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**HYDROGEN GENERATION IN SRAT WITH NITRIC ACID
AND LATE WASHING (U)**

by C. W. Hsu

Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

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Other Authors:

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CC: L. M. Poapouchado, 773-A
L. F. Landon, 704-T
J. T. Carter, 704-1T
M. J. Plodinec, 773-A
C. T. Randall, 704-T
J. R. Zamecnik, 704-1T
J. A. Ritter, 704-1T
N. E. Bibler, 773-A
D. M. Ferrara, 773-A
B. C. Ha, 773-A
SRTC Records (4)

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TO: E. W. HOLTZSCHEITER, 773-A

FROM: C. W. HSU, ^{CWkt} 704-1T

**HYDROGEN GENERATION IN SRAT
WITH NITRIC ACID AND LATE WASHING FLOWSHEETS (U)**

SUMMARY

Recently, SRTC recommended two process changes: 1) a final wash of the tetraphenylborate precipitate feed slurry and 2) the use of nitric acid to neutralize the sludge in the SRAT. The first change produced an aqueous hydrolysis product (PHA) with higher formic acid/formate and copper concentration, and reduced the nitrate content in the PHA by an order of magnitude. The second change is to substitute part of formic acid added to the SRAT with nitric acid, and therefore may reduce the hydrogen generated in the SRAT as well as provide nitrate as an oxidant to balance the redox state of the melter feed.

A series of bench-scale scoping experiments using sludge simulants containing noble metals were conducted to investigate the pertinent variables that could affect the hydrogen generation rate. The results are summarized in Table 2. With the new PHA from late-wash hydrolysis simulant

E. W. Holtzscheiter, 704-T
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added to the sludge at the maximum volume ratio, and the amount of acid added similar to the nominal amount, the peak hydrogen generation rate was 0.55 lb/hr DWPF scale. Other findings are described below.

- A longer induction period, a reduction of the peak hydrogen generation rate, and a more gradual rise in the hydrogen evolution resulted compared to those observed with the original formic acid flowsheet.
- The presence of mercury increased the hydrogen generation rate by a factor of 7. The effect of mercury seems to be highly related to the new PHA simulant from the late-washing hydrolysis.
- The hydrogen generation rate is affected by the amount of nitric acid added.
- The source of PHA affects the hydrogen generation rate. When PHA from the washed irradiated precipitate slurry was used, the hydrogen generation rate was only one third of the rate obtained when an unirradiated precipitate slurry was used.
- A reduction of PHA addition/evaporation rate by a factor of four reduced the peak hydrogen generation rate by a factor of 2.5.

INTRODUCTION

In the original DWPF flowsheets the hydroxylammonium nitrate (HAN) precipitate hydrolysis process produces sufficient oxidant (nitrate) such that the resulting blend of formic acid treated sludge and the aqueous product from hydrolysis (PHA) produces a melter feed of acceptable redox (i.e. $\text{Fe(II)}/\text{Fe(total)} < 0.33$). With the implementation of Late Washing to reduce the nitrite content of the tetraphenylborate slurry produced during In-Tank Precipitation to 0.01M or less, HAN is no longer required during hydrolysis.¹ As a result, the nitrate content of the melter feed will be reduced greater than an order-of-magnitude and the resulting melter feed produced will be too reducing.

If formic acid treatment of the sludge is retained, it will be necessary to trim the melter feed with an oxidant to attain a proper redox state of the glass melt. Rather than trimming the melter feed with an oxidant subsequent to the SRAT cycle in which formic acid is used to acidify the sludge, the Savannah River Technology Center (SRTC) has recommended this be accomplished by conversion to nitric acid

addition to the Sludge Receipt and Adjustment Tank (SRAT) in place of formic acid.²

The original formic acid flowsheet specified the treatment of the sludge by adding 90 wt% of formic acid at SRAT at $94 \pm 2^\circ\text{C}$, and then the mixture was digested at boiling for six hours. During the sludge treatment hydrogen (H_2) may be produced by noble-metals catalyzed decomposition of formic acid. Small amounts of noble metals are present in the actual sludge as fission products, and become active catalysts when chemically reduced by formic acid.

Previous laboratory studies showed that the hydrogen generation rate during sludge treatment with formic acid was significant enough that a controlled forced air purge and on-line hydrogen monitor system would be required for safe operation in the DWPF. A design basis was provided to DWPF for this fuel dilution approach.³ In addition, it was demonstrated both in the lab and IDMS that increasing the amount of formic acid added to the sludge increased the hydrogen generation rate dramatically, e.g. a 50% excess of formic acid increased the hydrogen generation rate to ten folds.⁴

In the new late-washing hydrolysis flowsheet, it is necessary to increase the amount of formic acid and copper catalyst to achieve the designed hydrolysis rate in the DWPF Salt Processing Cell. Therefore the PHA entering the SRAT will contain much higher formic acid, formate and copper. If formic acid flowsheet is retained, hydrogen generation may exceed the original design basis. By substituting part of formic acid with nitric acid, the total amount of formic acid/formate in the SRAT will be kept minimal, and may lower the hydrogen generation rate enough that the scope of the costly modification for DWPF CPC vessel may be substantially reduced.

OBJECTIVES

The purpose of this scoping study is to determine the pertinent variables that could affect the hydrogen generation rate with the new flowsheets. The results of the study have been used to guide two major process-demonstration efforts on this issue: characterization of the generation of hydrogen on an engineering scale with sludge simulant in IDMS and on a bench scale with actual SRS HLW sludges in the shielded cell.

In this study the effects of the following variables on the hydrogen generation rate were investigated:

- amount of nitric acid added at SRAT

- mercury content
- PHA source (irradiated or unirradiated)
- PHA addition and evaporation rate
- amount of formic acid/formate in the PHA (not complete)
- amount of PHA used (not complete)

In addition ammonium generation⁵ and mercury removal with the new flowsheets were also monitored and will be reported separately.

EXPERIMENTAL

Materials

The base sludge simulant used in most of the experiments presented here was a 12.6 wt% solids Purex type sludge prepared by Optima Chemicals, Inc. Its composition is listed in Table 1. 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 with trim chemicals added. 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 the noble metals were added to the alkali sludge prior to sludge treatment with nitric acid. Mercury was added as mercuric nitrate dissolved in hot deionized water and a few drops of concentrated nitric acid.

The PHA used in most of the experiments was prepared in Integrated Precipitate Hydrolysis System (IPHS) or Precipitate Hydrolysis Facility (PHEF) from simulated late-wash precipitate slurry similar to that to be used in the DWPF Cold Chemical Runs. In one experiment a PHA produced from hydrolysis of several irradiated precipitate slurry experiments was used. The acid and formate contents of the PHA's are listed in Table 2.

Experimental Equipment

The experimental equipment has been described in detail in WSRC-MS-92-270.⁴

Purchased gas standards were used to calibrate and check the MTI GC for its performance consistency before each cycle. The pH probe was calibrated with buffer solutions before each experiment.

Experimental Conditions

In most of the experiments, a predetermined amount of 8.3 M nitric acid, ranging from 42 to 95 mL, was added at a rate of 1.0 mL/min to 2.2 liters of sludge simulant preheated to between 92 and 96°C. The sludge was then refluxed at boiling conditions for one hour. During this cycle the reactor was purged with nitrogen at 300 scc/min. Afterwards four liters of PHA were added and evaporated at 4.2-5.0 mL/min to the reactor. In one experiment, the feed and evaporation rate of PHA was reduced to 1.0 mL/min. Following evaporation, the mixture was refluxed at boiling for an extended period to ensure the peaking of hydrogen generation. During the PHA cycle the nitrogen purge to the reactor was decreased to 100 scc/min to reduce dilution of hydrogen by the purge gas.

RESULTS AND DISCUSSION

The hydrogen generation rates and the experimental conditions are outlined in Table 2. The peak hydrogen evolution rates are expressed on a DWPF basis (6000-gallon batch at 19 wt% solids).

Offgas Generation During Nitric Acid Addition and Digestion

Figures 1 and 2 show the offgas and pH profiles during the titrations of an HM sludge (0.3 M nitrite) and a Purex sludge (0.06 M nitrite) with 8.3 M nitric acid at 93°C. Excess of nitric acid was added in both cases. The CO₂ in Figures 1 and 2 is the product of reactions between carbonates in the sludge and nitric acid. NO is generated from disproportionation of nitrous acid resulted from the nitric acid-nitrite interaction.⁶ Much less nitric acid than the indicated amount in Figures 1 and 2 will be required for the SRAT process because of the amount of free acid (0.2 to 0.3 M) already present in the late-washing PHA. During the actual sludge treatment the profiles will end wherever the appropriate amount of nitric acid is added to the reactor.

Offgas Generation During PHA Evaporation

CO₂, NO and sometimes a very minute amount of N₂O were generated during addition and evaporation of the PHA. The time dependence of the generation rates of these gases is strongly related to the amount of nitric acid used to treat the sludge prior to the PHA cycle. The initial CO₂ was attributed to the reaction of formic acid in the PHA with the remaining carbonates in the sludge, whereas CO₂ evolved later was the product of oxidation-reduction reactions between formic acid and other sludge components. NO was the product of the reaction between nitrite and formic acid. However,

because of the presence of noble metals in the sludge, a significant amount of hydrogen was generated during the second half of the PHA cycle and sometimes reached a maximum during the reflux period following the evaporation of PHA. An example of the gas profiles during the PHA cycle is shown in Figure 3.

Unlike formic acid, nitric acid by itself does not react with noble metals to generate hydrogen. Actually sufficient amounts of formic acid and formate in the incoming PHA activated the noble metals in the sludge. Then the formic acid in turn was decomposed catalytically to hydrogen and carbon dioxide. For example, profiles B and D in Figure 4 shows that even when nitric acid was not added at all, evaporating PHA with the sludge simulant already resulted in hydrogen evolution.

Effect of the Amount of Nitric Acid Added

From previous studies of hydrogen generation during treatment of sludge with formic acid, it was discovered that a small change in the amount of formic acid would influence the hydrogen generation rate dramatically.⁴ Figure 5 shows hydrogen concentration profiles from three experiments with different levels of nitric acid added to treat a sludge that did not contain any mercury. It is apparent that the hydrogen generation rate is affected by the amount of nitric acid added.

The set of four hydrogen profiles in Figure 4 further demonstrate the effect of nitric acid on the hydrogen generation. B and D are the profiles of adding only PHA to the sludge, where profiles A and C are the profiles where appropriate amount of nitric acid was added. The amount of nitric acid required to treat the sludge is defined in WSRC-RP-92-1056.⁶ The sludge used in experiments A and B contained mercury while the sludge used in experiments C and D did not. In both sets of conditions, the addition of nitric acid increased the hydrogen generation rate.

In the late-washing PHA, approximately half of the formate is in the form of acid and the other half is in the form of formate ions. Increasing the amount of nitric acid added to the sludge would reduce the amount of formic acid in PHA to react with the sludge components and therefore would leave more free formic acid in the system to react with the noble metals. Therefore even though nitric acid itself does not decompose to hydrogen, the amount of nitric acid can also influence the hydrogen generation rate.

Effect of Mercury Content of Sludge

Figure 4 shows the comparison of two sets of hydrogen concentration profiles of four experiments. The presence of mercury at 3.5 wt% of the sludge solids increased peak hydrogen evolution rate from 0.08 to 0.55 lb/hr, when the appropriate amount of nitric acid was added. (see Table 2) Even when only the PHA was used, the presence of mercury still increased the peak rate from .008 lb/hr to 0.22 lb/hr.

Effect of PHA Source

In one experiment PHA from hydrolysis of the late-washed irradiated precipitate slurry⁷ was used. The hydrogen generation rate was 0.16 lb/hr, compared to 0.55 lb/hr when PHA produced from an unirradiated precipitate slurry was used. (See Figure 6 and Table 2). More dramatically, hydrogen was barely detectable when the actual SRS Tank 11 sludge was treated with nitric acid and PHA from irradiated precipitate in the shielded cell.⁸ Factors that reduce the hydrogen generation rate due to the differences in the PHA's will be under investigation.

Effect of PHA Addition Rate

In most of the experiments the PHA was added and evaporated at the rate of 4.0-5.2 mL/min (12-14 gpm DWPF scale). In one experiment, the PHA addition/evaporation rate was intentionally slowed down to 1 mL/min to determine the effect of the PHA cycle time on the hydrogen generation rate. The results showed that by slowing down the PHA addition and evaporation rate, the peak hydrogen generation rate was reduced from 0.55 to 0.20 pph DWPF scale (see Table 2). The hydrogen profiles of these two experiments are shown in Figure 7.

The amount of formic acid/formate in the PHA affects the activation of the noble metals. The rate of addition and evaporation of the PHA determines the amount of the formic acid/formate coming in the SRAT and therefore affects the activation of the catalysts and the reaction rate of decomposition of formic acid. In addition, deactivation occurs during the course of hydrogen generation. Activation and deactivation may even occur simultaneously and partially cancel each other. When the activation exceeds the deactivation, an upward trend of hydrogen evolution is observed. When deactivation exceeds the activation, a downward trend is observed. Therefore when the cycle time of PHA addition/evaporation is lengthened, activation is slowed down and resulting in a lower peak hydrogen rate.

Change of Sludge pH During Treatment with Nitric Acid and PHA

The pH profiles during sludge treatment with nitric acid addition are shown in Figures 1 and 2. The end pH of this step depends on the amount of nitric acid added. Four pH profiles during the PHA cycles are shown in Figure 8. As discussed in the previous sections, higher amount of acids used often results in more active catalysts and higher hydrogen evolution rate and more ammonia generation.⁵

The disappearance of formic acid and the production of ammonium contribute to the upward drift of sludge pH. This reaction is very slow. This is very different from the case of the Cold Chemical Run where noble metals were not added to the sludge simulant.

CONCLUSIONS

- The combination of the new composition of the late-wash PHA simulant and the presence of mercury resulted in a condition that activates the noble metals very effectively. Though nitric acid itself does not generate hydrogen as formic acid, the amount of formic acid and formate and copper in the late-wash PHA still caused significant amount of hydrogen evolution even when nitric acid was not added.
- The amount of nitric acid used to treat the sludge and the formic acid/formate content of PHA affect the hydrogen evolution rate. Therefore it is imperative for DWPF to have tight controls over batching and analytical accuracies in both Chemical Processing Cell and in Salt Processing Cell processes.
- The rate of PHA addition and evaporation in the SRAT affects the peak hydrogen evolution rate. Therefore it is important for IDMS to match the cycle time designed for DWPF.
- Hydrogen evolution rate is noticeably reduced when processing PHA from irradiated and late-washed precipitate slurry compared to the rate when using the PHA from the unirradiated and unwashed precipitate.
- In contrast to the cold chemical runs, when more acid is added to treat the sludge containing noble metals, the final sludge pH may be higher.

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Table 1. Composition of Simulated Purex Sludge

<u>Element</u>	<u>wt%</u>
Ag	0.014
Al	3.828
Ba	0.275
Ca	2.415
Cr	0.242
Cs	0.003
Cu	0.121
Fe	25.543
Hg	3.503
K	0.223
Mg	0.242
Mn	5.083
Na	4.590
Nd	0.178
Ni	2.569
Pb	0.381
Pd	0.095
Rh	0.044
Ru	0.219
Se	0.004
Si	0.995
Te	0.049
Zn	0.260
Zr	0.136
CO ₃ ⁻²	4.005
NO ₃ ⁻¹	3.115
NO ₂ ⁻¹	3.020
PO ₄ ⁻²	0.005
SO ₄ ⁻²	0.752
Cl ⁻	1.095
F ⁻	0.108
I ⁻	0.019
Density (g/mL)	1.100
pH	12.500
Total Solids (wt% wet)	13.800
Total Organic Carbon	0.050

TABLE 2. SUMMARY OF BENCH-SCALE SCOPING EXPERIMENTS

Effect of HNO₃ Addition

<u>HNO₃, g-mol/l'</u>	<u>Hg, wt%</u>	<u>PHA, gpm</u>	<u>H₂, lb/hr^a</u>
1.06	0	12 - 14	0.23
0.70	0	12 - 14	0.08
0.45	0	12 - 14	0.04

Effect of Hg Content of Sludge

<u>HNO₃, g-mol/lb</u>	<u>Hg, wt%</u>	<u>PHA, gpm</u>	<u>H₂, lb/hr^a</u>
0.70	0	12 - 14	0.08
0.70	3.5	12 - 14	0.55

Effect of PHA Addition Rate

<u>HNO₃, g-mol/lb</u>	<u>Hg, wt%</u>	<u>PHA, gpm</u>	<u>H₂, lb/hr^a</u>
0.70	3.5	12 - 14	0.55
0.70	3.5	2.6	0.20

Effect of Source of PHA

<u>HNO₃, g-mol/lb</u>	<u>Hg, wt%</u>	<u>PHA, gpm</u>	<u>PHA Source</u>	<u>H₂, lb/hr^a</u>
0.70	3.5	12 - 14	Unirradiated ^b	0.55
0.70	3.5	12 - 14	Irradiated ^c	0.17

a. DWPF scale, 19 w% sludge solids

b. Unirradiated Late Wash PHA
acid in PHA 0.24 M
formate in PHA 23,400 mg/L
Cu 950 mg/L

c. Irradiated Late Wash PHA
acid in PHA 0.24 M
formate in PHA 18,700 mg/L

Figure 1. pH profile and offgas composition and flowrate profiles during treatment of sludge with nitric acid.

Figure 2. Offgas profiles and sludge pH profile during treatment of an HM sludge (low carbonate, high nitrite) with nitric acid

Figure 3. Off-gas and sludge pH profiles during a PHA cycle.
Sludge did not contain mercury.
0.45 g-mol nitric acid per lb sludge

Figure 4. Effect of mercury and nitric acid on hydrogen generation during PHA cycle. In the presence of 3.5 wt% mercury hydrogen evolved at fairly high rate even when nitric acid was not added at all. Nitric acid increases hydrogen evolution in the presence or absence of mercury.

Peak H₂ rate: (A) 0.55 lb/hr, (B) 0.22 lb/hr
(C) 0.08 lb/hr, (D) 0.008 lb/hr.

PHA evaporation stopped at 800-1000 min. following by reflux at boiling.

Figure 5. Effect of nitric acid on hydrogen evolution rates. Sludge simulant did not contain mercury. PHA contained 0.24 M acid and 23,400 mg/L formate.

Figure 6. Effect of PHA source. PHA produced from irradiated and washed precipitate slurry and from unirradiated precipitate slurry. (0.70 g-mole nitric acid/lb sludge in both cases)

Peak H₂ rate: unirradiated PHA, 0.55 lb/hr
irradiated PHA, 0.16 lb/hr.

Figure 7. Effect of PHA addition/evaporation rate on hydrogen generation.
Peak H₂ evolution rate: (A) 0.55 lb/hr
(B) 0.20 lb/hr

Figure 8. pH profiles of four runs. The graph shows that in the presence of active catalysts, higher pH could result from larger amount of acid added.

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