# DEVELOPMENT OF A NITRIC/FORMIC ACID PROCESS TO REDUCE HYDROGEN EMISSIONS DURING SLUDGE TREATMENT IN THE DWPF

C. W. Hsu, D. M. Ferrara, N. E. Bibler, B. C. Ha, and J. A. Ritter
Westinghouse Savannah River Company
Savannah River Technology Center
Aiken, South Carolina 29808

## ABSTRACT

A new Nitric/Formic Acid (N/FA) flowsheet was developed at the Savannah River Technology Center (SRTC) for use in the Chemical Processing Cell (CPC) of the Defense Waste Processing Facility (DWPF). The flowsheet was successfully demonstrated with simulated sludge using a 2 L bench-scale experimental system and a one-fifth scale (4,000 L) pilot facility, and with actual radioactive waste using a 0.1 L apparatus in one of the SRTC shielded cells. Overall, the new N/FA flowsheet compared to the original formic acid flowsheet reduced the peak $H_2$ generation rate by more than a factor of two and resulted in a more gradual rise in the $H_2$ evolution. Therefore, implementation of the new N/FA flowsheet in the DWPF CPC would result in an increased margin of safety and possibly a reduction in the scope and cost of modifying the DWPF CPC vessel vent system. Also, the new N/FA flowsheet would be compatible with Tank Farm processes and other DWPF flowsheets, and with the implementation of the new Late Wash flowsheet in the DWPF, it would be key to maintaining a proper redox balance of the melter feed.

## INTRODUCTION

At the Savannah River Site (SRS), the Defense Waste Processing Facility (DWPF) is being constructed to immobilize high-level radioactive liquid waste (HLW) into borosilicate glass using a slurry-fed melter (1). A few different flowsheets for various cells in the DWPF have been developed to treat the HLW sludge prior to being fed to the melter. Two of the most current DWPF flowsheets pertinent to this paper are the Hydroxylamine Nitrate (HAN) flowsheet and the Formic Acid (FA) flowsheet developed for the Salt Processing Cell (SPC) and the Chemical Processing Cell ( CPC), respectively. Recently, the HAN flowsheet was replaced with a new Late Wash (LW) flowsheet (2). However, the new LW flowsheet was not completely compatible with the FA flowsheet. Therefore, the main focus of this paper is on the replacement of the FA flowsheet with a new Nitric/Formic Acid (N/FA) flowsheet, which was developed, in part, to make the CPC compatible with the SPC and, in part, to mitigate the evolution of $H_2$.

The original FA flowsheet was developed to improve the processability of the sludge before and during melter operations. Formic acid was chosen because it is somewhat unique, as it functions as both a chemical reductant and as an acid, which are both essential to the reactions of sludge components. Formic acid reduces mercury(II) hydroxide to the elemental state for steam stripping, reduces $MnO_2$ to Mn(II) ion to prevent foaming in the melter, destroys nitrite, and acidifies the sludge to improve the slurry rheology. The formic acid requirement for treating the sludge has been defined and depends on the quantities of alkali metal hydroxides, alkali earth metal hydroxides, carbonates, mercury, $MnO_2$ and nitrite present in the sludge (3).

However, the HLW sludge also contains many transition metal hydroxides. Among them are small quantities of platinum group metals such as Ru, Rh and Pd that are fission products. During the treatment of simulated sludge with formic acid, it has been shown that a significant amount of $H_2$ is generated when the platinum group metals are included in the sludge (4). Hydrogen production during sludge treatment with formic acid also has been verified with actual SRS HLW sludges (5). The formic acid reduces the noble metals in the sludge to metallic states which then cause formic acid to decompose catalytically into $H_2$ and $CO_2$, usually with an induction period (6).

Since $H_2$ can constitute a flammability hazard in the DWPF, a major research effort was initiated at the Savannah River Technology Center (SRTC) to develop a means of mitigating the generation of $H_2$. One of the outcomes of this research effort was the development of a new Nitric/Formic Acid (N/FA) flowsheet. This paper presents results on the ability on the N/FA flowsheet to mitigate the generation of $H_2$ while, at the same time, making the CPC compatible with the SPC by balancing the redox potential of the melter feed. Experimental data are presented from tests performed with actual HLW (0.1 L tests) and from tests performed with simulated HLW (both 2 and 4,000 L tests).

## OVERVIEW OF TANK FARM AND DWPF PROCESSES

An excellent overview of the Tank Farm and DWPF processes has been given recently (1). The HLW is currently being stored at the SRS Tank Farm as a sludge and a salt cake in carbon steel, underground storage tanks. At the Tank Farm, the salt cake is re-dissolved and the cesium and strontium are precipitated with sodium tetraphenylborate and adsorbed on to sodium titanate, respectively. This In-Tank process removes the cesium and strontium from the supernate so that it can be processed as a low-level waste. In order to minimize the mass of waste glass per mass of sludge-slurry, the aluminum and soluble salt contents of the sludge are reduced by sodium hydroxide digestion, and washed with a dilute sodium nitrite solution (to inhibit tank corrosion). The precipitated slurry and the washed sludge are then ready to be transferred to the DWPF.

At the DWPF, the precipitated slurry is hydrolyzed in the SPC to produce, in part, an aqueous stream (denoted precipitate hydrolysis aqueous, PHA). The PHA is processed further along with the washed sludge in the CPC. In the CPC, the washed sludge is first treated with formic acid and then the PHA (which also contains formic acid/formate) is combined

with the sludge and excess water is evaporated. Afterwards, a glass-forming frit is added as the final melter feed preparation step.

## BACKGROUND ON $H_2$ GENERATION AND THE FORMIC ACID FLOWSHEET

Hydrogen generation from formic acid-treated sludge simulant, containing the noble metals Rh, Pd and Ru, was first reported by Wiemers (7) at the Pacific Northwest Laboratory and later confirmed by Hsu (8) at the SRS. Based on this limited experimental evidence, three major research efforts evolved at the SRTC to develop a means of mitigating the generation of $H_2$: A bench-scale experimental program, using 2 L of simulant per test, was chartered to investigate the pertinent process variables and conditions that could affect the $H_2$ generation rate and to explore alternative process flowsheets (4). A bench-scale experimental program in one of the SRTC shielded cells, using 0.1 L of actual HLW sludge per test, was chartered to validate the results of the tests with simulants (4). A one-fifth DWPF scale Integrated DWPF Melter System (IDMS), using 4,000 L of simulant per test, demonstrated the process under nearly prototypic conditions (9).

The 2 L bench-scale experiments showed that the most important process variables that would affect the $H_2$ generation rates and induction periods were (4): 1) the presence and quantities of noble metal in the sludge (Rh was found to be the most active catalyst, whereas Ru was found to be the most sustaining catalyst), 2) the amount of formic acid used to treat the sludge, and 3) the temperature of the sludge. These findings were also verified with tests performed in the shielded cell (5) and in the IDMS (9). Based on the results of these tests, a purged air system will be installed in the DWPF to control the $H_2$ concentration by fuel dilution.

However, there is an incentive to reduce the scope and cost of modifying the DWPF vessel vent system and to improve the margin of safety. Therefore, numerous experiments were conducted to investigate a means of reducing the $H_2$ generation rate to a level substantially below the original design basis (based on the FA flowsheet) (9). Some of these experiments have been described elsewhere (4). During the course of the experimentation it was found that the most attractive alternative was to replace formic acid with nitric acid in the CPC. This new N/FA flowsheet is described in detail below.

## NITRIC/FORMIC ACID FLOWSHEET FOR SLUDGE TREATMENT

The new N/FA flowsheet was developed in conjunction with the new Late Wash (LW) flowsheet, which was developed for the precipitate hydrolysis process in the SPC (2). The LW flowsheet produces a PHA which contains a higher concentration of formic acid/formate compared to the original HAN flowsheet. Therefore, the N/FA flowsheet uses nitric acid in lieu of formic acid to satisfy part of the total acid requirement while the formic acid/formate (i.e., the free acid) in the PHA is used to satisfy the remainder of the acid requirement as well as the requirement for redox reactions (10).

The LW flowsheet also produces a PHA which contains very little nitrate compared to the original HAN flowsheet (2). However, a proper balance must be maintained between formate and nitrate in the melter feed in order to ensure a proper redox state of the glass melt, which is essential for melter operations (11). Therefore, an additional advantage of adding nitric acid in the CPC is to supply the required nitrate.

The following criteria were set for accepting the N/FA flowsheet: the process must be compatible with the LW flowsheet, the maximum $H_2$ generation rate must not exceed the design basis established with the FA flowsheet, the removal of mercury must meet the 75% limit established with the FA flowsheet, and the $NO_x$ emissions must be within the permit limit. All of these criteria have been met with the N/FA flowsheet. However, in this paper only results of $H_2$ evolution are discussed in detail.

## EXPERIMENTAL

### Materials

The base sludge simulant used in the 2 and 4,000 L experiments was a 13.8 wt% solids Purex type sludge. Its composition is listed in Table I. Noble metals, mercuric nitrate and sodium nitrite were added as trim chemicals. When noble metals were added to the sludge, the loadings were 0.044 wt% Rh, 0.094 wt% Pd and 0.219 wt% Ru, based on the sludge solids. Rhodium was added as rhodium nitrate (5% rhodium in nitric acid), palladium was added as palladium nitrate (8.7% palladium in nitric acid), and ruthenium was added as ruthenium trichloride dissolved in deionized water. All of the noble metals were added to the alkali sludge prior to sludge treatment with nitric acid.

The actual radioactive waste sludges used in the 0.1 L shielded cell experiments were obtained from Tanks 11 and 15 of the SRS Tank Farm. These sludges were used in this study because they are high-activity wastes and should have the highest noble metal contents in the waste tanks. These sludges were washed at 80°C with a 4 to 5 M sodium hydroxide solution to remove part of the aluminum hydroxide in the sludge and later washed with a 0.01 M sodium hydroxide solution to remove the high levels of sodium hydroxide. The compositions of these washed sludges are also listed in Table I.

The PHA used in most of the experiments was made from a simulated LW precipitate slurry and prepared in either a 6 L bench-scale experimental system or a one-fifth scale pilot facility (12). However, one of the 2 L experiments and one of the 0.1 L experiments used PHA produced from the hydrolysis of an irradiated LW precipitate slurry. The composition of the unirradiated PHA simulant is listed in Table I. Both the amount of free acid and total formate (including formate in the formic acid and formate salt) in the PHA from the LW flowsheet were much higher than those in the PHA produced from the HAN flowsheet (0.2 to 0.3 M acid versus 0.1 M acid; and 23,000 mg/L formate versus 13,000 mg/L formate) (2).

### Equipment

The IDMS pilot-scale facility and the equipment used for both bench-scale systems have been reported in detail elsewhere (13, 4, 5). Therefore, only pertinent details of the offgas flow rate and gas analyzer systems are given here. On-line gas chromatographs (GC's) were used in all cases to analyze the process offgas. These GC's were capable of measuring $H_2$ down to 0.001 vol% or 10 ppm. The IDMS also utilized an on-line mass spectrometer for more rapid gas analyses, but its range was only for $H_2$ levels greater than 0.05 vol%. The gas

**TABLE I**
Simulated Purex and Actual HLW Sludges, and Simulated LW PHA[a]

| | Purex | Tank 11 | Tank 15 | LW PHA |
|---|---|---|---|---|
| Ag | 0.014 | 0.001 | 0.003 | |
| Al | 3.828 | 18.3 | 17.2 | 0.032 |
| B | | 0.04 | 0.0 | 4.356 |
| Ba | 0.275 | 0.11 | 0.06 | |
| Ca | 2.415 | 0.27 | 0.45 | 0.071 |
| Cr | 0.242 | 0.16 | | |
| Cs | 0.003 | | | 0.399 |
| Cu | 0.121 | | | 1.869 |
| Fe | 25.543 | 5.3 | 6.2 | 0.395 |
| Hg | 3.503 | 5.7 | 5.3 | |
| K | 0.223 | | | 12.322 |
| La | | 0.10 | 0.04 | |
| Li | | 0.01 | 0.00 | |
| Mg | 0.242 | 0.22 | 0.24 | 0.129 |
| Mn | 5.083 | 2.6 | 3.9 | 0.013 |
| Na | 4.590 | 9.7 | 9.0 | 12.772 |
| Nd | 0.178 | | | |
| Ni | 2.569 | 1.1 | 0.67 | |
| Pb | 0.381 | | | |
| Pd | 0.095 | 0.002 | 0.002 | |
| Rh | 0.044 | 0.025 | 0.036 | |
| Ru | 0.219 | 0.082 | 0.13 | |
| Se | 0.004 | | | |
| Si | 0.995 | | | 0.040 |
| U | | 0.02 | 0.02 | |
| Te | 0.049 | | | |
| Th | | 0.008 | 1.3 | |
| Ti | | 0.04 | 0.00 | |
| Zn | 0.260 | 0.35 | 0.34 | |
| Zr | 0.136 | | | |
| $COOH^{-1}$ | | | | 51.612 |
| $CO3^{-2}$ | 4.005 | | | |
| $NO3^{-1}$ | 3.115 | 0.066 | 0.285 | 10.247 |
| $NO2^{-1}$ | 3.020 | 8.364 | 15.307 | |
| $PO4^{-2}$ | 0.005 | | | |
| $SO4^{-2}$ | 0.752 | | | 0.23 |
| $Cl^{-1}$ | 1.095 | | | |
| $F^{-1}$ | 0.108 | | | |
| $I^{-1}$ | 0.019 | | | |
| pH | 12.5 | | | 3.7 |
| density (g/mL) | 1.10 | | | 1.04 |
| total solids (wt% wet) | 13.8 | 17.0 | 8.3 | 5.1 |
| total organic carbon | 0.05 | | | 18.42 |

[a] wt% dry unless noted; values not given were not determined

flow rates in the 2 L experiments were measured with a wet test meter and those in the shielded cell were determined by the inlet purge rate of argon and the argon content in the gas exiting the system. The IDMS facility used redundant orifice-type process flow meters to measure the offgas flow rates.

## Procedure and Conditions

In most of the 2 L experiments, a predetermined amount of 8.2 M nitric acid, ranging from 42 to 95 mL, was added at a rate of 1.0 mL/min to 2.2 L of sludge simulant preheated to between 92 and 96°C. The sludge was then refluxed at boiling conditions for 1 hr. During this part of the cycle, the reactor was purged with $N_2$ at 300 scc/min. Afterwards, 4 L of PHA were added to and evaporated from the reactor at a constant rate which ranged from 1.0 to 5.0 mL/min, depending on the experiment. Following evaporation, the mixture was refluxed at boiling conditions for an extended period of time to ensure the $H_2$ generation rate peaked. During the PHA cycle, the $N_2$

purge to the reactor was decreased to 100 scc/min to reduce the dilution of $H_2$.

In the shielded cell, the procedure was similar to that described above. In these experiments, 8.0 M nitric acid was added at a rate of 0.05 mL/min to 0.1 L of actual HLW sludge preheated to between 88 and 92°C. For the Tank 11 test, the amount of nitric acid added was based on that required to bring the pH of the sludge to 4, which corresponded closely to the nominal amount. However, for the Tank 15 test a 36% excess of nitric acid was used because so little was required by the sludge. Also, the PHA was added in small aliquots (15 mL each hour) through a separatory funnel instead of being metered in continuously. A 10 scc/min Ar purge was used in both tests.

The IDMS demonstration required 133 L of 7.5 M nitric acid, which was added at a rate of 1.6 L/min to 4,160 L of simulated Purex type sludge preheated to between 92 and 96°C. The temperature of the reactor was then increased to boiling conditions in order to add the PHA. The PHA was added in 8 equally sized batches which totaled 7,950 L. Continuous addition of PHA was not possible due to limitations of the system, but continuous evaporation was possible at about 2.65 L/min. In contrast to the 2 L experiments, there was no need to reflux the system following PHA addition/evaporation, as the $H_2$ generation rate peaked during the PHA cycle. It should be noted that this PHA evaporation rate was only about half of the DWPF prototypic rate. The purge gas used in this case was air, as in the DWPF.

## RESULTS AND DISCUSSION

The results of the tests performed in the three SRTC experimental facilities are described below. First, some of the general results from the 2 L experimental facility with simulated sludge are presented, followed by the 0.1 L shielded cell work with actual sludge, then a parametric study based on the 2 L experimental system is presented, and finally the IDMS demonstration with simulated sludge is discussed. Many of the findings with the N/FA flowsheet were consistent with the results of the previous work done on the FA flowsheet. Some of the important consistencies between the two flowsheets are highlighted below, along with some of the major differences. Note that the results of all the tests reported here are based on mol/min/kg sludge, where sludge indicates the total sludge solids.

### Offgas Generation during the PHA Cycle

During the PHA cycle, $CO_2$, NO and sometimes a minute amount of $N_2O$ were generated. An example of the offgas profiles during the PHA cycle are shown in Fig. 1. The time dependence of the generation rates of these gases was strongly related to the amount of nitric acid used to treat the sludge prior to the PHA cycle. The initial $CO_2$ was attributed to the reaction of formic acid in the PHA with the remaining carbonates in the sludge, whereas $CO_2$ evolved later was the product of oxidation-reduction reactions between formic acid and other sludge components and from the catalytic decomposition of formate. The NO was the product of the reaction between nitrite and formic acid. Similar to the FA flowsheet, only when the nitrite in the sludge was destroyed, as evidenced by the disappearance of NO, did the $H_2$ generation rate increase rapidly. Also, similar to the FA flowsheet, the significant amount of $H_2$ that was generated was due to the presence

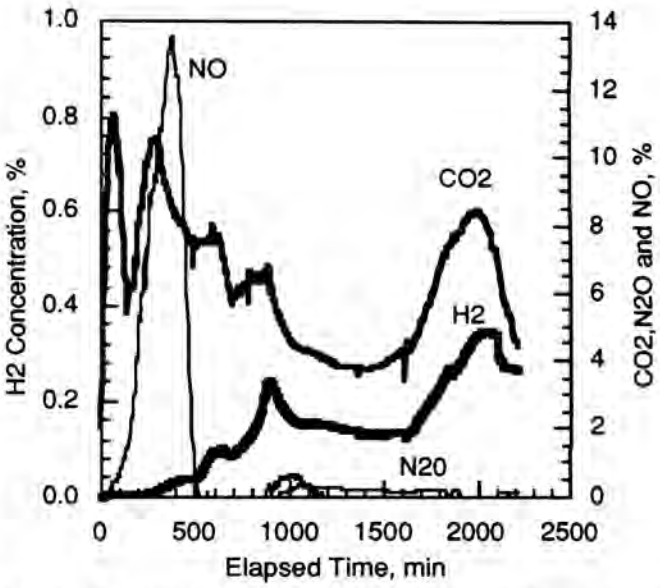


Fig. 1. Offgas profiles during a PHA cycle after treatment of sludge with nitric acid.

of noble metals in the sludge. However, the N/FA flowsheet did not generate a significant amount of $H_2$ until the second half of the PHA cycle.

Unlike formic acid, nitric acid alone could not react with the noble metals to generate $H_2$. However, during the PHA cycle the quantity of formic acid and formate present in the PHA was enough to activate the noble metals. Only then was the formic acid decomposed catalytically into $H_2$ and $CO_2$. Hydrogen was generated in the later part of the PHA cycle and often peaked after the PHA cycle ended. In contrast, the induction period was much shorter when treating the low nitrite sludge with formic acid (i.e., when using the FA flowsheet), as nearly all of the formic acid was added to the system before any PHA was added (3, 8).

### Comparison of $H_2$ Generation from the Formic Acid and Nitric/Formic Acid Flowsheets

Two experiments, one with formic acid and one with nitric acid, were conducted in order to make a direct comparison between the resulting $H_2$ generation profiles. In these experiments only 1.1 L of sludge simulant and 1.6 L of LW PHA simulant were used per test. The molar equivalence (0.45 mol) of formic acid added prior to the PHA cycle was the same as that of the nitric acid, but less than that originally defined for sludge treatment (3). This was done because credit was taken for the free formic acid in the LW PHA simulant, which was twice as high as that in the PHA from the HAN flowsheet.

The $H_2$ profiles from these two tests are shown in Fig. 2. The peak H2 generation rates for the FA and N/FA flowsheets were $4.17 \times 10^{-4}$ and $1.86 \times 10^{-4}$ mol/min/kg sludge, respectively. In addition, the rise of the $H_2$ evolution during the nitric acid run was much more gradual than for the formic acid run. These results showed that the N/FA flowsheet over the FA flowsheet provides a greater margin of safety and an opportunity for reducing the scope and cost of modifying the DWPF vessel vent system.

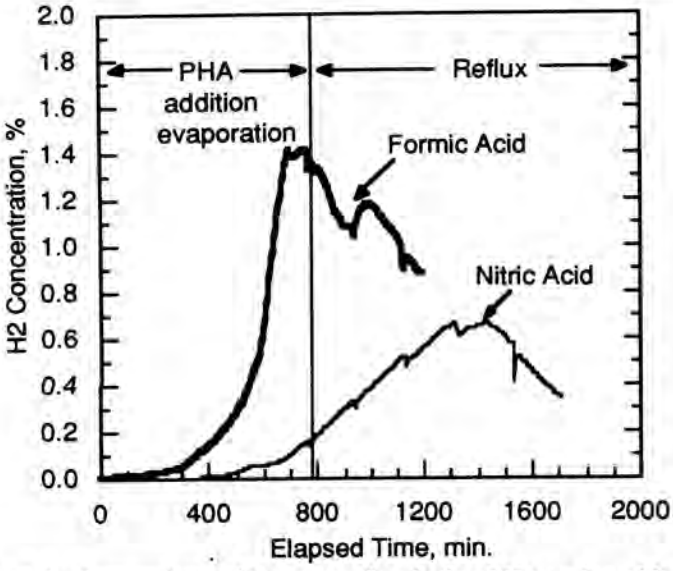


Fig. 2. Comparison of $H_2$ generation during PHA cycles with formic acid flowsheet and nitric acid flowsheet (zero elapsed time starts with the beginning of PHA evaporation).

## Generation of $H_2$ from Actual HLW Sludges from Tank 15 and Tank 11

Two experiments based on the N/FA flowsheet were done with actual radioactive sludge from Tanks 15 and 11. The resulting $H_2$ generation profiles are shown in Fig. 3 and Fig. 4, respectively. Even though both sludges had similar mercury and noble metal contents (see Table I), the activation and deactivation of the noble metals were quite different, as evidenced by the significantly different $H_2$ generation profiles. These results could not be interpreted, based simply on the mercury and/or noble metals contents of the sludges.

The peak $H_2$ generation rates from Tanks 15 and 11 were $6x10^{-5}$ and $2x10^{-4}$ mol/min/kg sludge, respectively. Both of these rates were considerably less than those observed from the FA and HAN flowsheets, which were $2x10^{-4}$ and $2x10^{-3}$ mol/min/kg sludge, respectively (4). In addition, the initial rise

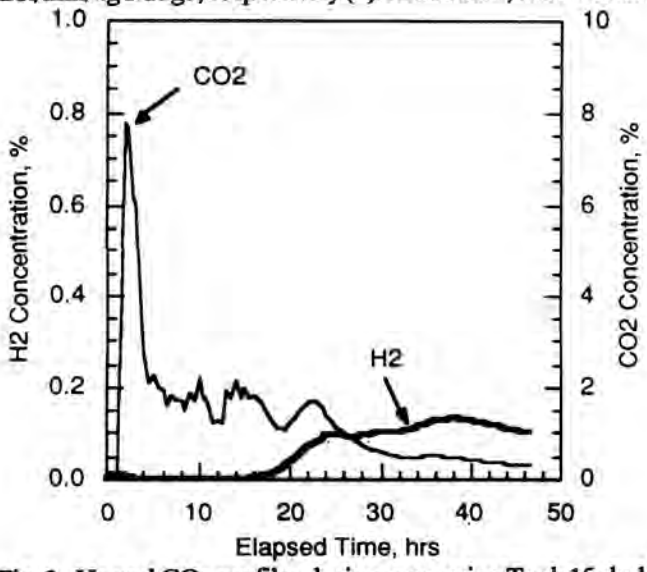


Fig. 3. $H_2$ and $CO_2$ profiles during processing Tank 15 sludge with nitric acid and PHA.

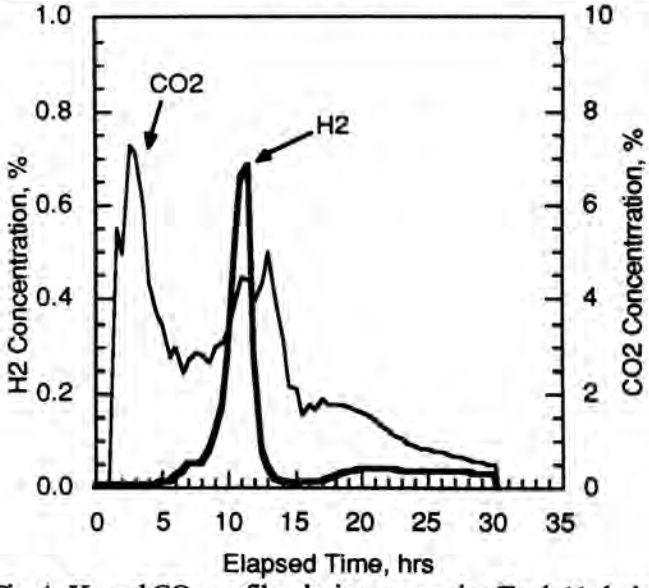


Fig. 4. $H_2$ and $CO_2$ profiles during processing Tank 11 sludge with nitric acid and PHA.

of the $H_2$ evolution (i.e., when the noble metals were first activated) was, in both cases, much more gradual compared to results of similar experiments based on the FA flowsheet (5). These significant differences in the $H_2$ generation rates and $H_2$ evolution from the N/FA and FA flowsheets were also observed using simulated sludge, as discussed above and shown in Fig. 2. Thus, these results also demonstrate that the N/FA flowsheet provides a wider margin of safety with actual sludge.

Moreover, the results from the Tank 11 sludge compared very well with the results from the 2 L experiments (see below) when performed under nearly similar conditions. The comparable peak $H_2$ generation rates were $2x10^{-4}$ (0.1 L test) and $4x10^{-4}$ (2 L test) mol/min/kg sludge, a remarkable agreement. This observation indicated that simulated sludges can be used to reliably predict the behavior of actual radioactive sludges.

In another test, nitric acid and a simulated LW PHA obtained from irradiated precipitate slurry were used to treat Tank 11 sludge. The amount of $H_2$ produced was barely detectable. The cause of this dramatic reduction of the $H_2$ generation due to irradiation of precipitate slurry is under investigation. A similar effect, but not so drastic, was also observed with simulated sludge (see below).

The $CO_2$ profiles from Tanks 15 and 11 are also displayed in Figs. 3 and 4. The initial $CO_2$ peak was the product of the reactions between the carbonates in the sludge and the nitric acid. Both profiles behaved similarly until about 5 hr into the cycle, which indicated that the sludge samples from these two tanks had similar amounts of carbonates. However, the $CO_2$ profiles after 5 hr were characteristically different. The Tank 11 sludge (Fig. 4) produced another $CO_2$ peak at about the time the $H_2$ peaked. This $CO_2$ was mostly likely the product of oxidation-reduction reactions between formic acid and other sludge components and from the catalytic decomposition of formate. In contrast, the Tank 15 sludge produced relatively little $CO_2$ after 5 hr, which was consistent with the amount of $H_2$ produced. Similar results were observed with the simulated sludge (see Figs. 2 and 9).

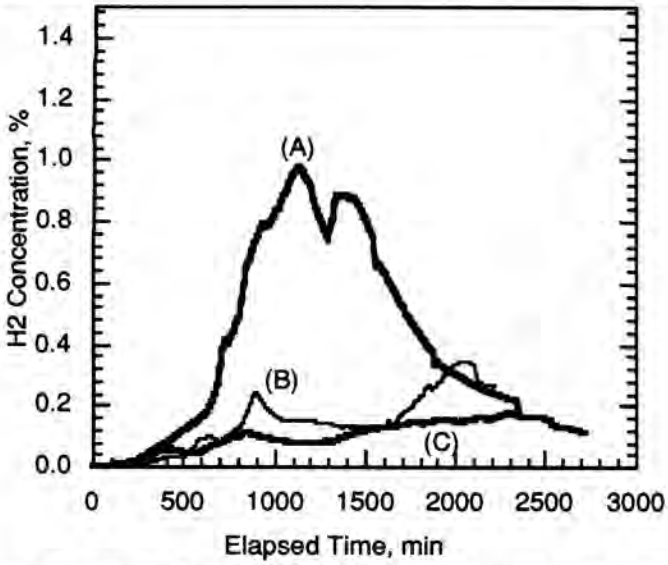


Fig. 5. Effect of nitric acid on $H_2$ generation: (A) 2.33, (B) 1.54 and (C) 1.12 mol nitric acid/kg sludge.

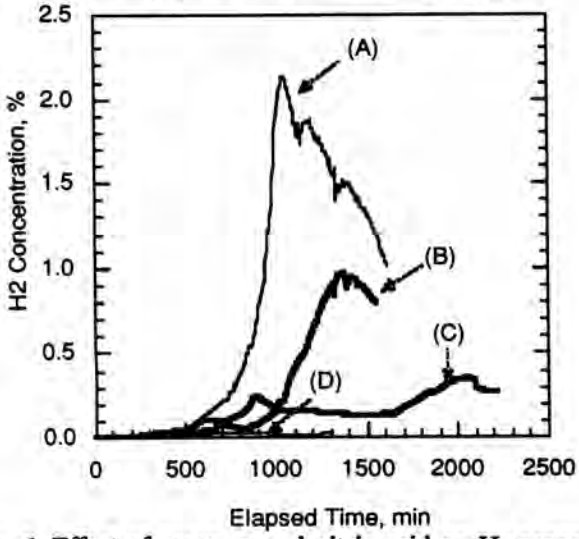


Fig. 6. Effect of mercury and nitric acid on $H_2$ generation during PHA cycle: (A)with Hg, 1.89 mol nitric acid per kg sludge, (B) with Hg, $HNO_3$ not added, (C) w/o Hg, 1.89 mole nitric acid per kg sludge, and (D) w/o Hg, $HNO_3$ not added.

## Investigation of Key Process Parameters with Sludge Simulant

The following variables were investigated in the 2 L experimental system using sludge simulant: the amount of nitric acid used, the presence of mercury in the sludge, the PHA addition and evaporation rate (cycle time), and the source of PHA. In all cases, 4 L of PHA were used with 2.2 L of sludge simulant. Note that this amount of PHA corresponded to 25% more than the nominal amount. The results are summarized in Table II and discussed in detail below.

The effect of the amount of nitric acid on the $H_2$ generation rate using simulated LW PHA is shown in Fig. 5 and Table II. The $H_2$ generation rate increased with an increase in the amount of nitric acid used. This result was similar to, but not quite as drastic as, the effect of formic acid on the $H_2$ generation rate based on the FA flowsheet (4, 9). In the extreme case tested, a 50% excess of formic acid increased the $H_2$ generation rate by a factor of 10 (4).

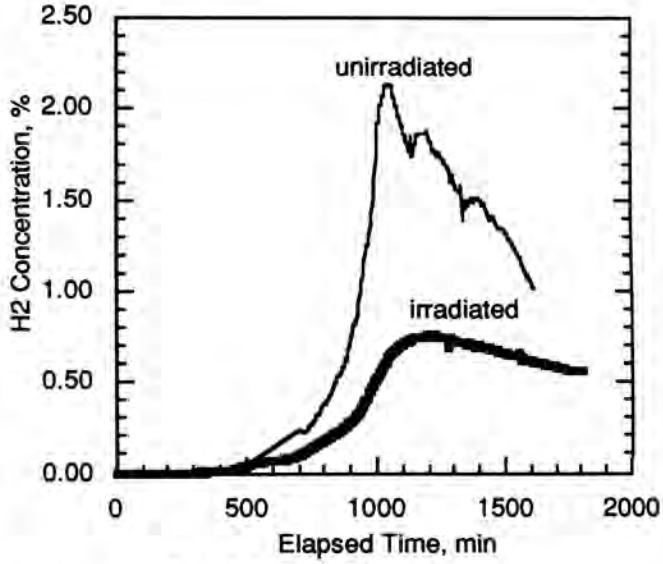


Fig. 7. Effect of PHA source.

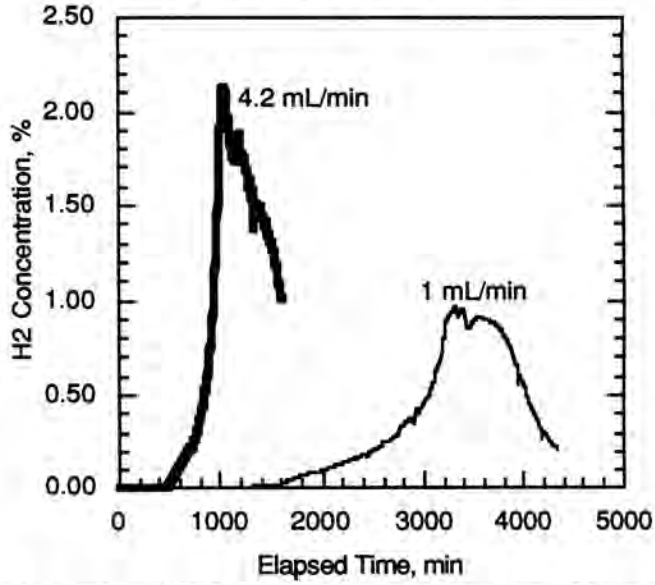


Fig. 8. Effect of PHA addition/evaporation rate on $H_2$ generation.

The effect of the presence of mercury on the $H_2$ generation rate is shown in Fig. 6 and Table II. The $H_2$ generation rate increased from $5.80 \times 10^{-5}$ to $3.99 \times 10^{-4}$ mol/min/kg sludge due to the presence of 3.5 wt% mercury when using the same amount of nitric acid and a simulated LW PHA. Even when only PHA was used (i.e., no nitric acid was added), the presence of mercury still increased the peak $H_2$ rate from $5.80E^{-6}$ to $1.60E^{-4}$ mol/min/kg sludge.

Figure 7 and Table II show the effect of the PHA source on the $H_2$ generation rate. In one of the experiments PHA made from the hydrolysis of an irradiated LW precipitate slurry was used. The $H_2$ generation rate was $1.19 \times 10^{-4}$ mol/min/kg sludge, compared to $3.99 \times 10^{-4}$ mol/min/kg sludge when PHA produced from an unirradiated precipitate slurry was used. The effect of the PHA source was even more marked when actual radioactive sludge from Tank 11 was treated with nitric acid and the same LW PHA obtained from

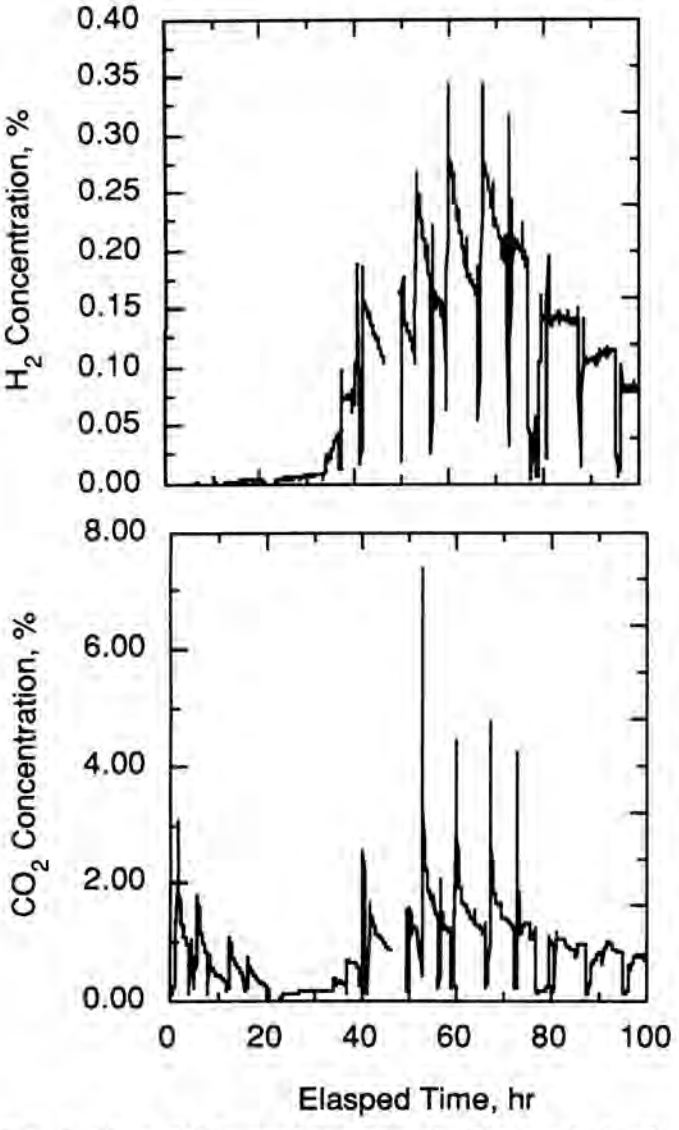


Fig. 9. $H_2$ and $CO_2$ profiles during the PHA cycle for the IDMS demonstration (spikes caused by offgas surges due to the "piston effect" during the onset of boiling).

the irradiated precipitate slurry. In this case, $H_2$ was barely detectable (see above).

The effect of the PHA addition/evaporation rate on the $H_2$ generation rate and induction period is shown in Fig. 8 and Table II. By slowing down the PHA addition/evaporation rate from about 5 to 1 mL/min, the peak $H_2$ generation rate was reduced from $3.99 \times 10^{-4}$ to $1.46 \times 10^{-4}$ mol/min/kg sludge and the induction period increased by a factor of three. These results were due to the effect of the amount of formic acid/formate in the PHA on the activation of the noble metals. The PHA addition/evaporation rate determined the amount of the formic acid/formate entering the system and therefore affected the activation of the catalysts and the reaction rate of decomposition of formic acid. Therefore, when the cycle time of PHA addition/evaporation was lengthened, activation was slowed down and deactivation was given more time, resulting in a lower peak $H_2$ generation rate and a longer induction period.

Moreover, deactivation may even occur during the course of $H_2$ generation, i.e., activation and deactivation may occur simultaneously and partially cancel each other. When the activation exceeds the deactivation, an upward trend of the $H_2$ evolution is observed, whereas when deactivation exceeds the activation, a downward trend is observed. This phenomenon was observed very clearly during the IDMS demonstration (see below).

**Nitric/Formic Acid Flowsheet Demonstration in the IDMS**

The nitric acid flowsheet was demonstrated in the IDMS using simulated sludge and simulated LW PHA. This IDMS run was, for the most part, prototypic of a nominal N/FA flowsheet run in the DWPF. Two exceptions are noted: 1) the PHA was not added continuously and it was evaporated too slowly (see above) and 2) a 30% excess of PHA was used. A qualitative indication of the effects of these non-prototypic conditions on the $H_2$ generation rate can be obtained from the results of the 2 L parametric study (see above).

Figure 9 displays the $H_2$ and $CO_2$ generation profiles during the PHA cycle. Note that the spikes in the offgas profiles were due to a "piston effect", i.e., due to offgas surges as a result of the onset of boiling. The peak $H_2$ generation rate of $1.38 \times 10^{-4}$ mol/min/kg sludge occurred at about two-thirds of the way through the PHA cycle. Both the induction period and the peak rate of this IDMS run compared very well with the 2 L experiment performed at a similar PHA addition/evaporation rate. Compare these IDMS results with the results shown in Fig. 8 and Table II for the 2 L experiment performed at 1 mL/min. Also, the peak $H_2$ generation rate for this nearly nominal IDMS demonstration of the N/FA flowsheet decreased by a factor of 4 to 5, compared to a similar nominal IDMS demonstration of the FA flowsheet (9). A conservative estimate, based on the 2 L experimental results and taking into account the effect of the slower PHA evaporation rate, suggested that more than a factor of two decrease would be expected under nominal conditions. Also, consistent with the 2 L experiment, a longer induction period, a reduction in the peak $H_2$ generation rate, and a more gradual rise in the $H_2$ evolution were observed for the N/FA flowsheet compared to the original FA flowsheet. The $CO_2$ profile was also consistent with both the 2 L and 0.1 L experiments, i.e., $CO_2$ tended to follow the generation of $H_2$.

The way in which the PHA was added in this IDMS demonstration (i.e., batchwise) also allowed for the observation of the simultaneous activation/deactivation of the catalysts. Fig. 9 shows that as the $H_2$ generation rate increased, the catalysts exhibited some deactivation, as evidenced by the local decreases in the $H_2$ generation rate while the overall rate was still increasing. Thus, as suggested above, activation/deactivation of the catalysts depends strongly on how the formic acid is added to the system.

This IDMS test also demonstrated that the melter feed prepared from the N/FA flowsheet can be processed through the melter. Satisfactory mercury removal without additional formic acid was also achieved. Overall, all of the criteria stated above for acceptance of the N/FA flowsheet were met during this run.

## CONCLUSIONS

The treatment of HLW sludge requires both an acid and a reductant, which are both supplied by formic acid in the original FA flowsheet. The new N/FA flowsheet consists of substituting a fraction of formic acid with nitric acid as the

**TABLE II**
Summary of the Two Liter Experiments with Simulated Sludge

| $HNO_3$ (mole/kg sludge) | Hg (wt% dry) | LWPHA (mL/min) | $H_2$ (mole/min/kg sludge) |
|---|---|---|---|
| | Effect of $HNO_3$ Addition | | |
| 2.33 | 0 | 4 to 5 | $1.71E^{-4}$ |
| 1.54 | 0 | 4 to 5 | $5.80E^{-5}$ |
| 1.12 | 0 | 4 to 5 | $9.07E^{-6}$ |
| | Effect of Hg Content of Sludge | | |
| 1.54 | 0 | 4 to 5 | $5.80E^{-5}$ |
| 1.54 | 3.5 | 4 to 5 | $3.99E^{-4}$ |
| | Effect of PHA Addition Rate | | |
| 1.54 | 3.5 | 4 to 5 | $3.99E^{-4}$ |
| 1.54 | 3.5 | 1 | $1.46E^{-4}$ |
| | Effect of PHA Source | | |
| 1.54 | 3.5 | 4 to 5[a] | $3.99E^{-4}$ |
| 1.54 | 3.5 | 4 to 5[b] | $1.19E^{-4}$ |

[a] unirradiated: acid: 0.24 M; formate: 23,400 mg/L; Cu :950 mg/L
[b] irradiated: acid: 0.24 M; formate: 18,700 mg/L

acid, and then relying on the formic acid supplied solely from the LW PHA as the reductant. The N/FA flowsheet was successfully demonstrated with both simulated sludge (2 and 4,000 L tests) and actual sludge (0.1 L tests). Moreover, the results from each facility compared very well when scaled to the same conditions. This observation indicated that simulated sludges can be used to reliably predict the behavior of actual radioactive sludges.

The key results of this study showed that the N/FA flowsheet compared to the FA flowsheet reduced the peak $H_2$ generation rate by more than a factor of two and resulted in a more gradual rise in the $H_2$ evolution. Therefore, implementation of the N/FA flowsheet in the DWPF CPC would result in an increased margin of safety and possibly a reduction in the scope and cost of modifying the DWPF CPC vessel vent system. Also, the N/FA flowsheet is compatible with Tank Farm processes and the Late Wash flowsheet, and is key to maintaining a proper redox balance of the melter feed with the implementation of the new Late Wash flowsheet in the DWPF.

The source of PHA had a marked effect on the $H_2$ generation rate. When the LW PHA was made from an irradiated precipitate slurry, as opposed to unirradiated precipitate slurry, the $H_2$ generation rates from both simulated sludge and actual radioactive sludge were significantly lower. In fact, with the actual sludge, $H_2$ was barely detectable. This phenomenon is under investigation at the SRTC.

## ACKNOWLEDGMENT

This paper was prepared in connection with work done under Contract No. DE-AC09-89SR18035 with the United States Department of Energy.

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