Increased CPC Batch Size Study for Tank 42 Sludge in the Defense Waste Processing Facility

by

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**INCREASED CHEMICAL PROCESS CELL (CPC) BATCH SIZE STUDY FOR TANK 42
SLUDGE IN THE DEFENSE WASTE PROCESSING FACILITY (DWPF) (U)**

A series of experiments have been completed at TNX for the sludge-only REDOX adjusted flowsheet using Tank 42 sludge simulant in response to the Technical Task Request HLW/DWPT/TTR-980013 to increase CPC batch sizes. By increasing the initial SRAT batch size, a melter feed batch at greater waste solids concentration can be prepared and thus increase melter output per batch by about one canister. The increased throughput would allow DWPF to dispose of more waste in a given time period thus shortening the overall campaign.

For the bench-scale experiments performed, hydrogen generation exceeds DWPF limits only when too much acid (340%) is added. Nitrite destruction may be a problem for a nominal acid addition of 155%. The required acid stoichiometry appears to be between 155% and 170%. The absence of an initial acid addition before concentrating (Pre-Boiling Acid Addition) does not appear to present any processing problems. However, because of the small scale of these experiments, potential problems such as mixing and/or heat transfer could not be quantified.

More experiments are necessary to properly quantify the operating conditions for an increased CPC batch but the current evidence does show it is feasible.

If you have additional questions regarding the attached report, please contact W. E. Daniel, 7-7759.

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INCREASED CPC BATCH SIZE STUDY FOR TANK 42 SLUDGE IN THE DEFENSE WASTE PROCESSING FACILITY (DWPF) (U)

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INCREASED CPC BATCH SIZE STUDY FOR TANK 42 SLUDGE IN THE DEFENSE WASTE PROCESSING FACILITY (DWPF) (U)

W. E. Daniel

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EXECUTIVE SUMMARY

A series of experiments have been completed at TNX for the sludge-only REDOX adjusted flowsheet using Tank 42 sludge simulant in response to the Technical Task Request HLW/DWPT/TTR-980013 to increase CPC batch sizes. By increasing the initial SRAT batch size, a melter feed batch at greater waste solids concentration can be prepared and thus increase melter output per batch by about one canister. The increased throughput would allow DWPF to dispose of more waste in a given time period thus shortening the overall campaign. In these experiments the following parameters were varied:

- Wt% Total Solids in Sludge feed: 20% and 22%
- SRAT Heel Volume: 1200 gal and 1500 gal
- Pre-Boiling Acid Addition without measurement/calculation: 133 gal and 0 gal
- Total Stoichiometric Acid Requirement: 340%, 197%, 175%, 170%, and 155%

Hydrogen generation exceeds DWPF limits only when too much acid (340%) is added. Nitrite destruction may be a problem for a nominal acid addition of 155%. The required acid stoichiometry appears to be between 155% and 170%. The absence of an initial acid addition before concentrating (Pre-Boiling Acid Addition) does not appear to present any processing problems. However, because of the small scale of these experiments, potential problems such as mixing and/or heat transfer could not be quantified.

The processing problems observed during the bench scale tests with the increased CPC batch (extra 1000 gal of sludge) are summarized below:

1. Nitrite destruction: Increased acid stoichiometry to compensate. Could boil longer.
2. Keeping slurry well-mixed especially during nitric acid addition: Increased mixing speed to compensate.
3. Pulling samples during SRAT cycle: Slurry very thick so must keep sampler clean to prevent blockage.

Despite these processing problems during the bench scale experiments, it appears DWPF could increase the solids content of a melter feed batch provided:

1. More acid is used (more than 155% but less than 170%)
2. DWPF mixing systems are capable of adequately mixing the higher solids slurry
3. Heat transfer coefficients do not fall below an unacceptable level

More experiments are necessary to properly quantify the operating conditions for an increased CPC batch.

FUTURE WORK

It is recommended that a series of bench-scale runs be completed with a total weight percent solids sludge closer to the current operating point (17 wt-%) and with acid stoichiometries ranging between 155% and 300%. These experiments would narrow the acid addition envelope required for an increased CPC batch operation. Since over acidification may exceed DWPF hydrogen safety limits, it is important to properly characterize the upper end of the acid stoichiometry.

Due to the small scale of the bench-scale experiments, a complete rheological profile of the sludge batch and the potential impact on coil fouling and heat transfer are not readily obtainable. Therefore, it is recommended that a melter feed process simulation at the greater solids content per batch be conducted in the Glass Feed Preparation System (GFPS - 1/240th scale SRAT) at the optimum processing parameters developed in the bench-scale experiments. In the GFPS, a complete profile of the rheological properties of the slurry through out the SRAT/SME cycles may be obtained along with on-line measurement of heat transfer coefficients. In addition, an assessment of (1) the DWPF mixing systems to maintain a homogeneous slurry of the SME product and (2) the Hydraguard sampler's ability obtain a representative sample can be evaluated.

These additional experiments could also be designed to determine why proportionally more acid is needed to destroy nitrite as the batch's weight percent solids increase. Additional research should be done into the basis for the required acid calculation for some unknown variable or variables that are not being taken into consideration.

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BACKGROUND

This work is in response to the DWPF Technical Task Request HLW/DWPT/TTR-980013 for developing strategies for increased CPC batch sizes. The Defense Waste Processing Facility (DWPF) wants to increase the batch sizes in its Chemical Processing Cell (CPC) to increase throughput or glass production per batch. DWPF would like to increase the number of canisters per SME cycle or to increase the SME to MFT batch size. By increasing the CPC batch size, higher melter feed solids can be prepared per batch and thus melter output per batch would increase by about one canister. The increased throughput would allow DWPF to dispose of more waste in a set amount of time thus shortening its overall campaign.

The current sludge batch being processed by DWPF is from Tank 42. Due to delays of In Tank Precipitation (ITP)¹, an alternative sludge-only REDOX adjusted flowsheet has been developed². Testing has been completed that demonstrates that this sludge-only REDOX process is feasible² for Tank 42 sludge. Based on the findings from this study, a series of Large Batch experiments were recommended that use this particular flowsheet.

A non-radioactive sludge simulant of Tank 42 was used for this study. Conservative Tank 42 levels of mercury and noble metals were targeted. The experiments were completed using a Tank 42 simulant prepared by trimming the Tank 51 simulant with aluminum, mercury, nickel, manganese, and noble metals.

This report documents the results from lab scale experiments to examine the technical feasibility of increasing the CPC batch size in DWPF.

INTRODUCTION

The objective of this study was to complete a series of laboratory scale experiments to simulate the SRAT and SME processing conditions for increasing the CPC batch size. DWPF had many concerns about the increased CPC batch process including hydrogen and nitrous oxide generation rates, SRAT coil fouling, the best acid addition strategy for the SRAT, boiling a caustic sludge, and the rheology of materials produced. To address these concerns, the following parameters were monitored during the bench-scale experiments:

- Maximum hydrogen generation rate during the SRAT and SME cycles.
- Maximum nitrous oxide (N₂O) generation rate during the SRAT and SME cycles.
- Minimum time necessary for steam stripping mercury to reach the 0.45 wt% limit in the SRAT product.
- Nitrite destruction rate during the SRAT cycle.
- Any process problems such as foaming, excessive offgas deposits leading to plugging, coil fouling, etc.
- Rheology of SRAT product

¹ D. M. Ferrara, B. C. Ha, D. P. Lambert, and N. E. Bibler, Technical Assessment of a Sludge-only Frit 200 Flowsheet with Copper (U), WSRC-RP-96-142, June 7, 1996.

² D. P. Lambert and C. S. Boley, Alternative Tank 51 Sludge-Only Process Development for the Defense Waste Processing Facility (DWPF) (U), WSRC-RP-97-40, Rev.1, March 13, 1997.

The bench-scale experiments were performed in glassware setup at TNX specifically fabricated to replicate the various DWPF processing vessels. These apparatus can simulate the following DWPF vessels: the Sludge Receipt and Adjustment Tank (SRAT)/ Slurry Mix Evaporator (SME), the SRAT/SME condenser, the Formic Acid Vent Condenser (FAVC), the Mercury Water Wash Tank (MWWT), and the Slurry Mix Evaporator Condensate Tank (SMECT).

After consultation with DWPF, the following strategy was decided upon for experimenting with increasing CPC batch size. A normal sludge transfer of 6000 gallons with 1000 gallons of wash water would be transferred into the SRAT with a 1200 to 1500 gallon heel. Any "Pre-Boiling Acid" would be added at this point, if desired. An arbitrary value of 133 gallons or 2/3 of the standard 200 gallons of 50-wt% nitric was chosen as the "Pre-Boiling Acid" amount. The SRAT volume would then be concentrated down to 6000 gallons by boiling. After this initial concentration, an additional 1000 gallons of sludge would be added to the SRAT and the remaining SRAT operations would take place, i.e. nitric and formic acid addition followed by concentration to 6000 gallons followed by refluxing. The appropriate amount of acid was added to meet the Total Acid Target and the $\text{Fe}^{+2}/\text{Fe}_{\text{total}}$ REDOX target of 0.22. Using this strategy, several bench-scale experiments were planned and carried out as discussed in the next section.

More details about this task can be found in the Task Technical & QA Plan "*Develop Strategy for Increased CPC Batch Size.*"³

³ W. E. Daniel, Develop Strategy for Increased CPC Batch Size, WSRC-RP-98-00354, Rev. 0, July 1, 1998.

DISCUSSION

Variability Experiments

The basic strategy for these bench-scale runs was to reduce the initial SRAT volume so additional sludge could be added and then processed. There were questions about how to add acid, before and/or after the initial concentration of sludge since boiling caustic sludge can lead to thick, gelatinous sludge. There were concerns about how higher weight percent solids could impact the process since the additional sludge would cause total solids to increase more than usual. There were questions about how the SRAT heel may affect the increased CPC batch, i.e. would a larger heel help by acting as a buffer or hurt the process by causing more processing problems. There was concern over what happens if the entire contents of the formic acid tank were emptied into the SRAT. To help answer these questions, a series of bench-scale experiments 1V through 5V were designed as described below.

- 1V. This first run was to be a bounding case where the SRAT sludge weight percent solids was high (22%) and no pre-boiling acid was added to the initial sludge transfer of 6000 gallons. A normal heel of 1500 gallons was assumed from a previous SRAT batch. To satisfy the Total Acid target, a nominal or normal acid addition stoichiometry was planned after the second sludge transfer of 1000 gallons. However, Run 2V was completed first and indicated that 155% stoichiometry was not destroying the nitrite so the value was changed to 197%. This run was to examine processing capabilities for high weight percent sludge with nominal acid addition after initial sludge transfer and concentration. This run was to represent the most expedient processing strategy.
- 2V. The second run was to emulate a normal batch where a nominal weight percent solids sludge (20%) was used with a heel of 1500 gallons. A nominal amount of Pre-Boiling acid (50 wt% nitric acid) was added after the initial sludge transfer of 6000 gallons without any sampling, analyses, or calculations. The Pre-Boiling acid quantity chosen for these experiments was to be 200 gallons based on typical DWPF runs. However, to allow some normal nitric acid addition later in the process, the value was changed to 133 gallons. The goal of this pre-boiling acid was to avoid boiling a caustic sludge, which has a gel-like consistency and can lower the heat transfer. After the second sludge transfer of 1000 gallons, the acid was added to satisfy the 155% stoichiometric total acid target.
- 3V. The third run was to emulate a high acid addition (340% Stoichiometry) with a nominal sludge (20 wt% solids) and a low heel (1200 gallons). This study simulated an over acidification of the sludge assuming all the formic acid feed tank was dumped into the SRAT.
- 4V. The fourth run was to simulate a worst case scenario with low acid addition (137.5%) with a high weight percent solids sludge and a small heel. In addition, the SRAT volume was to be concentrated below its nominal value (less than 6000 gallons). However, based on the observations from earlier experiments (Run 2V and 3V), the post concentration level of the SRAT volume was left at 6000 gallons and the stoichiometry was set at 175% since 155% from Run 2V did not appear to be destroying the nitrite.

5V. The fifth run was to verify the hydrogen production for a typical DWPF batch with 20 wt% solids (considered normal at the start of these experiments but now considered high) and a normal heel (1200 gal). This run was a repeat of Run 4V but with 20-wt% solids sludge and the correct amounts of noble metals.

These runs are summarized in Table I. The first column of Table I shows the run identification while the second column lists the targeted Tank 42 simulant sludge concentration. The third column shows the initial SRAT volume broken down into four component volumes: new sludge, water transferred in with new sludge or other additions, any existing SRAT heel, and the Pre-Boiling Acid or acid added right after the initial sludge transfer without any measurements, samples, or calculations. The next column indicates the SRAT volume after concentration and before reflux. The fifth column shows the amount of additional sludge to transfer into the SRAT after the initial concentration. The last column shows the desired acid requirement in terms of stoichiometric percent to satisfy Total Acid and REDOX targets.

Table I. Large CPC Batch Variability Runs

Run	Tank 42 Sludge Simulant	Initial SRAT Vol.				SRAT Vol. Post Conc.	Add Sludge Post Conc.	Acid Requirement
		Sludge	Water	Heel	Pre- Boiling Acid			
1V	high wt% solids (22%)	8500 gal				6000 gal	1000 gal	197% Stoichiometry*
		6000	1000	1500	0			
2V	normal wt% solids (20%)	8700 gal				6000 gal	1000 gal	155% Stoichiometry
		6000	1000	1500	133*			
3V	normal wt% solids (20%)	8200 gal				6000 gal	1000 gal	340% Stoichiometry
		6000	1000	1200	0			
4V	high wt% solids (22%)	8200 gal				6000 gal*	1000 gal	175% Stoichiometry*
		6000	1000	1200	0			
5V	normal wt% solids (20%)	8200 gal				6000 gal	1000 gal	170% Stoichiometry*
		6000	1000	1200	0			

*Original targets changed based on early experiments and observations

Some of the values in Table I changed from their original specifications due to early experiments and observations. The acid requirement in Run 1V was increased from a targeted 155% to 197% when no evidence of hydrogen was seen in Run 2V. The target acid requirement for Run 4V was increased to 175% since 155% did not seem sufficient for nitrite destruction. After these adjustments it was discovered that the noble metals had been under added in Runs 1V through 4V. This low noble metal addition was one of the reasons for the low hydrogen generation. Another bench-scale run (5V) was done with the correct amount of noble metals to re-examine the hydrogen generation.

During these experiments, slurry pH, offgas hydrogen, N₂O, and CO₂ concentrations, as well as flow rates were measured. Samples were pulled every two hours to monitor the nitrite, nitrate, and formate concentrations in the slurry. The "nominal" sludge used in each of these runs contained approximately 20 wt% solids as at the time this work was done that represented the expected weight percent solids for Tank 42. From current measurements, Tank 42 is closer to 17 wt% solids. Acid additions were based on the total acid to achieve the proper acid stoichiometry. Concentrated formic

acid (90 wt%) and nitric acid (50 wt%) were used during processing. In addition, Dow Corning 544 antifoam was added per the DWPF antifoam strategy (100 ppm on a total solution basis, 1 part antifoam:19 parts water).

All these experiments followed the sludge-only REDOX adjusted flowsheet² where the acid requirement is determined by a correlation developed by Kevin Brown⁴. Although the adjusted REDOX flowsheet was used, REDOX was not to be measured (only predicted) since glass quality was not the target of this investigation. However, [F-N] values are reported to gauge melter feed against past DWPF results. During these experiments the items of concern listed earlier, like H₂ and N₂O generation were monitored, as the results will show.

Experimental Setup and Preparation

Before the Large Batch experiments could begin, a SRAT heel had to be prepared. Details of this SRAT heel preparation for Runs 1V through 4V are contained in Appendix A-1. Due to usage of all the first heel, another heel had to be prepared for Run 5V, which is discussed in Appendix A-2. In summary, the SRAT Heel was created from the Optima Tank 51 simulant trimmed with Tank 42 levels of noble metals and mercury. A 20-weight percent solids sludge was targeted after the addition of trim chemicals (noble metals and mercury). This sludge was referred to as Sludge A' and its pre-trim measured as well as post-trim predicted elemental weight percent analyses are shown in Tables I and II in Appendix A-1 and Table XVIII and Table XIX in Appendix A-2. This sludge required approximately 12 hours of refluxing in the SRAT to steam strip mercury and meet the DWPF constraint of 0.45 wt % mercury.

Details of the large batch variability experiments 2V and 3V are contained in Appendix A-3. Runs 1V and 4V are documented in Appendix A-4. Run 5V is described in Appendix A-5. In summary, a 4-liter glass vessel was used to simulate the SRAT/SME tanks of DWPF. The lab scale setup included a 10°C and a 40°C condenser, a Mercury Water Wash Tank, a cooling dip leg, and a Slurry Mix Evaporator Condensate Tank. The lab scale experiments were performed in 772-T lab at TNX and were scaled at 1/11,355th DWPF size. More details on these experiments are contained in each of the run plans in Appendix A-3 through A-5.

A copy of the Conduct of R&D review is contained in Appendix B.

⁴ K. G. Brown, C. M. Jantzen, and J. B. Pickett, The Effects of Formate and Nitrate on Reduction/Oxidation (REDOX) Process Control for the Defense Waste Processing Facility (DWPF) (U), WSRC-RP-97-34, February 3, 1997.

RESULTS

Hydrogen and Nitrous Oxide Generation

One of DWPF chief concerns is that with more sludge there will be more noble metals in each batch. The additional noble metals are expected to increase the amount of hydrogen (H_2) and nitrous oxide (N_2O) being generated during a large CPC batch. Table II summarizes the maximum hydrogen and nitrous oxide generation observed in vol% and lb/hr at full DPWF scale for both the SRAT and SME cycles in Runs 1V through 5V.

Table II. Maximum Hydrogen and Nitrous Oxide Generation for Large CPC Batch

Run	SRAT				SME			
	Max H_2		Max N_2O		Max H_2		Max N_2O	
	vol%	lb/hr [†]	vol%	lb/hr [†]	vol%	lb/hr [†]	vol%	lb/hr [†]
1V	0.023	0.015	1.751	28.5	0.125	0.030	0.0	0.0
2V	0.0	0.0	0.869	9.2	0.0	0.0	0.0	0.0
3V	0.591	0.35	3.473	51.8	1.117	0.23 [‡]	0.0	0.0
4V	0.002	0.001	1.319	18.6	0.026	0.005	0.0	0.0
5V	0.013	0.009	2.401	49.9	0.076	0.021	0.0	0.0
DWPF Limit	--	0.65	--	--	--	0.23	--	--

[†]lb/hr at full DWPF scale, [‡]Exceeded DWPF hydrogen generation limit

Hydrogen and other gas generation data as well as anion data for Runs 1V through 5V are shown in Figure 1 through Figure 5, respectively. The top graph of each figure shows all GC and anion data plus mixer speed and torque. The bottom graphs of each figure show the hydrogen generation in pounds per hour for a 6000-gallon DWPF batch. Also in each graph the separate phases of the SRAT/SME cycles are identified by lines and lettering. D represents dewatering, N stands for Nitric acid addition, F is formic acid addition, and R is for reflux. The SRAT cycle ends at the end of the reflux section where upon the SME cycle begins.

After reviewing the sludge trimming done for Runs 1V through 4V, it was discovered that the noble metals (Pd, Rh, and Ru) were under added. The amount of under addition is summarized in Table III. Due to this under addition, the conditions of Run 4V were repeated in Run 5V except a 20-wt% solids sludge was used instead of a 22-wt% sludge.

Table III. Noble Metal Under Addition

Run	Pd	Rh	Ru
1V	280%	630%	17%
2V	250%	630%	17%
3V	240%	620%	17%
4V	280%	650%	17%

For Run 1V the maximum hydrogen generation occurred at the end of the SME cycle at 0.030 lb/hr. This was a momentary peak during the end of the second dewater phase in the SME cycle as shown in Figure 1. This value is artificially low due to the noble metal under addition especially considering the acid added was equivalent to 197% stoichiometry. However, all the nitrite had been destroyed

shortly after the reflux cycle started. This data indicates that the noble metal content of the sludge has a big impact on the hydrogen production. The maximum nitrous oxide generation for Run 1V was 24.2 lb/hr and took place in the SRAT cycle at the end of the formic addition and right before the SRAT dewatering phase as shown in Figure 1.

In Run 2V, there appeared to be no hydrogen generation, which corresponded to the slow destruction of nitrite, NO_2^- , as shown in Figure 2. It was not until the end of the SME cycle in Run 2V that all the nitrite was finally destroyed. The low hydrogen generation can also be attributed to the noble metal under addition. This data shows the impact of the acid addition as all the nitrite is destroyed at the beginning of the SRAT reflux cycle of Run 1V with 197% acid but in Run 2V with 155% acid it is not destroyed until the end of the SME cycle. This run can be furthered compared to an earlier Tank 42 experiment⁵ with 137.5% acid, 16-wt% solids sludge, and prototypic Tank 42 levels of noble metals. In this earlier experiment, 5 times as much Rh was added and the maximum hydrogen generation in the SRAT was 0.004 lb/hr and in the SME 0.085 lb/hr. Given the larger amount of acid (155%) and higher weight percent solids in Run 2V, the hydrogen generation should be at least as much as that seen in this earlier experiment. The maximum nitrous oxide generation for Run 2V was 12.0 lb/hr and took place in the SRAT cycle at the end of the formic addition and right before the SRAT dewatering phase as shown in Figure 2.

For Run 3V the maximum observed hydrogen generation occurred during the reflux stage of the SRAT cycle at 0.35 lb/hr. Although this value is high, it is still artificially low due to the noble metal under addition especially considering the high amount of acid added (340% stoichiometry). To draw a parallel with previous experiments⁵ with 17-wt% solids Tank 42 sludge and Tank 42 level of noble metals, a 254% acid addition gave a maximum of 0.31 lb/hr hydrogen generation in the SRAT and 0.162 lb/hr in the SME. In this earlier experiment, more than 5 times as much Rh had been added to the sludge. Given the higher weight percent solids sludge (20-wt%) and higher acid addition (340%) for Run 3V, the hydrogen generation would probably come close to the DWPF limit of 0.65 lb/hr or even beyond it. Even with the low noble metal content, Run 3V hydrogen generation in the SME is high enough (0.23 lb/hr) for the DWPF interlock, i.e. exceeds 25% LEL. Given the low noble metal content, if a complete dump of the formic acid feed tank did occur, there would be strong concerns for hydrogen generation in the SME although high results are expected because of the extreme amount of acid added. A more normal acid stoichiometry would give a more reasonable hydrogen peak as seen in Run 5V. The maximum nitrous oxide generation for Run 3V was 48.5 lb/hr during the large formic addition phase of the SRAT cycle, as shown in Figure 3.

For Run 4V the maximum observed hydrogen generation occurred at the end of the SME cycle at 0.005 lb/hr. This hydrogen peak occurred at the end of the second dewater phase in the SME cycle as shown in Figure 4. This hydrogen peak is artificially low due to the noble metal addition. However, as shown in the top graph of Figure 4, all the nitrite is destroyed by the end of the SRAT reflux cycle. The maximum nitrous oxide generation for Run 4V was 18.3 lb/hr and took place in the SRAT cycle at the beginning of the SRAT dewatering phase as shown in Figure 4.

For Run 5V the maximum hydrogen generation occurred at the end of the SME cycle at 0.021 lb/hr as shown in Figure 5. The maximum hydrogen generation in the SRAT cycle was 0.009 lb/hr. Since Run 5V was to emulate Run 4V except with the correct level of noble metals, a simple comparison

⁵D. P. Lambert, C. S. Boley, Tank 42 Sludge-Only Process Development for the Defense Waste Processing Facility (DWPF) (U), WSRC-RP-98-00149, June 2, 1998.

can be made if one assumes that the hydrogen production depends strictly on the amount of Rhodium (Rh) in the slurry. Please refer to Table IV for a comparison of Run 4V and 5V hydrogen generation rates. In Run 4V the maximum observed hydrogen rate in the SRAT was 0.0013 lb/hr, but linearly correcting for the 650% Rh under addition, the maximum hydrogen rate is estimated to be 0.0084 lb/hr. This correction is over simplified and does not take into account the reaction kinetics but does help to validate Run 5V results. If the same type of simple correction is applied to the Run 4V SME maximum of 0.0053 lb/hr, the estimated maximum would be 0.034 lb/hr. Again this value is similar to Run 5V SME maximum considering that Run 5V had less initial total solids (20-wt%) versus Run 4V (22-wt%). The maximum nitrous oxide generation for Run 5V was 49.9 lb/hr and took place in the SRAT cycle about half way through the SRAT dewatering phase as shown in Figure 5.

Table IV. Run 4V and 5V Hydrogen Generation

Run	g Rhodium	SRAT H ₂ , lb/hr	SME H ₂ , lb/hr
4V	0.00300	0.0013	0.0053
5V	0.02125	0.0091	0.0209
Ratio 5V/4V	7	7	4

The following figures represent the GC and other data collected during the previously described runs. In each figure, the top graphs represent multiple types of data plotted against the same numeric axes. The nitrogen (N₂), oxygen (O₂), and carbon dioxide (CO₂) are in volume percent and plotted versus the right hand axis. The formate (COOH⁻) and nitrate (NO₃⁻) are in parts per thousand (1 ppt is equivalent to 1000 ppm) and plotted against the right axis. The mixer speed divided by ten (RPM/10) and the torque (oz-in) are also plotted against the right axis. Helium (He), hydrogen (H₂) and nitrous oxide (N₂O) are in volume percent and plotted versus the left axis.

Figure 1. Large CPC Batch Run IV GC, Nitrite, Formate, and Nitrate Data.

Figure 2. Large CPC Batch Run 2V GC, Nitrite, Formate, and Nitrate Data.

Figure 3. Large CPC Batch Run 3V GC, Nitrite, Formate, and Nitrate Data.

Figure 4. Large CPC Batch Run 4V GC, Nitrite, Formate, and Nitrate Data.

Figure 5. Large CPC Batch Run 5V GC, Nitrite, Formate, and Nitrate Data.

Mercury Removal

Another DWPF SRAT processing constraint is the removal of mercury. For Runs 1V through 5V, mercury removal was accomplished beyond 0.45 wt% by the end of the SRAT cycle as shown in Table V. However, the normal reflux time of 12 hours had to be increased to 14 hours. The extended reflux times listed in Table V included the dewater time of the SRAT cycle plus extra time to see evidence of nitrite destruction or hydrogen generation. As can be seen from Runs 2V, 3V, 4V, and 5V, 14 hours of reflux is more than sufficient to remove Hg down to 0.45 wt%. The mercury analyses were done on the SRAT final samples, which were pulled at the end of the reflux period. The end of the reflux period was defined as the point where hydrogen generation had gone through a maximum providing evidence of nitrite destruction. For this reason, the Hg measurement for Run 1V occurred at 18 hours instead of the normal 14 hours.

Table V. Mercury Removal for Large CPC Batch

Run	Stoichiometry	SRAT	SME	Hg Recovered
1V	197%	0.37 wt% Hg (18.4 hrs Reflux) ⁶	0.032 wt% Hg	3.8 g
2V	155%	0.36 wt% Hg (13.5 hrs Reflux) ⁶	0.024 wt% Hg	4.0 g
3V	340%	0.083 wt% Hg (13.7 hrs Reflux) ⁶	0.024 wt% Hg	3.8 g
4V	175%	0.098 wt% Hg (14.7 hrs Reflux) ⁶	0.020 wt% Hg	2.8 g
5V	170%	0.26 wt% Hg (14.3 hrs Reflux) ⁶	0.044 wt% Hg	4.8 g

Nitrite Destruction

Another DWPF processing goal is the destruction of nitrite (NO_2^-) during the SRAT cycle. Table VI summarizes the levels of nitrite right before the addition of nitric acid (pre-nitric), right before reflux (pre-reflux), and right after reflux (post-reflux) in the SRAT cycles of these runs. The nitrite destruction can also be followed in Figure 1 through Figure 5 for Runs 1V through 5V. Note in these figures the nitrite (NO_2^-) levels correspond with the left axis and are in parts per thousand (ppt), i.e. 5700 ppm = 5.7 ppt. The important finding is that by the end of the SRAT cycle (after the reflux phase) only Run 2V still had nitrite, about 254 ppm. This result led to the increasing of acid stoichiometry in Run 1V and 4V to insure nitrite destruction. From this data it appears 170% stoichiometry is sufficient for nitrite destruction by the end of the SRAT cycle but 155% is not.

⁶ Reflux times included SRAT dewatering time and were longer than normal due to the wait for evidence of nitrite destruction or a peak in the hydrogen generation.

Table VI. Nitrite Destruction for Large CPC Batch

Run	Stoichiometry	SRAT Pre-Nitric NO ₂ ⁻	SRAT-Pre Reflux NO ₂ ⁻	SRAT-Post Reflux NO ₂ ⁻
1V	197%	5748 ppm	0 ppm	0 ppm
2V	155%	5487 ppm	1646 ppm	254 ppm
3V	340%	6006 ppm	0 ppm	0 ppm
4V	175%	6630 ppm	144 ppm	0 ppm
5V	170%	5532 ppm	91 ppm	0 ppm

F-N Calculation for SME Product

For all runs, the amount of acid used was based on the Total Acid Target and a Fe⁺²/Fe_{total} REDOX target of 0.22. Although the adjusted REDOX flowsheet was used, REDOX was not measured (only predicted) since glass quality was not the target of this investigation. However, since formate and nitrate measurements of the SME product were completed, [F-N] values for the four runs are shown in Table VII assuming a SME product with 45 wt% total solids for comparison with earlier data.

Table VII. SME Product [F-N] Values for Large CPC Batch

Run	Stoichiometry	SME [F-N]
1V	197%	0.471 mol/L
2V	155%	0.500 mol/L
3V	340%	0.929 mol/L
4V	175%	0.413 mol/L
5V	170%	0.456 mol/L

Product Compositions

The Mobile Lab and ADS analyzed both the SRAT and SME products for total solids, elemental solids, and densities. The predicted and measured weight percent solids and densities for the SRAT product are shown in Table VIII. The measured and predicted analyses for the SME products are shown in Table IX. The predicted and measured values compare quite well considering the variance in the measurement and sampling. Too much water was removed in SME Runs 2V and 3V because the initial concentration to 6000 gallons was not factored in properly. This extra water removal caused the higher than normal total weight percent solids (52-56 wt%).

Table VIII. Total and Elemental Weight Percent Solids for SRAT Product

Run	1V		2V		3V		4V		5V	
	Predicted	Measured	Predicted	Measured	Predicted	Measured	Predicted	Measured	Predicted	Measured
Total Wt% Solids	--	33.23%	--	31.06%	--	36.17%	--	32.17%	--	29.32%
Density (g/ml)	--	1.21	--	1.17	--	1.18	--	1.21	--	1.13
Species	wt% Dried Solids	wt% Dried Solids	wt% Dried Solids	wt% Dried Solids	wt% Dried Solids	wt% Dried Solids	wt% Dried Solids	wt% Dried Solids	wt% Dried Solids	wt% Dried Solids
Al	5.59%	5.51%	5.56%	5.51%	5.57%	4.89%	5.60%	5.38%	5.57%	7.18%
Ag	0.04%	--	0.04%	--	0.04%	--	0.04%	--	0.04%	--
Ca	2.38%	2.21%	2.01%	2.12%	2.01%	1.91%	2.39%	2.20%	2.01%	2.68%
Cd	0.09%	0.08%	0.09%	0.08%	0.09%	0.10%	0.09%	0.09%	0.11%	0.08%
Cl	0.03%	--	0.05%	--	0.05%	--	0.02%	--	0.03%	--
Cr	0.15%	--	0.16%	--	0.16%	--	0.15%	--	0.16%	0.11%
Cu	0.02%	0.02%	0.02%	0.02%	0.02%	0.01%	0.02%	0.02%	0.02%	0.01%
F	0.01%	--	0.01%	--	0.01%	--	0.01%	--	0.01%	
Fe	21.63%	19.90%	22.34%	19.20%	22.39%	17.00%	21.66%	21.15%	22.38%	20.50%
Hg	1.13%	0.37%	1.13%	0.36%	1.15%	0.08%	1.16%	0.10%	1.15%	0.26%
K	0.12%	0.16%	0.15%	0.15%	0.15%	0.19%	0.12%	0.15%	0.15%	0.29%
Li	0.01%	<0.01%	0.00%	<0.01%	0.00%	<0.01%	0.01%	<0.01%	0.00%	0.00%
Mg	1.04%	1.05%	1.07%	0.98%	1.08%	0.84%	1.04%	1.03%	1.08%	1.06%
Mn	4.23%	4.13%	4.36%	4.12%	4.37%	3.55%	4.23%	4.26%	4.36%	4.45%
Na	6.55%	6.59%	7.65%	6.80%	7.67%	5.93%	6.52%	6.62%	7.67%	5.02%
Ni	0.40%	0.37%	0.34%	0.31%	0.34%	0.27%	0.40%	0.38%	0.34%	0.33%
P	0.25%	0.28%	0.04%	0.26%	0.04%	0.27%	0.25%	0.28%	0.04%	0.19%
Pd	0.01%	<0.01%	0.01%	<0.01%	0.01%	<0.01%	0.01%	<0.01%	0.00%	0.00%
Rh	0.01%	<0.01%	0.01%	<0.01%	0.01%	<0.01%	0.01%	<0.01%	0.01%	0.01%
Ru	0.02%	0.04%	0.02%	0.04%	0.02%	0.03%	0.02%	0.04%	0.02%	0.02%
Si	1.14%	0.08%	1.53%	0.07%	1.54%	0.07%	1.13%	0.06%	1.54%	1.40%
Te	0.00%	<0.01%	0.00%	<0.01%	0.00%	<0.01%	0.00%	<0.01%	0.00%	0.00%
Ti	0.04%	0.04%	0.04%	0.04%	0.05%	0.04%	0.04%	0.04%	0.05%	0.03%
Zn	0.12%	0.12%	0.03%	0.11%	0.03%	0.10%	0.12%	0.12%	0.03%	0.12%

Table IX. Total and Elemental Weight Percent Solids for SME Product

Run	1V		2V		3V		4V		5V	
	Predicted	Measured	Predicted	Measured	Predicted	Measured	Predicted	Measured	Predicted	Measured
Total Wt% Solids	--	47.09%	--	52.51%	--	56.32%	--	48.06%	--	45.59%
Density (g/ml)	--	1.25	--	1.30	--	1.47	--	1.31	--	1.34
Species	wt% Dried Solids	wt% Dried Solids	wt% Dried Solids	wt% Dried Solids	wt% Dried Solids	wt% Dried Solids	wt% Dried Solids	wt% Dried Solids	wt% Dried Solids	wt% Dried Solids
Al	1.79%	1.73%	1.75%	1.89%	1.53%	1.71%	1.75%	1.87%	2.30%	2.40%
Ag	0.01%	--	0.01%	--	0.01%	--	0.01%	--	0.00%	--
B	2.77%	--	2.81%	--	2.78%	--	2.77%	--	2.76%	2.43%
Ca	0.72%	0.76%	0.67%	0.81%	0.60%	0.75%	0.71%	0.73%	0.89%	0.99%
Cd	0.03%	0.03%	0.03%	0.03%	0.03%	0.04%	0.03%	0.03%	0.03%	0.01%
Cl	0.00%	--	0.00%	--	0.00%	--	0.00%	--	0.00%	--
Cr	0.05%	--	0.01%	--	0.05%	--	0.05%	--	0.00%	0.03%
Cu	0.01%	<0.01%	0.01%	<0.01%	0.00%	0.01%	0.01%	<0.01%	0.00%	0.00%
F	0.00%	--	0.00%	--	0.00%	--	0.00%	--	0.00%	--
Fe	6.46%	6.30%	6.11%	6.85%	5.33%	6.37%	6.87%	6.95%	6.50%	6.60%
Hg	0.12%	0.03%	0.12%	0.02%	0.03%	0.02%	0.03%	0.02%	0.04%	0.04%
K	0.05%	<0.15%	0.05%	<0.15%	0.06%	0.11%	0.05%	<0.15%	0.10%	0.16%
Li	1.72%	1.27%	1.72%	1.43%	1.72%	1.43%	1.72%	1.31%	1.72%	0.00%
Mg	1.24%	0.99%	1.21%	1.07%	1.16%	1.08%	1.23%	1.03%	1.24%	1.11%
Mn	1.34%	1.30%	1.31%	1.37%	1.11%	1.31%	1.38%	1.36%	1.46%	1.43%
Na	8.18%	6.62%	8.20%	7.24%	7.90%	7.41%	8.19%	6.94%	7.63%	5.17%
Ni	0.12%	0.12%	0.10%	0.10%	0.08%	0.10%	0.12%	0.13%	0.10%	0.18%
P	0.09%	0.07%	0.08%	0.07%	0.08%	0.11%	0.09%	0.08%	0.06%	0.08%
Pd	0.00%	<0.10%	0.00%	<0.10%	0.00%	<0.10%	0.00%	<0.10%	0.00%	0.00%
Rh	0.00%	<0.10%	0.00%	<0.10%	0.00%	<0.10%	0.00%	<0.10%	0.00%	0.00%
Ru	0.01%	0.02%	0.01%	0.01%	0.01%	0.02%	0.01%	0.01%	0.01%	0.00%
Si	24.24%	20.7%	24.24%	22.3%	24.24%	21.3%	24.24%	21.7%	24.67%	23.00%
Te	0.00%	<0.01%	0.00%	<0.01%	0.00%	<0.01%	0.00%	<0.01%	0.00%	0.00%
Ti	0.01%	0.03%	0.01%	0.03%	0.01%	0.02%	0.01%	0.03%	0.01%	0.01%
Zn	0.04%	0.03%	0.04%	0.04%	0.03%	0.04%	0.04%	0.04%	0.04%	0.03%

Processing Problems

Mixing and Sampling

One problem encountered during all runs was keeping the slurry well-mixed especially during the nitric acid addition of the SRAT cycles. The sludge slurry for the large batches was thicker than a normal batch due to the higher weight percent solids sludge used, the presence of a SRAT heel, and the boiling or concentration of a caustic sludge. Caustic sludge is thicker due to the hydroxyl interactions between particles in the sludge. These interactions cause the sludge to become sticky and gelatinous. The sludge slurry was at its thickest (by appearance) after the first dewatering to make room for the additional 1000 gallons of sludge. In Run 2V where the equivalent of 133 gallons of concentrated nitric acid was added before the first dewatering, the slurry was as thick as the other runs based upon visual observations. Thus the pre-boiling acid may not be beneficial in terms of alleviating boiling a caustic sludge. However, for all runs the process was able to continue by increasing the mixer speed at various times. Table X gives a summary of the initial, maximum, and final mixer speeds for each run. For all runs, once the acid had been added in the SRAT cycle, the slurry was much less viscous and mixing was not a problem.

Table X. Mixer Speeds for Large Batch Runs

Run	Initial Speed (RPM)	Maximum Speed (RPM)	Maximum Speed Location	Final Speed (RPM)
1V	200	300	Before Nitric Addition	240
2V	200	250	Start of Formic Addition	200
3V	200	260	End of Nitric Addition	210
4V	200	300	Before Nitric Addition	200
5V	200	250	Start of Nitric Addition	200

Related to the mixing problem, pulling samples was difficult during the SRAT cycles due to the thickness of the slurry. This problem did not prevent the collection of samples, but it took longer to pull them.

Rheology

In order to understand the mixing and sampling problems encountered in the SRAT cycles, samples were pulled at the completion of the SRAT cycle for rheology analysis. Two samples, SRAT 1V and 3V products, were analyzed by a *TA Instruments* rheometer being demonstrated at TNX. The resulting shear stresses versus shear rate curves are shown in Figure 6. Note that Batch 3V with the excessive acid addition (340% stoichiometry) had a much lower yield stress of 31 dynes/cm² compared to Batch 1V with a yield stress of 287 dynes/cm² and less added acid (197% stoichiometry). Also Batch 3V's apparent viscosity of 14.3 cP was lower than Batch 1V's viscosity of

48.7 cP. This data confirms observations that the SRAT 3V product (high acid addition) was much thinner (i.e. lower shear stress) than the SRAT 1V product (nominal acid addition). The TA Instruments rheometer only needs a 3-ml sample to perform the shear stress measurements. Samples for all Runs 1V through 5V were analyzed later by a Haake rheometer. The shear stresses versus shear rate curves are shown in Figure 7. The yield stresses and apparent viscosities for all runs are shown in Table XI. The TA Instruments and Haake results agree well considering the different samples and techniques used. The shapes of the curves are very similar too. The Haake results confirm the TA Instruments findings, the high acid slurry (3V) was much thinner than all the other runs. Also, Run 4V and 5V were very similar from a rheological point of view as expected. Note the shear stress trajectories become more curved as the acid addition goes up but flattens out by the time 340% is reached.

To compare the thickness of the SRAT product of the increased CPC batch with a normal size batch, a Tank 42 sludge-only SRAT product (Tank 42 SRAT) from earlier experiments⁷ and the large batch SRAT heel for Runs 1V through 4V (SRAT Heel) described in Appendix A-1 were also analyzed. The Tank 42 sludge-only SRAT product was from a 25-wt% total solids sludge with 125% acid and the SRAT heel was a 20-wt% total solids sludge with 141% acid. The shear stress versus shear rate curves for these normal-sized batches are shown in Figure 8. The yield stresses and apparent viscosities for the normal-sized batches SRAT Heel and Tank 42 SRAT are included in Table XI. Note that the thinnest large batch SRAT product from Run 3V has a higher yield stress and apparent viscosity than either normal sized batch. These limited results support the observations about mixing and sampling, i.e. the mixing speeds were increased above normal, and sampling was more difficult than normal due to the thicker, more viscous slurry. The SRAT Heel yield stress and viscosity seem unnecessarily low and may be due to a poor sample. More rheological data needs to be collected to better characterize the normal versus large batch SRAT product. More data is especially needed after the first dewater step of the SRAT cycle when the slurry appears to be its thickest.

Table XI. Yield Stress and Apparent Viscosity for SRAT Products

Run	Acid Stoichiometry	Yield Stress Dynes/cm ²	Apparent Viscosity centipoise (cP)	Total Wt% Solids
1V	197%	179	36.5	33%
2V	155%	113.5	26.6	31%
3V	340%	34.8	16.7	36%
4V	175%	142	38	32%
5V	170%	140.5	41	29%
SRAT Heel	141%	1.1	2.2	20%
Tank 42 SRAT	125%	24	11	25%

⁷ D. P. Lambert, P. R. Monson, Hydrogen Generation Rate During Melter Feed Preparation of Tank 42 Sludge and CST in the Defense Waste Processing Facility (DWPF) (U), WSRC-TR-98-00297, Rev. 0, September 21, 1998.

Figure 6. Shear Stress versus Rate for SRAT 1V and 3V Products on TA Instruments

Figure 7. Shear Stress versus Rate for SRAT Products on Haake Rheometer

Figure 8. Large Batch 3V versus Normal Batch Tank 42 & LB Heel SRAT Rheology

Fouling

The cooling coil remained in the SRAT/SME vessel during the entire experiment. Water was only run through the coil when the vessel was cooled. There was no significant coil fouling as indicated in Table XII. The amount of fouling or accumulation was determined by subtracting the cooling dip leg's and stirrer's final weights from their initial weights and multiplying by the weight percent solids at the end of each run. The percentages represent the amount of solids left on the cooling coil and stirrer out of all the solids material added to the kettle. The fouling on the stirrer was reported to help verify the cooling dip leg's numbers. The stirrer's fouling numbers may be artificially inflated as the surface area and shape of its blades could cause more material to settle than on the cooling coil. Although counterintuitive, there appears to be more fouling as the acid stoichiometry or the amount of acid increases. This could be interpreted as more particles are dissolved or free to move about and stick to the cooling dip leg, stirrer, etc. as the acid increases. However, the percentage of fouling should not be a problem. For a better understanding of the cooling coil fouling, please refer to the

pictures in Figure 9 through Figure 12. Note Figure 10 and Figure 11 were taken with an older digital camera with lower resolution and so had to be pieced together from several photos. The other images were taken with a newer digital camera requiring only one picture.

Table XII. Coil Fouling for Large CPC Batch

Run	Acid Stoichiometry	Coil Fouling Solids	Coil Fouling % Solids	Stirrer Fouling Solids	Stirrer Fouling % Solids	Total Solids
2V	155%	0.03 g	0.00%	2.04 g	0.13%	1579.5
4V	175%	0.38 g	0.02%	3.12 g	0.20%	1556.9
5V	170%	0.87 g	0.06%	3.60 g	0.24%	1486.9
1V	197%	0.48 g	0.03%	3.85 g	0.24%	1584.8
3V	340%	1.63 g	0.11%	6.70 g	0.45%	1495.1

Figure 9. Cooling Dip Leg and Thermocouple for Large CPC Batch Run 1V.

Figure 10. Cooling Dip Leg for Large CPC Batch Run 2V.

Figure 11. Cooling Dip Leg for Large CPC Batch Run 3V.

Figure 12. Cooling Dip Leg and RTD for Large CPC Batch Run 3V.

CONCLUSIONS

These experiments demonstrated the feasibility of increasing the DWPF CPC batch size by adding more sludge to each batch and concentrating the sludge down to allow space for the addition of another 1000 gallons. After re-concentration, the CPC batch contains a greater waste solids loading for the same volume as a normal size batch. This increased waste loading should allow about one more canister to be poured per melter feed batch preparation.

From this limited set of runs, it appears DWPF could increase CPC batch size provided:

- More acid is used (somewhere between 155% and 170%)
- Slurry is kept well mixed at all times
- Heat Transfer coefficients do not fall to an unacceptable level

It should be noted that the sludge slurry is thicker than normal (especially during the beginning of the SRAT cycle) and DWPF mixing systems must be capable of mixing the higher solids slurry.

The processing problems observed during the increased CPC batch (extra 1000 gallons of sludge) bench scale experiments are summarized below:

- Exceeded hydrogen limit for large acid addition (340% stoichiometry). Lower acid additions like 155% to 175% should not present a problem.
- Difficulty destroying Nitrite: Increased acid stoichiometry from 155% to 175% to compensate.
- Difficulty keeping slurry well-mixed especially before nitric acid addition was complete: Increased mixing speed to compensate.
- Difficulty pulling samples during SRAT cycle: After samples were pulled, the sampler tube was cleared by blowing its contents back in to the kettle.

None of these problems are insurmountable. However, more experiments will be needed to answer questions raised by this work.

FUTURE WORK

Although by increasing the acid addition, the nitrite destruction can be met for the increased CPC batch process, this in turn may cause problems with equipment erosion and hydrogen generation. An optimum operating point needs to be found where the reaction kinetics are satisfied yet constraints on glass properties such as REDOX and limitations of physical equipment such as agitation are considered. To help answer these and other questions, it is recommended that another set of bench-scale runs be completed that look at the following items:

1. Acid targets between 150% and 170% to find optimum.
2. Tank 42 Sludge with HM levels of noble metals to bound response.
3. Complete Formic Acid Tank dump to bound response.

The bounding case of a complete acid tank dump needs to be repeated since the noble metals were low in the experiment done here and the hydrogen generation was still high. Once the bench-scale

experiments narrow the operating envelope for the CPC batch process, a series of 1/240th scale large CPC batch runs should be completed in the Glass Feed Preparation System (GFPS). These GFPS experiments should include a pre-boiling acid and no pre-boiling acid run. These large-scale runs would give a better indication of processing problems like foaming since the bench-scale is limited to a mass flux of about 4 lb/hr*ft² compared to DWPF's mass flux of about 50 lb/hr*ft². The GFPS scale would also allow a more complete rheological study of the sludge slurry as it goes through the process, i.e. more samples could be taken at various points in the process. As discussed earlier, the large batch slurry is definitely thicker than a normal batch and needs to be clearly defined to make sure DWPF mixing is adequate. With a *TA Instruments* rheometer these measurements would be quite easy, as only a 3-ml sample is needed. The larger scale experiments would also give a better representation of potential processing problems such as fouling, foaming, mixing, and heat transfer problems.

The anecdotal evidence in these and earlier experiments suggest that as the sludge's weight percent solids increase (16-wt% to 20-wt%) so does the required acid (137.5% to 170%). Research should be done on the basis of the required acid calculation for some unknown variable or variables that are not being taken into consideration. For higher weight percent solids sludge (greater than 20-wt% solids), it appears that more than the nominal 137.5% acid stoichiometry is needed for complete nitrite destruction by the end of the SRAT cycle. DWPF is currently using about 150% stoichiometry for the 17-wt% solids sludge of Tank 42.

ACKNOWLEDGMENTS

Thanks to John Occhipinti for providing quick answers to our questions and direction as needed.

Thanks to Frances Williams, Sammie King, John Duvall, Mary Johnson, Vickie Williams for their help in preparing for and performing the experiments. Their work is very much appreciated. I appreciate the extra hours and long weekends the technicians worked to complete these experiments.

I would also like to thank the excellent technical support (as always) from Dan Lambert, Paul Monson, and especially Russ Eibling who performed the Rheology tests and provided the corresponding data.

Thanks to Nick Odom for assisting with the temperature controllers.

We appreciated the quick turnaround for sample analyses by the Mobile lab and ADS.

APPENDIX A-1: LARGE BATCH SRAT HEEL PREPARATION

SRT-PTD-98-0016, Rev. 0

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November 20, 1998

TO: L. F. Landon, 704-1T

FROM: W. E. Daniel, 704-1T

Run Plan for Large Batch Heel Preparation for Variability Runs for Developing Strategies for Increased CPC Batch Sizes (U)

This run plan documents the preparation of the SRAT heel to be used in the variability runs for Developing Strategies for Increased CPC Batch Sizes as requested in DWPF Technical Task Request HLW/DWPT/TTR-980013. The experimental work will be controlled using the Laboratory Scale Chemical Process Cell Simulations (Manual L27, Procedure 2.02) and this run plan. The run plan includes many of the experimental details, the instructions for final sludge preparation, the scaling necessary for determining the operating conditions such as feed rates, purge rates, and the steps in completing the SRAT cycle. This document also summarizes the decisions made to complete these experiments.

- 1) The sludge used for the SRAT Heel preparation is a Tank 42-sludge simulant created from the Optima Tank 51 simulant with the following modifications.
 - a) A recipe is shown in Table XIII that targets a 20 weight percent solids sludge after the trim chemicals (noble metals and mercury) are added. This sludge will be referred to as Sludge A' and its pre-trim measured as well as post-trim predicted elemental weight percent analyses are shown in Table XIV.
 - b) Purex levels of noble metals and mercury will be added to the sludge batch as shown in Table XV. This will require approximately 12 hours of refluxing in the SRAT to steam strip mercury and meet the DWPF constraint of 0.45 wt % mercury.

Table XIII. Preparation Of Tank 42 Sludge 20 weight % (Trim Chemicals Missing)

Component	Amount, g	Comments
Tank 51 sludge simulant	16521.36	18.52 wt% solids initially
Tank 51 supernate	527.2	Added Supernate to lower wt% solids
Al ₂ O ₃	148.29	
Ni(NO ₃) ₂ *6H ₂ O	30.22	
SiO ₂	53.48	
MnO ₂ *x H ₂ O	221.77	Total Mass @ 27.2 wt% solids
Water	200.00	
Al ₂ O ₃	0.94	
Na ₂ C ₂ O ₄	4.87	
NaF	0.66	
NaOH	7.05	
NaCl	0.82	

Table XIV. Elemental Analyses of Large Batch 20 wt% Sludge A'

Insoluble Species	Measured Wt% Solids Pre-Trim	Predicted Wt% Solids Post-Trim	Soluble Species	Measured Wt% Solids Pre-Trim	Predicted Wt% Solids Post-Trim
Al	5.72%	7.58%	Al		0.02%
*Ag		0.04%	C2O4	0.28%	0.27%
Ca	2.04%	1.94%	Cl	0.04%	0.04%
*Cd		0.11%	CO3		1.81%
Cl		0.07%	Cr		0.00%
Cr		0.16%	F	0.01%	0.02%
Cu	0.02%	0.02%	K		0.00%
F		0.01%	Li		0.00%
Fe	23.08%	21.80%	Na		0.25%
*Hg		1.30%	NO2	4.38%	3.73%
K	0.16%	0.05%	NO3	1.80%	1.44%
Li	0.00%	0.00%	OH		0.12%
Mg	1.13%	1.11%	PO4	0.06%	0.05%
Mn	4.48%	3.64%	SO4	0.26%	0.21%
Na	7.88%	5.74%			
Ni	0.35%	0.34%			
P		0.00%			
*Pd		0.00%			
Pu		0.00%			
*Rh		0.01%			
*Ru		0.02%			
Se		0.00%			
Si	1.64%	1.80%			
Te		0.00%			
Ti	0.05%	0.05%			
U		0.00%			
Zn	0.01%	0.00			

Table XV. Trim Chemical Addition for Large Batch SRAT Heel Preparation

	Target Addition, g	Actual Addition, g	Wt% Solids	Target Solids, g	Actual Solids added, g
Sludge	3200.0	3200.0	19.3%	617.6	617.6
Trim Chemicals	Target Addition, grams	Actual Addition, grams	Elemental Solids Factor	Target Elemental Solids, g	Actual Elemental Solids, g
AgNO ₃	0.360	0.3606	0.6349	0.229	0.229
Cd(NO ₃) ₂ *4H ₂ O	1.864	0.0000	0.3644	0.679	0.000
HgO	8.669	8.6694	0.9261	8.029	8.029
Pd(NO ₃) ₂ *H ₂ O	0.032	0.0323	0.1527 [†]	0.014	0.014 [†]
Rh(NO ₃) ₃ *2H ₂ O	0.103	0.1034	0.0493 [†]	0.033	0.033 [†]
RuCl ₃	0.279	0.2795	0.4174 [†]	0.136	0.136 [†]

Element	Target Wt% Solids	Actual Wt% Solids
Ag	0.04%	0.04%
Cd	0.11%	0.00%
Hg	1.30%	1.30%
Pd	0.0022%	0.0008% [†]
Rh	0.0053%	0.0008% [†]
Ru	0.02%	0.019% [†]

[†]Values changed from original run plan to reflect noble metal under addition.

- 2) Calculated acid addition rates, boilup rates, purge rates, antifoam addition, etc. were based on scaling from DWPF settings as shown in Table XVI.
- 3) The acid additions were determined for 125% of stoichiometry with a redox target of $0.2 \text{ Fe}^{+2}/\Sigma\text{Fe}$. The redox calculation spreadsheet for the large batch heel are shown in Table XVII.
- 4) A review, as required by the Conduct of Research and Development has been completed.
- 5) The experiments are planned to be completed the week of November 23, 1998.

Table XVI. Scaling Calculations for Large Batch SRAT Heel Preparation

	DWPF	TNX 1W	Time
Scale factor	1	7,097 (8019) [†]	
Sludge Added Volume	6,000 gal	2832 ml	
Sludge Added Density	1.13	1.13	
Sludge Added Mass	25664 kg	3200.0 g	
SRAT Added Water	0 gal	0.0 ml	
SRAT purge air	188 scfm	750.1 scc/min	
SME purge air	66 scfm	263.3 scc/min	
Antifoam (100 ppm in Total Sludge)	5.66 lbs	0.32 g	
Antifoam Solution (20 to 1 solution)	113.16 lbs	6.40 g	
nitric acid feedrate	2 gpm	1.062 ml/min	2.3 hrs
formic acid feedrate	2 gpm	1.067 ml/min	1.1 hrs
Boilup rate	5,000 lb/hr	5.33 g/min	
Formic Molarity	23.55 M	23.55 M	
Nitric Molarity	10.35 M	10.40 M	
Formic Volume	269.2 gal	143.61 ml	
Formic Mass		172.96 g	
Nitric Volume	133.6 gal	70.90 ml	
Nitric Mass		92.92 g	
Formic feed time	134.6 min	134.6 min	
Nitric feed time	66.8 min	66.8 min	
Total Volume		3046.37 ml	

[†]Correct scale factor in parentheses, value off due to improper density correction.

Table XVII. Large Batch SRAT Heel Preparation Redox Calculation

Stoichiometry ratio

125.0% (141%)[†]

Date: 11/20/98

Stream	PHA	Sludge	Frit	SME	
Oxide Contribution (%) (in SME)	0.0%	26.0%	74.0%	15399.2	kg Calc. Basis
Density (kg/L)	1.0355	1.130	n/a	137.0%	
Total Solids (%)	5.38%	19.30%	n/a	48.0%	
Calcine Factor (ox/sol)	1.00	0.81	n/a	n/a	
Hydroxide (M)	n/a	0.646	n/a	n/a	
Mercury (ppm)	n/a	2509.0	n/a	n/a	
Total Mn (wt% solids)	n/a	4.48	n/a	n/a	
Soluble Mn (ppm)	n/a	0.00	n/a	n/a	
*TIC (ppm)	n/a	0.00	n/a	n/a	
Total Acid (M)	0.240	n/a	n/a	n/a	
Nitrite (ppm)	0.0	8452.0	0.0 (kg/100kg frit)		
NO2 Destruction	0.0%	100.0%	0.0%		
Nitrate (ppm)	1012.1	3466.0	0.0 (kg/100kg frit)		
% nitrite to nitrate conversion		35.0%			
Formate (ppm)	22808.9	0.0	1.0 (kg/100kg frit)		
Reaction formate destruction, kg		140.25			
Factor for total formate destruction		15.0%			
Total formate destruction, kg		21.04			
Oxide Mass (kg)	0.0	4003.8	11395.4	15399.2	
Solids Mass (kg)	0.00	4953.40	11395.39	16348.79	
Total Mass (kg)	0.00	25665.29	n/a	34059.98	
Volume (L)	0.00	22,712.65	n/a	24861.30	
% Stoichiometry	n/a	125.0%	n/a	n/a	
Volume HNO3@50% (L)	n/a	2,824.87	n/a	n/a	
NO2 Contribution (kg)	0.000	216.923	0.000	216.923	
NO2 Remaining (kg)	0.000	0.000	0.000	0.000	
NO3 Contribution (kg)	0.000	1977.649	0.000	1977.649	
COOH Contribution (kg)	0.000	-140.25	93.843	-46.41	
NO2 (Molar@45%)				0.000	
NO3 (Molar@45%)				1.352	
COOH (Molar@45%)				-0.044	
Predicted Fe(II)/□Fe			0.09	≤ BDL@0.03	≤ 0.1
Volume HCOOH@90% (L)			3442.56	3167.03	3488.54
% Stoichiometry	n/a	125.0%	n/a	n/a	
Volume HCOOH@90% (L)	n/a	1,241.38	n/a	n/a	
NO2 Contribution (kg)	0.000	216.923	0.000	216.923	
NO2 Remaining (kg)	0.000	0.000	0.000	0.000	
NO3 Contribution (kg)	0.000	164.879	0.000	164.879	
COOH Contribution (kg)	0.000	1295.096	93.843	1388.940	
NO2 (Molar@45%)				0.000	
NO3 (Molar@45%)				0.113	
COOH (Molar@45%)				1.308	
Predicted Fe(II)/□Fe			0.09	≤	0.468 ≤ 0.1
Volume HNO3@50% (L)			1221.59		1186.77

[†]Value in parentheses represents corrected value due to scale factor error.

Table XVII. Large Batch SRAT Heel Preparation Redox Calculation Continued

mol% Nitric	n/a	17.9%	n/a	n/a
Volume HCOOH@90% (L)	n/a	1,019.17	n/a	n/a
Volume HNO3@50% (L)		505.65		
NO2 Contribution (kg)	0.000	216.923	0.000	216.923
NO2 Remaining (kg)	0.000	0.000	0.000	0.000
NO3 Contribution (kg)	0.000	489.365	0.000	489.365
COOH Contribution (kg)	0.000	940.291	0.000	940.291
NO2 (Molar@45%)				0.000
NO3 (Molar@45%)				0.335
COOH (Molar@45%)				0.886
Predicted Fe(II)/□Fe			0.09	≤ 0.200 (0.211) [†] ≤ 0.1

† Value in parentheses represents corrected value due to scale factor error.

kgb 9/16/96

Run # Large CPC Heel

Date: 11/23/98

PREREQUISITES

1. ☒ Signed TAR requesting work.
2. ☒ Issued Testing scope and task assignment.
3. ☒ Analyze sludge for density, total base (pH 5.5), nitrate, manganese, nitrite, density, solids.
4. ☒ Calibrate GC. Calibrate for nitrogen, oxygen, N₂O, hydrogen, and carbon dioxide.
5. ☒ Prepare sufficient 90% formic acid and 50% nitric acid.
6. ☒ Prepare sufficient antifoam solution or make sure sufficient solution is available.
7. ☒ Calculate batching and scaling for experiment based on DWPF parameters.
8. ☒ Calculate redox for experiment based on DWPF parameters.
9. ☒ Setup experimental rig per sketch below.
10. ☒ Complete leak check and water run.

Run # Large CPC Heel

Date: 11/23/98

PREPARATION FOR SRAT CYCLE

Note: Do not insulate kettle until acid addition is complete

1. ☒ Add 3200 g of Sludge A' to kettle.
2. ☒ Add trim_chemicals (from Table XV) directly to the kettle.
3. ☒ Transfer 100 grams of wash water to the kettle (to rinse all containers used for adding sludge, noble metals, mercury, etc.).
4. ☒ Calibrate pH probe with pH 4 and 10 buffer. Record measured pH of pH 7 buffer 7.125.
5. ☒ Install pH probe in kettle. Record initial pH of sludge 11.827.
6. ☒ Turn on the air purge to kettle at 750.1 sccm. Connect the outlet flowmeter to perform the leak check. The outlet flow should be 700-800 sccm. If it is not, tighten all connections until the system is leak tight. Write down the leak check in the logbook.
7. ☒ Disconnect outlet flowmeter.
8. ☒ Turn on kettle agitator. Setpoint = 150 rpm.
9. ☒ Turn on cooling water to SRAT condenser. Setpoint = 40°C.
10. ☒ Turn on cooling water to Chilled (FAVC) condenser. Setpoint = 5°C.
11. ☒ Make sure the GC computer has enough memory space for the run (at least 40 Mbyte).
12. ☒ Set the GC computer time equal to the clock time. Record the time in the log book.
13. ☒ Install the calibration gas cylinder to the GC and let the GC run five times. If at the end of five runs the GC reading is within 10% of the gas composition in the cylinder, print the calibration check results and write down "pre-cal check and run number" on the printout. Otherwise, select "Calibration" "Level 1" "OK" to calibrate the GC five times. At the end of five runs the GC reading should be within 10% of the gas composition in the cylinder. If it is not, contact the engineer. Print the calibration check results and write down "pre-cal check and run number" on the printout.
14. ☒ Start the GC for this run beginning with baseline reading for a few minutes. Write down the GC time, filename etc. in the logbook. Record the baseline data on the data sheet.

Run # Large CPC Heel

Date: 11/24/98

SRAT CYCLE

1. ☒ Add 2.2 g 1:10 antifoam solution and 2.2 g water directly to the kettle (100 ppm antifoam).
2. ☒ Start heating the kettle (Turn on power, setpoint at 93°C). Record the run data every 20 minutes on the data sheet.
3. ☒ Add 70.90 ml of 50-wt% nitric acid @ 1.062 ml/min (reference Table XVI) to the kettle.
4. ☒ Add 143.61 ml of 90% formic acid @ 1.067 ml/min (reference Table XVI) to the kettle.
5. ☒ Add 2.2 g 1:10 antifoam solution and 2.2 g water directly to the kettle (100 ppm antifoam).
6. ☒ Bring kettle contents to boiling. If slurry begins to foam over, switch off heating and turn on the cooling coil water pump to bring the temperature down rapidly. Then switch off the cooling coil water pump and slowly heat up the kettle again to the point of boiling.
7. ☒ Dewater until kettle volume is approximately 3.2 L. (*Boiled off 323 g*)
8. ☒ Reflux the slurry for 12 hours at 5.33 g/min boil-up, then turn off the heat to cool the kettle to sub-boiling.
9. ☒ Pull a 125 ml sample (LB SRAT Heel) from the kettle, record the weight on the run sheet. Label and send to lab for analyses.

APPENDIX A-2: LARGE BATCH SRAT HEEL PREPARATION 2

SRT-PTD-99-0029, Rev. 1

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June 15, 1999

TO: L. F. Landon, 704-1T

FROM: W. E. Daniel, 704-1T

Run Plan for Large Batch Heel Preparation for Extra Variability Run for Increased CPC Batch Size Study (U)

This run plan documents the preparation of a SRAT heel to be used in an extra variability run for Developing Strategies for Increased CPC Batch Sizes as requested in DWPF Technical Task Request HLW/DWPT/TTR-980013. The experimental work will be controlled using the Laboratory Scale Chemical Process Cell Simulations (Manual L27, Procedure 2.02) and this run plan. The run plan includes many of the experimental details, the instructions for final sludge preparation, the scaling necessary for determining the operating conditions such as feed rates, purge rates, and the steps in completing the SRAT cycle. This document also summarizes the decisions made to complete these experiments.

- 1) The sludge used for the SRAT Heel preparation is a Tank 42-sludge simulant created from the Optima Tank 51 simulant with the following modifications.
 - a) A recipe is shown in Table XVIII that targets a 20 weight percent solids sludge after the trim chemicals (noble metals and mercury) are added. This sludge will be referred to as Sludge A' and its pre-trim measured as well as post-trim predicted elemental weight percent analyses are shown in Table XIX.
 - b) Purex levels of noble metals and mercury will be added to the sludge batch as shown in Table XX. This will require approximately 13 hours of refluxing in the SRAT to steam strip mercury and meet the DWPF constraint of 0.45 wt % mercury.

Table XVIII. Preparation Of Tank 42 Sludge 20 weight % (Trim Chemicals Missing)

Component	Amount, g	Comments
Tank 51 sludge simulant	16521.36	18.52 wt% solids initially
Tank 51 supernate	527.2	Added Supernate to lower wt% solids
Al ₂ O ₃	148.29	
Ni(NO ₃) ₂ *6H ₂ O	30.22	
SiO ₂	53.48	
MnO ₂ *x H ₂ O	221.77	Total Mass @ 27.2 wt% solids
Water	200.00	
Al ₂ O ₃	0.94	
Na ₂ C ₂ O ₄	4.87	
NaF	0.66	
NaOH	7.05	
NaCl	0.82	

Table XIX. Elemental Analyses of Large Batch 20 wt% Sludge A'

Insoluble Species	Measured Wt% Solids Pre-Trim	Predicted Wt% Solids Post-Trim	Soluble Species	Measured Wt% Solids Pre-Trim	Predicted Wt% Solids Post-Trim
Al	5.72%	7.58%	Al		0.02%
*Ag		0.04%	C2O4	0.28%	0.27%
Ca	2.04%	1.94%	Cl	0.04%	0.04%
*Cd		0.11%	CO3		1.81%
Cl		0.07%	Cr		0.00%
Cr		0.16%	F	0.01%	0.02%
Cu	0.02%	0.02%	K		0.00%
F		0.01%	Li		0.00%
Fe	23.08%	21.80%	Na		0.25%
*Hg		1.30%	NO2	4.38%	3.73%
K	0.16%	0.05%	NO3	1.80%	1.44%
Li	0.00%	0.00%	OH		0.12%
Mg	1.13%	1.11%	PO4	0.06%	0.05%
Mn	4.48%	3.64%	SO4	0.26%	0.21%
Na	7.88%	5.74%			
Ni	0.35%	0.34%			
P		0.00%			
*Pd		0.00%			
Pu		0.00%			
*Rh		0.01%			
*Ru		0.02%			
Se		0.00%			
Si	1.64%	1.80%			
Te		0.00%			
Ti	0.05%	0.05%			
U		0.00%			
Zn	0.01%	0.00			

Table XX. Trim Chemical Addition for Large Batch SRAT Heel 2 Preparation

		Target Addition, g	Actual Addition, g	Wt% Solids w/o Trim	Target Solids w/Trim, g ⁹	Actual Solids added, g ⁹
<i>Sludge A'</i>		2100.0	2100.0	19.3%	423.6	423.6
Trim Chemicals	Wt% Species in Solution	Target Addition, grams	Actual Addition, grams	Elemental Solids Factor	Target Elemental Solids, g	Actual Elemental Solids, g
<i>AgNO3</i>	100.00%	0.252	0.254	0.6349	0.160	0.161
<i>HgO</i>	100.00%	5.885	5.8852	0.9261	5.450	5.450
<i>Pd(NO3)2*H2O</i>	15.27% ⁸	0.061	0.0609	0.1527	0.0093	0.0093
<i>Rh(NO3)3*2H2O</i>	4.93% ⁸	0.452	0.4526	0.0493	0.0223	0.0223
<i>RuCl3</i>	41.74% ⁸	0.220	0.2197	0.4174	0.0920	0.0917
<i>Cd(NO3)2*4H2O</i>	100.00% ⁸	1.262	1.2649	0.3644	0.460	0.461

Element		Target Wt% Solids ⁹	Actual Wt% Solids
Ag		0.04%	0.04%
Hg		1.30%	1.30%
Pd		0.0022%	0.0022%
Rh		0.0053%	0.0053%
Ru		0.022%	0.022%
Cd		0.11%	0.11%

- 2) Calculated acid addition rates, boilup rates, purge rates, antifoam addition, etc. were based on scaling from DWPF settings as shown in Table XXI.
- 3) The acid additions were determined for 125% of stoichiometry with a redox target of $0.2 \text{ Fe}^{+2}/\Sigma\text{Fe}$. The redox calculation spreadsheet for the large batch heel are shown in Table XXII.
- 4) A review, as required by the Conduct of Research and Development has been completed.
- 5) The experiments are planned to be completed the week of June 14, 1999.

⁸ These values represent the weight percent of elemental Pd, Rh, or Ru in their respective solutions.

⁹ These values include the weight and/or solids of the added trim chemicals.

Table XXI. Scaling Calculations for Large Batch SRAT Heel 2 Preparation

	DWPF	TNX LBH2	Time
Scale factor	1	10,814 (12220) [†]	
Sludge Added Volume	6,000 gal	1858 ml	
Sludge Heel Volume	0 gal	0 ml	
Sludge Added Density	1.13	1.13	
Sludge Heel Density	1.15	1.15	
Sludge Added Mass	25664 kg	2100.0 g	
Sludge Heel Mass	0 kg	0.0 g	
SRAT Added Water	1,000 gal	309.7 ml	2.2 hrs boil
SRAT purge air [‡]	188 scfm	489.8 scc/min	
SRAT He purge	0.50 vol %	2.46 scc/min	
SME purge air [‡]	66 scfm	172.0 scc/min	
SME He purge	0.50 vol %	0.86 scc/min	
Antifoam (100 ppm in Total Sludge)	5.66 lbs	0.21 g	
Antifoam Solution (20 to 1 solution)	113.16 lbs	4.20 g	
nitric acid feedrate	2 gpm	0.697 ml/min	1.0 hrs feed
formic acid feedrate	2 gpm	0.700 ml/min	2.5 hrs feed
boilup rate	5,000 lb/hr	3.50 g/min	
Formic Molarity	23.55 M	21.3 M	
Nitric Molarity	10.35 M	10.40 M	
Formic Volume	270.6 gal	104.74 ml	
Formic Mass		126.15 g	
Nitric Volume	134.3 gal	46.77 ml	
Nitric Mass		61.30 g	
formic feed time	135.3 min	135.3 min	
Nitric feed time	67.1 min	67.1 min	
Total Vol		2319.66 ml	

[†]Correct scale factor in parentheses, value off due to improper density correction.

[‡]Actual SRAT/SME Gas Purge equivalent to this Air purge plus the Helium Purge.

Table XXII. Large Batch SRAT Heel Preparation Redox Calculation

Stoichiometry ratio	125.0% (140%) [†]			Date: 6/15/99
Stream	PHA	Sludge	Frit	SME
Oxide Contribution (%) (in SME)	0.0%	26.0%	74.0%	15399.2 kg Calc. Basis
Density (kg/L)	1.0355	1.130	n/a	137.0%
Total Solids (%)	5.38%	19.88%	n/a	48.0%
Calcine Factor (ox/sol)	1.00	0.78	n/a	n/a
Hydroxide (M)	n/a	0.646	n/a	n/a
Mercury (ppm)	n/a	2584.4	n/a	n/a
Total Mn (wt% solids)	n/a	4.45	n/a	n/a
Soluble Mn (ppm)	n/a	0.00	n/a	n/a
*TIC (ppm)	n/a	0.00	n/a	n/a
Total Acid (M)	0.240	n/a	n/a	n/a
Nitrite (ppm)	0.0	8452.0	0.0 (kg/100kg frit)	
NO2 Destruction	0.0%	100.0%	0.0%	
Nitrate (ppm)	1012.1	3466.0	0.0 (kg/100kg frit)	
% nitrite to nitrate conversion		35.0%		
Formate (ppm)	22808.9	0.0	1.0 (kg/100kg frit)	
Reaction formate destruction, kg		142.37		
Factor for total formate destruction		15.0%		
Total formate destruction, kg		21.36		
Oxide Mass (kg)	0.0	4003.8	11395.4	15399.2
Solids Mass (kg)	0.00	5102.26	11395.39	16497.65
Total Mass (kg)	0.00	25665.29	n/a	34370.10
Volume (L)	0.00	22,712.65	n/a	25087.67
% Stoichiometry	n/a	125.0%	n/a	n/a
Volume HNO3@50% (L)	n/a	2,839.60	n/a	n/a
NO2 Contribution (kg)	0.000	216.923	0.000	216.923
NO2 Remaining (kg)	0.000	0.000	0.000	0.000
NO3 Contribution (kg)	0.000	1987.098	0.000	1987.098
COOH Contribution (kg)	0.000	(142.37)	93.843	(48).530
NO2 (Molar@45%)				0.000
NO3 (Molar@45%)				1.359
COOH (Molar@45%)				-0.046
Predicted Fe(II)/ΣFe			0.09	≤ BDL@0.03 ≤ 0.1
Volume HCOOH@90% (L)			3458.10	3180.09 3504.50
% Stoichiometry	n/a	125.0%	n/a	n/a
Volume HCOOH@90% (L)	n/a		n/a	n/a
		1,247.85		
NO2 Contribution (kg)	0.000	216.923	0.000	216.923
NO2 Remaining (kg)	0.000	0.000	0.000	0.000
NO3 Contribution (kg)	0.000	164.879	0.000	164.879
COOH Contribution (kg)	0.000	1301.639	93.843	1395.482
NO2 (Molar@45%)				0.000
NO3 (Molar@45%)				0.113
COOH (Molar@45%)				1.314
Predicted Fe(II)/ΣFe			0.09	≤ 0.470 ≤ 0.1
Volume HNO3@50% (L)			1230.65	1195.51

[†]Value in parentheses represents corrected value due to scale factor error.

Table XXII. Large Batch SRAT Heel Preparation Redox Calculation Continued

mol% Nitric	n/a	17.9%	n/a	n/a
Volume HCOOH@90% (L)	n/a	1,024.48	n/a	n/a
Volume HNO3@50% (L)		508.29		
NO2 Contribution (kg)	0.000	216.923	0.000	216.923
NO2 Remaining (kg)	0.000	0.000	0.000	0.000
NO3 Contribution (kg)	0.000	491.056	0.000	491.056
COOH Contribution (kg)	0.000	943.805	0.000	943.805
NO2 (Molar@45%)				0.000
NO3 (Molar@45%)				0.336
COOH (Molar@45%)				0.889
Predicted Fe(II)/ΣFe			0.09	≤ 0.200 (0.210) [†] ≤ 0.1

[†]Value in parentheses represents corrected value due to scale factor error.

kgb 9/16/96

Run # LBH2

Date: 6-15-99

PREREQUISITES

1. ☒ Signed TAR requesting work.
2. ☒ Issued Testing scope and task assignment.
3. ☒ Analyze sludge for density, total base (pH 5.5), nitrate, manganese, nitrite, density, solids.
4. ☒ Calibrate GC. Calibrate for nitrogen, oxygen, N₂O, hydrogen, and carbon dioxide.
5. ☒ Prepare sufficient 90% formic acid and 50% nitric acid.
6. ☒ Prepare sufficient antifoam solution or make sure sufficient solution is available.
7. ☒ Calculate batching and scaling for experiment based on DWPF parameters.
8. ☒ Calculate redox for experiment based on DWPF parameters.
9. ☒ Setup experimental rig per sketch below.
10. ☒ Complete leak check and water run.

Run # LBH2

Date: 6-15-99

PREPARATION FOR SRAT CYCLE

Note: Do not insulate kettle until acid addition is complete

1. ☒ Add 2100 g of Sludge A' to kettle.
2. ☒ Turn on kettle agitator. Setpoint = 200 rpm. Mark Sludge Level in Kettle as De-water Level for later de-watering and concentration.
3. ☒ Turn on cooling water to SRAT condenser. Setpoint = 40°C.
4. ☒ Turn on cooling water to Chilled (FAVC) condenser. Setpoint = 10°C.
5. ☒ Add trim chemicals (from) directly to the kettle.
6. ☒ Transfer 309.7 g of distilled water to the kettle (use to rinse all containers used for adding sludge, noble metals, mercury, etc.).
7. ☒ Calibrate pH probe with pH 4 and 10 buffer. Record measured pH of pH 7 buffer 7.131.
8. ☒ Install pH probe in kettle. Record initial pH of sludge 12.068.
9. ☒ Turn on the air purge to kettle at 100.0 sccm. Connect the outlet flowmeter to perform the leak check. The outlet flow should be 90-110 sccm. If it is not, tighten all connections until the system is leak tight. Write down the leak check in the logbook.
10. ☒ Disconnect outlet flowmeter.
11. ☒ Set the air flow to kettle at 490 sccm. Set the He flow to 2.46 sccm.
12. ☒ Make sure the GC computer has enough memory space for the run (at least 40 Mbyte).
13. ☒ Set the GC computer time equal to the clock time. Record the time in the log book.
14. ☒ Install the calibration gas cylinder to the GC and let the GC run five times. If at the end of five runs the GC reading is within 10% of the gas composition in the cylinder, print the calibration check results and write down "pre-cal check and run number" on the printout. Otherwise, select "Calibration" "Level 1" "OK" to calibrate the GC five times. At the end of five runs the GC reading should be within 10% of the gas composition in the cylinder. If it is not, contact the engineer. Print the calibration check results and write down "pre-cal check and run number" on the printout.
15. ☒ Start the GC for this run beginning with baseline reading for a few minutes. Write down the GC time, filename etc. in the logbook. Record the baseline data on the data sheet.

Run # LBH2

Date: 6-16-99

SRAT CYCLE

1. ☒ Add 2.1 g 1:10 antifoam solution and 2.1 g water directly to the kettle (100 ppm antifoam).
2. ☒ Start heating up the kettle with the TEMP-O-TROL Model TOT-VOVC (yellow box) temperature controller. Turn on its power switch, turn the voltage output dial to maximum (115), press and hold the up [Δ] and down [∇] keys simultaneously until display flashes between TUNE and OFF, then press the up [Δ] key until display says SPrr, now press and hold the enter [*] key and the display should show 60 for °C per hour the system will ramp up to reach its setpoint. If the display shows something other than 60 then while pressing the enter [*] key, press the up or down keys to adjust the value to 60. To return to the normal temperature display, press and hold up [Δ] and down [∇] keys simultaneously until the temperature is shown. Now press and hold the enter [*] key to check the current setpoint which should be 93. If the display shows something other than 93 then while pressing the enter [*] key, press the up or down keys to adjust the value to 93. Once you release the enter [*] key, a little flashing block [] should appear in the upper left corner of the display and the ON light should illuminate indicating power to the heating mantle. The temperature should ramp to 93°C then hold there. Record the run data every 20 minutes on the data sheet.
3. ☒ If slurry begins to foam over at any time, switch off heating and turn on the cooling coil water pump to bring the temperature down rapidly. Add antifoam solution as shown in Step 1. Then switch off the cooling coil water pump and slowly heat up the kettle again to the point of boiling.
4. ☒ Once at 93°C, add 46.77 ml of 50-wt% nitric acid at 0.697 ml/min (reference Table XXI) to the kettle. Should take about 1.1 hour.
5. ☒ Now add 104.74 ml of 90-wt% formic acid at 0.700 ml/min (reference Table XXI) to the kettle. Should take about 2.3 hours.
6. ☒ Add 2.1 g 1:10 antifoam solution and 2.1 g water directly to the kettle (100 ppm antifoam).
7. ☒ Adjust the setpoint on the TEMP-O-TROL to 110°C by pressing and holding the enter [*] key and pressing the up [Δ] and down [∇] keys. Adjust voltage output to 3.5 g/min boil-up rate and bring the kettle contents to boiling.
8. ☒ Dewater until remove 469.6 g of water in the SMECT leaving approximately 2 L in the kettle (kettle volume should be close to De-water Level marked in Step 2 of PREPARATION FOR SRAT CYCLE). Should take about 2.2 hours.
9. ☒ Reflux the slurry for a total of 13 hours (including the dewater times in step 8) at 3.5 g/min boil-up. Continue refluxing until there is evidence of nitrite destruction (hydrogen release) and the hydrogen has reached its peak. Then turn off the heat to cool the kettle to sub-boiling.
10. ☒ Pull a 125 ml sample (LB SRAT Heel 2) from the kettle, record the weight here 121.0. Label and send to lab for analyses.
11. ☒ After vessel has cooled, hook up pump to remove a set amount of SRAT product in preparation of the large batch run.

APPENDIX A-3: LARGE BATCH RUNS 2V & 3V

SRT-PTD-98-0039, Rev. 1

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January 7, 1999

TO: L. F. Landon, 704-1T

FROM: W. E. Daniel, 704-1T

Run Plan for Large Batch Variability Runs with Normal Weight% Solids Sludge for Developing Strategies for Increased CPC Batch Sizes (U)

This run plan documents the variability runs with normal weight percent solids sludge as detailed in the Task Technical Plan for Developing Strategy for Increased CPC Batch Size (WSRC-RP-98-00354) as requested in DWPF Technical Task Request HLW/DWPT/TTR-980013. The experimental work will be controlled using the Laboratory Scale Chemical Process Cell Simulations (Manual L27, Procedure 2.02) and this run plan. This run plan includes many of the experimental details, the instructions for final sludge preparation, the scaling necessary for determining the operating conditions such as feed rates, purge rates, and the steps in completing the SRAT and SME cycles. This document also summarizes the decisions made to complete these experiments.

- 1) The sludge used for the SRAT Heel preparation is a Tank 42-sludge simulant created from the Optima Tank 51 simulant with the following modifications.
 - a) A recipe is shown in Table XXIII that targets a 20 weight percent solids sludge after the trim chemicals (noble metals and mercury) are added. This sludge will be referred to as Sludge A' and its pre-trim measured as well as post-trim predicted elemental weight percent analyses are shown in Table XXIV. Analyses of the SRAT Heel used in these experiments are shown in Table XXV.
 - b) Tank 42 levels of noble metals and mercury will be added to the sludge batches as shown in Table XXVI and Table XXX. These levels will require approximately 14 hours of refluxing in the SRAT to steam strip mercury and meet the DWPF constraint of 0.45 wt % mercury.

Table XXIII. Preparation Of Tank 42 Sludge 20 weight % (Trim Chemicals Missing)

Component	Amount, g	Comments
Tank 51 sludge simulant	16521.36	18.52 wt% solids initially
Tank 51 supernate	527.2	Added Supernate to lower wt% solids
Al ₂ O ₃	148.29	
Ni(NO ₃) ₂ *6H ₂ O	30.22	
SiO ₂	53.48	
MnO ₂ *x H ₂ O	221.77	Total Mass @ 27.2 wt% solids
Water	200.00	
Al ₂ O ₃	0.94	
Na ₂ C ₂ O ₄	4.87	
NaF	0.66	
NaOH	7.05	
NaCl	0.82	

Table XXIV. Elemental Analyses of Large Batch 20 wt% Sludge A'

Insoluble Species	Measured Wt% Solids Pre-Trim	Predicted Wt% Solids Post-Trim	Soluble Species	Measured Wt% Solids Pre-Trim	Predicted Wt% Solids Post-Trim
Al	5.72%	7.58%	Al		0.02%
*Ag		0.04%	C2O4	0.28%	0.27%
Ca	2.04%	1.94%	Cl	0.04%	0.04%
*Cd		0.11%	CO3		1.81%
Cl		0.07%	Cr		0.00%
Cr		0.16%	F	0.01%	0.02%
Cu	0.02%	0.02%	K		0.00%
F		0.01%	Li		0.00%
Fe	23.08%	21.80%	Na		0.25%
*Hg		1.30%	NO2	4.38%	3.73%
K	0.16%	0.05%	NO3	1.80%	1.44%
Li	0.00%	0.00%	OH		0.12%
Mg	1.13%	1.11%	PO4	0.06%	0.05%
Mn	4.48%	3.64%	SO4	0.26%	0.21%
Na	7.88%	5.74%			
Ni	0.35%	0.34%			
P		0.00%			
*Pd		0.00%			
Pu		0.00%			
*Rh		0.01%			
*Ru		0.02%			
Se		0.00%			
Si	1.64%	1.80%			
Te		0.00%			
Ti	0.05%	0.05%			
U		0.00%			
Zn	0.01%	0.00			

Table XXV. Elemental Analyses of Large Batch 20.4 wt% SRAT Heel prepared from Sludge A'

Insoluble Species	Measured Wt% Solids	Soluble Species	Measured Wt% Solids
Al	5.30%	Al	--
*Ag	--	C2O4	0.04%
Ca	2.04%	Cl	0.16%
*Cd	0.00%	CO3	--
Cl	--	Cr	--
Cr	--	F	--
Cu	0.01%	K	--
F	--	Li	--
Fe	20.80%	Na	--
*Hg	--	NO2	0.12%
K	0.14%	NO3	9.07%
Li	0.00%	OH	--
Mg	0.89%	PO4	0.04%
Mn	4.17%	SO4	0.10%
Na	7.26%		
Ni	0.32%		
P	0.24%		
*Pd	0.045%		
Pu	--		
*Rh	0.0053%		
*Ru	0.032%		
Se	--		
Si	1.17%		
Te	0.00%		
Ti	0.03%		
U	--		
Zn	0.11%		

Table XXVI. Trim Chemical Addition for First Sludge Addition for Run 2V

	Target Addition, g	Actual Addition, g	Wt% Solids	Target Solids, g	Actual Solids added, g
Sludge A'	2000.0	2000.0	19.3%	386.0	386.0
Trim Chemicals	Target Addition, grams	Actual Addition, grams	Elemental Solids Factor	Target Elemental Solids, g	Actual Elemental Solids, g
AgNO ₃	0.225	0.2252	0.6349	0.143	0.143
Cd(NO ₃) ₂ *4H ₂ O	1.165	1.1646	0.3644	0.425	0.424
HgO	5.126	5.125	0.9261	4.748	4.746
Pd(NO ₃) ₂ *H ₂ O	0.020	0.021	0.1527 [†]	0.008	0.003 [†]
Rh(NO ₃) ₃ *2H ₂ O	0.065	0.064	0.0493 [†]	0.020	0.003 [†]
RuCl ₃	0.174	0.174	0.4174 [†]	0.085	0.073 [†]

Element	Target Wt% Solids	Actual Wt% Solids
Ag	0.04%	0.04%
Cd	0.11%	0.11%
Hg	1.30%	1.23%
Pd	0.0022%	0.0008% [†]
Rh	0.0053%	0.0008% [†]
Ru	0.022%	0.019% [†]

[†]Values changed from original run plan to reflect noble metal under addition.

Table XXVII. Trim Chemical Addition for Second Sludge Addition for Run 2V

	Target Addition, g	Actual Addition, g	Wt% Solids	Target Solids, g	Actual Solids added, g
Sludge A'	333.3	333.3	19.3%	64.3	64.3
Trim Chemicals	Target Addition, grams	Actual Addition, grams	Elemental Solids Factor	Target Elemental Solids, g	Actual Elemental Solids, g
AgNO ₃	0.037	0.0373	0.6349	0.024	0.024
Cd(NO ₃) ₂ *4H ₂ O	0.194	0.194	0.3644	0.070	0.070
HgO	0.903	0.904	0.9261	0.836	0.837
Pd(NO ₃) ₂ *H ₂ O	0.003	0.003	0.1527 [†]	0.002	0.002
Rh(NO ₃) ₃ *2H ₂ O	0.010	0.010	0.0493 [†]	0.004	0.004
RuCl ₃	0.029	0.029	0.4174 [†]	0.014	0.014

Element	Target Wt% Solids	Actual Wt% Solids
Ag	0.04%	0.04%
Cd	0.11%	0.11%
Hg	1.30%	1.30%
Pd	0.0022%	0.0007% [†]
Rh	0.0053%	0.0008% [†]
Ru	0.022%	0.019% [†]

[†]Values changed from original run plan to reflect noble metal under addition.

Table XXVIII. Trim Chemical Addition for First Sludge Addition for Run 3V

	Target Addition, g	Actual Addition, g	Wt% Solids	Target Solids, g	Actual Solids added, g
<i>Sludge A'</i>	2000.0	2000.0	19.3%	386.0	386.0
Trim Chemicals	Target Addition, grams	Actual Addition, grams	Elemental Solids Factor	Target Elemental Solids, g	Actual Elemental Solids, g
AgNO ₃	0.225	0.225	0.6349	0.143	0.143
Cd(NO ₃) ₂ *4H ₂ O	1.165	1.164	0.3644	0.425	0.424
HgO	5.168	5.168	0.9261	4.786	4.786
Pd(NO ₃) ₂ *H ₂ O	0.020	0.022	0.1527 [†]	0.008	0.003 [†]
Rh(NO ₃) ₃ *2H ₂ O	0.065	0.065	0.0493 [†]	0.020	0.003 [†]
RuCl ₃	0.174	0.174	0.4174 [†]	0.085	0.073 [†]

Element	Target Wt% Solids	Actual Wt% Solids
Ag	0.04%	0.04%
Cd	0.11%	0.11%
Hg	1.30%	1.30%
Pd	0.0022%	0.0009% [†]
Rh	0.0053%	0.0008% [†]
Ru	0.022%	0.019% [†]

[†]Values changed from original run plan to reflect noble metal under addition.

Table XXIX. Trim Chemical Addition for Second Sludge Addition for Run 3V

	Target Addition, g	Actual Addition, g	Wt% Solids	Target Solids, g	Actual Solids added, g
<i>Sludge A'</i>	333.3	333.3	19.3%	64.3	64.3
Trim Chemicals	Target Addition, grams	Actual Addition, grams	Elemental Solids Factor	Target Elemental Solids, g	Actual Elemental Solids, g
AgNO ₃	0.037	0.038	0.6349	0.024	0.024
Cd(NO ₃) ₂ *4H ₂ O	0.194	0.194	0.3644	0.070	0.070
HgO	0.910	0.907	0.9261	0.843	0.840
Pd(NO ₃) ₂ *H ₂ O	0.003	0.004	0.1527 [†]	0.002	0.0006 [†]
Rh(NO ₃) ₃ *2H ₂ O	0.010	0.0105	0.0493 [†]	0.004	0.0005 [†]
RuCl ₃	0.029	0.031	0.4174 [†]	0.014	0.013 [†]

Element	Target Wt% Solids	Actual Wt% Solids
Ag	0.04%	0.04%
Cd	0.11%	0.11%
Hg	1.30%	1.31%
Pd	0.0022%	0.0001% [†]
Rh	0.0053%	0.0008% [†]
Ru	0.022%	0.020% [†]

[†]Values changed from original run plan to reflect noble metal under addition.

- 2) The batching of the materials is designed to produce a glass containing 26 wt % calcined sludge solids and 74 wt % frit 200. A batching summary is shown in Table XXX.
- 3) Calculated acid addition rates, boilup rates, purge rates, antifoam addition, etc. were based on scaling from DWPF settings as shown in Table XXXI.
- 4) Run 2V simulates normal acid additions for 137.5% of stoichiometry with a redox target of $0.2 \text{ Fe}^{+2}/\Sigma\text{Fe}$ while Run 3V simulates high acid additions for 300% stoichiometry. The original task plan called for 200 gallons of pre-acid for Run 2V but after consultation with DWPF, it was decided to add two-thirds of 200 gallons so there would be some acid left for the regular addition. At the current TNX scale, this means 39 ml of pre-acid will be added for Run 2V leaving 3 ml for later to match the required stoichiometric amount. The amount of nitric for Run 3V is the same as with 137.5% stoichiometry and a redox target of $0.2 \text{ Fe}^{+2}/\Sigma\text{Fe}$ but the amount of formic is increased to give 300% stoichiometry. The redox calculation spreadsheets for the Variability Run 2V and 3V are shown in Table XXXII and Table XXXIII, respectively.
- 5) A review, as required by the Conduct of Research and Development has been completed and is included in Appendix B.
- 6) The experiments should be completed the week of January 11, 1999.

Table XXX. Batching Summary for Variability Runs 2V and 3V

Batching Summary	Run 2V	Run 3V
Sludge & Heel Mass	2833.3 g	2733.3 g
Nitric Acid Volume, ml	42.15 ml	44.91 ml
Formic Acid Volume, ml	106.60 ml	260.73 ml
SRAT Product Sample, ml	125	125
Frit 200 Addition #1, g	563.86 g	544.64 g
SME Water Addition #1, g	1035.68 g	1000.39 g
SME 90 wt% Formic Acid Addition #1, g	11.49 g	11.10 g
Frit 200 Addition #2, g	563.86 g	544.64 g
SME Water Addition #2, g	1035.68 g	1000.39 g
SME 90 wt% Formic Acid Addition #2, g	11.49 g	11.10 g
SRAT Air Purge [†] , scc/min	466.5	466.5
SRAT Helium purge, scc/min	2.34	2.34
SME Air Purge [†] , scc/min	163.8	163.8
SME Helium purge, scc/min	0.82	0.82

[†]Actual SRAT Gas Purge equivalent to this Air purge plus the Helium Purge.

Table XXXI. Scaling Calculations for Large Batch Variability Runs 2V and 3V

	DWPF	TNX 2V	Time	DWPF	TNX 3V	Time
Scale factor		11,355 (12831) [†]			11,355 (12831) [†]	
Sludge Added Volume	7,000 gal	2065 ml		7,000 gal	2065 ml	
Sludge Heel Volume	1,500 gal	442 ml		1,200 gal	354 ml	
Sludge Added Density	1.13	1.13		1.13	1.13	
Sludge Heel Density	1.13	1.13		1.13	1.13	
Sludge Added Mass	29941 kg	2333.3 g		29941 kg	2333.3 g	
Sludge Heel Mass	6416 kg	500.0 g		5133 kg	400.0 g	
SRAT Added Water	1,000 gal	295.0 ml	2.2 hrs	1,000 gal	295.0 ml	3.0 hrs boil
SRAT purge air [‡]	188 scfm	466.5 scc/min		188 scfm	466.5 scc/min	
SRAT He purge	0.50 vol %	2.34 scc/min		0.50 vol %	2.34 scc/min	
SME purge air [‡]	66 scfm	163.8 scc/min		66 scfm	163.8 scc/min	
SME He purge	0.50 vol %	0.82 scc/min		0.50 vol %	0.82 scc/min	
Antifoam (100 ppm in Total Sludge)	8.02 lbs	0.23 g		7.73 lbs	0.23 g	
Antifoam Solution (20 to 1 solution)	160.31 lbs	4.67 g		154.65 lbs	4.67 g	
Elemental Hg to Reduce					46.10 g	
nitric acid feedrate	2 gpm	0.669 ml/min	1.0 hrs	2 gpm	0.669 ml/min	1.1 hrs
formic acid feedrate	2 gpm	0.687 ml/min	2.7 hrs	2 gpm	0.687 ml/min	6.5 hrs
boilup rate	5,000 lb/hr	3.33 g/min		5,000 lb/hr	3.33 g/min	
Formic Molarity	23.55 M	22.85 M		23.55 M	22.85 M	
Nitric Molarity	10.35 M	10.32 M		10.35 M	10.32 M	
Formic Volume	310.3 gal	106.60 ml		758.9 gal	260.73 ml	
Formic Mass		128.39 g			314.02 g	
Nitric Volume	126.1 gal	42.15 ml		134.3 gal	44.91 ml	
Nitric Mass		55.15 g			58.77 g	
formic feed time	155.1 min	155.1 min		379.4 min	379.4 min	
Nitric feed time	63.0 min	63.0 min		67.2 min	67.2 min	
Total Vol		2951.07 ml			3019.46 ml	
Frit Volume, gallons	3,759 gal	1253.018 g		3,631 gal	1210.319 g	
Frit Density	1.5			1.5		
Frit wt % solids	60%			60%		
Frit Solids	28,231.0 lbs	1127.716 g		27,269.0 lbs	1089.287 g	
Formic Acid	517.6 lbs	20.675 g		499.9 lbs	19.970 g	
Water	33,987.0 lbs	1357.645 g		32,828.9 lbs	1311.381 g	
Transfer Water	17,924.5 lbs	716.010 g		17,313.7 lbs	691.611 g	
Total Water	51,911.5 lbs	2073.655 g		50,142.5 lbs	2002.992 g	
Total	80,660.1 lbs	3222.045 g		77,911.5 lbs	3112.249 g	

[†]Correct scale factor in parentheses, value off due to improper density correction.

[‡]Actual SRAT Gas Purge equivalent to this Air purge plus the Helium Purge.

Table XXXI. Scaling Calculations for Large Batch Variability Runs 2V and 3V Continued

	DWPF	TNX 2V	Time	DWPF	TNX 3V	Time
frit 200	28,231.0 lbs	1127.716 g		27,269.0 lbs	1089.287 g	
90 wt % formic acid	575.1 lbs	22.972 g		555.5 lbs	22.189 g	
water	51,854.0 lbs	2071.357 g		50,087.0 lbs	2000.773 g	
Total	80,660.1 lbs	3222.045 g		77,911.5 lbs	3112.249 g	
frit 200 Addition 1	14,115.5 lbs	563.858 g		13,634.5 lbs	544.644 g	
90 wt % formic addition 1	287.5 lbs	11.486 g		277.7 lbs	11.095 g	
water addition 1	25,927.0 lbs	1035.679 g	5.2 hrs	25,043.5 lbs	1000.386 g	5.0 hrs
frit 200 Addition 2	14,115.5 lbs	563.858 g		13,634.5 lbs	544.644 g	
90 wt % formic addition 2	287.5 lbs	11.486 g		277.7 lbs	11.095 g	
water addition 2	25,927.0 lbs	1035.679 g	5.2 hrs	25,043.5 lbs	1000.386 g	5.0 hrs

Table XXXII. Large Batch Variability Run 2V Redox Calculation

Stoichiometry ratio:	137.5% (155%) [†]			Date:	1/4/99
Stream	PHA	Sludge	Frit	SME	
Oxide Contribution (%) (in SME)	0.0%	26.0%	74.0%	17538.9	kg Calc. Basis
Density (kg/L)	1.0355	1.130	n/a	137.0%	
Total Solids (%)	5.38%	19.49%	n/a	48.0%	
Calcine Factor (ox/sol)	1.00	0.78	n/a	n/a	
Hydroxide (M)	n/a	0.542	n/a	n/a	
Mercury (ppm)	n/a	2208.2	n/a	n/a	
Total Mn (wt% solids)	n/a	4.37	n/a	n/a	
Soluble Mn (ppm)	n/a	0.00	n/a	n/a	
*TIC (ppm)	n/a	0.00	n/a	n/a	
Total Acid (M)	0.240	n/a	n/a	n/a	
Nitrite (ppm)	0.0	7070.8	0.0	(kg/100kg frit)	
NO2 Destruction	0.0%	100.0%	0.0%		
Nitrate (ppm)	1012.1	6002.1	0.0	(kg/100kg frit)	
% nitrite to nitrate conversion		35.0%			
Formate (ppm)	22808.9	0.0	1.0	(kg/100kg frit)	
Reaction formate destruction, kg		150.28			
Factor for total formate destruction		15.0%			
Total formate destruction, kg		22.54			
Oxide Mass (kg)	0.0	4560.1	12978.8	17538.9	
Solids Mass (kg)	0.00	5837.09	12978.80	18815.89	
Total Mass (kg)	0.00	29942.84	n/a	39199.77	
Volume (L)	0.00	26,498.09	n/a	28612.97	
% Stoichiometry	n/a	137.5%	n/a	n/a	
Volume HNO3@50% (L)	n/a	3,149.86	n/a	n/a	
NO2 Contribution (kg)	0.000	211.719	0.000	211.719	
NO2 Remaining (kg)	0.000	0.000	0.000	0.000	
NO3 Contribution (kg)	0.000	2275.144	0.000	2275.144	
COOH Contribution (kg)	0.000	(150.28)	93.843	(56).441	

[†]Value in parentheses represents corrected value due to scale factor error.

Table XXXII. Large Batch Variability Run 2V Redox Calculation Continued

Stoichiometry ratio:	137.5% (155%) [†]				Date:	1/4/99
Stream	PHA	Sludge	Frit		SME	
NO2 (Molar@45%)					0.000	
NO3 (Molar@45%)					1.556	
COOH (Molar@45%)					-0.053	
Predicted Fe(II)/ΣFe			0.09	≤	BDL@0.03	≤ 0.1
Volume HCOOH@90% (L)			3962.99		3645.89	4015.91
% Stoichiometry	n/a	137.5%	n/a		n/a	
Volume HCOOH@90% (L)	n/a	1,384.19	n/a		n/a	
NO2 Contribution (kg)	0.000	211.719	0.000		211.719	
NO2 Remaining (kg)	0.000	0.000	0.000		0.000	
NO3 Contribution (kg)	0.000	253.822	0.000		253.822	
COOH Contribution (kg)	0.000	1445.008	93.843		1538.851	
NO2 (Molar@45%)					0.000	
NO3 (Molar@45%)					0.174	
COOH (Molar@45%)					1.450	
Predicted Fe(II)/ΣFe			0.09	≤	0.458	≤ 0.1
Volume HNO3@50% (L)			1262.94			1222.87
mol% Nitric	n/a	15.2%	n/a		n/a	
Volume HCOOH@90% (L)	n/a	1,174.49	n/a		n/a	
Volume HNO3@50% (L)		477.20				
NO2 Contribution (kg)	0.000	211.719	0.000		211.719	
NO2 Remaining (kg)	0.000	0.000	0.000		0.000	
NO3 Contribution (kg)	0.000	560.053	0.000		560.053	
COOH Contribution (kg)	0.000	1094.933	0.000		1094.933	
NO2 (Molar@45%)					0.000	
NO3 (Molar@45%)					0.383	
COOH (Molar@45%)					1.031	
Predicted Fe(II)/ΣFe			0.09	≤	0.200 (0.217) [†]	≤ 0.1

[†]Value in parentheses represents corrected value due to scale factor error.

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Table XXXIII. Large Batch Variability Run 3V Redox Calculation

Stoichiometry ratio	300% (340%) [†]			Date:	1/7/99	
Stream	PHA	Sludge	Frit		SME	
Oxide Contribution (%) (in SME)	0:0%	26.0%	74.0%		17621.3	kg Calc. Basis
Density (kg/L)	1.0355	1.130	n/a		137.0%	
Total Solids (%)	5.38%	19.46%	n/a		48.0%	
Calcine Factor (ox/sol)	1.00	0.79	n/a		n/a	
Hydroxide (M)	n/a	0.560	n/a		n/a	
Mercury (ppm)	n/a	2250.2	n/a		n/a	
Total Mn (wt% solids)	n/a	4.38	n/a		n/a	
Soluble Mn (ppm)	n/a	0.00	n/a		n/a	
*TIC (ppm)	n/a	0.00	n/a		n/a	
Total Acid (M)	0.240	n/a	n/a		n/a	
Nitrite (ppm)	0.0	7308.7	0.0	(kg/100kg frit)		
NO2 Destruction	0.0%	100.0%	0.0%			
Nitrate (ppm)	1012.1	5565.6	0.0	(kg/100kg frit)		
% nitrite to nitrate conversion		35.0%				
Formate (ppm)	22808.9	0.0	1.0	(kg/100kg frit)		
Reaction formate destruction, kg		152.31				
Factor for total formate destruction		15.0%				
Total formate destruction, kg		22.85				
Oxide Mass (kg)	0.0	4581.5	13039.8		17621.3	
Solids Mass (kg)	0.00	5827.17	13039.78		18866.95	
Total Mass (kg)	0.00	29942.84	n/a		39306.14	
Volume (L)	0.00	26,498.09	n/a		28690.62	
% Stoichiometry	n/a	300.0%	n/a		n/a	
Volume HNO3@50% (L)	n/a	7,045.36	n/a		n/a	
NO2 Contribution (kg)	0.000	218.842	0.000		218.842	
NO2 Remaining (kg)	0.000	0.000	0.000		0.000	
NO3 Contribution (kg)	0.000	4764.377	0.000		4764.377	
COOH Contribution (kg)	0.000	(152.31)	93.843		(58).463	
NO2 (Molar@45%)					0.000	
NO3 (Molar@45%)					3.258	
COOH (Molar@45%)					-0.055	
Predicted Fe(II)/ΣFe			0.09	≤	BDL@0.03	≤ 0.1
Volume HCOOH@90% (L)			9024.87		8701.99	9078.73
% Stoichiometry	n/a	300.0%	n/a		n/a	
Volume HCOOH@90% (L)	n/a	3,096.05	n/a		n/a	
NO2 Contribution (kg)	0.000	218.842	0.000		218.842	
NO2 Remaining (kg)	0.000	0.000	0.000		0.000	
NO3 Contribution (kg)	0.000	243.245	0.000		243.245	
COOH Contribution (kg)	0.000	3259.655	93.843		3353.498	

[†]Value in parentheses represents corrected value due to scale factor error.

Table XXXIII. Large Batch Variability Run 3V Redox Calculation Continued

Stoichiometry ratio:	300% (340%) [†]			Date:	1/7/99	
Stream	PHA	Sludge	Frit		SME	
NO2 (Molar@45%)					0.000	
NO3 (Molar@45%)					0.166	
COOH (Molar@45%)					3.159	
Predicted Fe(II)/ΣFe			0.09	≤	0.888	≤ 0.1
Volume HNO3@50% (L)			2590.82			2550.56
mol% Nitric	n/a	7.2%	n/a		n/a	
Volume HCOOH@90% (L)	n/a	2,872.58	n/a		n/a	
Volume HNO3@50% (L)		508.53				
NO2 Contribution (kg)	0.000	218.842	0.000		218.842	
NO2 Remaining (kg)	0.000	0.000	0.000		0.000	
NO3 Contribution (kg)	0.000	569.580	0.000		569.580	
COOH Contribution (kg)	0.000	2893.264	0.000		2893.264	
NO2 (Molar@45%)					0.000	
NO3 (Molar@45%)					0.390	
COOH (Molar@45%)					2.725	
Predicted Fe(II)/ΣFe			0.09	≤	0.615 (0.688) [†]	≤ 0.1

[†]Value in parentheses represents corrected value due to scale factor error.

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Run # 2V & 3V

Date: 1/13/99

PREREQUISITES

1. ☒ Signed TAR requesting work.
2. ☒ Issued Testing scope and task assignment.
3. ☒ Analyze sludge for density, total base (pH 5.5), nitrate, manganese, nitrite, density, solids.
4. ☒ Calibrate GC. Calibrate for nitrogen, oxygen, N₂O, hydrogen, and carbon dioxide.
5. ☒ Prepare sufficient 90% formic acid and 50% nitric acid.
6. ☒ Prepare sufficient antifoam solution or make sure sufficient solution is available.
7. ☒ Calculate batching and scaling for experiment based on DWPF parameters.
8. ☒ Calculate redox for experiment based on DWPF parameters.
9. ☒ Setup 2 experimental rigs per sketch below.
10. ☒ Complete leak checks and water runs.

Run # 2V

Date: 1/12/99

PREPARATION FOR SRAT CYCLE

Note: Do not insulate kettle until acid addition is complete

1. ☒ Add 2000 g of Sludge A' to kettle using 2-liter transfer bottle or beaker.
2. ☒ Add 500.0 g of SRAT Heel A' to kettle using 2-liter transfer bottle or beaker.
3. ☒ Turn on kettle agitator. Setpoint = 200 rpm. Mark Sludge Level in Kettle as De-water Level for later de-watering and concentration.
4. ☒ Add first batch of trim chemicals (from Table XXVI) directly to the kettle.
5. ☒ Transfer 295 ml of distilled water to the kettle (use to rinse all containers used for adding sludge, noble metals, mercury, etc.).
6. ☒ Calibrate pH probe with pH 4 and 10 buffer. Record measured pH of pH 7 buffer 7.031.
7. ☒ Install pH probe in kettle. Record initial pH of sludge 11.70.
8. ☒ Turn on the air purge to kettle at 100.0 sccm. Connect the outlet flowmeter to perform the leak check. The outlet flow should be 90-110 sccm. If it is not, tighten all connections until the system is leak tight. Write down the leak check in the logbook.
9. ☒ Disconnect outlet flowmeter.
10. ☒ Turn on the air purge to kettle at 466.5 sccm. Turn on He purge and set to 2.34 sccm.
11. ☒ Turn on cooling water to SRAT condenser. Setpoint = 40°C.
12. ☒ Turn on cooling water to Chilled (FAVC) condenser. Setpoint = 10°C.
13. ☒ Make sure the GC computer has enough memory space for the run (at least 40 Mbyte).
14. ☒ Set the GC computer time equal to the clock time. Record the time in the log book.
15. ☒ Install the calibration gas cylinder to the GC and let the GC run five times. If at the end of five runs the GC reading is within 10% of the gas composition in the cylinder, print the calibration check results and write down "pre-cal check and run number" on the printout. Otherwise, select "Calibration" "Level 1" "OK" to calibrate the GC five times. At the end of five runs the GC reading should be within 10% of the gas composition in the cylinder. If it is not, contact the engineer. Print the calibration check results and write down "pre-cal check and run number" on the printout.
16. ☒ Start the GC for this run beginning with baseline reading for a few minutes. Write down the GC time, filename etc. in the logbook. Record the baseline data on the data sheet.

Run # 2V

Date: 1/13/99

SRAT CYCLE

1. ☒ Add 2.3 g 1:10 antifoam solution and 2.3 g water directly to the kettle (100-ppm antifoam).
2. ☒ Start heating up the kettle with the Therm-O-Watch (yellow box) temperature controller. Turn on its power switch, press the [SEL] key for 3 seconds until display shows "roFF". Press the [^] key until display shows "rrUn" then press and hold the [SEL] key until the normal display appears. The Therm-O-Watch will ramp up to 93°C and hold at 93°C. Record the run data every 20 minutes on the data sheet.
3. ☒ Once at 93°C, add 39.33 ml of 50-wt% nitric acid at 0.669 ml/min (reference Table XXVIII) to the kettle. Should take about 1 hour.
4. ☒ Switch off the Therm-O-Watch, hook the heating mantle to the Cole-Parmer (gray box) temperature controller, and switch on the Cole-Parmer unit. Bring the kettle contents to boiling.
5. ☒ If slurry begins to foam over at any time, switch off heating and turn on the cooling coil water pump to bring the temperature down rapidly. Add antifoam solution as shown in Step 1. Then switch off the cooling coil water pump and slowly heat up the kettle again to the point of boiling.
6. ☒ Dewater until kettle volume returns to De-water Level marked in Step 3 of PREPARATION FOR SRAT CYCLE (approximately 2.2 L). Should take about 1 hour and 45 minutes. (339g)
7. ☒ When dewatering is complete, turn off the heat to kettle, turn on water to cooling coil, and cool the kettle to sub-boiling (90°C).
8. ☒ Add 333.3 g of Sludge A' to the kettle using 2-liter transfer bottle or beaker.
9. ☒ Add second batch of trim chemicals (from Table XXVII) directly to the kettle.
10. ☒ Transfer 50 ml of distilled water to the kettle (use to rinse all containers used for adding sludge, noble metals, mercury, etc.). (50.4 g used)
11. ☒ Allow slurry to cool to 50°C, monitoring torque every 20 minutes.
12. ☒ Pull 10 ml sample for nitrate, nitrite, and formate analysis. Add 1 ml of 1 N NaOH solution and label the sample LB SRAT 2V*-0N.
13. ☒ Start heating up the kettle with the Therm-O-Watch (yellow box) temperature controller. Turn on its power switch, press the [SEL] key for 3 seconds until display shows "roFF". Press the [^] key until display shows "rrUn" then press and hold the [SEL] key until the normal display appears. The Therm-O-Watch will ramp up to 93°C and hold at 93°C. Record the run data every 20 minutes on the data sheet.
14. ☒ Once at 93°C, add 2.82 ml of 50-wt% nitric acid at 0.669 ml/min (reference Table XXVIII) to the kettle. Should take about 5 minutes.
15. ☒ Add 106.60 ml of 90-wt% formic acid at 0.687 ml/min (reference Table XXVIII) to the kettle. Should take about 2 hours and 45 minutes.
16. ☒ Add 2.3 g 1:10 antifoam solution and 2.3 g water directly to the kettle (100 ppm antifoam).
17. ☒ Switch off the Therm-O-Watch, hook the heating mantle to the Cole-Parmer (gray box) temperature controller, and switch on the Cole-Parmer unit. Bring the kettle contents to boiling.

Run # 2V

Date: 1/13/99

SRAT CYCLE (continued)

18. ☒ Dewater until collect **892 g of H₂O** in the SMECT leaving approximately 1.8 L in the kettle. Should take about 4.5 hours. *(Collected 896.3 g)*
19. ☒ Pull **10 ml** sample for nitrate, nitrite, and formate analysis. Add **1 ml** of **1 N NaOH** solution and label **LB SRAT 2V*-1N**.
20. ☒ Add **2.3 g 1:10 antifoam solution** and **2.3 g water** directly to the kettle (100 ppm antifoam).
21. ☒ Reflux the slurry for a total of **14 hours** (including the dewater time in step 18) at **3.4 g/min boil-up** taking **10 ml** sample for nitrate, nitrite, and formate analysis **every 2 hours** and **one at the end** then turn off the heat to cool the kettle to sub-boiling. Add **1 ml** of **1 N NaOH** solution to each sample and label as **LB SRAT 2V*-2N, 4N, 6N, 8N, and 10N**.
22. ☒ Pull a **125** ml sample from the kettle, record the weight on the run sheet. Label as **LB SRAT 2V*final** and send to lab for analyses.
23. ☒ Pulled *extra 125-ml sample LB SRAT-12N for Rheology.*

Run # 2V

Date: 1/14/99

SME CYCLE

1. ☒ Add 2.3 g 1:10 antifoam solution and 2.3 g water directly to the kettle (100 ppm antifoam).
2. ☒ Add 522.6 g frit 200 to the kettle (1st frit addition - Table XXX)¹⁰.
3. ☒ Add 11.26 g of 90-wt% formic acid to the kettle (1st formic addition - Table XXX) 10.
4. ☒ Add 1015.0 g of water to the kettle (1st water addition - Table XXX) 10.
5. ☒ Change air (ch 2) to 0.164 slm and He (ch 1) to 0.82 sccm.
6. ☒ Bring kettle contents to boiling. Record the run data every 20 minutes on the data sheet.
7. ☒ When dewatering is complete (about 4 hours and 40 minutes), turn off the heat to cool the kettle to sub-boiling¹⁰. (Remove 921.3 g)
8. ☒ Add 522.6 g frit 200 to the kettle (2nd frit addition - Table XXX) 10.
9. ☒ Add 11.26 g of 90-wt% formic acid to the kettle (2nd formic addition - Table XXX) 10.
10. ☒ Add 1015.0 g of water to the kettle (2nd water addition - Table XXX) 10.
11. ☒ When dewatering is complete (about 4 hours and 40 minutes), turn off the heat to cool the kettle to sub-boiling¹⁰. Turn on cooling water to cooling coil dip-leg. (Remove 921.3 g)
☒ Take pictures of cooling coil, pH probe by pulling up in kettle.
12. ☒ Pull a 125-ml sample from the kettle, record the weight on the run sheet. Label as LB SME 2V* and send to lab for analyses.
13. ☒ Stop GC and record the GC time and clock time in the logbook. Stop recording run data on the data sheet.
14. ☒ Install the calibration gas cylinder to the GC and run the post-cal check. If the check indicates OK, print a copy and write "post-cal check and run number" on the printout, then place the GC in standby. If the check is not within 10% of the cal gas composition, notify the engineer.
15. ☒ Pump kettle contents into a tared bottle. Record the weight on the run sheet.
16. ☒ Complete pH meter post calibration check. Record measured pH in pH 7 buffer 7.43.
17. ☒ Install the outlet flow meter to the purge gas. *Change channel 2 to 100 sccm and turn off helium before leak checking.*
18. ☒ When the kettle is cool (<50 °C), record the outlet purge flow in the log book. (All channels).
19. ☒ Turn off all instruments.
☒ Weigh all kettle pieces and record in lab book.
☒ Take pictures of pH probe, cooling coil, RTD, stirring rod, and thermocouple. Set cooling coil, pH probe, RTD, and thermocouple aside for later examination.
☒ Start setting up rigs for next experiment.

¹⁰ Modified from original value because of extra 125-ml sample pulled for Rheology.

Run # 3V

Date: 1/12/99

PREPARATION FOR SRAT CYCLE

Note: Do not insulate kettle until acid addition is complete

1. ☒ Add 2000 g of Sludge A' to kettle using 2-liter transfer bottle or beaker.
2. ☒ Add 400.0 g of SRAT Heel A' to kettle using 2-liter transfer bottle or beaker.
3. ☒ Turn on kettle agitator. Setpoint = 200 rpm. Mark Sludge Level in Kettle as De-water Level for later de-watering and concentration.
4. ☒ Add first batch of trim chemicals (from Table XXVIII) directly to the kettle.
5. ☒ Transfer 295 ml of distilled water to the kettle (use to rinse all containers used for adding sludge, noble metals, mercury, etc.).
6. ☒ Calibrate pH probe with pH 4 and 10 buffer. Record measured pH of pH 7 buffer 7.124. (glass probe)
7. ☒ Install pH probe in kettle. Record initial pH of sludge 13.18.
8. ☒ Turn on the air purge to kettle at **100.0 sccm**. Connect the outlet flowmeter to perform the leak check. The outlet flow should be 90-110 sccm. If it is not, tighten all connections until the system is leak tight. Write down the leak check in the logbook.
9. ☒ Disconnect outlet flowmeter.
10. ☒ Turn on the air purge to kettle at **466.5 sccm**. Turn on He purge and set to **2.34 sccm**.
11. ☒ Turn on cooling water to SRAT condenser. Setpoint = **40°C**.
12. ☒ Turn on cooling water to Chilled (FAVC) condenser. Setpoint = **10°C**.
13. ☒ Make sure the GC computer has enough memory space for the run (at least 40 Mbyte).
14. ☒ Set the GC computer time equal to the clock time. Record the time in the log book.
15. ☒ Install the calibration gas cylinder to the GC and let the GC run five times. If at the end of five runs the GC reading is within 10% of the gas composition in the cylinder, print the calibration check results and write down "pre-cal check and run number" on the printout. Otherwise, select "Calibration" "Level 1" "OK" to calibrate the GC five times. At the end of five runs the GC reading should be within 10% of the gas composition in the cylinder. If it is not, contact the engineer. Print the calibration check results and write down "pre-cal check and run number" on the printout.
16. ☒ Start the GC for this run beginning with baseline reading for a few minutes. Write down the GC time, filename etc. in the logbook. Record the baseline data on the data sheet.

Run # 3V

Date: 1/13/99

SRAT CYCLE

1. ☒ Add 2.3 g 1:10 antifoam solution and 2.3 g water directly to the kettle (100 ppm antifoam).
2. ☒ Start heating up the kettle with the Therm-O-Watch (yellow box) temperature controller. Turn on its power switch, press the [SEL] key for 3 seconds until display shows "roFF". Press the [^] key until display shows "rrUn" then press and hold the [SEL] key until the normal display appears. The Therm-O-Watch will ramp up to 93°C and hold at 93°C. Record the run data every 20 minutes on the data sheet.
3. ☒ Switch off the Therm-O-Watch, hook the heating mantle to the Cole-Parmer (gray box) temperature controller, and switch on the Cole-Parmer unit. Bring the kettle contents to boiling.
4. ☒ If slurry begins to foam over at any time, add antifoam solution as shown in Step 1. If still foaming then switch off heating and turn on the cooling coil water pump to bring the temperature down rapidly. Then switch off the cooling coil water pump and slowly heat up the kettle again to the point of boiling.
5. ☒ Dewater until kettle volume returns to De-water Level marked in **Step 3 of PREPARATION FOR SRAT CYCLE** (approximately 2.1 L). Should take about 1 hour and 30 minutes. (300g)
6. ☒ When dewatering is complete, turn off the heat to kettle, turn on water to cooling coil, and cool the kettle to sub-boiling (90°C).
7. ☒ Add 333.3 g of Sludge A' to the kettle using 2-liter transfer bottle or beaker.
8. ☒ Add second batch of trim chemicals (from Table XXIX) directly to the kettle.
9. ☒ Transfer 50 ml of distilled water to the kettle (use to rinse all containers used for adding sludge, noble metals, mercury, etc.). *Added an additional 31.3 grams.*
10. ☒ Allow slurry to cool to 50°C, monitoring torque every 20 minutes.
11. ☒ Pull 10 ml sample for nitrate, nitrite, and formate analysis. Label LB SRAT 3V*-0N.
12. ☒ Start heating up the kettle with the Therm-O-Watch (yellow box) temperature controller. Turn on its power switch, press the [SEL] key for 3 seconds until display shows "roFF". Press the [^] key until display shows "rrUn" then press and hold the [SEL] key until the normal display appears. The Therm-O-Watch will ramp up to 93°C and hold at 93°C. Record the run data every 20 minutes on the data sheet.
13. ☒ Once at 93°C, add 44.90 ml of 50-wt% nitric acid at 0.669 ml/min (reference Table XXXI) to the kettle. Should take about 1 hour and 6 minutes.
14. ☒ Add 260.73 ml of 90-wt% formic acid at 0.687 ml/min (reference Table XXXI) to the kettle. Should take about 6 hours and 30 minutes.
15. ☒ Add 2.3 g 1:10 antifoam solution and 2.3 g water directly to the kettle (100 ppm antifoam).
16. ☒ Switch off the Therm-O-Watch, hook the heating mantle to the Cole-Parmer (gray box) temperature controller, and switch on the Cole-Parmer unit. Bring the kettle contents to boiling.
17. ☒ Dewater until collect 1031 g of H₂O in the SMECT leaving approximately 1.8 L in the kettle. Should take about 5 hours. *(Removed extra 31 g for additional water added earlier)*
18. ☒ Pull 10 ml sample for nitrate, nitrite, and formate analysis. Label LB SRAT 3V*-1N.
19. ☒ Add 2.3 g 1:10 antifoam solution and 2.3 g water directly to the kettle (100 ppm antifoam).

Run # 3V

Date: 1/14/99

SRAT CYCLE (continued)

20. ☒ Reflux the slurry for a total of 14 hours (including the dewater time in step 17) at 3.4 g/min boil-up taking 10 ml sample for nitrate, nitrite, and formate analysis every 2 hours and one at the end then turn off the heat to cool the kettle to sub-boiling. Add 1 ml of 1 N NaOH solution to each sample and label as LB SRAT 3V*-2N, 4N, 6N, 8N, and final N.
21. ☒ Pull a 125-ml sample from the kettle, record the weight on the run sheet. Label as LB SRAT 3V* and send to lab for analyses.

Run # 3V

Date: 1/14/99

SME CYCLE

1. ☒ Add 2.3 g 1:10 antifoam solution and 2.3 g water directly to the kettle (100 ppm antifoam).
2. ☒ Add 525.32 g of frit 200 to the kettle (1st frit addition - Table XXX)¹¹.
3. ☒ Add 10.70 g of 90-wt% formic acid to the kettle (1st formic addition - Table XXX)¹¹.
4. ☒ Add 964.9 g of water to the kettle (1st water addition - Table XXX)¹¹.
☒ Change air (ch 2) to 0.164 slm and He (ch 1) to 0.82 sccm.
5. ☒ Bring kettle contents to boiling. Record the run data every 20 minutes on the data sheet.
6. ☒ When dewatering is complete (about 4 hours and 25 minutes), turn off the heat to cool the kettle to sub-boiling. (Remove 870.1 g)
7. ☒ Add 525.32 g of frit 200 to the kettle (2nd frit addition - Table XXX)¹¹.
8. ☒ Add 10.70 g of 90-wt% formic acid to the kettle (2nd formic addition - Table XXX)¹¹.
9. ☒ Add 964.9 g of water to the kettle (2nd water addition - Table XXX)¹¹.
10. ☒ When dewatering is complete (about 4 hours and 25 minutes), turn off the heat to cool the kettle to sub-boiling. Turn on cooling water to cooling coil dip-leg. (Remove 870.1 g)
11. ☒ Pull a 125-ml sample from the kettle, record the weight on the run sheet. Label as LB SME 3V* and send to lab for analyses.
12. ☒ Stop GC and record the GC time and clock time in the log book. Stop recording run data on the data sheet.
13. ☒ Install the calibration gas cylinder to the GC and run the post-cal check. If the check indicates OK, print a copy and write "post-cal check and run number" on the printout, then place the GC in standby. If the check is not within 10% of the cal gas composition, notify the engineer.
14. ☒ Pump kettle contents into a tared bottle. Record the weight on the run sheet.
15. ☒ Complete pH meter post calibration check. Record measured pH in pH 7 buffer 3.8.
16. ☒ Install the outlet flow meter to the purge gas. Change channel 2 to 100 sccm and turn off helium before leak checking.
17. ☒ When the kettle is cool (<50 °C), record the outlet purge flow in the log book. (All channels).
18. ☒ Turn off all instruments.
☒ Weigh all kettle pieces and record in lab book.
☒ Take pictures of pH probe, cooling coil, RTD, stirring rod, and thermocouple. Set cooling coil, pH probe, RTD, and thermocouple aside for later examination.
☒ Start setting up rigs for next experiment.

¹¹ Modified from original value because of extra 125-ml sample pulled for Rheology

APPENDIX A-4: LARGE BATCH RUNS 1V & 4V

SRT-PTD-99-0004, Rev. 0

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January 18, 1999

TO: L. F. Landon, 704-1T

FROM: W. E. Daniel, 704-1T

Run Plan for Large Batch Variability Runs with High Weight% Solids Sludge for Developing Strategies for Increased CPC Batch Sizes (U)

This run plan documents the variability runs with high weight percent solids sludge as detailed in the Task Technical Plan for Developing Strategy for Increased CPC Batch Size (WSRC-RP-98-00354) as requested in DWPF Technical Task Request HLW/DWPT/TTR-980013. The experimental work will be controlled using the Laboratory Scale Chemical Process Cell Simulations (Manual L27, Procedure 2.02) and this run plan. This run plan includes many of the experimental details, the instructions for final sludge preparation, the scaling necessary for determining the operating conditions such as feed rates, purge rates, and the steps in completing the SRAT and SME cycles. This document also summarizes the decisions made to complete these experiments.

- 1) The sludge used for the SRAT Heel preparation is a Tank 42-sludge simulant created from the Optima Tank 51 simulant with the following modifications.
 - a) A recipe is shown in Table XXXIV that targets a 20 weight percent solids sludge after the trim chemicals (noble metals and mercury) are added. This sludge will be referred to as Sludge A' and its pre-trim measured as well as post-trim predicted elemental weight percent analyses are shown in Table XXXV. Analyses of the SRAT Heel used in these experiments are shown in Table XXXVI.
 - b) Tank 42 levels of noble metals and mercury will be added to the sludge batches as shown in Table XXXVII through Table XL. These levels will require approximately 14 hours of refluxing in the SRAT to steam strip mercury and meet the DWPF constraint of 0.45 wt % mercury.

Table XXXIV. Preparation Of Tank 42 Sludge 22 weight % (Trim Chemicals Missing)

Component	Amount, g	Comments
Tank 51 sludge simulant	14613.20	18.52 wt% solids initially
Tank 51 supernate	373.20	Added Supernate to lower wt% solids
Al ₂ O ₃	194.98	
Ni(NO ₃) ₂ *6H ₂ O	37.65	
SiO ₂	25.73	
MnO ₂ *x H ₂ O	133.49	Total Mass @ 71.4 wt% solids
Water	200.00	
Al ₂ O ₃	1.50	
Na ₂ C ₂ O ₄	0.00	
NaF	0.88	
NaOH	8.69	
NaCl	0.34	

Table XXXV. Elemental Analyses of Large Batch 22 wt% Sludge B'

Insoluble Species	Measured Wt% Solids Pre-Trim	Predicted Wt% Solids Post-Trim	Soluble Species	Measured Wt% Solids Pre-Trim	Predicted Wt% Solids Post-Trim
Al	5.76%	8.63%	Al		0.02%
*Ag		0.04%	C2O4	0.12%	0.15%
Ca	2.50%	1.98%	Cl	0.02%	0.02%
*Cd		0.11%	CO3		1.79%
Cl		0.02%	Cr		0.00%
Cr		0.17%	F	0.01%	0.02%
Cu	0.02%	0.02%	K		0.00%
F		0.01%	Li		0.00%
Fe	22.19%	22.23%	Na		0.17%
*Hg		1.30%	NO2	3.74%	3.69%
K	0.12%	0.05%	NO3	1.62%	1.55%
Li	0.01%	0.00%	OH		0.11%
Mg	1.09%	1.13%	PO4	0.00%	0.05%
Mn	4.31%	4.11%	SO4	0.21%	0.21%
Na	6.51%	5.86%			
Ni	0.42%	0.41%			
P		0.00%			
*Pd		0.00%			
Pu		0.00%			
*Rh		0.01%			
*Ru		0.02%			
Se		0.00%			
Si	1.15%	1.49%			
Te		0.00%			
Ti	0.05%	0.05%			
U		0.00%			
Zn	0.12%	0.00			

**Table XXXVI. Elemental Analyses of Large Batch 20.4 wt% SRAT Heel
prepared from Sludge A'**

Insoluble Species	Measured Wt% Solids	Soluble Species	Measured Wt% Solids
Al	5.30%	Al	--
*Ag	--	C2O4	0.04%
Ca	2.04%	Cl	0.16%
*Cd	0.00%	CO3	--
Cl	--	Cr	--
Cr	--	F	--
Cu	0.01%	K	--
F	--	Li	--
Fe	20.80%	Na	--
*Hg	--	NO2	0.12%
K	0.14%	NO3	9.07%
Li	0.00%	OH	--
Mg	0.89%	PO4	0.04%
Mn	4.17%	SO4	0.10%
Na	7.26%		
Ni	0.32%		
P	0.24%		
*Pd	0.045%		
Pu	--		
*Rh	0.0053%		
*Ru	0.032%		
Se	--		
Si	1.17%		
Te	0.00%		
Ti	0.03%		
U	--		
Zn	0.11%		

Table XXXVII. Trim Chemical Addition for First Sludge Addition for Run 1V

	Target Addition, g	Actual Addition, g	Wt% Solids	Target Solids, g	Actual Solids added, g
Sludge B'	2000.0	2000.0	20.2%	404.0	404.0
Trim Chemicals	Target Addition, grams	Actual Addition, grams	Elemental Solids Factor	Target Elemental Solids, g	Actual Elemental Solids, g
AgNO ₃	0.235	0.236	0.6349	0.149	0.150
Cd(NO ₃) ₂ *4H ₂ O	1.220	1.224	0.3644	0.444	0.446
HgO	5.366	5.366	0.9261	4.969	4.969
Pd(NO ₃) ₂ *H ₂ O	0.021	0.021	0.1527 [†]	0.009	0.003 [†]
Rh(NO ₃) ₃ *2H ₂ O	0.068	0.068	0.0493 [†]	0.021	0.003 [†]
RuCl ₃	0.182	0.183	0.4174 [†]	0.089	0.076 [†]

Element	Target Wt% Solids	Actual Wt% Solids
Ag	0.04%	0.04%
Cd	0.11%	0.11%
Hg	1.30%	1.30%
Pd	0.0022%	0.0008% [†]
Rh	0.0053%	0.0008% [†]
Ru	0.022%	0.019% [†]

[†]Values changed from original run plan to reflect noble metal under addition.

Table XXXVIII. Trim Chemical Addition for Second Sludge Addition for Run 1V

	Target Addition, g	Actual Addition, g	Wt% Solids	Target Solids, g	Actual Solids added, g
Sludge B'	333.3	333.3	19.3%	64.3	64.3
Trim Chemicals	Target Addition, grams	Actual Addition, grams	Elemental Solids Factor	Target Elemental Solids, g	Actual Elemental Solids, g
AgNO ₃	0.040	0.041	0.6349	0.025	0.026
Cd(NO ₃) ₂ *4H ₂ O	0.203	0.204	0.3644	0.074	0.074
HgO	0.945	0.945	0.9261	0.875	0.875
Pd(NO ₃) ₂ *H ₂ O	0.003	0.003	0.1527 [†]	0.001	0.00046 [†]
Rh(NO ₃) ₃ *2H ₂ O	0.011	0.011	0.0493 [†]	0.004	0.00054 [†]
RuCl ₃	0.031	0.031	0.4174 [†]	0.015	0.013 [†]

Element	Target Wt% Solids	Actual Wt% Solids
Ag	0.04%	0.04%
Cd	0.11%	0.11%
Hg	1.30%	1.30%
Pd	0.0022%	0.0007% [†]
Rh	0.0053%	0.0008% [†]
Ru	0.022%	0.020% [†]

[†]Values changed from original run plan to reflect noble metal under addition.

Table XXXIX. Trim Chemical Addition for First Sludge Addition for Run 4V

	Target Addition, g	Actual Addition, g	Wt% Solids	Target Solids, g	Actual Solids added, g
Sludge B'	2000.0	2000.0	20.2%	404.0	404.0
Trim Chemicals	Target Addition, grams	Actual Addition, grams	Elemental Solids Factor	Target Elemental Solids, g	Actual Elemental Solids, g
AgNO ₃	0.235	0.233	0.6349	0.149	0.148
Cd(NO ₃) ₂ *4H ₂ O	1.220	1.221	0.3644	0.444	0.445
HgO	5.453	5.452	0.9261	5.050	5.049
Pd(NO ₃) ₂ *H ₂ O	0.021	0.021	0.1527 [†]	0.009	0.003 [†]
Rh(NO ₃) ₃ *2H ₂ O	0.068	0.066	0.0493 [†]	0.021	0.003 [†]
RuCl ₃	0.182	0.182	0.4174 [†]	0.089	0.076 [†]

Element	Target Wt% Solids	Actual Wt% Solids
Ag	0.04%	0.04%
Cd	0.11%	0.11%
Hg	1.25%	1.25%
Pd	0.0022%	0.0008% [†]
Rh	0.0053%	0.0008% [†]
Ru	0.022%	0.019% [†]

[†]Values changed from original run plan to reflect noble metal under addition.

Table XL. Trim Chemical Addition for Second Sludge Addition for Run 4V

	Target Addition, g	Actual Addition, g	Wt% Solids	Target Solids, g	Actual Solids added, g
Sludge B'	333.3	333.3	19.3%	64.3	64.3
Trim Chemicals	Target Addition, grams	Actual Addition, grams	Elemental Solids Factor	Target Elemental Solids, g	Actual Elemental Solids, g
AgNO ₃	0.040	0.039	0.6349	0.025	0.025
Cd(NO ₃) ₂ *4H ₂ O	0.203	0.201	0.3644	0.074	0.073
HgO	0.909	0.908	0.9261	0.842	0.841
Pd(NO ₃) ₂ *H ₂ O	0.003	0.003	0.1527 [†]	0.001	0.00046 [†]
Rh(NO ₃) ₃ *2H ₂ O	0.011	0.010	0.0493 [†]	0.004	0.00049 [†]
RuCl ₃	0.031	0.030	0.4174 [†]	0.015	0.0125 [†]

Element	Target Wt% Solids	Actual Wt% Solids
Ag	0.04%	0.04%
Cd	0.11%	0.11%
Hg	1.30%	1.31%
Pd	0.0022%	0.0007% [†]
Rh	0.0053%	0.0008% [†]
Ru	0.023%	0.019% [†]

[†]Values changed from original run plan to reflect noble metal under addition.

- 2) The batching of the materials is designed to produce a glass containing 26 wt % calcined sludge solids and 74 wt % frit 200. A batching summary is shown in Table XLI.
- 3) Calculated acid addition rates, boilup rates, purge rates, antifoam addition, etc. were based on scaling from DWPF settings as shown in Table XLII.
- 4) Run 1V simulates an ideal processing case with high weight percent solids sludge and an elevated acid addition for 170.0% of stoichiometry with a redox target of $0.2 \text{ Fe}^{+2}/\Sigma\text{Fe}$. The higher stoichiometry was chosen since 137.5% stoichiometry proved inadequate for nitrite destruction in the earlier large batch runs and to help define the minimum acid addition necessary for the large batch operating strategy. This run simulates DWPF most expedient option for increased CPC batch operation. The redox calculation spreadsheets for the Variability Run 1V are shown in Table XLIII.
- 5) Run 4V simulates a worst case scenario where sludge solids are high and the SRAT is concentrated down to below the normal 6000 gallon mark. Originally a low acid stoichiometry (100%) was going to be used but after the first set of large batch runs it was decided to add a slightly elevated acid quantity (150% stoichiometry) to evaluate nitrite destruction. The redox calculation spreadsheets for the Variability Run 4V are shown in Table XLIV.
- 6) In both runs (1V & 4V), the reflux time in the SRAT cycle will be extended until there is evidence of nitrite destruction. The SME cycles may be postponed to a later date.
- 7) A review, as required by the Conduct of Research and Development was completed and is contained in Appendix B.
- 8) The experiments should be completed the week of January 18, 1999.

Table XLI. Batching Summary for Variability Runs 1V and 4V

Batching Summary	Run 1V	Run 4V
Sludge & Heel Mass	2820.4 g	2722.9 g
Nitric Acid Volume, ml	59.61 ml	52.37 ml
Formic Acid Volume, ml	128.69 ml	117.14 ml
SRAT Product Sample, ml	125	125
Frit 200 Addition #1, g	559.04 g	540.04 g
SME Water Addition #1, g	1026.83 g	991.93 g
SME 90 wt% Formic Acid Addition #1, g	11.39 g	11.00 g
Frit 200 Addition #2, g	559.04 g	540.04 g
SME Water Addition #2, g	1026.83 g	991.93 g
SME 90 wt% Formic Acid Addition #2, g	11.39 g	11.00 g
SRAT Air Purge ¹ , scc/min	466.5	466.5
SRAT Helium purge, scc/min	2.34	2.34
SME Air Purge ¹ , scc/min	163.8	163.8
SME Helium purge, scc/min	0.82	0.82

¹Actual SRAT Gas Purge equivalent to this Air purge plus the Helium Purge.

Table XLII. Scaling Calculations for Large Batch Variability Runs 1V and 4V

	DWPF	TNX 1V	Time	DWPF	TNX 4V	Time
Scale factor		11,355 (13172) [†]			11,355 (13172) [†]	
Sludge Added Volume	7,000 gal	2011 ml		7,000 gal	2011 ml	
Sludge Heel Volume	1,500 gal	431 ml		1,200 gal	345 ml	
Sludge Added Density	1.16	1.16		1.16	1.16	
Sludge Heel Density	1.13	1.13		1.13	1.13	
Sludge Added Mass	30736 kg	2333.3 g		30736 kg	2333.3 g	
Sludge Heel Mass	6416 kg	487.1 g		5133 kg	389.6 g	
SRAT Added Water	1,000 gal	287.4 ml	2.4 hrs	1,000 gal	287.4 ml	2.3 hrs
SRAT purge air [‡]	188 scfm	466.5 scc/min		188 scfm	466.5 scc/min	
SRAT He purge	0.50 vol %	2.34 scc/min		0.50 vol %	2.34 scc/min	
SME purge air [‡]	66 scfm	163.8 scc/min		66 scfm	163.8 scc/min	
SME He purge	0.50 vol %	0.82 scc/min		0.50 vol %	0.82 scc/min	
Antifoam (100 ppm in Total Sludge)	8.19 lbs	0.23 g		7.91 lbs	0.23 g	
Antifoam Solution (20 to 1 solution)	163.81 lbs	4.67 g		158.15 lbs	4.67 g	
Elemental Hg to Reduce						
nitric acid feedrate	2 gpm	0.669 ml/min	1.4 hrs	2 gpm	0.669 ml/min	1.3 hrs
formic acid feedrate	2 gpm	0.687 ml/min	3.2 hrs	2 gpm	0.687 ml/min	2.9 hrs
boilup rate	5,000 lb/hr	3.33 g/min		5,000 lb/hr	3.33 g/min	
Formic Molarity	23.55 M	22.85 M		23.55 M	22.85 M	
Nitric Molarity	10.35 M	10.32 M		10.35 M	10.32 M	
Formic Volume	374.6gal	128.69 ml		340.9 gal	117.14 ml	
Formic Mass		155.00 g			141.09 g	
Nitric Volume	178.3 gal	59.61 ml		156.7 gal	52.37 ml	
Nitric Mass		78.00 g			68.53 g	
formic feed time	187.3 min	187.3 min		170.5 min	170.5 min	
Nitric feed time	89.2 min	89.2 min		78.3 min	78.3 min	
Total Vol		2918.15 ml			2813.16 ml	
Frit Volume, gallons	3,727 gal	1242.317 g		3,600 gal	1200.085 g	
Frit Density	1.5			1.5		
Frit wt % solids	60%			60%		
Frit Solids	27,989.9 lbs	1118.085 g		27,038.4 lbs	1080.076 g	
Formic Acid	513.1 lbs	20.498 g		495.7 lbs	19.801 g	
Water	33,696.8 lbs	1346.051 g		32,551.3 lbs	1300.292 g	
Transfer Water	17,771.4 lbs	709.895 g		17,167.3 lbs	685.763 g	
Total Water	51,468.2 lbs	2055.946 g		49,718.5 lbs	1986.055 g	
Total	79,971.3 lbs	3194.530 g		77,252.7 lbs	3085.933 g	

[†]Value in parentheses represents corrected value due to scale factor error.

[‡]Actual SRAT Gas Purge equivalent to this Air purge plus the Helium Purge.

Table XLII. Scaling Calculations for Large Batch Variability Runs 1V and 4V Continued

	DWPF	TNX 1V	Time	DWPF	TNX 4V	Time
frit 200	27,989.9 lbs	1118.085 g		27,038.4 lbs	1080.076 g	
90 wt % formic acid	570.2 lbs	22.776 g		550.8 lbs	22.002 g	
water	51,411.1 lbs	2053.668 g		49,663.4 lbs	1983.855 g	
Total	79,971.3 lbs	3194.530 g		77,252.7 lbs	3085.933 g	
frit 200 Addition 1	13,995.0 lbs	559.043 g		13,519.2 lbs	540.038 g	
90 wt % formic addition 1	285.1 lbs	11.388 g		275.4 lbs	11.001 g	
water addition 1	25,705.6 lbs	1026.834 g	5.1 hrs	24,831.7 lbs	991.927 g	5.0 hrs
frit 200 Addition 2	13,995.0 lbs	559.043 g		13,519.2 lbs	540.038 g	
90 wt % formic addition 2	285.1 lbs	11.388 g		275.4 lbs	11.001 g	
water addition 2	25,705.6 lbs	1026.834 g	5.1 hrs	24,831.7 lbs	991.927 g	5.0 hrs

Table XLIII. Large Batch Variability Run 1V Redox Calculation

Stoichiometry ratio:	170.0% (197%) [†]			Date:	1/18/99
Stream	PHA	Sludge	Frit	SME	
Oxide Contribution (%) (in SME)	0.0%	26.0%	74.0%	18968.8	kg Calc. Basis
Density (kg/L)	1.0355	1.155	n/a	137.0%	
Total Solids (%)	5.38%	20.23%	n/a	48.0%	
Calcine Factor (ox/sol)	1.00	0.80	n/a	n/a	
Hydroxide (M)	n/a	0.548	n/a	n/a	
Mercury (ppm)	n/a	2302.5	n/a	n/a	
Total Mn (wt% solids)	n/a	4.24	n/a	n/a	
Soluble Mn (ppm)	n/a	0.00	n/a	n/a	
*TIC (ppm)	n/a	0.00	n/a	n/a	
Total Acid (M)	0.240	n/a	n/a	n/a	
Nitrite (ppm)	0.0	6305.2	0.0	(kg/100kg frit)	
NO2 Destruction	0.0%	100.0%	0.0%		
Nitrate (ppm)	1012.1	5879.0	0.0	(kg/100kg frit)	
% nitrite to nitrate conversion		35.0%			
Formate (ppm)	22808.9	0.0	1.0	(kg/100kg frit)	
Reaction formate destruction, kg		149.02			
Factor for total formate destruction		15.0%			
Total formate destruction, kg		22.35			
Oxide Mass (kg)	0.0	4931.9	14036.9	18968.8	
Solids Mass (kg)	0.00	6191.26	14036.88	20228.15	
Total Mass (kg)	0.00	30597.50	n/a	42141.97	
Volume (L)	0.00	26,498.09	n/a	30760.56	
% Stoichiometry	n/a	150.0%	n/a	n/a	
Volume HNO3@50% (L)	n/a	3,901.51	n/a	n/a	
NO2 Contribution (kg)	0.000	192.924	0.000	192.924	
NO2 Remaining (kg)	0.000	0.000	0.000	0.000	
NO3 Contribution (kg)	0.000	2751.074	0.000	2751.074	
COOH Contribution (kg)	0.000	(149.02)	93.843	(55).176	

[†]Value in parentheses represents corrected value due to scale factor error.

Table XLIII. Large Batch Variability Run 1V Redox Calculation Continued

Stoichiometry ratio:	170.0% (197%) [†]				Date:	1/18/99
Stream	PHA	Sludge	Frit		SME	
NO2 (Molar@45%)					0.000	
NO3 (Molar@45%)					1.881	
COOH (Molar@45%)					-0.052	
Predicted Fe(II)/ΣFe			0.09	≤	BDL@0.03	≤ 0.1
Volume HCOOH@90% (L)			4875.67		4534.09	4932.67
% Stoichiometry	n/a	170.0%	n/a		n/a	
Volume HCOOH@90% (L)	n/a	1,714.50	n/a		n/a	
NO2 Contribution (kg)	0.000	192.924	0.000		192.924	
NO2 Remaining (kg)	0.000	0.000	0.000		0.000	
NO3 Contribution (kg)	0.000	247.406	0.000		247.406	
COOH Contribution (kg)	0.000	1795.398	93.843		1889.241	
NO2 (Molar@45%)					0.000	
NO3 (Molar@45%)					0.169	
COOH (Molar@45%)					1.78	
Predicted Fe(II)/ΣFe			0.09	≤	0.543	≤ 0.1
Volume HNO3@50% (L)			1567.01			1523.92
mol% Nitric	n/a	17.3%	n/a		n/a	
Volume HCOOH@90% (L)	n/a	1,417.89	n/a		n/a	
Volume HNO3@50% (L)		674.96				
NO2 Contribution (kg)	0.000	192.924	0.000		192.924	
NO2 Remaining (kg)	0.000	0.000	0.000		0.000	
NO3 Contribution (kg)	0.000	680.541	0.000		680.541	
COOH Contribution (kg)	0.000	1354.260	0.000		1354.260	
NO2 (Molar@45%)					0.000	
NO3 (Molar@45%)					0.465	
COOH (Molar@45%)					1.276	
Predicted Fe(II)/ΣFe			0.09	≤	0.200 (0.221) [†]	≤ 0.1

[†]Value in parentheses represents corrected value due to scale factor error. kgb 9/16/96

Table XLIV. Large Batch Variability Run 4V Redox Calculation

Stoichiometry ratio	150.0% (175%) [†]			Date:	1/18/99	
Stream	PHA	Sludge	Frit		SME	
Oxide Contribution (%) (in SME)	0.0%	26.0%	74.0%		19102.8	kg Calc. Basis
Density (kg/L)	1.0355	1.156	n/a		137.0%	
Total Solids (%)	5.38%	20.23%	n/a		48.0%	
Calcine Factor (ox/sol)	1.00	0.80	n/a		n/a	
Hydroxide (M)	n/a	0.566	n/a		n/a	
Mercury (ppm)	n/a	2348.1	n/a		n/a	
Total Mn (wt% solids)	n/a	4.24	n/a		n/a	
Soluble Mn (ppm)	n/a	0.00	n/a		n/a	
*TIC (ppm)	n/a	0.00	n/a		n/a	
Total Acid (M)	0.240	n/a	n/a		n/a	
Nitrite (ppm)	0.0	6520.4	0.0	(kg/100kg frit)		
NO2 Destruction	0.0%	100.0%	0.0%			
Nitrate (ppm)	1012.1	5431.4	0.0	(kg/100kg frit)		
% nitrite to nitrate conversion		35.0%				
Formate (ppm)	22808.9	0.0	1.0	(kg/100kg frit)		
Reaction formate destruction, kg		151.08				
Factor for total formate destruction		15.0%				
Total formate destruction, kg		22.66				
Oxide Mass (kg)	0.0	4966.7	14136.1		19102.8	
Solids Mass (kg)	0.00	6194.30	14136.06		20330.36	
Total Mass (kg)	0.00	30621.45	n/a		42354.92	
Volume (L)	0.00	26,498.09	n/a		30916.00	
% Stoichiometry	n/a	150.0%	n/a		n/a	
Volume HNO3@50% (L)	n/a	3,529.96	n/a		n/a	
NO2 Contribution (kg)	0.000	199.664	0.000		199.664	
NO2 Remaining (kg)	0.000	0.000	0.000		0.000	
NO3 Contribution (kg)	0.000	2501.439	0.000		2501.439	
COOH Contribution (kg)	0.000	(151.08)	93.843		(57).236	
NO2 (Molar@45%)					0.000	
NO3 (Molar@45%)					1.711	
COOH (Molar@45%)					-0.054	
Predicted Fe(II)/ΣFe			0.09	≤	BDL@0.03	≤ 0.1
Volume HCOOH@90% (L)			4366.21		4023.48	4423.40
% Stoichiometry	n/a	150.0%	n/a		n/a	
Volume HCOOH@90% (L)	n/a	1,551.23	n/a		n/a	
NO2 Contribution (kg)	0.000	199.664	0.000		199.664	
NO2 Remaining (kg)	0.000	0.000	0.000		0.000	
NO3 Contribution (kg)	0.000	236.200	0.000		236.200	
COOH Contribution (kg)	0.000	1621.981	93.843		1715.824	

[†]Value in parentheses represents corrected value due to scale factor error.

Table XLIV. Large Batch Variability Run 4V Redox Calculation Continued

Stoichiometry ratio:	150.0% (175%) [†]		Date:	1/18/99	
Stream	PHA	Sludge	Frit	SME	
NO2 (Molar@45%)				0.000	
NO3 (Molar@45%)				0.162	
COOH (Molar@45%)				1.616	
Predicted Fe(II)/ΣFe			0.09	≤	0.509 ≤ 0.1
Volume HNO3@50% (L)			1462.28		1418.97
mol% Nitric	n/a	16.8%	n/a		n/a
Volume HCOOH@90% (L)	n/a	1,290.62	n/a		n/a
Volume HNO3@50% (L)		593.03			
NO2 Contribution (kg)	0.000	199.664	0.000		199.664
NO2 Remaining (kg)	0.000	0.000	0.000		0.000
NO3 Contribution (kg)	0.000	616.760	0.000		616.760
COOH Contribution (kg)	0.000	1217.264	0.000		1217.264
NO2 (Molar@45%)					0.000
NO3 (Molar@45%)					0.422
COOH (Molar@45%)					1.147
Predicted Fe(II)/ΣFe			0.09	≤	0.200 (0.221) [†] ≤ 0.1

[†]Value in parentheses represents corrected value due to scale factor error.

kgb 9/16/96

Run # 1V & 4V

Date: 1/19/99

PREREQUISITES

1. ☒ Signed TAR requesting work.
2. ☒ Issued Testing scope and task assignment.
3. ☒ Analyze sludge for density, total base (pH 5.5), nitrate, manganese, nitrite, density, solids.
4. ☒ Calibrate GC. Calibrate for nitrogen, oxygen, N₂O, hydrogen, and carbon dioxide.
5. ☒ Prepare sufficient 90% formic acid and 50% nitric acid.
6. ☒ Prepare sufficient antifoam solution or make sure sufficient solution is available.
7. ☒ Calculate batching and scaling for experiment based on DWPF parameters.
8. ☒ Calculate redox for experiment based on DWPF parameters.
9. ☒ Setup 2 experimental rigs per sketch below.
10. ☒ Complete leak checks and water runs.

Run # 1V

Date: 1/20/99

PREPARATION FOR SRAT CYCLE

Note: Do not insulate kettle until acid addition is complete

1. ☒ Add 2000 g of Sludge B' to kettle using 2-liter transfer bottle or beaker.
2. ☒ Add 487.1 g of SRAT Heel A' to kettle using 2-liter transfer bottle or beaker.
3. ☒ Turn on kettle agitator. Setpoint = 200 rpm. Mark Sludge Level in Kettle as De-water Level for later de-watering and concentration.
4. ☒ Add first batch of trim chemicals (from Table XXXVII) directly to the kettle.
5. ☒ Transfer 287.4 ml of distilled water to the kettle (use to rinse all containers used for adding sludge, noble metals, mercury, etc.).
6. ☒ Calibrate pH probe with pH 4 and 10 buffer. Record measured pH of pH 7 buffer 7.033.
7. ☒ Install pH probe in kettle. Record initial pH of sludge 11.623.
8. ☒ Turn on the air purge to kettle at 100.0 sccm. Connect the outlet flowmeter to perform the leak check. The outlet flow should be 90-110 sccm. If it is not, tighten all connections until the system is leak tight. Write down the leak check in the logbook.
9. ☒ Disconnect outlet flowmeter.
10. ☒ Set the air flow to kettle at 466.5 sccm. Set the He flow to 2.34 sccm.
11. ☒ Turn on cooling water to SRAT condenser. Setpoint = 40°C.
12. ☒ Turn on cooling water to Chilled (FAVC) condenser. Setpoint = 10°C.
13. ☒ Make sure the GC computer has enough memory space for the run (at least 40 Mbyte).
14. ☒ Set the GC computer time equal to the clock time. Record the time in the log book.
15. ☒ Install the calibration gas cylinder to the GC and let the GC run five times. If at the end of five runs the GC reading is within 10% of the gas composition in the cylinder, print the calibration check results and write down "pre-cal check and run number" on the printout. Otherwise, select "Calibration" "Level 1" "OK" to calibrate the GC five times. At the end of five runs the GC reading should be within 10% of the gas composition in the cylinder. If it is not, contact the engineer. Print the calibration check results and write down "pre-cal check and run number" on the printout.
16. ☒ Start the GC for this run beginning with baseline reading for a few minutes. Write down the GC time, filename etc. in the logbook. Record the baseline data on the data sheet.

Run # 1V

Date: 1/20/99

SRAT CYCLE

1. ☒ Add 2.3 g 1:10 antifoam solution and 2.3 g water directly to the kettle (100-ppm antifoam).
2. ☒ Start heating up the kettle with the Therm-O-Watch (yellow box) temperature controller. Turn on its power switch, press the [SEL] key for 3 seconds until display shows "roFF". Press the [^] key until display shows "rrUn" then press and hold the [SEL] key until the normal display appears. The Therm-O-Watch will ramp up to 93°C and hold at 93°C. Record the run data every 20 minutes on the data sheet.
3. ☒ Hook the heating mantle to the Cole-Parmer (gray box) temperature controller, and switch on the Cole-Parmer unit. Bring the kettle contents to boiling.
4. ☒ If slurry begins to foam over at any time, switch off heating and turn on the cooling coil water pump to bring the temperature down rapidly. Add antifoam solution as shown in Step 1. Then switch off the cooling coil water pump and slowly heat up the kettle again to the point of boiling.
5. ☒ Dewater until remove 287.4 g of water (kettle volume should be close to De-water Level marked in Step 3 of PREPARATION FOR SRAT CYCLE). Should take about 1 hour and 30 minutes.
6. ☒ When dewatering is complete, turn off the heat to kettle, turn on water to cooling coil, and cool the kettle to sub-boiling (90°C).
7. ☒ Add 333.3 g of Sludge B' to the kettle using 2-liter transfer bottle or beaker.
8. ☒ Add second batch of trim chemicals (from Table XXXVIII) directly to the kettle.
9. ☒ Transfer 50 ml of distilled water to the kettle (use to rinse all containers used for adding sludge, noble metals, mercury, etc.).
10. ☒ Allow slurry to cool to 50°C, monitoring torque every 20 minutes.
11. ☒ Pull 10 ml sample for nitrate, nitrite, and formate analysis. Weigh and record in lab book. Add 1 ml of 1 N NaOH solution, reweigh, and record in lab book. Label the sample LB SRAT 1V*-0N.
12. ☒ Start heating up the kettle with the Therm-O-Watch (yellow box) temperature controller. Press the [SEL] key for 3 seconds until display shows "roFF". If display shows "rrUn", press the [^] or [v] key until display shows "roFF". Press the [^] or [v] key until display shows "rrUn" then press and hold the [SEL] key until the normal display appears. The Therm-O-Watch will ramp up to 93°C and hold at 93°C. Record the run data every 20 minutes on the data sheet.
13. ☒ Once at 93°C, add 59.61 ml of 50-wt% nitric acid at 0.669 ml/min (reference Table XLII) to the kettle. Should take about 1 hour and 30 minutes.
14. ☒ Add 128.69 ml of 90-wt% formic acid at 0.687 ml/min (reference Table XLII) to the kettle. Should take about 3 hours and 15 minutes.
15. ☒ Add 2.3 g 1:10 antifoam solution and 2.3 g water directly to the kettle (100 ppm antifoam).
16. ☒ Hook the heating mantle to the Cole-Parmer (gray box) temperature controller and switch on the Cole-Parmer unit. Bring the kettle contents to boiling.

Run # 1V

Date: 1/21/99

SRAT CYCLE (continued)

17. ☒ Dewater until collect 927 g of H₂O in the SMECT leaving approximately 1.7 L in the kettle. Should take about 4.6 hours.
18. ☒ Pull 10 ml sample for nitrate, nitrite, and formate analysis. Weigh and record in lab book. Add 1 ml of 1 N NaOH solution, reweigh, and record in lab book. Label LB SRAT 1V*-1N.
19. ☒ Add 2.3 g 1:10 antifoam solution and 2.3 g water directly to the kettle (100 ppm antifoam).
20. ☒ Reflux the slurry for 14.6 hours or more (including the dewater time in step 18) at 3.4 g/min boil-up taking 10 ml sample for nitrate, nitrite, and formate analysis every 2 hours and one at the end. Continue refluxing until there is evidence of nitrite destruction (hydrogen release) and the hydrogen has reached its peak. Then turn off the heat to cool the kettle to sub-boiling. Weigh samples and record in lab book. Add 1 ml of 1 N NaOH solution to each sample, reweigh, and record in lab book. Label as LB SRAT 1V*-2N, 4N, 6N, 8N, 10N, etc. (18.5 hours total)
21. ☒ Pull a 125 ml sample from the kettle, record the weight on the run sheet. Label as LB SRAT 1V* and send to lab for analyses.
22. ☒ Pull a 125 ml sample from the kettle, record the weight on the run sheet. Label as LB SRAT 1V* Rheology and send to lab for Rheology.
23. ☒ Remove Sampler and insert rubber stopper in port. (Weigh and record at 157.24 g)

Run # 1V

Date: 1/21/99

SME CYCLE

1. ☒ Add 2.3 g 1:10 antifoam solution and 2.3 g water directly to the kettle (100 ppm antifoam).
2. ☒ Add about 559.04 g frit 200 to the kettle (1st frit addition - Table XLI). Actual amount of frit to add: 550.91 g¹²
3. ☒ Add about 11.39 g of 90-wt% formic acid to the kettle (1st formic addition - Table XLI). Actual amount of formic to add: 11.22 g¹²
4. ☒ Add about 1026.83 g of water to the kettle (1st water addition - Table XLI). Actual amount of water to add: 1011.89 g¹²
5. ☒ Bring kettle contents to boiling. Record the run data every 20 minutes on the data sheet.
6. ☒ Remove about 1027 g of water (about 5 hours). Actual amount of water to remove: 648.8 g¹³
7. ☒ When dewatering is complete, turn off the heat to cool the kettle to sub-boiling.
8. ☒ Add about 559.04 g frit 200 to the kettle (2nd frit addition - Table XLI). Actual amount of frit to add: 550.91 g¹²
9. ☒ Add about 11.39 g of 90-wt% formic acid to the kettle (2nd formic addition - Table XLI). Actual amount of formic to add: 11.22 g¹²
10. ☒ Add about 1026.83 g of water to the kettle (2nd water addition - Table XLI). Actual amount of water to add: 1011.89 g¹²
11. ☒ Bring kettle contents to boiling. Record the run data every 20 minutes on the data sheet.
12. ☒ Remove about 1027 g of water (about 5 hours). Actual amount of water to remove: 648.8 g¹³
13. ☒ When dewatering is complete, turn off the heat to cool the kettle to sub-boiling. Turn on cooling water to cooling coil dip-leg.
14. ☒ Pull a 125-ml sample from the kettle, record the weight on the run sheet. Label as LB SME 1V*
Final and send to lab for analyses.
15. ☒ Stop GC and record the GC time and clock time in the logbook. Stop recording run data on the data sheet
16. ☒ Install the calibration gas cylinder to the GC and run the post-cal check. If the check indicates OK, print a copy and write "post-cal check and run number" on the printout, then place the GC in standby. If the check is not within 10% of the cal gas composition, notify the engineer.
17. ☒ Pump kettle contents into a tared bottle. Record the weight on the run sheet.
18. ☒ Complete pH meter post calibration check. Record measured pH in pH 7 buffer 7.3.
19. ☒ Install the outlet flow meter to the purge gas. *Perform leak check.*
20. ☒ When the kettle is cool (<50 °C), record the outlet purge flow in the log book. (All channels).
21. ☒ Turn off all instruments.

¹² Actual amounts calculated after account for SRAT samples pulled and other losses.

¹³ Amounts recalculated to reach 45 wt% solids in SME product after account for samples pulled and other losses.

Run # 4V

Date: 1/19/99

PREPARATION FOR SRAT CYCLE

Note: Do not insulate kettle until acid addition is complete

1. ☒ Add 2000 g of Sludge B' to kettle using 2-liter transfer bottle or beaker.
2. ☒ Add 389.6 g of SRAT Heel A' to kettle using 2-liter transfer bottle or beaker.
3. ☒ Turn on kettle agitator. Setpoint = 200 rpm. Mark Sludge Level in Kettle as De-water Level for later de-watering and concentration.
4. ☒ Add first batch of trim chemicals (from Table XXXIX) directly to the kettle.
5. ☒ Transfer 287.4 ml of distilled water to the kettle (use to rinse all containers used for adding sludge, noble metals, mercury, etc.).
6. ☒ Calibrate pH probe with pH 4 and 10 buffer. Record measured pH of pH 7 buffer 6.930.
7. ☒ Install pH probe in kettle. Record initial pH of sludge 11.531.
8. ☒ Turn on the air purge to kettle at 100.0 sccm. Connect the outlet flowmeter to perform the leak check. The outlet flow should be 90-110 sccm. If it is not, tighten all connections until the system is leak tight. Write down the leak check in the logbook.
9. ☒ Disconnect outlet flowmeter.
10. ☒ Set the air flow to kettle at 466.5 sccm. Set the He flow to 2.34 sccm.
11. ☒ Turn on cooling water to SRAT condenser. Setpoint = 40°C.
12. ☒ Turn on cooling water to Chilled (FAVC) condenser. Setpoint = 10°C.
13. ☒ Make sure the GC computer has enough memory space for the run (at least 40 Mbyte).
14. ☒ Set the GC computer time equal to the clock time. Record the time in the log book.
15. ☒ Install the calibration gas cylinder to the GC and let the GC run five times. If at the end of five runs the GC reading is within 10% of the gas composition in the cylinder, print the calibration check results and write down "pre-cal check and run number" on the printout. Otherwise, select "Calibration" "Level 1" "OK" to calibrate the GC five times. At the end of five runs the GC reading should be within 10% of the gas composition in the cylinder. If it is not, contact the engineer. Print the calibration check results and write down "pre-cal check and run number" on the printout.
16. ☒ Start the GC for this run beginning with baseline reading for a few minutes. Write down the GC time, filename etc. in the logbook. Record the baseline data on the data sheet.

Run # 4V

Date: 1/20/99

SRAT CYCLE

1. ☒ Add **2.3 g 1:10 antifoam solution** and **2.3 g water** directly to the kettle (100 ppm antifoam).
2. ☒ Start heating up the kettle with the Therm-O-Watch (yellow box) temperature controller. Turn on its power switch, press the [SEL] key for 3 seconds until display shows "roFF". Press the [^] key until display shows "rrUn" then press and hold the [SEL] key until the normal display appears. The Therm-O-Watch will ramp up to 93°C and hold at 93°C. Record the run data every 20 minutes on the data sheet.
3. ☒ Hook the heating mantle to the Cole-Parmer (gray box) temperature controller, and switch on the Cole-Parmer unit. Bring the kettle contents to boiling.
4. ☒ If slurry begins to foam over at any time, switch off heating and turn on the cooling coil water pump to bring the temperature down rapidly. Add antifoam solution as shown in Step 1. Then switch off the cooling coil water pump and slowly heat up the kettle again to the point of boiling.
5. ☒ Dewater until remove **287.4 g of water** (kettle volume should be close to De-water Level marked in Step 3 of PREPARATION FOR SRAT CYCLE). Should take about 1 hour and 30 minutes. (*Collected 289.5 g*)
6. ☒ When dewatering is complete, turn off the heat to kettle, turn on water to cooling coil, and cool the kettle to sub-boiling (90°C).
7. ☒ Add **333.3 g of Sludge B'** to the kettle using 2-liter transfer bottle or beaker.
8. ☒ Add second batch of trim chemicals (from Table XL) directly to the kettle.
9. ☒ Transfer **50 ml** of distilled water to the kettle (use to rinse all containers used for adding sludge, noble metals, mercury, etc.).
10. ☒ Allow slurry to cool to **50°C**, monitoring torque every 20 minutes.
11. ☒ Pull **10 ml sample** for nitrate, nitrite, and formate analysis. Label **LB SRAT 4V*-0N**.
12. ☒ Start heating up the kettle with the Therm-O-Watch (yellow box) temperature controller. Press the [SEL] key for 3 seconds until display shows "roFF". If display shows "rrUn", press the [^] or [v] key until display shows "roFF". Press the [^] or [v] key until display shows "rrUn" then press and hold the [SEL] key until the normal display appears. The Therm-O-Watch will ramp up to 93°C and hold at 93°C. Record the run data every 20 minutes on the data sheet.
13. ☒ Once at 93°C, add **52.37 ml of 50-wt% nitric acid at 0.669 ml/min** (reference Table XLII) to the kettle. Should take about 1 hour and 20 minutes.
14. ☒ Add **117.14 ml of 90-wt% formic acid at 0.687 ml/min** (reference Table XLII) to the kettle. Should take about 2 hours and 55 minutes.
15. ☒ Add **2.3 g 1:10 antifoam solution** and **2.3 g water** directly to the kettle (100 ppm antifoam).
16. ☒ Hook the heating mantle to the Cole-Parmer (gray box) temperature controller and switch on the Cole-Parmer unit. Bring the kettle contents to boiling.
17. ☒ Dewater until collect **846 g of H₂O** in the SMECT leaving approximately **1.7 L in the kettle**. Should take about 4 hours and 15 minutes. (*Collected 847.4 g*)
18. ☒ Pull **10 ml sample** for nitrate, nitrite, and formate analysis. Label **LB SRAT 4V*-1N**.

Run # 4V

Date: 1/20/99

SRAT CYCLE (continued)

19. ☒ Add 2.3 g 1:10 antifoam solution and 2.3 g water directly to the kettle (100 ppm antifoam).
20. ☒ Reflux the slurry for 14.6 hours or more (including the dewater time in step 18) at 3.4 g/min boil-up taking 10 ml sample for nitrate, nitrite, and formate analysis every 2 hours and one at the end. Continue refluxing until there is evidence of nitrite destruction (hydrogen release) and the hydrogen has reached its peak. Then turn off the heat to cool the kettle to sub-boiling. Weigh samples and record in lab book. Add 1 ml of 1 N NaOH solution to each sample, reweigh, and record in lab book. Label as LB SRAT 4V*-2N, 4N, 6N, 8N, 10N, etc.
21. ☒ Pull a 125 ml sample from the kettle, record the weight on the run sheet. Label as LB SRAT 4V* and send to lab for analyses.
22. ☒ Pull a 125 ml sample from the kettle, record the weight on the run sheet. Label as LB SRAT 4V* Rheology and send to lab for Rheology.
23. ☒ Remove Sampler and insert rubber stopper in port.

Run # 4V

Date: 1/21/99

SME CYCLE

1. ☒ Add 2.3 g 1:10 antifoam solution and 2.3 g water directly to the kettle (100 ppm antifoam).
2. ☒ Add about 540.04 g of frit 200 to the kettle (1st frit addition - Table XLI). Actual amount of frit to add: 541.15 g¹⁴ (Added 541.2 g)
3. ☒ Add about 11.00 g of 90-wt% formic acid to the kettle (1st formic addition - Table XLI). Actual amount of formic to add: 11.02 g¹⁴
4. ☒ Add about 991.93 g of water to the kettle (1st water addition - Table XLI). Actual amount of water to remove: 993.98 g¹⁴ (Added 994.0 g)
5. ☒ Bring kettle contents to boiling. Record the run data every 20 minutes on the data sheet.
6. ☒ Remove about 992 g of water (about 5 hours). Actual amount of water to remove: 672.5 g¹⁵
7. ☒ When dewatering is complete (about 3.4 hours), turn off the heat to cool the kettle to sub-boiling.
8. ☒ Add about 540.04 g of frit 200 to the kettle (1st frit addition - Table XLI). Actual amount of frit to add: 541.15 g¹⁴ (Added 541.2 g)
9. ☒ Add about 11.00 g of 90-wt% formic acid to the kettle (1st formic addition - Table XLI). Actual amount of formic to add: 11.02 g¹⁴
10. ☒ Add about 991.93 g of water to the kettle (1st water addition - Table XLI). Actual amount of water to remove: 993.98 g¹⁴ (Added 994.0 g)
11. ☒ Bring kettle contents to boiling. Record the run data every 20 minutes on the data sheet.
12. ☒ Remove about 992 g of water (about 5 hours). Actual amount of water to remove: 672.5 g¹⁵
(Removed 674.8 g)
13. ☒ When dewatering is complete, turn off the heat to cool the kettle to sub-boiling. . Turn on cooling water to cooling coil dip-leg.
14. ☒ Pull a 125-ml sample from the kettle, record the weight on the run sheet. Label as LB SME 4V* and send to lab for analyses.
15. ☒ Stop GC and record the GC time and clock time in the log book. Stop recording run data on the data sheet.
16. ☒ Install the calibration gas cylinder to the GC and run the post-cal check. If the check indicates OK, print a copy and write "post-cal check and run number" on the printout, then place the GC in standby. If the check is not within 10% of the cal gas composition, notify the engineer.
17. ☒ Pump kettle contents into a tared bottle. Record the weight on the run sheet.
18. ☒ Complete pH meter post calibration check. Record measured pH in pH 7 buffer 7.25.
19. ☒ Install the outlet flow meter to the purge gas.
20. ☒ When the kettle is cool (<50 °C), record the outlet purge flow in the log book. (All channels). Perform Leak Check.
21. ☒ Turn off all instruments.

¹⁴ Actual amounts calculated after account for SRAT samples pulled and other losses.

¹⁵ Amounts recalculated to reach 45 wt% solids in SME product after account for samples pulled and other losses

APPENDIX A-5: LARGE BATCH RUNS 5V

SRT-PTD-99-0031, Rev. 0

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June 16, 1999

TO: L. F. Landon, 704-1T

FROM: W. E. Daniel, 704-1T

**Run Plan for Extra Large Batch Variability Run
for Developing Strategies for Increased CPC Batch Sizes (U)**

This run plan documents an extra variability run regarding the Task Technical Plan for Developing Strategy for Increased CPC Batch Size (WSRC-RP-98-00354) as requested in DWPF Technical Task Request HLW/DWPT/TTR-980013. The experimental work will be controlled using the Laboratory Scale Chemical Process Cell Simulations (Manual L27, Procedure 2.02) and this run plan. This run plan includes many of the experimental details, the instructions for final sludge preparation, the scaling necessary for determining the operating conditions such as feed rates, purge rates, and the steps in completing the SRAT and SME cycles. This document also summarizes the decisions made to complete these experiments.

- 1) The sludge used for the SRAT Heel preparation is a Tank 42-sludge simulant created from the Optima Tank 51 simulant with the following modifications.
 - a) A recipe is shown in Table XLV that targets a 20 weight percent solids sludge after the trim chemicals (noble metals and mercury) are added. This sludge will be referred to as Sludge A' and its pre-trim measured as well as post-trim predicted elemental weight percent analyses are shown in Table XLVI. Estimated elementals of the SRAT Heel used in this experiment are shown in Table XLVII.
 - b) Tank 42 levels of noble metals and mercury will be added to the sludge batches as shown in Table XLVIII and Table XLIX. These levels will require approximately 14 hours of refluxing in the SRAT to steam strip mercury and meet the DWPF constraint of 0.45 wt % mercury.

Table XLV. Preparation Of Tank 42 Sludge 22 weight % (Trim Chemicals Missing)

Component	Amount, g	Comments
Tank 51 sludge simulant	14613.20	18.52 wt% solids initially
Tank 51 supernate	373.20	Added Supernate to lower wt% solids
Al ₂ O ₃	194.98	
Ni(NO ₃) ₂ *6H ₂ O	37.65	
SiO ₂	25.73	
MnO ₂ *x H ₂ O	133.49	Total Mass @ 71.4 wt% solids
Water	200.00	
Al ₂ O ₃	1.50	
Na ₂ C ₂ O ₄	0.00	
NaF	0.88	
NaOH	8.69	
NaCl	0.34	

Table XLVI. Elemental Analyses of Large Batch 20 wt% Sludge A'

Insoluble Species	Measured Wt% Solids Pre-Trim	Predicted Wt% Solids Post-Trim	Soluble Species	Measured Wt% Solids Pre-Trim	Predicted Wt% Solids Post-Trim
Al	5.72%	7.58%	Al		0.02%
*Ag		0.04%	C2O4	0.28%	0.27%
Ca	2.04%	1.94%	Cl	0.04%	0.04%
*Cd		0.11%	CO3		1.81%
Cl		0.07%	Cr		0.00%
Cr		0.16%	F	0.01%	0.02%
Cu	0.02%	0.02%	K		0.00%
F		0.01%	Li		0.00%
Fe	23.08%	21.80%	Na		0.25%
*Hg		1.30%	NO2	4.38%	3.73%
K	0.16%	0.05%	NO3	1.80%	1.44%
Li	0.00%	0.00%	OH		0.12%
Mg	1.13%	1.11%	PO4	0.06%	0.05%
Mn	4.48%	3.64%	SO4	0.26%	0.21%
Na	7.88%	5.74%			
Ni	0.35%	0.34%			
P		0.00%			
*Pd		0.00%			
Pu		0.00%			
*Rh		0.01%			
*Ru		0.02%			
Se		0.00%			
Si	1.64%	1.80%			
Te		0.00%			
Ti	0.05%	0.05%			
U		0.00%			
Zn	0.01%	0.00			

Table XLVII. Estimated Elementals for Second SRAT Heel prepared from Sludge A'

Insoluble Species	Estimated Wt% Solids	Soluble Species	Estimated Wt% Solids
Al	5.55%	Al	0.02%
Ag	0.037%	C2O4	0.27%
Ca	1.98%	Cl	0.04%
Cd	0.11%	CO3	1.70%
Cl	0.06%	Cr	0.00%
Cr	0.16%	F	0.01%
Cu	0.02%	K	0.00%
F	0.01%	Li	0.00%
Fe	22.4%	Na	0.24%
Hg	1.30%	NO2	4.25%
K	0.16%	NO3	1.84%
Li	0.00%	OH	0.12%
Mg	1.10%	PO4	0.06%
Mn	4.35%	SO4	0.25%
Na	7.65%		
Ni	0.34%		
P	0.00%		
Pd	0.0022%		
Pu	0.00%		
Rh	0.0053%		
Ru	0.022%		
Se	0.00%		
Si	1.59%		
Te	0.00%		
Ti	0.05%		
U	0.00%		
Zn	0.01%		

Table XLVIII. Trim Chemical Addition for First Sludge Addition for Run LB 5V

		Target Addition, g	Actual Addition, g	Wt% Solids w/o Trim	Target Solids w/Trim, g ⁹	Actual Solids added, g ⁹
Sludge A'		2000.0		19.3%	393.1	
Trim Chemicals	Wt% Species in Solution	Target Addition, grams	Actual Addition, grams	Elemental Solids Factor	Target Elemental Solids, g	Actual Elemental Solids, g
AgNO3	100.00%	0.236		0.6349	0.150	
HgO	100.00%	5.626		0.9261	5.210	
Pd(NO3)2*H2O	15.27% ¹⁶	0.058		0.1527	0.00883	
Rh(NO3)3*2H2O	4.93% ⁸	0.431		0.0493	0.02125	
RuCl3	41.74% ⁸	0.211		0.4174	0.0881	
Cd(NO3)2*4H2O	100.00%	1.208		0.3644	0.440	

Element	Target Wt% Solids ¹⁷	Actual Wt% Solids
Ag	0.037%	
Hg	1.30%	
Pd	0.0022%	
Rh	0.0053%	
Ru	0.022%	
Cd	0.11%	

Table XLIX. Trim Chemical Addition for Second Sludge Addition for Run LB 5V

		Target Addition, g	Actual Addition, g	Wt% Solids w/o Trim	Target Solids w/Trim, g ⁹	Actual Solids added, g ⁹
Sludge A'		333.3		19.3%	65.5	
Trim Chemicals	Wt% Species in Solution	Target Addition, grams	Actual Addition, grams	Elemental Solids Factor	Target Elemental Solids, g	Actual Elemental Solids, g
AgNO3	100.00%	0.039		0.6349	0.025	
HgO	100.00%	0.937		0.9261	0.868	
Pd(NO3)2*H2O	15.27% ⁸	0.010		0.1527	0.00147	
Rh(NO3)3*2H2O	4.93% ⁸	0.072		0.0493	0.00354	
RuCl3	41.74% ⁸	0.035		0.4174	0.0147	
Cd(NO3)2*4H2O	100.00%	0.203		0.3644	0.074	

Element	Target Wt% Solids ⁹	Actual Wt% Solids
Ag	0.037%	
Hg	1.30%	
Pd	0.0022%	
Rh	0.0053%	
Ru	0.022%	
Cd	0.11%	

¹⁶ These values represent the weight percent of elemental Pd, Rh, or Ru in their respective solutions.

¹⁷ These values include the weight and/or solids of the added trim chemicals.

- 2) The batching of the materials is designed to produce a glass containing 26 wt % calcined sludge solids and 74 wt % frit 200. A batching summary is shown in Table XXX.
- 3) Calculated acid addition rates, boilup rates, purge rates, antifoam addition, etc. were based on scaling from DWPF settings as shown in Table LI.
- 4) Run 5V simulates a processing scenario where the sludge solids are high (about 20 wt%) and a 150% acid stoichiometry is used to ensure nitrite destruction. The redox calculation spreadsheets for the Variability Run LB 5V are shown in Table LII.
- 5) The reflux time in the SRAT cycle will be extended until there is evidence of nitrite destruction.
- 6) A review, as required by the Conduct of Research and Development was completed and is contained in Appendix B.
- 7) The experiments should be completed the week of June 14, 1999.

Table L. Batching Summary for Variability Run LB 5V

Batching Summary	Run LB 5V
Sludge & Heel Mass	2733.3 g
Nitric Acid Volume, ml	51.18 ml
Formic Acid Volume, ml	117.87 ml
SRAT Product Sample, ml	125
Frit 200 Addition #1, g	534.23 g
SME Water Addition #1, g	981.25 g
SME 90 wt% Formic Acid Addition #1, g	10.88 g
Frit 200 Addition #2, g	534.23 g
SME Water Addition #2, g	981.25 g
SME 90 wt% Formic Acid Addition #2, g	10.88 g
SRAT Air Purge [‡] , scc/min	466.5
SRAT Helium purge, scc/min	2.34
SME Air Purge [‡] , scc/min	163.8
SME Helium purge, scc/min	0.82

[‡]Actual SRAT Gas Purge equivalent to this Air purge plus the Helium Purge.

Table LI. Scaling Calculations for Large Batch Variability Runs 5V

	DWPF	TNX LB 5V	Time
Scale factor		11,355 (12831) [†]	
Sludge Added Volume	7,000 gal	2065 ml	
Sludge Heel Volume	1,200 gal	354 ml	
Sludge Added Density	1.13	1.13	
Sludge Heel Density	1.13	1.13	
Sludge Added Mass	29941 kg	2333.3 g	
Sludge Heel Mass	5133 kg	400.0 g	
SRAT Added Water	1,000 gal	295.0 ml	2.3 hrs boil
SRAT purge air [‡]	188 scfm	466.5 scc/min	
SRAT He purge	0.50 vol %	2.34 scc/min	
SME purge air [‡]	66 scfm	163.8 scc/min	
SME He purge	0.50 vol %	0.82 scc/min	
Antifoam (100 ppm in Total Sludge)	7.73 lbs	0.23 g	
Antifoam Solution (20 to 1 solution)	154.65 lbs	4.67 g	
nitric acid feedrate	2 gpm	0.663 ml/min	1.2 hrs feed
formic acid feedrate	2 gpm	0.687 ml/min	3.0 hrs feed
boilup rate	5,000 lb/hr	3.33 g/min	
Formic Molarity	23.55 M	22.85 M	
Nitric Molarity	10.35 M	10.40 M	
Formic Volume	343.1 gal	117.87 ml	
Formic Mass		141.97 g	
Nitric Volume	154.3 gal	51.18 ml	
Nitric Mass		67.07 g	
formic feed time	171.5 min	171.5 min	
Nitric feed time	77.1 min	77.1 min	
Total Vol		2882.88 ml	
Frit Volume, gallons	3,561 gal	1187.170 g	
Frit Density	1.5		
Frit wt % solids	60%		
Frit Solids	26,747.4 lbs	1068.453 g	
Formic Acid	490.4 lbs	19.588 g	
Water	32,201.0 lbs	1286.298 g	
Transfer Water	16,982.5 lbs	678.383 g	
Total Water	49,183.5 lbs	1964.681 g	
Total	76,421.3 lbs	3052.722 g	

[†]Value in parentheses represents corrected value due to scale factor error.

[‡]Actual SRAT/SME Gas Purge equivalent to this Air purge plus the Helium Purge.

Table LI. Scaling Calculations for Large Batch Variability Run LB 5V Continued

	DWPF	TNX LB 5V	Time
frit 200	26,747.4 lbs	1068.453 g	
90 wt % formic acid	544.9 lbs	21.765 g	
water	49,129.0 lbs	1962.505 g	
Total	76,421.3 lbs	3052.722 g	
frit 200 Addition 1	13,373.7 lbs	534.226 g	
90 wt % formic addition 1	272.4 lbs	10.882 g	
water addition 1	24,564.5 lbs	981.252 g	4.9 hrs boil
frit 200 Addition 2	13,373.7 lbs	534.226 g	
90 wt % formic addition 2	272.4 lbs	10.882 g	
water addition 2	24,564.5 lbs	981.252 g	4.9 hrs boil

Table LII. Large Batch Variability Run 5V Redox Calculation

Stoichiometry ratio:	150.0% (141%) [†]			Date:	6/16/99
Stream	PHA	Sludge	Frit	SME	
Oxide Contribution (%) (in SME)	0.0%	26.0%	74.0%	18380.1	kg Calc. Basis
Density (kg/L)	1.0355	1.130	n/a	137.0%	
Total Solids (%)	5.38%	19.96%	n/a	48.0%	
Calcine Factor (ox/sol)	1.00	0.80	n/a	n/a	
Hydroxide (M)	n/a	0.560	n/a	n/a	
Mercury (ppm)	n/a	2298.5	n/a	n/a	
Total Mn (wt% solids)	n/a	4.36	n/a	n/a	
Soluble Mn (ppm)	n/a	0.00	n/a	n/a	
*TIC (ppm)	n/a	0.00	n/a	n/a	
Total Acid (M)	0.240	n/a	n/a	n/a	
Nitrite (ppm)	0.0	7277.0	0.0 (kg/100kg frit)		
NO2 Destruction	0.0%	100.0%	0.0%		
Nitrate (ppm)	1012.1	5617.9	0.0 (kg/100kg frit)		
% nitrite to nitrate conversion		35.0%			
Formate (ppm)	22808.9	0.0	1.0 (kg/100kg frit)		
Reaction formate destruction, kg		154.24			
Factor for total formate destruction		15.0%			
Total formate destruction, kg		23.14			
Oxide Mass (kg)	0.0	4778.8	13601.3	18380.1	
Solids Mass (kg)	0.00	5975.42	13601.30	19576.72	
Total Mass (kg)	0.00	29942.84	n/a	40784.83	
Volume (L)	0.00	26,498.09	n/a	29769.95	
% Stoichiometry	n/a	150.0%	n/a	n/a	
Volume HNO3@50% (L)	n/a	3,539.25	n/a	n/a	
NO2 Contribution (kg)	0.000	217.893	0.000	217.893	
NO2 Remaining (kg)	0.000	0.000	0.000	0.000	
NO3 Contribution (kg)	0.000	2515.677	0.000	2515.677	
COOH Contribution (kg)	0.000	(154.24)	93.843	(60).394	
NO2 (Molar@45%)				0.000	
NO3 (Molar@45%)				1.720	
COOH (Molar@45%)				-0.057	
Predicted Fe(II)/ΣFe			0.09	≤ BDL@0.03	≤ 0.1
Volume HCOOH@90% (L)			4426.78	4096.52	4481.89
% Stoichiometry	n/a	150.0%	n/a	n/a	
Volume HCOOH@90% (L)	n/a	1,555.31	n/a	n/a	
NO2 Contribution (kg)	0.000	217.893	0.000	217.893	
NO2 Remaining (kg)	0.000	0.000	0.000	0.000	
NO3 Contribution (kg)	0.000	244.480	0.000	244.480	
COOH Contribution (kg)	0.000	1625.834	93.843	1719.677	
NO2 (Molar@45%)				0.000	
NO3 (Molar@45%)				0.167	
COOH (Molar@45%)				1.620	
Predicted Fe(II)/ΣFe			0.09	≤ 0.505	≤ 0.1
Volume HNO3@50% (L)			1430.20		1388.50

[†]Value in parentheses represents corrected value due to scale factor error.

Table XVII. Large Batch Variability Run 5V Redox Calculation Continued

Stoichiometry ratio:	150.0% (141%) [†]			Date:	6/16/99
mol% Nitric	n/a	16.5%	n/a	n/a	
Volume HCOOH@90% (L)	n/a	1,298.68	n/a	n/a	
Volume HNO3@50% (L)		583.98			
NO2 Contribution (kg)	0.000	217.893	0.000	217.893	
NO2 Remaining (kg)	0.000	0.000	0.000	0.000	
NO3 Contribution (kg)	0.000	619.227	0.000	619.227	
COOH Contribution (kg)	0.000	1222.652	0.000	1222.652	
NO2 (Molar@45%)				0.000	
NO3 (Molar@45%)				0.423	
COOH (Molar@45%)				1.152	
Predicted Fe(II)/ΣFe			0.09	≤ 0.200 (0.211) [†]	≤ 0.1
					kgb 9/16/96

[†]Value in parentheses represents corrected value due to scale factor error.

Run # 5V

Date: 6-17-99

PREREQUISITES

1. ☒ Signed TAR requesting work.
2. ☒ Issued Testing scope and task assignment.
3. ☒ Analyze sludge for density, total base (pH 5.5), nitrate, manganese, nitrite, density, solids.
4. ☒ Calibrate GC. Calibrate for nitrogen, oxygen, N₂O, hydrogen, and carbon dioxide.
5. ☒ Prepare sufficient 90% formic acid and 50% nitric acid.
6. ☒ Prepare sufficient antifoam solution or make sure sufficient solution is available.
7. ☒ Calculate batching and scaling for experiment based on DWPF parameters.
8. ☒ Calculate redox for experiment based on DWPF parameters.
9. ☒ Setup experimental rig per sketch below.
10. ☒ Complete leak checks and water runs.

Run # 5V

Date: 6-17-99

PREPARATION FOR SRAT CYCLE

Note: ☒ Do not insulate kettle until acid addition is complete

1. ☒ While agitating kettle, remove all of **SRAT Heel A'** from previous experiment but **400.0 g**. Amount to be removed is 1564 g = 1675 g - 121.0 g (wt of LB SRAT Heel 2 sample) (*1573 g removed*)
2. ☒ Add **2000 g** of **Sludge A'** to kettle using 2-liter transfer bottle or beaker. (*1999.92 g added*)
3. ☒ Set mixer speed to **200 rpm**. Mark **Sludge Level in Kettle** as *De-water Level* for later de-watering and concentration.
4. ☒ Add first batch of trim chemicals (from **Table XLVIII**) directly to the kettle.
5. ☒ Transfer **295.0 g** of distilled water to the kettle (use to rinse all containers used for adding sludge, noble metals, mercury, etc.).
6. ☒ Calibrate pH probe with pH 4 and 10 buffer. Record measured pH of pH 7 buffer *done*¹⁸.
7. ☒ Install pH probe in kettle. Record initial pH of sludge *done*¹⁸.
8. ☒ Turn on the air purge to kettle at **100.0 sccm**. Connect the outlet flowmeter to perform the leak check. The outlet flow should be **90-110 sccm**. If it is not, tighten all connections until the system is leak tight. Write down the leak check in the logbook.
9. ☒ Disconnect outlet flowmeter.
10. ☒ Set the air flow to kettle at **466.5 sccm**. Set the He flow to **2.34 sccm**.
11. ☒ Turn on cooling water to SRAT condenser. **Setpoint = 40°C**.
12. ☒ Turn on cooling water to Chilled (FAVC) condenser. **Setpoint = 10°C**.
13. ☒ Make sure the GC computer has enough memory space for the run (at least 40 Mbyte).
14. ☒ Set the GC computer time equal to the clock time. Record the time in the log book.
15. ☒ Install the calibration gas cylinder to the GC and let the GC run five times. If at the end of five runs the GC reading is within 10% of the gas composition in the cylinder, print the calibration check results and write down "pre-cal check and run number" on the printout. Otherwise, select "Calibration" "Level 1" "OK" to calibrate the GC five times. At the end of five runs the GC reading should be within 10% of the gas composition in the cylinder. If it is not, contact the engineer. Print the calibration check results and write down "pre-cal check and run number" on the printout.
16. ☒ Start the GC for this run beginning with baseline reading for a few minutes. Write down the GC time, filename etc. in the logbook. Record the baseline data on the data sheet.

¹⁸ Performed in SRAT Heel Preparation Step described in previous run plan.

Run # 5V

Date: 6-17-99

SRAT CYCLE

1. ☒ Add 2.33 g 1:10 antifoam solution and 2.33 g water directly to the kettle (100-ppm antifoam).
2. ☒ Start heating up the kettle with the TEMP-O-TROL Model TOT-VOVC (yellow box) temperature controller. Turn on its power switch, turn the voltage output dial to maximum (115), press and hold the up [Δ] and down [∇] keys simultaneously until display flashes between TUNE and OFF, then press the up [Δ] key until display says SPrr, now press and hold the enter [*] key and the display should show 60 for $^{\circ}\text{C}$ per hour the system will ramp up to reach its setpoint. If the display shows something other than 60 then while pressing the enter [*] key, press the up or down keys to adjust the value to 60. To return to the normal temperature display, press and hold up [Δ] and down [∇] keys simultaneously until the temperature is shown. Now press and hold the enter [*] key to check the current setpoint which should be 93. If the display shows something other than 93 then while pressing the enter [*] key, press the up or down keys to adjust the value to 93. Once you release the enter [*] key, a little flashing block [] should appear in the upper left corner of the display and the ON light should illuminate indicating power to the heating mantle. The temperature should ramp to 93°C then hold there. Record the run data every 20 minutes on the data sheet.
3. ☒ Adjust the setpoint on the TEMP-O-TROL to 110°C by pressing and holding the enter [*] key and pressing the up [Δ] and down [∇] keys. Adjust voltage output to 3.33 g/min boil-up rate and bring the kettle contents to boiling.
4. ☒ If slurry begins to foam over at any time, switch off heating and turn on the cooling coil water pump to bring the temperature down rapidly. Add antifoam solution as shown in Step 1. Then switch off the cooling coil water pump and slowly heat up the kettle again to the point of boiling.
5. ☒ Dewater until remove 300 g of water (kettle volume should be close to De-water Level marked in Step 3 of PREPARATION FOR SRAT CYCLE). Should take about 1 hour and 30 minutes.
6. ☒ When dewatering is complete, turn off the heat to kettle, turn on water to cooling coil, and cool the kettle to sub-boiling (90°C).
7. ☒ Add 333.3 g of Sludge A' to the kettle using 2-liter transfer bottle or beaker.
8. ☒ Add second batch of trim chemicals (from Table XLIX) directly to the kettle.
9. ☒ Transfer 50 g of distilled water to the kettle (use to rinse all containers used for adding sludge, noble metals, mercury, etc.). (125.9 g water used)
10. ☒ Allow slurry to cool to 50°C , monitoring torque every 20 minutes.
11. ☒ Pull 10 ml sample for nitrate, nitrite, and formate analysis. Weigh and record in lab book. Add 1 ml of 1 N NaOH solution, reweigh, and record in lab book. Label the sample LB SRAT 5V*-0N.

Run # 5V

Date: 6-17-99

SRAT CYCLE (continued)

12. ☒ Start heating up the kettle with the TEMP-O-TROL Model TOT-VOVC (yellow box) temperature controller. Turn on its power switch, turn the voltage output dial to maximum (115), press and hold the up [Δ] and down [∇] keys simultaneously until display flashes between TUNE and OFF, then press the up [Δ] key until display says SPrr, now press and hold the enter [*] key and the display should show 60 for $^{\circ}\text{C}$ per hour the system will ramp up to reach its setpoint. If the display shows something other than 60 then while pressing the enter [*] key, press the up or down keys to adjust the value to 60. To return to the normal temperature display, press and hold up [Δ] and down [∇] keys simultaneously until the temperature is shown. Now press and hold the enter [*] key to check the current setpoint which should be 93. If the display shows something other than 93 then while pressing the enter [*] key, press the up or down keys to adjust the value to 93. Once you release the enter [*] key, a little flashing block [] should appear in the upper left corner of the display and the ON light should illuminate indicating power to the heating mantle. The temperature should ramp to 93°C then hold there. Record the run data every 20 minutes on the data sheet.
13. ☒ Once at 93°C , add 51.18 ml of 50-wt% nitric acid at 0.663 ml/min (reference Table LI) to the kettle. Should take about 1 hour and 15 minutes.
14. ☒ Add 117.87 ml of 90-wt% formic acid at 0.687 ml/min (reference Table LI) to the kettle. Should take about 3 hours.
15. ☒ Add 2.33 g 1:10 antifoam solution and 2.33 g water directly to the kettle (100 ppm antifoam).
16. ☒ Adjust the setpoint on the TEMP-O-TROL to 110°C by pressing and holding the enter [*] key and pressing the up [Δ] and down [∇] keys. Adjust voltage output to 3.33 g/min boil-up rate and bring the kettle contents to boiling.
17. ☒ Dewater until collect 947 g of H_2O in the SMECT leaving approximately 1.7 L in the kettle. Should take about 4.7 hours. *(Collected 1023 g due to additional water added earlier)*
18. ☒ Pull 10 ml sample for nitrate, nitrite, and formate analysis. Weigh and record in lab book. Add 1 ml of 1 N NaOH solution, reweigh, and record in lab book. Label LB SRAT 5V*-1N.
19. ☒ Add 2.33 g 1:10 antifoam solution and 2.33 g water directly to the kettle (100 ppm antifoam).
20. ☒ Reflux the slurry for 14.2 hours or more (including the dewater time in step 18) at 3.33 g/min boil-up taking 10 ml sample for nitrate, nitrite, and formate analysis every 2 hours and one at the end. Continue refluxing until there is evidence of nitrite destruction (hydrogen release) and the hydrogen has reached its peak. Then turn off the heat to cool the kettle to sub-boiling. Weigh samples and record in lab book. Add 1 ml of 1 N NaOH solution to each sample, reweigh, and record in lab book. Label as LB SRAT 5V*-2N, 4N, 6N, 8N, 10N, etc.
21. ☒ Pull a 125 ml sample from the kettle, record the weight on the run sheet. Label as LB SRAT 5V* and send to lab for analyses.
22. ☒ Pull a 125 ml sample from the kettle, record the weight on the run sheet. Label as LB SRAT 5V* Rheology and send to lab for Rheology.
23. ☒ Remove Sampler and insert rubber stopper in port.

Run # 5V

Date: 6-21-99

SME CYCLE

1. ☒ Set the air flow to kettle at 163.8 sccm. Set the He flow to 0.82 sccm.
2. ☒ Add 2.33 g 1:10 antifoam solution and 2.33 g water directly to the kettle (100 ppm antifoam).
3. ☒ Add about 534.23 g frit 200 to the kettle (1st frit addition - Table L). Actual amount of frit to add: 518.67 g¹⁹
4. ☒ Add about 10.88 g of 90-wt% formic acid to the kettle (1st formic addition - Table L). Actual amount of formic to add: 10.57 g¹²
5. ☒ Add about 981.25 g of water to the kettle (1st water addition - Table L). Actual amount of water to add: 952.69 g¹²
6. ☒ Bring kettle contents to boiling. Record the run data every 20 minutes on the data sheet.
7. ☒ Remove about 674 g of water (about 3.4 hours). Actual amount of water to remove: 651 g¹²
8. ☒ When dewatering is complete, turn off the heat to cool the kettle to sub-boiling.
9. ☒ Add about 534.23 g frit 200 to the kettle (2nd frit addition - Table L). Actual amount of frit to add: 518.67 g¹²
10. ☒ Add about 10.88 g of 90-wt% formic acid to the kettle (2nd formic addition - Table L). Actual amount of formic to add: 10.57 g¹²
11. ☒ Add about 981.25 g of water to the kettle (2nd water addition - Table L). Actual amount of water to add: 952.69 g¹²
12. ☒ Bring kettle contents to boiling. Record the run data every 20 minutes on the data sheet.
13. ☒ Remove about 674 g of water (about 3.4 hours). Actual amount of water to remove: 651 g¹²
14. ☒ When dewatering is complete, turn off the heat to cool the kettle to sub-boiling. Turn on cooling water to cooling coil dip-leg.
15. ☒ Pull a 125-ml sample from the kettle, record the weight on the run sheet. Label as LB SME 5V* and send to lab for analyses.
16. ☒ Stop GC and record the GC time and clock time in the logbook. Stop recording run data on the data sheet.
17. ☒ Install the calibration gas cylinder to the GC and run the post-cal check. If the check indicates OK, print a copy and write "post-cal check and run number" on the printout, then place the GC in standby. If the check is not within 10% of the cal gas composition, notify the engineer.
18. ☒ Pump kettle contents into a tared bottle. Record the weight on the run sheet.
19. ☒ Complete pH meter post calibration check. Record measured pH in pH 7 buffer 7.37.
20. ☒ Install the outlet flow meter to the purge gas.
21. ☒ When the kettle is cool (<50 °C), record the outlet purge flow in the log book. (All channels).
22. ☒ Turn off all instruments.

¹⁹ Actual amounts calculated after account for SRAT samples pulled and other losses.

APPENDIX B: CONDUCT OF R&D REVIEW

Review of Conduct of R&D for Large CPC Batch Task

The Conduct of R&D from SRTC²⁰ as it pertains to the scoping and variability experiments for the DWPF Large CPC Batch study has been reviewed. Please see the attached figures from the Conduct of R&D document, which have been marked appropriately for the Large CPC Batch work.

Following the logic laid out in the Conduct of R&D, no new Job or Process Hazards Review is needed for the Large Batch study as similar equipment, procedures, and chemicals that have been used in past experiments will be used in these new experiments. Should the task change then the Conduct of R&D can be reviewed again to assure all proper protocols are being followed.

²⁰ Conduct of Research and Development, Savannah River Technology Center, March 31, 1998, WSRC-IM-97-00024.

Figure 1
Conduct of R&D Summary Flow Diagram

Figure 2
Work Initiation Process Flow Diagram

Process Flowchart

Work initiated through requests, phone calls, and e-mails with customer.

Examined reports on previous work, various literature sources, and spoke with other researchers.

This work is Non-baseline and is for R&D.

A preliminary plan and schedule was developed so funding and other administration requirements

Meetings were held with the customer so a TTR could be written to meet everyone's needs.

The customer (DWPF) signed off on the TTR and so did we (ITS).

Figure 2 (contd)
Work Initiation Process Flow Diagram
Process Flowchart

A task leader and principal investigator was assigned to the DWPF large batch work.

A technical task plan was drafted, reviewed, and signed by the customer and other participants.

See Figure 3 for R&D Hazards checklist.

Figure 3 R&D Hazards Screening Checklist

Listed below are characteristics of an experiment/project that may present hazards above normal risks to SRTC. Circle YES or NO for each item listed. For each "yes" answer you will be directed to a secondary hazard review or reviews that will direct completion of specific actions need to manage/mitigate the identified hazard.

ENERGIES

- A. Electricity (exposed energized parts > 50V).
YES ☒ NO
See Figures 4 & 11.
- B. Fissionable materials.
YES ☒ NO
Specify: _____
See Figures 4, 5, 6, 7, 9, & 11.
- C. High noise levels (>85dBA).
YES ☒ NO
See Figures 4, 8, & 11.
- D. Microwave/radiofrequencies (30 KHz- 300 GHz), electric or magnetic fields.
YES ☒ NO
See Figures 4, 8, & 11.
- E. Lasers (other than class 1).
YES ☒ NO
See Figures 4, 8, & 11.
- F. Moving equipment (exposed belts, chins, gears, pinch rollers, pulleys, rotating shafts/blades, wheels, etc.)
☒ YES NO
See Figures 4 & 11.
- G. Radioactive materials.
YES ☒ NO
Specify: Radionuclides: _____
Amount: _____
Physical Form: _____
See Figures 4, 5, 6, 7, 9, & 11.
- H. Static magnetic fields > 600 Gauss.
YES ☒ NO
See Figures 4, 8, & 11.

Figure 3
R&D Hazards Screening Checklist

- I. Sub-radiofrequency (<30 KHz) electric and magnetic fields.
YES ☒ NO
See Figures 4, 8, & 11.
- J. Temperatures (<32°F or >150°F). Consider furnaces, ovens, dryers, boilers, steam systems, heaters, dewars, chillers, and release of compressed gases.
☒ YES NO
See Figures 4, 8, 10, & 11.
- K. Vacuum (external pressure > 15PSI).
YES ☒ NO
See Figures 4, 8, & 11.
- L. Pressure (compressible materials > 30PSI; or noncompressible materials > 150PSI).
YES ☒ NO
See Figures 4, 8, & 11.
- M. Pressure vessels (> 15PSI and >6"ID; and/or contain toxic, corrosive, or nuclear materials).
YES ☒ NO
See Figures 4, 8 & 11.

WORKSITE ENVIRONMENTAL CONDITIONS

- A. Boating or work over water.
YES ☒ NO
See Figure 4, 8, & 11.
- B. Cold or heat stress conditions.
YES ☒ NO
See Figure 4, 8, & 11.
- C. Confined spaces/trenches/or evacuations.
YES ☒ NO
See Figures 4, 8, & 11.
- D. Flammable atmospheres (> 10% LEL).
YES ☒ NO
See Figures 4, 8, 10, & 11.
- E. Oxygen deficient atmospheres (<19.5% O₂).
YES ☒ NO
See Figures 4, 8, & 11.

Figure 3 (continued)

R&D Hazards Screening Checklist

- F. Toxic atmosphere (airborne contaminant concentrations expected to exceed 50% of the Threshold Limit Value)
YES ☒ NO
See Figures 4, 5, 8, & 11.
- G. Activity performed in a nuclear facility.
YES ☒ NO
See Figure 6.
- H. Work with radioactive or contaminated material or entry into controlled area.
YES ☒ NO
See Figures 6 & 7.

HAZARDOUS MATERIALS

- A. Biological Agents.
YES ☒ NO
See Figures 4, 5, 8, 9, & 11.
- B. Carcinogens, mutagens, teratogens.
YES ☒ NO
Specify: _____
See Figures 4, 5, 8, 9, & 11.
- C. Corrosives.
☒ YES ☐ NO
See Figures 4, 5, 8, 9, & 11.
- D. Cryogenic gases/liquids.
YES ☒ NO
See Figures 4, 8, & 11.
- E. Flammable/combustible gases, liquids, solids.
YES ☒ NO
Specify: _____ Amount: _____
See Figures 4, 5, 8, 9, 10, & 11.
- F. Toxic Chemicals.
☒ YES ☐ NO
Specify: Mercury, Cadmium Amount: 40 grams, 10 grams
See Figures 4, 5, 8, 9, & 11.

Figure 3 (continued)

R&D Hazards Screening Checklist

- G. Oxidizers
☒ YES ☐ NO
Specify: Nitric Acid Amount: 220 ml
See Figures 4, 5, 8, 9, 10, & 11.
- H. Hydrocarbons (>55 gallons).
☐ YES ☒ NO
See Figures 4, 5, 8, 9, & 11.
- I. Any hazardous substance.
☒ YES ☐ NO
Specify: Formic Acid
See Figures 4, 5, 8, 9, & 11.

ENVIRONMENTAL COMPLIANCE

- A. Release of regulated gas or particulate to the environment.
☒ YES ☐ NO
See Figure 9.
Experiments fall within permitted limits of hoods.
- B. Release of regulated materials to a waste disposal system.
☐ YES ☒ NO
See Figure 9.
- C. Waste disposal problems (including equipment).
☐ YES ☒ NO
See Figure 9.
- D. Creation of radioactive waste.
☐ YES ☒ NO
See Figure 9.

Figure 4
Job Hazards Analysis (JHA) Flowchart

Process Flowchart

Figure 5
Process Hazards Review (PHR) Flowchart

Technicians will be working with 50 weight percent nitric acid and 90 weight percent formic acid solutions.

Technicians have worked with these and other hazardous materials and are not exposed at any greater risk than in past experiments.

Figure 8
Industrial Hygiene & Chemical Control Flowchart

Figure 9
Environmental Protection & Waste Management Flowchart
Process Flowchart

The technicians have dealt with these type of materials in the past and are trained on how to handle it.

Figure 10
Fire Protection Flowchart

The experimental equipment includes a heating mantle that has been used in many previous experiments and meets all safety guidelines.

Figure 11
Safety Inspection (SMI-51) Flowchart
Process Flowchart

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