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# Key Results from SB8 Simulant Flowsheet Studies

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# EXECUTIVE SUMMARY

Key technically reviewed results are presented here in support of the Defense Waste Processing Facility (DWPF) acceptance of Sludge Batch 8 (SB8). This report summarizes results from simulant flowsheet studies of the DWPF Chemical Process Cell (CPC). Results include:

- Hydrogen generation rate for the Sludge Receipt and Adjustment Tank (SRAT) and Slurry Mix Evaporator (SME) cycles of the CPC on a 6,000 gallon basis.
- Volume percent of nitrous oxide, $N_2O$, produced during the SRAT cycle.
- Ammonium ion concentrations recovered from the SRAT and SME off-gas.
- Dried weight percent solids (insoluble, soluble, and total) measurements and density.

These items relate to Safety Class (SC) items in HLW-TTR-2012-0004, Rev. 0 as called out in an attachment, a copy of which can be found in Appendix A.

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| | |
|---|---|
| ARP | Actinide Removal Process |
| CPC | Chemical Process Cell |
| DWPF | Defense Waste Processing Facility |
| GC | Gas Chromatograph |
| MCU | Modular Caustic-side solvent extraction Unit |
| MWWT | Mercury Water Wash Tank |
| SB | Sludge Batch, e.g. SB7b, SB8 |
| SC | Safety Class |
| SME | Slurry Mix Evaporator |
| SMECT | Slurry Mix Evaporator Condensate Tank |
| SRAT | Sludge Receipt and Adjustment Tank |
| SRNL | Savannah River National Laboratory |
| TTR | Task Technical Request |
| TTQAP | Task Technical & Quality Assurance Plan |

# 1.0 Introduction

This brief report summarizes key quantities needed by DWPF to support documentation related to Safety Class (SC) items in their Sludge Batch 8 (SB8) acceptance paperwork. The work was authorized by a Technical Task Request[1] and performed by Savannah River National Laboratory (SRNL) under a Task Technical and Quality Assurance Plan (TTQAP)[2]. A complete description of experimental methods and flowsheet study findings will be reported in SRNL-STI-2013-00106[3]. Details of simulant preparation and lab-scale process simulations were recorded in controlled laboratory notebooks SRNL-NB-2012-00108 and -00110.

# 2.0 Results and Discussion

Key SB8 starting simulant properties are given in Table 2-1. Key properties include wt.% total, soluble, and insoluble solids along with density. The simulant was pre-concentrated by caustic boiling prior to acid addition in the SRAT cycle to 18.7 wt.% total solids. The concentrated slurry was selected as the scaling basis (concentrated simulant was set equivalent to 6000 gallons of fresh sludge from Tank 40; that is, 3,300 g at 18.7 wt% total solids and a density of 1.16 g/mL was assumed equivalent to 6,000 gallons of fresh sludge in the DWPF SRAT with no constraint on whether the 6,000 gallons fresh sludge were actually some larger volume that had been caustic concentrated down to 6,000 gallons as long as the wt.% total solids was not increased above 18.7 wt.% total solids on a heel-free basis.).

**Table 2-1. SB8-Tank 40 Simulant Properties**

| | SB8-Tank 40 |
|---|---|
| Wt.% total solids | 16.5 |
| Wt. % insoluble solids | 9.0 |
| Wt. % soluble solids | 7.5 |
| Wt. % calcined solids | 12.6 |
| Slurry density, g/mL | 1.138 |
| Supernate density, g/mL | 1.066 |

Five flowsheet simulations were performed (different acid stoichiometries and trim chemicals). Runs D1-D4 were sludge-only flowsheet tests while D5 used the coupled flowsheet. Table 2-2 gives a brief summary of the five runs, the acid stoichiometry and flowsheet used, and the weight percent mercury in the trimmed starting sludge (on a wt. % dried solids basis).

**Table 2-2. Mercury Concentrations and Process Demonstration Information**

| Run ID | Flowsheet | Stoich.-KMA | Stoich.-DWPF | Wt% Hg-sludge |
|---|---|---|---|---|
| D1 | Sludge-only | 105% | 110% | 2.142 |
| D2 | Sludge-only | 140% | 147% | 2.142 |
| D3 | Sludge-only | 120% | 126% | 1.638 |
| D4 | Sludge-only | 140% | 147% | 1.250 |
| D5 | Coupled | 120% | 125% | 1.638 |

Table 2-3 gives the noble metal concentrations as wt.% on a dried solids basis in the SB8-Tank 40 starting sludge simulant used in all five runs (including the coupled flowsheet run). No noble metals were trimmed into the Actinide Removal Process slurry that made up a small portion of the coupled flowsheet CPC simulation feed, since it is essentially free of sludge solids.

**Table 2-3. Noble metal concentration for SB8-Tank 40**

| | SB8-Tank 40 Blend wt. % |
|---|---|
| Ag | 0.0164 |
| Pd | 0.0034 |
| Rh | 0.0175 |
| Ru | 0.0830 |

Table 2-4 presents the solids and density results for the five SRAT products.

**Table 2-4. SRAT Product Properties**

| | D1 | D2 | D3 | D4 | D5 |
|---|---|---|---|---|---|
| Wt. % total solids | 27.30 | 27.20 | 27.43 | 27.36 | 29.69 |
| Wt. % dissolved solids[1] | 15.85 | 17.50 | 16.78 | 17.77 | 18.92 |
| Wt. % insoluble solids[2] | 13.60 | 11.80 | 12.81 | 11.67 | 13.29 |
| Wt. % soluble solids[2] | 13.70 | 13.45 | 14.63 | 15.69 | 16.40 |
| Wt. % calcined solids | 17.25 | 16.55 | 17.28 | 16.71 | 18.30 |
| Slurry density, g/mL | 1.203 | 1.208 | 1.203 | 1.213 | 1.232 |
| Supernate density, g/mL | 1.108 | 1.123 | 1.112 | 1.124 | 1.134 |
| Slurry pH | 7.92 | 6.10 | 7.56 | 5.68 | 6.67 |

1 – dissolved solids are the non-water, non-volatile species on an aqueous phase mass basis
2 – insoluble and soluble solids are calculated from the measured total and dissolved solids

Table 2-5 contains the corresponding data for the five SME products.

**Table 2-5. SME Product Properties**

| | D1 | D2 | D3 | D4 | D5 |
|---|---|---|---|---|---|
| Wt. % total solids | 51.67 | 50.17 | 50.68 | 51.55 | 55.46 |
| Wt. % dissolved solids[1] | 19.81 | 19.35 | 20.38 | 20.27 | 24.05 |
| Wt. % insoluble solids[2] | 39.72 | 38.22 | 38.06 | 39.23 | 41.35 |
| Wt. % soluble solids[2] | 11.94 | 11.95 | 12.63 | 12.32 | 14.11 |
| Wt. % calcined solids | 42.91 | 40.80 | 41.84 | 42.42 | 45.55 |
| Slurry density, g/mL | 1.420 | 1.387 | 1.399 | 1.354[3] | 1.484 |
| Supernate density, g/mL | 1.136 | 1.136 | 1.140 | 1.141 | 1.172 |
| Slurry pH | 7.60 | 6.57 | 7.44 | 6.64 | 6.78 |

1 – dissolved solids are the non-water, non-volatile species on an aqueous phase basis
2 – insoluble and soluble solids are calculated from the measured total and dissolved solids
3 – this slurry density result is somewhat suspicious (low)

Approximate changes in major anions during processing were calculated from material balances coupled with analytical results, Table 2-6.

**Table 2-6. Changes in Major Anions**

| | D1 | D2 | D3 | D4 | D5 |
|---|---|---|---|---|---|
| KMA factor | 105% | 140% | 120% | 140% | 120% |
| | SRAT | SRAT | SRAT | SRAT | SRAT |
| Formate Loss | 22% | 37% | 34% | 33% | 28% |
| Nitrite Loss | 100% | 100% | 100% | 100% | 100% |
| Nitrite-to-nitrate | 26% | 2% | 9% | 5% | 8% |
| | SME | SME | SME | SME | SME |
| Formate Loss | 11% | 7% | 6% | 9% | 2% |
| Nitrate Loss | 11% | 4% | 3% | 6% | 1% |

Individual calculated values for SRAT formate loss, SRAT nitrite-to-nitrate conversion, and SME losses have been shown to have only about one significant figure.[4]

The SRAT cycle hydrogen generation rate at DWPF scale is plotted as a function of time relative to the end of formic acid addition in Figure 1. The DWPF limit for the SRAT is 0.65 lbs hydrogen/hour. Gas mass flowrate calculations were performed per equation 2 in WSRC-STI-2008-00131.[4]

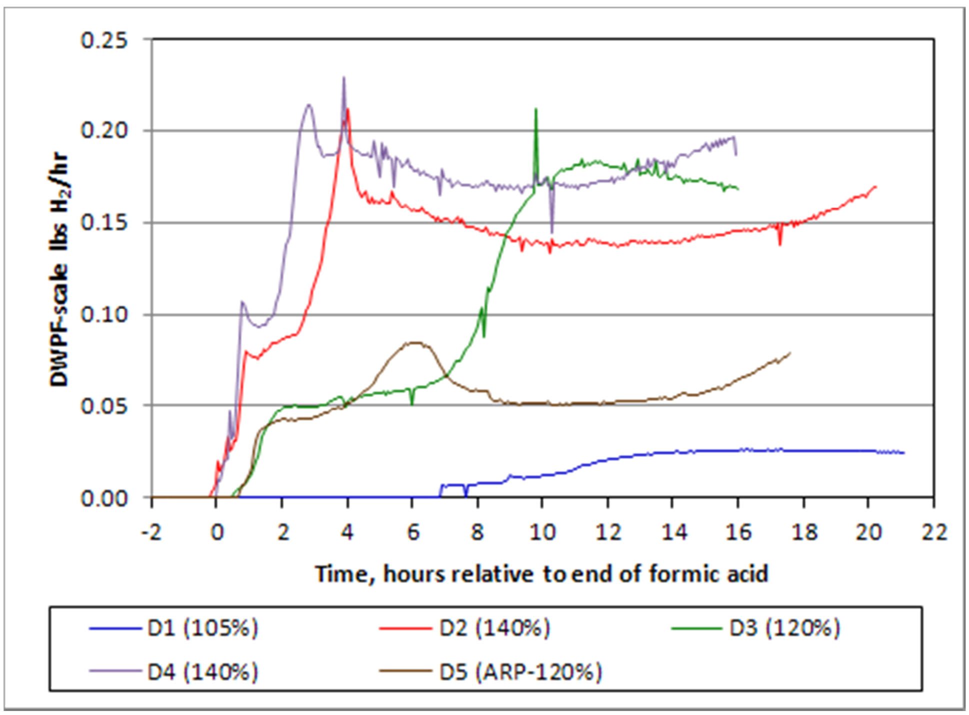


**Figure 1. SRAT cycle hydrogen generation rates at DWPF scale**

The SME cycle hydrogen generation rates are presented in Figure 2.

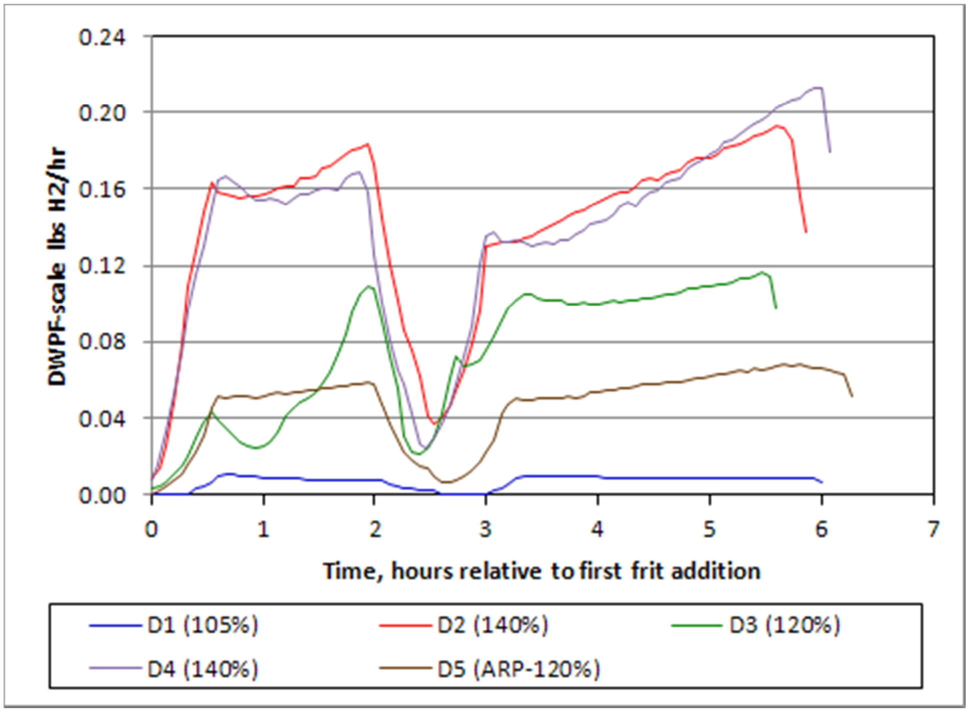


**Figure 2. SME cycle hydrogen generation rates at DWPF scale**

The DWPF limit for the SME cycle is 0.223 lbs hydrogen/hour. The DWPF limit was approached quite closely in the two runs at 140% stoichiometry (Koopman Minimum Acid eqn., or 147% Hsu acid eqn.) just as the heat was turned off to end the SME cycle. Maximum hydrogen generation rates for the five SRAT and SME cycles are given numerically in Table 2-7 on a DWPF scale basis.

**Table 2-7. SRAT and SME Maximum Hydrogen Generation Rate**

| | D1 | D2 | D3 | D4 | D5 |
|---|---|---|---|---|---|
| SRAT, DWPF-scale lbs $H_2$/hr | 0.027 | 0.21 | 0.21 | 0.23 | 0.085 |
| SME, DWPF-scale lbs $H_2$/hr | 0.011 | 0.19 | 0.12 | 0.21 | 0.068 |

Nitrous oxide generation rates were only about half that seen in SB7b simulant testing. This occurred with complete nitrite destruction combined with some nitrate destruction during the SB8 tests. Simulant nitrite is relatively closely matched to projected actual waste nitrite, so a reduction in $N_2O$ generation may also be seen in DWPF after transitioning to SB8. Peak $N_2O$ generation rates remained below 15 lb/hr at DWPF scale in the five tests. The SB8 coupled flowsheet run, D5, produced more $N_2O$ than the four sludge-only runs. The maximum volume percent of $N_2O$ was observed in D5 at 0.88%. The D5 SRAT produced 53 pounds of $N_2O$ at DWPF scale, and the (relatively short) SME cycle produced an additional 4 pounds during six hours of processing. Assuming 60 pounds in the SRAT and 40 pounds in the SME (60 hours processing with no loss in rate should be conservative for the DWPF SME cycle), gives 100 pounds of $N_2O$ for one SRAT-SME cycle as a very conservative estimate. At a basis of 47 SRAT cycles per year of this size to meet a canister production target of 275/year, this equates to 4,700 pounds of $N_2O$ per year (2.35 tons) which is trivial compared to the DWPF annual production rate WAC limit of 103.5 tons $NO_x$/year.

Decomposition of nitrate ion can lead to ammonium ion formation. In the SB8 flowsheet runs, the ammonia scrubber solution was sampled following the SRAT and again following the SME cycle to check for captured ammonium ion. Table 2-8 below shows the amount of ammonium ion found in the equivalent of approximately 1,600 gallons of SMECT condensate. The result after the SME cycle includes the ammonium collected during the SRAT cycle (is part SRAT ammonium plus part new ammonium ion recovery).

**Table 2-8. Ammonium ion recovery in the SMECT**

| | After SRAT, mg/L | After SME, mg/L |
|---|---|---|
| D1 | 9 | 11 |
| D2 | <5 | <5 |
| D3 | 31 | 40 |
| D4 | <5 | <5 |
| D5 | <1 | <1 |

These data, combined with observations of $N_2O$ generation throughout the SME cycle, suggest that ammonium ion formation was being inhibited, and formation of gaseous nitrogen oxides promoted, compared to other recent DWPF sludge batches.

## 3.0 Recommendations

DWPF should begin SB8 processing by targeting 115-120% stoichiometry by the current DWPF acid equation (Hsu equation) for the initial SRAT batches.

DWPF should initially assume 30-35% formate loss in the SRAT cycle and a 5-10% gain in nitrate ion from conversion of nitrite to nitrate. Extended SRAT processing time (from lower steaming rates) could increase formate loss and reduce nitrate gain (increase nitrate loss). SME formate losses could be in the neighborhood of 1% per hour at boiling, while SME nitrate losses could be 0.5% per hour. (The effects of long SME boiling time durations would need to studied further before better recommendations could be made.)

After the initial SB8 SRAT batches, DWPF should still constrain processing of SB8 to 110-126% of the DWPF acid equation due to uncertainties in the inputs to the stoichiometric acid equation and potential unknowns in the ARP slurry and MCU (strip effluent) stream as well as the hydrogen generation rate tendencies in the upper half of the processing window simulated (126-147% of DWPF acid equation). DWPF processing experience with early SB8 SRAT/SME batches can be used as a guide to moving toward higher acid stoichiometries if this seems necessary due to processing issues.

Higher wt.% total solids targets for SB8 processing should be used to counter the lower insoluble solids fractions in SB8 feed due to the higher molarity sodium wash endpoint. These higher wt.% solids levels will be necessary to produce reasonable yield stress slurries and achieve DWPF canister production goals with minimal caustic pre-concentration times. The higher total solids targets will apply to the incoming sludge, SRAT product, and SME product, but especially in the SME cycle where frit must stay suspended.. Soluble solids are projected to account for 5-6 wt.% of the feed slurry compared to ~3% in SB1. The Tank Farm is projecting 17.2 wt.% total solids in their SB8-Tank 40 estimate of 4/22/2013 which are divided into 11.6% insoluble solids and 5.6% soluble solids (vs. 9.5% and 4.3% at the end of SB7b).

The current DWPF WAC limit for $NO_x$ production will suffice for SB8.

## 4.0 References

[1] Bricker, J. M., *Sludge Batch 8 Flowsheet Studies*, HLW-DWPF-TTR-2012-0004, December 6, 2011.

[2] Newell, J. D., *Task Technical and Quality Assurance Plan for Sludge Batch 8 Simulant Flowsheet Studies*, SRNL-RP-2011-01679, SRNL, Aiken, SC, 29808 (December 2011).

[3] Koopman, D. C., *DWPF Simulant Flowsheet Studies for SB8*, SRNL-STI-2013-00106, SRNL, Aiken, SC, 29808 (May 2013).

[4] Koopman, D. C., D. R. Best, and B. R. Pickenheim, *SRAT Chemistry and Acid Consumption during Simulated DWPF Melter Feed Preparation*, WSRC-TR-2008-00131, SRNL, Aiken, SC, 29808 (December 2008).

# Appendix A
## Clarification of Safety Class Items for TTR

Attachment 1 per e-mail for HLW-DWPF-TTR-2012-0004, Revision 0.

Clarification of Safety Class (SC) items for HLW-DWPF-TTR-2012-0004, Revision 0

Data used to Evaluate DWPF Technical Safety Requirement (TSR) Safety Administrative Controls (SACs) 5.8.2.11 and 5.8.2.25

- Dried weight percent solids (soluble, insoluble, and total) measurements and Density
- Hydrogen Generation/Nitrous Oxide Concentration: Hydrogen generation rate for SRAT and SME on 6000 gallon basis. Volume percent of nitrous oxide produced during the SRAT cycle.
- Ammonium concentration for the condensate generated from the SRAT and SME

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