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**AMMONIA EMISSION PROJECTIONS FOR DWPF RECYCLE  
DURING MACROBATCH 3 CAMPAIGN (U)**

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A. S. Choi

**Savannah River Technology Center  
Westinghouse Savannah River Company  
Aiken, SC 29808**

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**APPROVALS**

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A. S. Choi, Author  
Process Development – Hanford RPP, ITS/SRTC

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Date

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J. R. Zamecnik, Technical Reviewer  
Process Development – Hanford RPP, ITS/SRTC

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Date

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D. A. Crowley, Manager  
Process Development – Hanford RPP, ITS/SRTC

---

Date

---

E. W. Holtzscheiter, Manager  
Immobilization Technology Section (ITS)/SRTC

---

Date

## SUMMARY

The expected concentration of ammonia in the DWPF liquid recycle during the Macrobatch 3 campaign was estimated using the CPES model. The resulting projections are:

- 130 ppm  $\text{NH}_4^+$  in the SMECT transfer to the RCT
- 22 ppm aqueous  $\text{NH}_3$  in the RCT transfer to the Tank Farm.

The generation of hydrogen and ammonia during the SRAT/SME cycles was modeled using the same chemistry bases that have been used in all previous CPES model runs made since 1993. In this study, however, the current model basis for calculating the total ammonia production during a coupled operation was reformulated into a more useful form equally applicable to a sludge-only operation as well. The ammonia projections given above were calculated using this new basis: 0.1 mole ammonia per mole of formic acid added.

The composition of the Macrobatch 3 feed for the model run was developed from recent analytical data for the Tank 40 samples that were washed to 0.565 molar Na during the acceptance evaluation test in the SRTC's Shielded Cells. The total acid requirement for the Macrobatch 3 sludge and subsequent partitioning of the total acid between formic and nitric acids were calculated in the model according to the current DWPF blending scheme to achieve the glass iron redox ratio of ~0.22 with no addition of formic acid to the SME.

## INTRODUCTION

Much of the settled sludge in Tank 8 was slurried up and transferred to Tank 40, where it was blended with the existing Tank 40 sludge inventory, thus forming Macrobatch 3 feed for the Defense Waste Processing Facility (DWPF). Prior to feeding to DWPF, samples of the macrobatch 3 sludge slurry were sent to SRTC for the acceptance evaluation tests in the Shielded Cells.<sup>1</sup> The as-received samples contained 1.86 M sodium (Na) and were washed to 0.565 M before the Sludge Receipt and Adjustment Tank (SRAT) processing. The washing endpoint of 0.565 M Na used by the Savannah River Technology Center (SRTC) personnel was set a little higher than the actual Tank Farm target of 0.5 M Na as a conservative measure. This is because more free acids would be required to neutralize and reduce appropriate sludge constituents present at higher concentrations, which would in turn result in a greater quantity of excess formic acid and, therefore, higher generation rates of flammable gases such as  $\text{H}_2$  and  $\text{NH}_3$ .

The results of the SRTC acceptance tests, however, showed that the measured maximum hydrogen generation rate for the Macrobatch 3 sludge was much less than that for the Macrobatch 2 sludge at comparable noble metal concentrations. One possible explanation for this lower-than-expected hydrogen generation rate would be the fact that excess free acid added to the Macrobatch 3 sludge was less than that added to the Macrobatch 2, i.e., 125 vs. 137% of the stoichiometric requirements, respectively.<sup>2</sup> Similar comparisons could not be made for the ammonia generation, since the SRTC's Shielded Cells are not equipped with the ammonia monitoring system.

Tracking the fate of ammonia is, however, important, since unlike hydrogen a significant quantity of ammonia can remain dissolved in the liquid phase only to be released later under different pH conditions, thus creating a potential for flammability in a tank. One particular flammability concern that DWPF needs to address prior to the startup of the Macrobatches 3 campaign is whether the contents of the Recycle Collection Tank (RCT) would ever reach the lower flammability limit.<sup>3</sup> The primary objective of this study was therefore to provide the projection on the total ammonia concentration in the DWPF liquid recycle to the Tank Farm for an input to such calculations.

## MODEL BASES

All the key bases and assumptions used in the CPES model to calculate the concentration of ammonia in the liquid recycle during the Macrobatches 3 campaign are described next.

### Tank 40 Composition

Available analytical data for the SRTC washed Tank 40 sludge slurry and supernate were used to develop the composition of the Macrobatches 3 sludge feed to the SRAT shown in Table 1.<sup>1,4</sup> The concentrations of some of the important radionuclides such as Cs, Sr, Tc and Pu were determined by adding all the isotopic data given in wt% dried sludge slurry.<sup>5</sup> Despite their negligible impact on the overall slurry properties, most of the remaining trace-level radionuclides were still included either as Group A (soluble) or Group B (insoluble), each at a prescribed wt% distribution.<sup>6</sup> The concentrations of Group A and Group B given in Table 1 are the same as those used in the earlier CPES runs made in support of the HLW System Plan Revision 9.<sup>7</sup>

The as-given analytical data for the supernate phase showed a charge imbalance of close to 20%.<sup>4</sup> As a result, the concentration of free hydroxide was adjusted by 240% from the given value of 0.038 M to 0.131 M to achieve the charge balance. The resulting Tank 40 sludge composition used in the model run included 36 g of soluble solids and 188 g of insoluble solids per liter of slurry. These soluble and insoluble solids concentrations are approximately 5% lower and 12% higher than their respective values calculated using the bulk slurry data such as density and wt% solids given in Table 2 of Reference 1. It is estimated that ~27% of the total sodium in Tank 40 is insoluble and represented as Na<sub>2</sub>O in Table 1. The analytical data also showed that ~60% of total inorganic carbon (TIC) is in insoluble carbonate form, while 17% of the total aluminum exists as soluble aluminate.

### Acid Addition

In DWPF, the stoichiometric acid requirement for each SRAT batch is calculated as:<sup>8</sup>

$$\begin{aligned}
 & \text{DWPF stoichiometric moles acid required} \\
 & = 1.2 * [MnO_2] + 0.75 * [NO_2^-] + [HgO] + 2 * [CO_3^{-2}] + [OH^-] \quad (1)
 \end{aligned}$$

**TABLE 1. Composition of Tank 40 Sludge Slurry Washed to 0.565 M Na.**

| Solubles     | Mole/L SN  | g/L slurry | Insolubles | mole/L slurry | g/L slurry |
|--------------|------------|------------|------------|---------------|------------|
| NaNO2        | 1.6400E-01 | 1.0458E+01 | Fe(OH)3    | 8.7081E-01    | 9.3046E+01 |
| NaNO3        | 7.5400E-02 | 5.9230E+00 | Al(OH)3    | 3.6549E-01    | 2.8511E+01 |
| NaOH         | 1.3128E-01 | 4.8614E+00 | MnO2       | 1.2041E-01    | 1.0468E+01 |
| Na2SO4       | 1.1200E-02 | 1.4702E+00 | CaCO3      | 4.9037E-02    | 4.9077E+00 |
| Na2C2O4      | 7.3500E-03 | 9.1021E-01 | U3O8       | 2.1957E-02    | 1.8490E+01 |
| NaCOOH       | 7.4900E-04 | 4.7069E-02 | Mg(OH)2    | 1.5598E-01    | 9.0952E+00 |
| NaAl(OH)4    | 8.1406E-02 | 8.8774E+00 | HgO        | 2.0034E-03    | 4.3391E-01 |
| NaF          | 3.9400E-03 | 1.5289E-01 | Ca3(PO4)2  | 2.1024E-02    | 6.5211E+00 |
| NaCl         | 3.9600E-04 | 2.1388E-02 | Ni(OH)2    | 4.1771E-02    | 3.8721E+00 |
| Na2CO3       | 3.4398E-02 | 3.3696E+00 | Cr(OH)3    | 5.8834E-03    | 6.0611E-01 |
| Ba(OH)2      | 0          | 0          | Cu(OH)2    | 1.4431E-03    | 1.4077E-01 |
| Ca(OH)2      | 1.3540E-05 | 9.2695E-04 | TiO2       | 7.8732E-04    | 6.2907E-02 |
| CsOH         | 5.3691E-06 | 7.4380E-04 | SiO2       | 8.7172E-02    | 5.2382E+00 |
| Group A*     | N/A        | 9.2942E-03 | Na2O       | 8.8517E-02    | 5.4863E+00 |
| Group B*     | N/A        | 2.2463E-05 | ThO2       | 0             | 0          |
| KOH          | 0          | 0          | Zn(OH)2    | 0             | 0          |
| NH4OH        | 0          | 0          | PuO2       | 1.1522E-04    | 3.1213E-02 |
| Na2CrO4      | 3.6696E-04 | 5.4930E-02 | RuO2       | 6.7694E-04    | 9.0081E-02 |
| Na2B4O7      | 4.1000E-06 | 7.6251E-04 | RhO2       | 1.5560E-04    | 2.0991E-02 |
| Na2MoO4      | 1.3500E-05 | 2.5691E-03 | PdO        | 1.7141E-05    | 2.0981E-03 |
| Na2RhO4      | 0          | 0          | Ag2O       | 1.0059E-04    | 2.3311E-02 |
| Na2RuO4      | 0          | 0          | SrCO3      | 7.7615E-05    | 1.1458E-02 |
| Na2SiO3      | 1.4170E-04 | 1.5986E-02 | BaSO4      | 5.5223E-04    | 1.2888E-01 |
| Na3PO4       | 2.9601E-04 | 4.4849E-02 | PbCO3      | 8.5237E-04    | 2.2775E-01 |
| NaAg(OH)2    | 1.4309E-06 | 2.1801E-04 | TcO2       | 1.5419E-05    | 2.0184E-03 |
| NaI          | 0          | 0          | Group A    | 0             | 0          |
| NaTcO4       | 0          | 0          | Group B    | 0             | 0          |
| Na2PuO2(OH)4 | 0          | 0          | CaSO4      | 0             | 0          |
| Pd(NO3)2     | 0          | 0          | CaCO3(14)  | 2.4705E-09    | 2.4730E-07 |
| Sr(OH)2      | 0          | 0          | CaF2       | 0             | 0          |
| UO2(OH)2     | 1.5185E-05 | 4.2666E-03 | CaO        | 8.1958E-03    | 4.5962E-01 |
| H2O          |            | 9.1392E+02 | CaC2O4     | 0             | 0          |
| Total        |            | 9.5015E+02 | Total      |               | 1.8788E+02 |

where all concentrations are given in terms of total number of moles in one SRAT batch. Each of the first three terms of Eq. (1) represents the number of moles of acid required to reduce each respective species shown to a target completion, while the latter two terms represent the number of moles of acid required to completely neutralize carbonate or hydroxide. In the CPES model, additional neutralization reactions besides those included in Eq. (1) are allowed, most notably of aluminate and oxalate. So, the stoichiometric acid requirement used in the CPES model was calculated as:

$$\begin{aligned} & \text{CPES stoichiometric moles acid required} \\ & = \text{DWPf stoichiometric moles acid required} + [AlO_2^-] + 2 * [C_2O_4^{-2}] \end{aligned} \quad (2)$$

Finally, the total acid addition to each SRAT batch was calculated at 125% of the CPES stoichiometric acid requirement:

$$\text{Total acid addition} = 1.25 * \text{CPES stoichiometric moles acid required} \quad (3)$$

The total acid addition calculated from Eq. (3) was then split between formic and nitric acids at a ratio of 83.35 mol% : 16.65 mol% according to the DWPF spreadsheet results tailored to achieve the target glass redox ratio,  $Fe^{+2}/Fe^{total}$ , of ~0.22.<sup>8</sup> The concentrations of formic and nitric acids used in the model were 90 and 50 wt%, respectively.

### SME Blending

The amount of Frit 200 to be added during the Slurry Mix Evaporator (SME) cycle was calculated to be 330 grams per 722 ml of Macrobatch 3 SRAT product for the Shielded Cells runs.<sup>9</sup> The corresponding sludge loading in the Macrobatch 3 glass is 27.73 wt%, which was subsequently used in the CPES model. The addition of free formic acid to the SME was calculated by trial-and-error to satisfy the following glass iron redox ratio:<sup>10</sup>

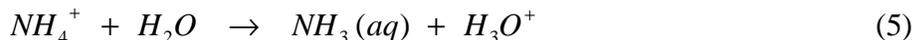
$$\frac{Fe^{+2}}{Fe^{total}} = 0.217 + 0.253[COOH^{-}] - 0.739[NO_3^{-}] \approx 0.22 \quad (4)$$

where the concentrations are in molar.

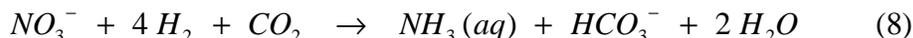
### Hydrogen and Ammonia Source Terms in Chemical Cell

The current bases for the hydrogen and ammonia source terms during the SRAT/SME cycles were derived from the limited data obtained during the Integrated DWPF Melter System (IDMS) coupled flowsheet runs.<sup>11</sup> Specifically, the ammonium balance of the PX4 run data showed that when the precipitate hydrolysis aqueous (PHA) feed did not contain ammonium ion, the total quantity of ammonia produced during one SRAT cycle was about 1.74E-4 lbmole per gallon of PHA added at 0.2 M total acid. When the PHA feed contained ammonium ion during HM4 and PX5 runs, the net production of ammonia was found to be minimal.

Based on these limited IDMS data, the generation of ammonia during a coupled operation is described in the CPES model to follow two different paths.<sup>6</sup> First, when the PHA feed contains ammonium ion, ammonia is produced simply by the decomposition alone:



However, when the PHA feed does not contain ammonium ion, ammonia is generated by the reduction of nitrate by  $H_2$ :



The catalytic decomposition of formate in the presence of  $H^+$  by Reaction (6) is the primary source term for hydrogen, and the subsequent reduction of nitrate by Reaction (8) to produce ammonia is indeed consistent with the earlier bench-scale data;<sup>12</sup> when the PHA feed contained no ammonium ion, the production of ammonia or ammonium ion closely followed the production of hydrogen. The same bench-scale data also showed that ammonium ions were generated during the SRAT/SME cycles when the noble-metal containing sludge was treated with either formic acid or nitric acid/late-washed PHA. This means that the same hydrogen and ammonia generation schemes as described by Reactions (6) to (8) for a coupled operation would also apply to the Macrobatch 3 sludge-only operation, where the PHA feed is effectively substituted by the addition of formic acid. This was not unexpected, since the PHA is essentially a dilute formic acid solution containing several organic and inorganic salts at low concentrations.

The current CPES model basis for the ammonia production during a coupled operation is that regardless of whether the PHA contains ammonium ion or not, the total quantity of ammonia produced during one SRAT cycle is  $1.74E-4$  lbmole per gallon of PHA added at 0.2 molar total acid. Based on the findings of the bench-scale run,<sup>12</sup> this ammonia production basis can now be cast into a more useful form that is universally applicable to both coupled and sludge-only operations:

$$\left( \frac{1.74 E - 4 \text{ lbmole } NH_3}{\text{gal PHA}} \right) \left( \frac{453.6 \text{ gmole } NH_3}{\text{lbmole } NH_3} \right) \left( \frac{\text{gal PHA}}{3.785 \text{ L PHA}} \right) \left( \frac{\text{L PHA}}{0.2 \text{ gmole HCOOH}} \right)$$

$$= \frac{0.104 \text{ gmole } NH_3}{\text{gmole HCOOH}}$$

The reformulated ammonia production basis says that whether formic acid is contained in the PHA or added as a cold chemical, about one-tenth of formic acid present would be converted into ammonia during a SRAT cycle. The ammonia production during the Macrobatch 3 sludge-only operation was modeled using this reformulated basis. It is assumed in the CPES model that 40% of ammonia thus produced would be released later during the SME cycle; however, the net ammonia production during the SME cycle continues to be set at zero.

The maximum hydrogen production during the SRAT/SME cycles in the Shielded Cells was estimated to be less than 0.32 lb or 12% of the design basis value of 2.67 lb. Despite this lower-than-expected hydrogen production during the acceptance evaluation test, the target hydrogen production rate for the Macrobatch 3 CPES model run was set right at the design basis value, as in all previous model runs.<sup>6</sup> The model also assumes that 75% of the total hydrogen produced or 2 lb would be released during the SRAT cycle, while the remaining 25% or 0.67 lb released during the SME cycle. Setting the target hydrogen production rate high at the design basis value should not affect the ammonia source term, as long as a sufficient quantity of formic acid remains after the completion of acid/base and redox reactions.

## MODEL RESULTS

The CPES model was run on a VAXstation 4000 with the Macrobatches 3 input discussed earlier. Since the simulation is concerned only with processing washed sludge through the DWPF canyon, it took only 1 ½ CPU hours to achieve the convergence within a prescribed tolerance. Some of the key results of Macrobatches 3 simulation included that:

- The instantaneous sludge feed rate required to meet the design basis glass production rate of 228 lb/hr is 0.77 GPM at 19.6 wt% total solids or 4,000 gallons per 86-hour SRAT cycle.
- The formic acid addition to the SRAT is 157 gallons per 4,000 gallon sludge batch.
- The nitric acid addition to the SRAT is 77 gallons per 4,000 gallon sludge batch.
- The total ammonia production in the SRAT was 4.4 lb per 4,000 gallon sludge batch.
- The SMECT liquid transfer to the RCT includes  $\text{NH}_4^+$  at 130 ppm.
- The final RCT content after adjustments includes aqueous  $\text{NH}_3$  at 22 ppm.
- Under the conditions assumed in this Macrobatches 3 flowsheet simulation, the required formic acid addition to the SME product to maintain the target glass iron redox ratio of 0.22 was calculated to be less than 1 gallon per 4,000 gallon sludge batch, which is in essence consistent with the current DWPF blending scheme.

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