni	1.54	NO_2^{-}	7.33
Cs	0.0046	Pb	0.278	NO_3^{-}	0.504
Cu	0.105	Si	1.44	Cl^{-}	0.980
Fe	22.8	Sr	0.060	F^{-}	0.124
K	0.248	Zn	0.185	I^{-}	0.0184
Mg	0.156	Zr	0.768	OH^{-}*	0.738

Organic Carbon (wt%) < 0.05
Total Solids (wt%) 15.4
Insoluble Solids (wt%) 12.96

* soluble

Formic acid was added to the sludge to: 1) reduce mercuric oxide to the elemental form for subsequent steam stripping, 2) reduce Mn(IV) to Mn(II) to decrease the potential for foaming in the melter; 3) improve the rheology of the melter feed; and 4) destroy nitrite. The major reactions of formic acid are listed in Table 2.[4]

The formic acid was added at 93 to 96 deg C (in order to minimize evaporation) at a feed rate of 0.4 liters/min per 1000 liters of sludge. The addition was followed by a six hour period where the SRAT contents were boiled at total reflux. Figure 4 shows the off-gas evolution during a typical formic acid addition and reflux.

Table 2.
Major Reactions of Sludge in the SRAT

Neutralization:			
$NaOH + HCOOH$	$\rightarrow$	$NaCOOH + H_2O$	(1)
$KOH + HCOOH$	$\rightarrow$	$KCOOH + H_2O$	(2)
$CaCO_3 + 2HCOOH$	$\rightarrow$	$Ca(COOH)_2 + H_2O + CO_2$	(3)
$SrCO_3 + 2HCOOH$	$\rightarrow$	$Sr(COOH)_2 + H_2O + CO_2$	(4)
$Ni(OH)_2 + 2HCOOH$	$\rightarrow$	$Ni(COOH)_2 + 2H_2O$	(5)
Redox & Other:			
$2HNO_2 + HCOOH$	$\rightarrow$	$2NO + CO_2 + 2H_2O$	(6)
$MnO_2 + 3HCOOH$	$\rightarrow$	$Mn(COOH)_2 + 2H_2O + CO_2$	(7)
$HgO + HCOOH$	$\rightarrow$	$Hg + H_2O + CO_2$	(8)
$3HNO_2$	$\leftrightarrow$	$HNO_3 + 2NO + H_2O$	(9)

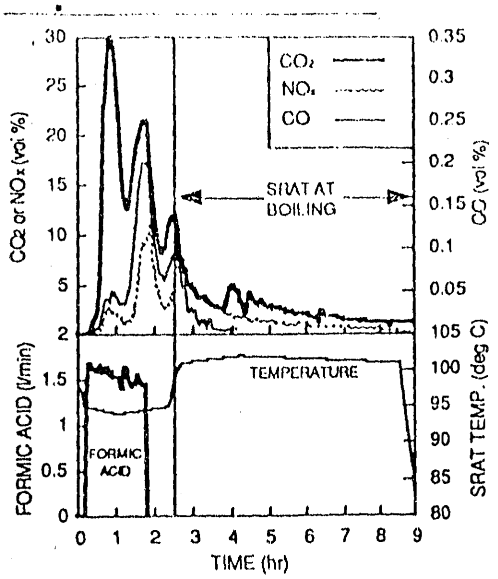

Figure 4. Typical SRAT Offgas Composition During Batch 1 Operations.

The offgas from the SRAT contains predominantly air, NO, and CO_2. Nitrogen dioxide is formed from the reaction of NO with oxygen in the vapor space above the SRAT and in the offgas lines:

$$2\,NO + O_2 \rightarrow 2\,NO_2 \qquad (10)$$

The major reactions in the offgas condensate are those that form nitrous and nitric acids:

$$NO_2 + H_2O \leftrightarrow HNO_2 + HNO_3 \qquad (11)$$
$$3\,HNO_2 \leftrightarrow HNO_3 + 2\,NO + H_2O \qquad (12)$$

The condensate from the SRAT Condenser was very acidic with the pH of this stream ranging from <1 to about 4.

During the three runs with sludge containing mercury, soluble mercury was measured in the SRAT condenser condensate at concentrations ranging from .03 to .05 M. Dissolved mercury was then returned through the decanter overflow back into the SRAT, and was expected to adversely affect the overall mercury steam stripping efficiency. However, this efficiency for the three IDMS runs ranged from 60 to 90 %, about 2 to 3 times better than predicted from bench-scale studies. This increased efficiency could significantly decrease the DWPF melter feed preparation cycle time, especially for sludges containing large concentrations of mercury.

The design final concentration of mercury in the sludge is 0.45 wt%. This concentration was determined based on the fact that, according to the available data at the time, stripping beyond this point becomes increasingly inefficient. However, in the IDMS mercury runs, the end point concentration of the sludge ranged from 0.08 to 0.25 wt %, well exceeding the design concentration. In these cases, approximately 80 - 90% of the mercury originally present in the sludge was removed.

During the PHA addition and in the SME cycle, the temperature at the exit of the SRAT Condenser was typically 30 to 40 deg C. During formic acid adjustment, however, this temperature rose to as high as 60 deg C because of the exothermic reaction of NO with O_2 to form NO_2 (reaction 10). This reaction is very exothermic (ΔH = -13.64 kcal/mol) and the formation of NO_2 is thermodynamically favorable ($K \approx 10^6$). Moreover, contrary to most reactions, it has a negative apparent activation energy of -2,984 cal/mol, which implies the reaction rate increases with a decrease in temperature.

Of the NO_x measured at the FAVC exit, approximately 80% was NO_2, the rest being NO. The O_2 in the offgas system comes from the SRAT vessel purge and the tank purges (see Figure 1). Figure 5 shows the NO_x concentration at the FAVC exit and the O_2 concentration at the SRAT Condenser exit. The first minimum in O_2 concentration was due mostly to a decrease in mole fraction due to the large amount of CO_2 produced. The mass flow of O_2 at this time was not substantially different than when there was no CO_2 evolution.

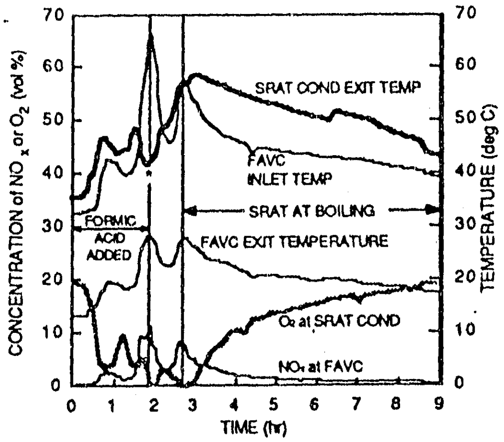

Figure 5. Typical SRAT Offgas Temperature Profile During Batch 1 Operations

The second and third minima, however, were due both to CO_2 and NO_x decreasing the mole fraction and to reaction of O_2 with NO. These two minima both occurred at the maxima in NO_x concentration. In fact, the concentration of O_2 became zero at these minima.

The very exothermic reaction of nitric oxide with oxygen caused the temperature at the inlet to the FAVC to be greater than the temperature at the exit of the SRAT Condenser. Figure 5 shows the offgas temperatures at the SRAT Condenser exit (≈3 meters downstream of the condenser), the FAVC inlet, and the FAVC exit for two runs. The FAVC inlet temperature reached as high as 68 deg C, a temperature increase of approximately 25 deg C from the exit of the SRAT Condenser. Figure 5 shows that the maxima in FAVC inlet temperature occurred at the maxima in NO_x evolution. Note also that, in one case (*), the SRAT Condenser exit temperature actually dropped while the FAVC inlet temperature increased. This temperature drop occurred due to the depletion of O_2 at the SRAT Condenser exit. However, the reaction again occurred between the temperature measurement point and the FAVC inlet because of the addition of the air purges to the offgas line.

During the three runs containing mercury, a high temperature at the FAVC vapor exit would trigger an interlock which would stop formic acid addition, discontinue steam to the SRAT, and initiate cooling of the vessel. In an effort to avoid the NOx surges and the associated temperature increases, the formic acid was added at approximately 0.2 liters/min per 1000 liters of sludge, about half the rate used in the earlier operations. The result was a more gradual production of NOx gas and more controllable temperatures in the offgas system.

Melter System

The melter offgas system is designed to remove virtually all radionuclides from the offgas. These radionuclides are present as entrainment from the melter and as volatile salts. The Quencher is designed to remove the majority of the entrained solids, while the SAS units, HEME, and HEPA filters remove both entrained solids and volatile salts. The Offgas Condenser is designed to remove water and mercury. The efficiency of these devices is measured as a decontamination factor, or DF, which is defined as:

$$DF = \frac{\text{mass flow of species entering device}}{\text{mass flow of species exiting device}}$$

The major radionuclides emitted into the offgas are Cs, Ru, Pu, U, Tc, and Th. Cesium is present both as the oxide and volatile chloride, whereas the others are present only as oxides. Since the volatile salts are harder to remove, Cs was chosen to measure the DFs. The Cs was measured by isokinetic sampling of particulates with subsequent analysis by ICP-MS. Table 3 shows the DWPF design DF's and those measured in the IDMS. The HEPA filter DF could not be measured since the exit concentration of Cs was too small to be detected. The overall DF found for the IDMS was a factor of 100 better than the design basis. Even excluding the exceptionally high DF in the melter, the IDMS overall DF was almost an order of magnitude better than design.

Table 3.
Decontamination Factors (DF)
for Cesium

Device	DWPF Design		Measured		Measured/Design
Melter	6.		135.		22.5
Quencher	1.5	≈3000	2.7	≈24000	1.82
SAS/Cond.	50.		28.5		0.57
HEME	40.		314.		7.9
OVERAL	1.75×10^4		3.20×10^6		

The chemistry of mercury in the melter offgas system is important since mercuric halides are very corrosive and it is suspected that mercurous chloride (calomel) may foul the HEME. Measurements of dissolved and total mercury in the offgas condensate indicate that > 99% of the mercury is soluble (probably as mercuric chloride and/or mercuric oxide). Virtually no elemental mercury or calomel have been found. Moreover, particulate samples taken have been analyzed by X-ray fluorescence and no mercury has been found. Preliminary measurements of mercury concentrations in the offgas vapor have shown that the concentration of mercury is near what would be expected if mercuric chloride were the primary volatile species.

COLD FEED OPERATIONS

The IDMS facility is currently performing a series of runs in which the processability of at least three of the feed compositions planned for the DWPF Cold Runs will be demonstrated. These runs will also be used to demonstrate the DWPF statistical process control methodology through the use of the Product Composition Control System developed at SRL. Further, these runs will be used to evaluate the effects of noble metals on the DWPF feed preparation and melter systems.

Each of the simulated sludges used during this operation will contain reference amounts of noble metals (Ru, Rh, Pd, and Ag) and amalgamating/alloying agents (Te, Se, and Hg), as shown in Table 4.

Table 4.
Nominal Noble Metal Composition for "Blend" Sludge

Cation	Wt % (dry)	Cation	Wt % (dry)
Ag	0.014	Pd	0.045
Ru	0.100	Rh	0.018
Se	0.002	Hg	1.588
Te	0.022		

The ease of reduction and high densities of these metals and their alloys increase the possibility of accumulation on the floor of the glass melter. Vitrification facilities worldwide have experienced operational difficulties due to such deposition; in some cases, melter operation had to be discontinued. The runs in the IDMS will be used to evaluate the long-term effects of the processing of feeds containing noble metals on a DWPF-type melter.

Noble metals are known to be very good catalysts for the decomposition of formic acid via the following overall reaction:

$$\mathrm{HCOOH} \xrightarrow{\text{cat.}} \mathrm{H_2 + CO_2} \qquad (13)$$

In bench-scale studies at SRL, qualitative measurements indicated the presence of hydrogen during the formic acid treatment of a noble metal containing sludge simulant. In the second IDMS run using "Blend" sludge, hydrogen concentrations exiting the SRAT Condenser were measured to be as high as 8 to 9 vol% during the formic acid reflux period. During this time the feed preparation system was inerted with a nitrogen blanket. Work in this area is ongoing.

Ruthenium is expected to be present in the melter offgas as volatile RuO_4 and as particulate RuO_2. Much of the ruthenium in the melter feed will be present as Ru-107, a radioactive isotope. Therefore, the melter offgas system must remove it. Work on the determination of the DF's for Ru in the melter offgas system is ongoing.

CONCLUSIONS

1. High concentrations of CO_2 and NO_x are evolved during the formic acid adjustment of Savannah River Site sludge.
2. The NO_x evolution causes the formation of nitrous and nitric acids in the SRAT Condenser condensate, with pHs of <1 to 4, but this did not have a significant effect on the overall efficiency of mercury stripping.
3. The NO_x evolution can cause large increases in offgas temperature due to the reaction of NO with O_2.
4. The mercury stripping efficiency was higher than anticipated based on bench-scale operations. The final mercury concentration was much lower than expected.
5. The measured Cs DF's were similar in magnitude to the DWPF design basis.
6. Most of the mercury in the melter offgas exists either as $HgCl_2$ or HgO. Little evidence for the formation of calomel (Hg_2Cl_2) was found.
7. Hydrogen is produced when treating sludge containing noble metals with formic acid.

ACKNOWLEDGMENTS

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