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by

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ABSTRACT

The Integrated Defense Waste Processing Facility (DWPF) Melter System (IDMS), operated by the Savannah River Laboratory, is a one-fifth scale pilot facility used in support of the start-up and operation of the Department of Energy's DWPF. Five IDMS runs determined the effect of the presence of noble metals in HLW sludge on the H_2 generation rate during the preparation of melter feed with formic acid. Overall, the results clearly showed that H_2 generation in the DWPF SRAT could, at times, exceed the lower flammable limit of H_2 in air (4 vol%), depending on such factors as offgas generation and air inleakage of the DWPF vessels. Therefore, the installation of a forced air purge system and H_2 monitors were recommended to the DWPF to control the generation of H_2 during melter feed preparation by fuel dilution.

INTRODUCTION

The Defense Waste Processing Facility (DWPF), located at the Savannah River Site (SRS), will be the United States' first facility to immobilize high-level radioactive waste (HLW) in a borosilicate glass matrix for storage in an off-site geologic repository.¹ The Savannah River Laboratory (SRL) operates two engineering-scale demonstration facilities to support the DWPF: the Precipitate Hydrolysis Experimental Facility (PHEF)² and the Integrated DWPF Melter System (IDMS).^{3,4} This paper is concerned with the one-fifth scale IDMS feed preparation system, as related to the generation of H_2 .

The generation of H_2 during the treatment of HLW with formic acid was considered extremely important because of the possibility of forming a flammable atmosphere in the vapor spaces above the feed preparation reactor and associated tanks and offgas lines of an air laden system. In 1988, Wiemers⁵ at the Pacific Northwest Laboratory was the first to report the generation of significant amounts of H_2 during the treatment of

Hanford simulated HLW with formic acid. The H_2 was purportedly caused by the noble metal-catalyzed decomposition of the formic acid. Formic acid is used to treat HLW to improve its chemical and rheological properties, and noble metals occur naturally in HLW as fission products. In 1990, Hsu⁶ at the SRL confirmed that SRS noble metal-containing simulated HLW would also produce H_2 . Therefore, five IDMS runs were performed to characterize the generation of H_2 during the preparation of melter feed with formic acid and to obtain design information for the DWPF.

The primary and long-term objective of IDMS noble metals runs was to determine the effect of noble metals deposition in the melter. However, based on the work by Hsu,⁶ a secondary, but equally important, objective was to characterize the generation of H_2 during melter feed preparation. Three types of SRS simulated HLW sludges were tested: Blend (BL), Heavy Metal (HM) and Purex (PX). Table 1 compares the sludges, along with the precipitate hydrolysis aqueous (PHA) product obtained from the PHEF. Table 2 lists the concentrations and chemical forms of the noble and other metals added to the sludges prior to each run. Note that only BL contained Hg. Since mercury is known to form amalgams with noble metals, it was not added to the other sludges in an attempt to produce the highest possible H_2 generation rate.

METAL-CATALYZED DECOMPOSITION OF AQUEOUS FORMIC ACID

Metal-catalyzed decomposition of gaseous or aqueous formic acid produces H_2 according to the following reaction:

This reaction is postulated to proceed via a heterogeneous mechanism involving a surface formate ion intermediate.⁷ The metal catalyzed

decomposition of gaseous formic acid to produce H_2 has been studied extensively as evidenced by the inclusion of this topic in most text books dealing with heterogeneous catalysis (e.g., see Satterfield)⁸. However, the same is not true for the decomposition of aqueous formic acid, where much less work has been done.^{9,10,11}

Table 1. Characterization of Three SRS Sludges and PHA^a

Species or Measurement	BL	PX	HM	PHA
Al	6.86	6.33	8.68	0.04
B	---	---	---	3.15
Ba	0.30	0.52	0.19	---
Ca	1.55	3.30	1.11	0.09
Cr	0.05	0.01	0.06	---
Cs	---	---	---	0.55
Cu	0.16	0.19	0.06	0.47
Fe	20.92	22.32	4.31	0.34
K	0.34	---	0.18	8.56
Mg	0.14	0.11	0.12	0.03
Mn	4.79	8.00	4.72	0.16
Na	4.28	3.55	7.76	8.35
Nd	0.18	0.35	1.37	0.01
Ni	1.87	4.28	0.96	0.05
P	0.07	0.13	0.06	---
Pb	0.44	0.99	0.26	---
Si	3.90	2.65	3.71	0.05
Zn	0.33	0.49	0.13	0.01
Zr	0.14	---	---	---
COOH ⁻¹	---	---	---	25.36
SO ₄ ⁻²	0.50	0.97	0.44	0.28
NO ₃ ⁻¹	0.88	0.42	1.42	24.03
NO ₂ ⁻¹	8.62	2.14	9.31	---
Cl ⁻¹	0.70	0.01	---	0.16
F ⁻¹	0.54	---	---	0.01
Density (g/ml)	1.09	1.09	1.09	1.02
pH	11.31	11.10	10.96	3.80
Total Solids ^b	14.3	14.2	14.9	6.1
Total Acid (M)	---	---	---	0.13
TOC	0.10	0.10	0.08	10.54
TIC	0.26	0.78	0.25	0.12

^a wt% dry unless noted; ^b wt% wet

Müller and Loerpabel⁹ investigated the platinum metals (Pd, Ir, Rh, Pt, Os and Ru) in aqueous solutions of formic acid and showed that at 100 °C only CO₂ and H₂ were produced by all of these metals, and their catalytic activity approximately decreased in the order listed. They also demonstrated that an induction period existed for some of the metals (Os and Ru), which was the time for formic acid to reduce the metal to a catalytically active form. The induction time was strongly dependent on the metal, temperature and presence of anions, and generally a shorter or no

induction period resulted in a higher maximum gas generation rate. Furthermore, after a maximum gas generation rate was exhibited, the catalytic activity decreased and, in general, more rapidly with higher maximum gas generation rates. This decrease in catalytic activity was attributed to the time dependent agglomeration of the fine metal catalyst particles thereby decreasing their active surface area.

Table 2. Noble and Other Metals in the Simulated HLW*

Element	Species	IDMS Sludge		
		BL	HM	PX
Ru	RuNO(OH) ₃	0.100	0.217	0.239
Rh	Rh(NO ₃) ₂	0.018	0.041	0.038
Pd	Pd(NO ₃) ₂	0.045	0.085	0.079
Ag	AgNO ₃	0.014	0.015	0.014
Se	SeO ₂	0.002	0.004	0.004
Te	TeO ₂	0.022	0.051	0.048
Hg	Hg(NO ₃) ₂	1.588	0.000	0.000

* wt% elemental dry basis

Ruthven and Upadhye¹⁰ studied the Pd catalyzed decomposition of aqueous formic acid in 0.05 to 0.9 M solutions and also showed that no other gaseous products were detected other than CO₂ and H₂. Moreover, the heat of adsorption was comparable to that found in vapor phase studies which possibly indicated a similarity in vapor and liquid phase mechanisms. Also, their Pd catalyst continuously deactivated during the course of reaction, but they attributed it to the adsorption of the H₂ product. A square root dependence of the rate of H₂ production on the formic acid concentration was also observed.

Hill and Winterbottom¹¹ investigated the Pd catalyzed decomposition of aqueous formic acid in various sodium formate solutions. They reported activation energies ranging from 21 to 42 kJ/mol, where the higher values occurred at the extremes of the composition range. Moreover, they observed a reaction rate dependence ranging from 0.33 to 1.07 depending on whether formic acid or formate was predominantly present in solution. This range was in good agreement with that reported by Ruthven and Upadhye.¹⁰

MELTER FEED PREPARATION

The IDMS feed preparation system consists of a reactor (SRAT) and an offgas system, which has two condensers in series. Since H₂ is generated in the SRAT, a potential exists for the lower flammable limit (LFL) of H₂ in air (4 vol%) to be exceeded in the offgas lines after the condensers. A detailed description of the IDMS feed preparation equipment, along with the processing cycle, has been given elsewhere.^{1,3,4}

However, in order to understand the discussion on the generation of H_2 , a brief summary of the processing cycle is given below.

Typically, for each run made in the IDMS, approximately 4,000 L of simulated alkaline sludge were transferred to the reactor (SRAT). Mercury was added to the SRAT (BL runs only) as mercuric nitrate, selenium and tellurium as dissolved dioxides, ruthenium as nitrosyl ruthenium hydroxide and the three remaining noble metals (Ag, Pd and Rh) as soluble nitrate salts (see Table 2). The temperature of the SRAT was increased to between 93 and 96°C to add formic acid. Depending on the type of sludge (see Table 3, below), 114 to 227 L of 90 wt% formic acid were added at 0.4 L/min per 1,000 L of sludge. After formic acid addition, the SRAT was boiled and refluxed for 6 to 8 hr to allow the slower reactions to proceed and steam strip mercury (when present) from the sludge. Next, approximately 7,200 L of PHA (from the PHEF) were added at 7.6 L/min and, at the same time, condensate was removed from the system. This step required an additional 13 hr during which time more mercury stripping occurred. When all the PHA was added, a slurry consisting of water, borosilicate glass frit and 4 L of formic acid was added to the SRAT at 80 L/min while still in the concentration mode. After this addition, 10 hr were required to concentrate the sludge to a specified solids concentration for feeding to the melter.

RESULTS AND DISCUSSION

BL1 was the first noble metals run in the IDMS, but only very low levels of H_2 were detected during the time when H_2 was monitored. BL2 was the second noble metals run and the first time a significant amount H_2 was detected in the offgas during feed preparation. This result redirected the objectives of future noble metals runs in the IDMS. The next four IDMS runs (HM2, HM3, PX1 and PX2) were designed to 1) characterize H_2 generation from HM (HM2) and PX (PX1), as these sludges have the highest noble metals concentrations of all the different sludges, 2) determine the effect of a vessel heel on the H_2 generation rate (HM3 contained a heel from HM2), 3) determine the effect of nitrite on the H_2 generation rate by comparing PX1 with HM2 (the level of corrosion inhibitor, nitrite, added to actual HLW could vary by a factor of five), and 4) determine the effect of excess formic acid on the H_2 generation rate by adding 25% more formic acid to PX2 than PX1.

Each of these IDMS runs is discussed in detail below within the realm of a parametric study. The variables which had the greatest impact on the H_2 generation rate were determined from a laboratory study.¹² Also, all of the sludges were essentially equivalent, except for the presence of a few species, e.g., noble metals, nitrite and mercury. Table 3 shows that, except

for BL2 and PX2 (explanations are given below), even the amount of formic acid required¹³ for each run did not vary widely.

Table 3. Formic Acid (FA), Sludge Volume and Solids Content

Run	FA(L)	Sludge(L)	wt% Solids
BL1	121	4,428	19.0
BL2	227 ^a	4,164	30.0
HM2	117	4,164	14.9
HM3	98	5,360	18.5
PX1	136	3,883	14.5
PX2	170 ^b	4,315	14.2

^a 91 L due to caustic heel; ^b 34 L to test effect of excess FA (see text)

It should be noted that all of the runs exhibited very low levels of H_2 early in formic acid addition and reflux. These levels were of little concern, however, as they were far below the LFL. The H_2 generation rates of interest were those which increased rapidly to levels that could have easily exceeded the LFL.

BL Runs: First Noble Metals Operations

For BL1, a H_2 monitor was available only from the beginning of the run to a few hours into PHA addition. During that time, the H_2 generation rate never exceeded 0.008 mol/min. Therefore, it was concluded that the generation of H_2 was not critical during HLW processing. However, it is seen from Figure 1 that NO_x was produced (from nitrite)⁴ throughout formic acid addition and even during reflux. Note that the oscillations in the profiles were due to slight fluctuations in temperature, as the SRAT was apparently not at boiling. The broad NO_x profile indicated that there was a significant amount of unreacted nitrite remaining in the sludge, which was later verified by liquid analyses. The impact of this residual nitrite on the H_2 generation rate was not known at that time and understood only after several months of research.

For BL2, approximately twice the formic acid was added at twice the feed rate of BL1. The additional formic acid was required to neutralize a caustic heel (from an IDMS waste water process malfunction). Figure 2 shows that, in contrast to the BL1 results, the NO_x profile was quite narrow and decreased below the detection limit after about 7 hr. Both of these results were probably caused by a combination of the faster feed rate and greater amount of formic acid added in BL2. The interesting result was that a significant amount of H_2 was not generated until the NO_x concentration decreased to below the detection limit, at which time the H_2 generation rate rapidly increased, but peaked three times. The

first two peaks were again caused by fluctuations in temperature, but this time they were due to process shutdowns for safety concerns, as this was the first time that the H_2 generation rate was on the order of the LFL. After the first peak, the system was inerted with a N_2 purge instead of air. When reflux operations continued, the H_2 generation rate rapidly increased again, peaked and slowly decreased until reflux was finished at approximately 18 hr.

Figure 1. Offgas composition profiles for BL1 during formic acid addition and reflux.

It is clear from these results for BL2 that, during the latter part of PHA addition of BL1, a significant amount of H_2 was probably generated; and, the delay or induction period was most likely caused by the unreacted nitrite in the sludge. Low levels of NO_x were indeed observed well into PHA addition. However, it must be emphasized that, during BL1, a potential safety hazard did not exist since, during PHA addition, a N_2 purge has always been used to inert the SRAT.

During PHA addition of BL2 (not shown), the H_2 generation rate continuously decreased and eventually leveled off at about 0.1 mol/min. The profile corresponded approximately to a first order decrease in the H_2 generation rate. The deactivation may be explained by agglomeration of the catalyst particles,⁹ or by irreversible adsorption of H_2 .¹⁰ In either case, the catalyst structure was apparently altered and rendered

somewhat inactive. Note that, although mercury is well known to form amalgams with noble metals and thus deactivate their catalytic activity, in this case, the effect of mercury is not clearly understood.

Figure 2. Offgas composition profiles for BL2 during formic acid addition and reflux.

The maximum H_2 generation rate observed during BL2 corresponded to levels that exceeded the LFL in the IDMS SRAT. Thus, since there is presently no forced air purge system on the DWPF SRAT, based on its design air leakage, the possibility of exceeding the LFL during feed preparation also existed. This result redirected the IDMS program to address this potential DWPF safety hazard. The results of this redirection form the basis of the remainder of this paper.

HM Runs: Effect of SRAT Heel

The DWPF SRAT will be operated with a 30 vol% heel, which contains noble metals as well as formate. These species may both adversely affect the H_2 generation rate; therefore, two IDMS runs were performed with HM sludge to ascertain the effect of a well characterized vessel heel. Also, actual HM is one of the sludges which contain the highest noble metals concentrations; thus, it was imperative that it be characterized with respect to H_2 generation.

HM2 was performed without a heel, whereas HM3 contained a 22 vol% heel from HM2.

Table 3 shows that the volume of new sludge and consequently the amount of formic acid added to each run were similar. It was not surprising then, that the CO_2 and NO_x profiles displayed in Figure 3 for HM2 were similar to those for HM3 (not shown). This result indicated that the heel had no effect on the non-catalytic reactions. The effect on the catalytic reaction which produced H_2 (Equ. 1) was not as clear, however.

Figure 3. Offgas composition profiles for HM2 during formic acid addition and reflux.

It is seen from Figure 4 that, when the heel was present, there was a 7 hr delay before the rapid increase in the H_2 generation rate occurred. However, part of the delay exhibited in HM3 may have been caused by the large decrease in the SRAT temperature (due to safety interlocks), which occurred just prior to the rapid increase in H_2 . A similar temperature decrease was seen in HM2, which may have also delayed the increase in H_2 .

Figure 4 also shows that there was a significant decrease in the maximum H_2 generation rate when the heel was present. However, this effect was more than likely caused by the 3 hr time span (at about 30 hr) during which the SRAT temperature was well below boiling. Moreover, constant boiling conditions were not attained until approximately 37 hr, which was when HM3 exhibited its maximum H_2 generation rate of 0.038 mol/min. Conversely,

HM2, which reached boiling much faster, exhibited a maximum H_2 generation rate of 0.159 mol/min.

Figure 4. H_2 generation rates for HM2 and HM3 through PHA addition.

Clearly, based on the data presented in Figure 4, it is not apparent what the maximum H_2 generation rate would have been for HM3 if no interruptions occurred. However, it did appear that the maximum H_2 generation rate for HM3 would not have exceeded that exhibited by HM2. This result suggested that the excess formate and the residual noble metals in the heel had little effect on the production of H_2 , which was also verified in the laboratory.¹² Also, since the additional volume of sludge, due to the heel, diluted the incoming formic acid, the effect of formic acid would have been less (see below).

HM and PX Runs: Effect of Nitrite

Table 1 shows that the only significant difference between HM and PX was the concentration of nitrite: PX was prepared with

one-fifth of that added to HM. Moreover, it is seen from Table 2 that the same amounts of noble metals were also added to each sludge. Table 3 shows that similar amounts of formic acid were required by HM2 and PX1, where the difference was essentially due to the difference in the nitrite.

It is seen from Figures 3 and 5 that the NO_x concentrations for HM2 and PX1 peaked at about 25 and 0.6 vol%, respectively. This result was a direct consequence of the initial level of nitrite in each sludge. For PX1, a significant amount of H_2 was generated at about 10 hr into the cycle, whereas for HM2, it took over 17 hr. An even shorter induction period probably would have resulted if the formic acid feed rate of PX1 was not reduced part way through the cycle (for process operation reasons), resulting in a slower nitrite destruction rate.

Figure 5. Offgas composition profiles for PX1 during formic acid addition and reflux.

These results showed that the induction period was reduced by 41% and the peak H_2 generation rate increased by a factor of four. The nitrite apparently impeded the formation of the active form of the noble metals. A similar effect of the presence of anions in solution has also been reported, but with no explanation.⁹

Based on these results, the same delay should have occurred in BL2. However, it was possible that formic acid in excess of that

required¹³ may have been used. The excess formic acid accelerated the destruction of nitrite (compare the NO_x levels of BL1 and BL2) and thus shortened the induction period for H_2 generation. The rapid destruction of the nitrite, in conjunction with the proven effect of excess formic acid (see below), may have contributed to the unusually high maximum H_2 generation rate exhibited in BL2.

BL2 was unusual in that it contained about half of the noble metals as PX (see Table 2), yet the peak H_2 generation rate was similar to PX1. Laboratory results showed that the peak H_2 generation rate was essentially proportional to the amount of noble metals and that excess formate had little effect on the H_2 generation rate.¹² These laboratory results further verified the supposition that excess formic acid may have been inadvertently added to BL2. However, the role that mercury may have played in BL2 was also not clear.

PX Runs: Effect of Excess Formic Acid

Laboratory experiments demonstrated that the amount of formic acid added to the sludge had a marked effect on the H_2 generation rate.¹² As a result, two IDMS runs were performed to test this hypothesis on a large scale. A nominal amount of formic acid was added to PX1 and 25 % excess to PX2 (see Table 3). Note that PX was also prepared with one-fifth the nitrite that was added to the other sludges (see Table 1). Therefore, based on results just discussed on the effect of nitrite, the laboratory work and the fact that PX has one of the highest noble metal contents (see Table 2), it was anticipated that the PX runs would exhibit the highest H_2 generation rates of all the IDMS runs.

Figure 5 shows that very little H_2 was produced up to the end of reflux. Nevertheless, it is seen from Figure 6 that, at about 10 hr, the H_2 generation rate increased rapidly and caused numerous process interlocks, as is apparent from the erratic temperature profile. Nevertheless, a distinct peak-like shape spanning from 10 to 20 hr was exhibited. The maximum H_2 generation rate ranged from 0.4 to 0.61 mol/min. The higher value may have been due to a surge of offgas from the SRAT, which always results just before the SRAT reaches boiling conditions. The characteristic deactivation (i.e., the first order decrease in the H_2 generation rate) of the catalysts was also very apparent during this run. Figure 7 shows that similar results were observed for PX2. A very distinct peak of 0.76 mol/min was observed, along with a rapid decrease to below 0.15 mol/min. These results were consistent with results reported in the literature,⁹ i.e., for shorter induction periods, higher maximum H_2 generation rates and faster deactivations can occur. However, it has recently been shown that this may not always be the case.¹²

A comparison of the graphs shows that the 25 % excess formic acid resulted in a 53 % increase in the maximum H_2 generation rate (based on the lower value of 0.4 mol/min). It also shortened the induction period by 2 to 3 hr. Overall, these results clearly exemplified the importance of determining the correct formic acid requirement for each sludge, based on the method developed by Hsu.¹²

Figure 6. H_2 generation rate for PX1 through PHA addition.

It is noteworthy that these results also compared well with laboratory scale experiments performed with both simulated¹² and actual HLW sludges. As a result, they were used to redesign the DWPF feed preparation system. A forced air purge system and H_2 monitors were recommended to control the generation of H_2 during feed preparation by fuel dilution.

BL, HM and PX: Activation Energies

The H_2 generation rate during heating and cooling of the SRAT was used to determine an apparent activation energy. An average value of 110 kJ/mol was determined from all of the runs. Furthermore, laboratory studies showed that the most active catalyst in the HLW was Rh, followed by Ru and then Pd, which was relatively much less active.¹² These results suggested that the apparent activation energy was probably related to the activity of either Rh or Ru.

Bond⁷ listed numerous activation energies for the decomposition of formic acid by various metals in different bulk forms, i.e., supported, film, powder, etc., and at different conditions. The values ranged from 27 to 209 kJ/mol, where these extreme values corresponded to Pt foil and Fe powder, respectively. A value of 105 kJ/mol was,

however, reported for Rh, which was nearly the same as that obtained in this work.

Figure 7. H_2 generation rate for PX2 through the end of the feed preparation cycle.

It should be noted that much of the literature data were obtained at temperatures ranging from 120 to 160 °C, compared to 80 to 100 °C in this study. Furthermore, the data reported by Bond⁷ were obtained using formic acid vapor. Nevertheless, similar results have been reported using aqueous formic acid.¹⁰

CONCLUSIONS

The levels of H_2 observed in this study were such that the LFL of H_2 in air (4 vol%) could be exceeded in DWPF vessels, which do not presently have air purges. Therefore, the installation of a forced air purge system and H_2 monitors were recommended to the DWPF to control the generation of H_2 in the feed preparation system by fuel dilution.

The results of the parametric study showed the following: All the IDMS runs exhibited an induction period, followed by a rapid increase in the H_2 generation rate to a fairly sharp maximum and then a continuous decrease to levels far below the maximum. A laboratory study showed that the most active metals were Rh and Ru, and that their reduction by formic acid to an active metallic state was the cause of the induction period. The induction period also decreased with lower concentrations of nitrite and with higher concentrations of formic acid. Higher maximum H_2 generation rates also resulted for lower nitrite and higher formic acid concentrations. However, the H_2 generation rate was insensitive to higher concentrations of formate.

There was also considerable evidence, based on comparing the results of this study with those reported in the literature, which supported the supposition that the H_2 was produced via heterogeneous catalysis. The formic acid first reduced the noble metals to a catalytically active metallic state. Then the active metals adsorbed and decomposed the formic acid into H_2 and CO_2 , according to Equation 1. It should be emphasized that the inherent obscurity of heterogeneous catalytic reactions, (i.e., the reaction rate generally depends on unknown parameters, e.g., the particle size, surface area, etc.), combined with the inhomogeneity of simulated (and of course actual) HLW sludge, understandably made the results of this study, in some cases, difficult to interpret.

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