Hydrogen Generation during Melter Feed Preparation of Tank 42 Sludge and Salt Washed Loaded CST in the Defense Waste Processing Facility

by

W. E. Daniel

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

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S. F. Piccolo, Team Leader
Salt Disposition Systems Engineering Team

HYDROGEN GENERATION DURING MELTER FEED PREPARATION OF TANK 42 SLUDGE AND SALT WASHED LOADED CST IN THE DEFENSE WASTE PROCESSING FACILITY (DWPF) (U)

The attached report summarizes the bench-scale research requested by the salt disposition team to examine the effect of crystalline silicotitanate (CST) resin with adsorbed noble metals on the maximum hydrogen generation rate produced during the DWPF melter feed preparation processes (Task 13, HLW-SDT-TTR-99-13.0)¹. CST is one of the options under consideration to replace the current In-Tank precipitation process. CST is a non-elutable resin used to remove cesium from the supernate fraction of SRS High Level Waste. The CST would be combined with the sludge in the SRAT to replace the PHA that is currently part of DWPF's coupled flowsheet. Frit would then be added to the SRAT product as is typical in a DWPF SME cycle.

Testing was completed using a non-radioactive Tank 42 sludge simulant. A 1/10,000th scale laboratory setup at TNX was used and the results then scaled for DWPF operations. 110% of Tank 42 levels of noble metals and 100% of Tank 42 levels of mercury were added to the sludge. The CST concentration was targeted to produce 10 wt% CST in the glass. The CST was loaded with non-radioactive cesium and noble metals.

These bench-scale experiments showed that the loaded CST (as-received and size-reduced) did not produce any more hydrogen than the sludge-only process and all hydrogen production was well below DWPF limits. The loaded bench-scale CST runs did not have any foaming problems but this was at a limited mass flux of about 4 lb/hr*ft² compared to DWPF's mass flux of about 50 lb/hr*ft². Loaded CST experiments are being conducted in the 1/240th scale GFPS to better match DWPF's mass flux to determine if they are any real foaming issues.

If there are additional questions regarding the attached report, please contact W. E. Daniel at 7-7759.

W. L. Tamosaitis, Manager

SRTC - Waste Processing Section

¹ CST-DWPF Processing Hydrogen and Foaming, F. G. Smith, February 10, 1999, WSRC-RP-99-00229.

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**HYDROGEN GENERATION DURING MELTER FEED
PREPARATION OF TANK 42 SLUDGE AND SALT WASHED
LOADED CST IN THE DEFENSE WASTE PROCESSING
FACILITY (DWPF) (U)**

W. E. Daniel

Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

SAVANNAH RIVER SITE

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PREPARATION OF TANK 42 SLUDGE AND SALT WASHED
LOADED CST IN THE DEFENSE WASTE PROCESSING
FACILITY (DWPF) (U)**

W. E. Daniel

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APPROVALS

W. E. Daniel
W. E. Daniel, Author

8-26-99
Date

D. P. Lambert
D. P. Lambert, Technical Reviewer

8-30-99
Date

L. F. Landon
L. F. Landon, Manager

8-26-99
Date

W. L. Tamosaitis
W. L. Tamosaitis, Waste Processing Technology

8/31/99
Date

K. J. Rueter
K. J. Rueter, Salt Disposition Systems Engineering Team

9/1/99
Date

J. T. Carter
J. T. Carter, Manager, HLW Process Engineering

9/1/99
Date

Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

SAVANNAH RIVER SITE

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY UNDER CONTRACT NO. DE-AC09-96SR18500

EXECUTIVE SUMMARY

The salt disposition team requested ITS to examine the effect of crystalline silicotitanate (CST) resin with adsorbed noble metals on the maximum hydrogen generation rate produced during the DWPF melter feed preparation processes (Task 13, HLW-SDT-TTR-99-13.0)¹.

CST is one of several process options under evaluation to replace the current In-Tank precipitation process. CST is a non-elutable resin used to remove cesium from the supernate fraction of SRS High Level Waste. The CST would be combined with the sludge in the SRAT to replace the PHA that is currently part of DWPF's coupled flowsheet. Frit would then be added to the SRAT product as is typical in a DWPF SME cycle.

Testing was completed using a non-radioactive Tank 42 sludge simulant. A 1/10,000th scale laboratory setup was used and the results then scaled for DWPF operations. 110% Tank 42 levels of noble metals and 100% Tank 42 levels of mercury were added to the sludge. The CST concentration was targeted to produce 10 wt% CST in the glass. The CST was loaded with non-radioactive cesium and noble metals.

Major conclusions from the testing are:

- The maximum SRAT hydrogen generation rate was 0.005 lb/hr in the Sludge-Only Run 2LC, based on a 6000 gallon DWPF sludge batch. The maximum hydrogen generation occurred near the end of the SRAT reflux cycle and is less than 1% of the current DWPF limit of 0.65 lb/hr. A complete listing of the hydrogen generation rates is given in Table I.
- The maximum SME hydrogen generation rate was 0.016 lb/hr based on a 6000-gallon DWPF sludge batch in the Sludge-Only Run 2LC. This maximum hydrogen generation occurred at the beginning of the SME dewater cycle and is less than 7% of the current DWPF limit of 0.23 lb/hr.
- The runs containing loaded CST did not produce more hydrogen than the sludge-only run. In fact, the loaded CST runs appear to produce less hydrogen than sludge-only. In earlier Phase III runs, the opposite finding was observed but these earlier runs contained HM levels of noble metals (34 times as much palladium, five times as much rhodium, and nine times as much as ruthenium), and three times as much mercury as well as a non-loaded CST that was less washed and from a different batch.
- The size-reduced CST runs produced slightly more hydrogen than the as-received CST but still less than the sludge-only run and below DWPF limits.
- There were no foaming or other processing problems during the runs. However, at the bench scale it is difficult to conclude if DWPF would have any problems so foaming tests are being conducted in the 1/240th GFPS that more closely match the scale of DWPF.

¹ CST-DWPF Processing Hydrogen and Foaming, F. G. Smith, February 10, 1999, WSRC-RP-99-00229.

Table I. Hydrogen Generation Summary for Loaded CST & Sludge-Only Runs

	As-Received Loaded CST	Sludge-Only (No CST)	Size-Reduced Loaded CST	DWPF Limit
SRAT H₂ Peak, lb/hr	0.002	0.005	0.004	0.65
SME H₂ Peak, lb/hr	0.006	0.016	0.010	0.228

- **Recommendations for Future Work**

Should non-elutable CST ion exchange be selected, future work should include experiments to test the following items:

1. Repeat the size-reduced loaded CST experiment with HM (maximum concentration levels) of noble metals and mercury in the bench-scale apparatus and run until SRAT hydrogen peak reached.
2. Repeat the size-reduced loaded CST experiment with HM (maximum concentration levels) of noble metals and mercury in the 1/240th Glass Feed Preparation System. This large-scale run would give a better indication of foaming problems due to the limited mass flux of about 4 lb/hr*ft² in the bench-scale rig compared to DWPF's mass flux of about 50 lb/hr*ft².

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BACKGROUND

The Defense Waste Processing Facility began processing radioactive Tank 51 Sludge in 1996. Because of delays in the start-up of the In-Tank Precipitation (ITP) process, DWPF began processing sludge-only instead of the planned coupled sludge and Precipitate Hydrolysis Aqueous (PHA) feed. Because of these and other problems with the ITP process, alternative methods for removing cesium have been investigated. CST is one of the process options being considered as a replacement for ITP. CST is a non-elutable resin used to remove Cs from the supernate of SRS High Level Waste. The CST would be combined with the sludge in the SRAT cycle to replace the PHA that is currently part of DWPF's coupled flowsheet. The frit would be added to the SRAT product as normal in the DWPF SME cycle.

The salt disposition team asked ITS to examine the effect of blending CST resin with adsorbed cesium and noble metals with Tank 42 sludge on the maximum hydrogen generation rate during the DWPF melter feed preparation processes (Task 13, HLW-SDT-TTR-99-13.0).

Testing was completed using a non-radioactive Tank 42 sludge simulant. A 1/10,000th scale laboratory setup was used and the results then scaled for DWPF operations. 110% Tank 42 levels of noble metals and 100% Tank 42 levels of mercury were added to the sludge. The CST concentration was targeted to produce 10 wt% CST in the glass. The CST was loaded with cesium and noble metals.

This document details the testing performed to determine the maximum hydrogen generation expected with a coupled flowsheet of sludge, loaded CST, and frit.

INTRODUCTION

The main objective of these scoping tests was to measure the rate of hydrogen generation in a series of experiments designed to duplicate the expected SRAT and SME processing conditions in laboratory scale vessels. The experiments were completed with a non-radioactive Tank 42 sludge simulant. The specific objectives of these tests were:

- Determine the maximum hydrogen generation rate during each SRAT and SME processing cycle.
- Determine if any foaming problems were encountered when using the loaded CST.
- Determine any processing problems while completing SRAT/SME cycles with CST.

DISCUSSION

Experimental

Method

Three four-liter bench scale SRAT/SME processing runs were completed in the 772-T lab at TNX. Each of the runs consisted of a typical DWPF SRAT and SME cycle. The experimental setup was designed to volumetrically scale the DWPF vessels, flows, and feed-rates. For

example, 2.0 L of sludge was set equivalent to a 6000-gallon DWPF sludge batch in each of the bench scale runs. These amounts give a scale factor of approximately $1/11,105^{\text{th}}$ of DWPF scale based on a 6000-gallon DWPF sludge batch. However, due to an improper density correction, a scaling factor of $1/10,004^{\text{th}}$ was used in these experiments. Since this larger scale factor was used, these experiments are still conservative, i.e. more acid was added than normal for this amount of sludge. For sludge processing and chemical reaction requirements, a target of 137.5% stoichiometry had been chosen but due to the scaling factor error, the acid addition was closer to 150% stoichiometry. With the $1/10,004^{\text{th}}$ scale factor a DWPF 2-gallon/minute acid addition rate is scaled down to 0.76 ml/min. The experiments were controlled using two laboratory run plans (Appendix A and B). The run plans contain sketches of the experimental setup and the scaled conditions used for the experiments.

The SRAT cycle includes the key DWPF processing steps shown in Table II. The key activities in the DWPF SRAT cycle include the acid addition to the sludge, the reduction of various metals including manganese and mercury, and the destruction of nitrite. Key data to be collected included hydrogen generation rate, foaming conditions, and any processing anomalies.

The SME cycle also includes the key DWPF processing steps shown in Table II. Key data includes hydrogen generation rate, foaming problems, and processing issues.

Table II. Key Steps in the SRAT and SME Cycles

SRAT Cycle Steps	SME Cycle Steps
1. SRAT sludge preparation, sludge analysis, batching calculations	1. First addition of a frit-water-formic acid slurry
2. Heat-up to 93°C	2. Boil off water added with the frit.
3. Addition of nitric acid at 93°C	3. Second addition of a frit-water-formic acid slurry
4. Addition of formic acid at 93°C	4. Boil off water to reach a target solids loading of 45 wt% total solids
5. First CST slurry addition	5. Cool down and sample
6. Heat-up to boiling	
7. Concentration down to 6000 gallons	
8. Second CST slurry addition	
9. Concentration down to 6000 gallons	
10. Reflux for at least 8 hours to remove Hg.	
11. Cool down and sample.	

Three runs were completed, two with loaded CST and one with no CST, i.e. sludge-only. The first experiment was with as-received CST particles (Run 1LC) and the second was with sludge-only (Run 2LC) or no CST. The third experiment was with size-reduced CST particles (Run

3LC). The three runs are summarized in Table III. All runs started with the same Tank 42 sludge simulant with the same levels of noble metals and mercury.

Table III. Bench-Scale Loaded CST Run Summary

Run	Description	Sludge	Noble Metals	CST	Acid Target
1LC	Sludge plus As-Received CST	Tank 42	110% Tank 42	As-Received, Loaded with Noble Metals	150% ²
2LC	Sludge-only	Tank 42	110% Tank 42	None	150%
3LC	Sludge plus Size-Reduced CST	Tank 42	110% Tank 42	Size-Reduced, Loaded with Noble Metals	150%

In all of the runs, the nitric and formic acids were fed to the sludge-slurry at 93 °C. After the acid addition, the first batch of loaded CST was added followed by dewatering. The second batch of loaded CST was then added followed by dewatering. The SRAT cycle then continued as normal into the reflux stage. The total boiling and reflux time in the SRAT was between 10 to 12 hours to get the mercury down to 0.45 wt% solids and to insure nitrite destruction. The SME cycle was carried out as normal with two frit-water-formic additions and two dewatering steps to achieve 45-wt% solids.

Sludge Preparation

The sludge simulant used in these runs contained approximately 17 wt % solids and was made up to match the Tank 42 sludge that DWPF is processing. The sludge was prepared using a Tank 51 sludge-simulant, a non-radioactive simulant containing all the major sludge components. The Tank 51 simulant was chosen because its composition is the closest to the Tank 42 composition. The Tank 51 simulant was doped with aluminum, nickel, and manganese since these components are significantly higher in the Tank 42 sludge. The noble metals and mercury were added prior to each run. The pre-noble Tank 42 simulant was analyzed for solids, elementals, total base (pH 5.5) and density. The composition of the sludge before and after noble metal addition is summarized in the run plans in Appendix A and B.

CST Preparation

The CST used in these experiments was loaded with cesium and noble metals to simulate several salt washes in the proposed ITP process for DWPF. About 500 grams of Batch 5 (Lot No. 999098810005) CST was loaded using a 6 liter salt solution with Cs and noble metals amounts shown in Table IV. After 3 days of loading in an up flow column, the Cs concentration had dropped to 35 PPM. At 110°C the weight percent solids of the un-loaded CST was determined to be 94.86%. However, calcining the loaded CST at 610°C gave a calcined weight percent solids of 77.2%. This calcine weight percent was used to determine the 140 g of "air-dry" loaded CST that was added in these experiments to give 10-wt% CST in the glass on an oxide basis. To produce the size-reduced CST, a special apparatus was used that pumped the CST slurry between two annular vessels until the proper size CST settled out. More details on the apparatus used and

² The target stoichiometry was 137.5% but due to a scaling factor error the actual stoichiometry is closer to 150%.

the loading of the CST are contained in a separate report.³ For the size-reduced CST experiment, 140 g of "air-dry" CST was dissolved in about 1400 g of water. This 9-wt% CST slurry was then added to the bench-scale setup in two additions like the "air-dry" CST.

Table IV. CST Loading Salt Solution Makeup

Elements	Target Conc., ppm
Pd	2.5
Rh	1.7
Ru	6.1
Cs	1845

Acid Addition Strategy

Concentrated formic acid (90-wt %) and nitric acid (50-wt%) were added to neutralize the sludge and complete the desired REDOX and nitrite destruction reactions. Total acid additions were based on total acid to achieve 137.5% stoichiometry using a scale factor of 1/10,004th and an acid mix to produce a REDOX target of $0.2 \text{ Fe}^{2+}/\Sigma\text{Fe}$ in the glass. After discovering that the scale factor was indeed 1/11,105th, the amounts of acids actually added were equivalent to about 150% stoichiometry with a REDOX target of $0.2 \text{ Fe}^{2+}/\Sigma\text{Fe}$. This extra acid is conservative and is closer to what DWPF actually runs.

CST Addition Strategy

The CST was not metered into the SRAT during boiling like PHA. It was batched in during non-boiling conditions. For the as-received CST Run 1LC, the CST was added dry through a funnel to the kettle, followed by enough water to simulate a 10-wt % CST-water slurry. The amount of "air-dry" CST added was 138.9 g to give 107.3 g of calcined CST. For the size-reduced CST Run 3LC, a 9-wt% solution was provided with about 140 g of "air-dry" CST. Although this value was higher than the requested 138.9 g, it was deemed close enough considering variances in the measurements and the makeup of the CST solution.

Antifoam Addition Strategy

To prevent a loss of solids due to foaming, Dow Corning 544 antifoam was added per the DWPF antifoam strategy (100 ppm on a total solution basis, 1 part antifoam: 19 parts water every twelve hours) and as needed to control foaming in the experiments. No antifoam had to be added outside the normal amounts during the experiments.

Frit Addition Strategy

Two equal amounts of frit, water, and formic acid were added to the SME to simulate the frit-water slurry. Frit 202 was added to the loaded CST runs since it is the frit used during coupled experiments. For the sludge-only experiment, Frit 200 was used as it is normally used for sludge-only experiments. No water was added to simulate the addition of frit-decon water to the SME. The frit was added dry through a funnel to the bench-scale kettle, followed by 90-weight percent formic acid, and enough water to simulate a 35-wt% frit slurry. The frit addition for the

³ CST/Frit 202 Settling, CST Particle Size Reduction, and CST Loading, M. A. Baich, WSRC-TR-99-00244.

sludge-only run was based on a target of 74-wt% frit in the glass and for the loaded CST runs was based on 64 wt % frit in the glass.

Results

Offgas Composition

The main purpose of the experiments was to monitor the hydrogen generation rate. In order to calculate the hydrogen generation rate, the offgas flow and composition were measured. Since it is difficult to measure the offgas flow accurately throughout the SRAT and SME cycle, an internal helium standard was used to calculate the outlet flow. The helium and air purges were metered in using MKS mass flow controllers. The MKS mass flow controllers were calibrated prior to the runs using a MKS GRBOR Mass Flow Controller Calibrator. In addition, flow meters were zeroed under no flow conditions to ensure accurate readings and leak checks were performed prior to each experiment to demonstrate that the bench-scale system was leak free.

The offgas composition was monitored using a Gas Chromatograph (GC). The MTI gas chromatographs were calibrated prior to and after each run to ensure the measured composition of the calibration standard was within 10% of the certification concentration.

Hydrogen Generation

The maximum hydrogen generation during the SRAT cycle was 0.005 lb/hr in the Sludge-Only Run 2LC based on 6000 gallons of 17-wt% solids sludge. This peak occurred close to the end of the SRAT cycle reflux. This maximum SRAT hydrogen value is significantly lower than the DWPF SRAT hydrogen limit of 0.65 lb/hr. The maximum hydrogen generation for the SME cycle was 0.016 lb/hr for the Sludge-Only Run 2LC which is significantly less than the DWPF SME hydrogen limit 0.23 lb/hr. This hydrogen peak occurred at the start of the second SME dewatering. It is normal to have peaks at the onset of boiling because hydrogen accumulates in the kettle during the non-boiling conditions (like after cooling to add materials to the kettle) due to poor mass transfer. If this peak is ignored, the maximum SME hydrogen value is 0.014 lb/hr and occurs at the end of the second SME dewatering step. Note that 110% Tank 42 levels of noble metals were used in these experiments.

Figure 1, Figure 2, and Figure 3 show the hydrogen generation rates for the As-Received CST Run 1LC, the Sludge-Only Run 2LC, and the Size-Reduced CST Run 3LC, respectively. Note that the sludge-only run (2LC) hydrogen peaks were about the same as the size-reduced (3LC) run values. The sudden drops in hydrogen concentration were due to cooling down the vessel to make additions. Table V shows the peak hydrogen generation rates for all three runs. More detailed charts of the GC and other run data for the As-Received Loaded CST Run (1LC), the Sludge-only Run (2LC), and the Size-Reduced Loaded CST are shown in Figure 4, Figure 5, and Figure 6, respectively.

Table V. Hydrogen Generation Rate for Loaded CST & Sludge-Only Runs

	As-Received Loaded CST	Sludge-Only (No CST)	Size-Reduced Loaded CST	DWPF Limit
Run ID	1LC	2LC	3LC	
772-T Lab Room #	112	112	112	
Date (1999)	6/9-6/10	6/9-6/10	6/16-6/17	
SRAT H₂ Peak, vol %	0.003	0.007	0.006	
SRAT H₂ Peak, lb/hr	0.002	0.005	0.004	0.65
SRAT H₂ Peak, scc/min	0.015	0.039	0.034	
SME H₂ Peak, vol %	0.031	0.068	0.042	
SME H₂ Peak, lb/hr	0.006	0.016	0.010	0.228
SME H₂ Peak, scc/min	0.052	0.134	0.083	

Discussion of Hydrogen Generation

The hydrogen generation for the Sludge-Only Run 2LC was slightly higher than either loaded CST runs 1LC and 3LC. Whether this difference is significant would require further testing at larger scales such as the 1/240th GFPS system. The Size-Reduced CST Run 3LC had higher peaks of hydrogen than the As-Received CST Run 1LC (0.004 lb/hr versus 0.002 lb/hr in the SRAT and 0.01 lb/hr versus 0.006 lb/hr in the SME). This difference may be due in part to the longer SRAT boil time in the Size-Reduced CST Run 3LC (13.5 hours) versus the As-Received CST Run 1LC (10.4 hours). The Size-Reduced CST Run 3LC took longer to dewater as its boil-up rate drifted lower than the As-Received CST Run 1LC.

Looking at all three runs collectively there appears to be no significant hydrogen increase when adding CST that has been loaded with Cesium and noble metals to the DWPF SRAT/SME cycle. In fact, the loaded CST may somehow inhibit the release of hydrogen but further testing would be required to verify this hypothesis. In earlier Phase III testing, the opposite was observed or the CST runs produced more hydrogen than the sludge-only run. However, it is difficult to compare these latest results with the earlier findings since a different batch (#999096810004) of CST was used and the earlier experiments used sludge with HM levels of noble metals and mercury. In any case, the difference between Phase III testing and the latest runs may be due to the preparation of the CST. The Phase III CST was ground by hand, soaked for 37-43 hours in caustic, air-dried, and titrated back to a normal pH. The loaded CST under went multiple flushings for longer periods than Phase III. These flushings may have changed the CST activity or propensity to generate hydrogen. Since these latest runs more closely mimic the treatment of CST in the proposed ITP operations, the latest findings may reflect a more accurate picture of how the loaded CST will behave. To better answer this question, more experiments are suggested as discussed in the *Future Work* section.

Figure 1. As-Received CST Run 1LC Hydrogen Generation on DWPF Scale

Figure 2. Sludge-Only Run 2LC Hydrogen Generation on DWPF Scale

Figure 3. Size-reduced CST Run 3LC Hydrogen Generation on DWPF Scale

Figure 4. As-Received CST Run 1LC GC and Run Data

Figure 5. Sludge-Only Run 2LC GC and Run Data

Figure 6. Size-Reduced CST Run 3LC GC and Run Data

Foaming

None of the three experiments with sludge-only, as-received CST, and size-reduced CST had any problems with foaming. DOW Corning 544 antifoam was added as 100 PPM on a total solution basis at the beginning of the SRAT cycle before heat up, then after acid addition but before the CST addition, and at the beginning of the SME cycle. The loaded CST runs had no more foam than the sludge-only experiment, and even that was small (less than half an inch). However, the mass flux for these bench-scale runs was around 4 lb/hr*ft² compared to DWPF's 50 lb/hr*ft². At a higher flux, foaming may become an issue and testing the larger scale like the 1/240th GFPS will help answer this question.

Processing Issues

No unusual processing problems were encountered in the runs with loaded CST. There were no mixing, heating, or sampling problems. At times, the mixer speed was increased to insure good mixing but nothing out of the ordinary. Tests are being conducted on a larger scale (the 1/240th GFPS and TFL sampler mock-up) to better quantify any processing problems.

FUTURE WORK

These scoping experiments were designed to measure hydrogen generation using loaded CST in DWPF SRAT/SME cycles with Tank 42 levels of noble metals and mercury. Earlier experiments with unloaded CST showed more hydrogen (about 40%) than the sludge-only experiment done at the same time. In these earlier experiments, the maximum hydrogen in the SRAT was 0.41 lb/hr and the maximum hydrogen in the SME was 0.22 lb/hr on a DWPF basis. These earlier experiments were done with Tank 42 sludge but with HM (maximum concentration) levels of noble metals and mercury. The HM Tank 42 sludge from these earlier experiments had 34 times as much palladium, five times as much rhodium, and nine times as much as ruthenium, and three times as much mercury as the Tank 42 sludge used in these loaded CST experiments. These earlier experiments were also made with a different CST (UOP IONSIV IE-911, Lot #999096810004, 8/3/98) which could have affected the results.

Based on the current results and the earlier experimental findings, it is recommended that a bench-scale size-reduced loaded CST experiment be performed to see the impact of HM levels on hydrogen generation. A 1/240th run should also be performed in the Glass Feed Preparation System to see how well the results scale.

ACKNOWLEDGMENTS

Thanks to Roy Jacobs and Joe Carter for providing quick answers to questions and direction as needed.

Thanks to Frances Williams, Sammie King, John Duvall, Mary Johnson, Vickie Williams, and Tony Burckhalter for doing an excellent job preparing for and carrying out the planned experiments. Their team approach toward work is very much appreciated. The long hours and especially the long nights they worked to accomplish these experiments on time is to be commended.

The technical support from Dan Lambert, Dave Koopman, Paul Monson, and Russ Eibling is also very much appreciated.

SRT-PTD-99-0004, Rev. 0

CC: E. W. Holtzscheiter, 773-A
J. E. Occhipinti, 704-27S
S. L. Marra, 704-25S
R. E. Edwards, 704-25S
R. E. Eibling, 704-1T
P. R. Monson, 704-1T
D. P. Lambert, 704-1T
M. F. Williams, 704-1T
J. W. Duvall, 704-1T
M. L. Johnson, 772-T
S. O. King, 677-T
V. J. Williams, 677-T
T. O. Burckhalter, 677-T
D. C. Koopman, 704-T

June 7, 1999

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

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

Run Plan For Hydrogen Study During Melter Feed Preparation Of Tank 42 Sludge And Loaded CST In The Defense Waste Processing Facility (DWPF) (U)

This run plan documents the runs with Tank 42 sludge and loaded CST to support the CST Homogeneity and DWPF Chemistry activities for impact of CST on hydrogen evolution and foaming (SDT-TTR-99-13). 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 trimming, 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) Two Bench Scale runs will be completed. Run 1LC will refer to the loaded CST and Tank 42 sludge run. Run 2LC will refer to the Tank 42 Sludge only, no CST run. Both runs will be completed in parallel.
- 2) The sludge used for the Loaded CST experiments is a Tank 42-sludge simulant prepared by Dave Koopman from several barrels of the Optima Tank 51 simulant.
 - a) Dave's recipe targets a 17.26 weight percent solids sludge after the trim chemicals (noble metals and mercury) are added. This sludge will be referred to as Loaded CST Tank 42 Sludge and its pre-trim measured as well as post-trim predicted elemental weight percent analyses are shown in Table VI.
 - b) 110% of Tank 42 levels of noble metals and 100% of Tank 42 levels of mercury will be added to the sludge batches as shown in Table VII and Table VIII. These levels will require approximately 8 hours of refluxing in the SRAT to steam strip mercury and meet the DWPF constraint of 0.45 wt % mercury.

Table VI. Elemental Analyses of Loaded CST Tank 42 Sludge

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	9.08%	8.98%	Al		0.00%
*Ag		0.04%	C2O4	0.15%	0.14%
Ca	2.69%	2.66%	Cl		0.00%
Cd		0.00%	CO3	2.20%	2.18%
Cl		0.02%	Cr		0.00%
Cr		0.19%	F	0.03%	0.03%
Cu	0.03%	0.03%	K		0.00%
F		0.00%	Li		0.00%
Fe	27.12%	26.83%	Na		0.00%
*Hg		1.05%	NO2	3.40%	3.36%
K	0.13%	0.13%	NO3	1.41%	1.43%
Li	0.00%	0.00%	OH	1.78%	1.76%
Mg	1.37%	1.35%	PO4	1.65%	1.64%
Mn	3.83%	3.79%	SO4	0.20%	0.20%
Na	6.63%	6.56%			
Ni	0.37%	0.37%			
P		0.31%			
*Pd		0.0023%			
Pu		0.00%			
*Rh		0.0056%			
*Ru		0.023%			
Se		0.00%			
Si	0.90%	0.89%			
Te		0.00%			
Ti	0.04%	0.04%			
U		0.00%			
Zn	0.14%	0.14%			

*These materials added in the Post-Trim

Table VII. Trim Chemical Addition for Sludge for Run 1LC

		Target Addition, g	Actual Addition, g	Wt% Solids w/o Trim	Target Solids w/Trim, g ⁵	Actual Solids added, g ⁵
<i>Tank 42 Sludge</i>		2270.0	2270.0	16.8%	385.7	3857
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%	0.244	0.244	0.6349	0.155	0.155
HgO	100.00%	4.373	4.373	0.9261	4.050	4.050
Pd(NO3)2*H2O	15.27%⁴	0.058	0.058	0.1527	0.0090	0.0090
Rh(NO3)3*2H2O	4.93%⁴	0.438	0.438	0.0493	0.0216	0.0216
RuCl3	41.74%⁴	0.213	0.213	0.4174	0.0890	0.0890

Element		Target Wt% Solids ⁵	Actual Wt% Solids
Ag		0.04%	0.04%
Hg		1.05%	1.05%
Pd		0.0023%	0.0023%
Rh		0.0056%	0.0056%
Ru		0.023%	0.023%

Table VIII. Trim Chemical Addition for Sludge for Run 2LC

		Target Addition, g	Actual Addition, g	Wt% Solids w/o Trim	Target Solids w/Trim, g ⁵	Actual Solids added, g ⁵
<i>Tank 42 Sludge</i>		2270.0	2269.6	16.8%	385.7	385.63
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%	0.244	0.244	0.6349	0.155	0.155
HgO	100.00%	4.373	4.373	0.9261	4.050	4.050
Pd(NO3)2*H2O	15.27%⁴	0.058	0.058	0.1527	0.0090	0.0090
Rh(NO3)3*2H2O	4.93%⁴	0.438	0.438	0.0493	0.0216	0.0216
RuCl3	41.74%⁴	0.213	0.213	0.4174	0.0890	0.0890

Element		Target Wt% Solids ⁵	Actual Wt% Solids
Ag		0.04%	0.04%
Hg		1.05%	1.05%
Pd		0.0023%	0.0023%
Rh		0.0056%	0.0056%
Ru		0.023%	0.023%

⁴ These values represent the weight percent of elemental Pd, Rh, or Ru in their respective forms added.

⁵ These values include the weight and/or solids of the added trim chemicals.

- 3) The batching of the materials for Run 1LC is designed to produce a glass containing 26-wt % calcined sludge solids, 10-wt % CST, and 64-wt % frit 202. The batching for Run 2LC is designed to produce a glass containing 26 wt % calcined sludge solids and 74-wt % frit 200. A batching summary is shown in Table IX.
- 4) Calculated acid addition rates, boilup rates, purge rates, antifoam addition, etc. were based on scaling from DWPF settings as shown in Table X.
- 5) Run 1LC simulates a processing case with a 17 weight percent solids sludge and loaded CST or CST exposed to several salt washes. A nominal acid addition of 137.5% of stoichiometry was targeted but due to an error in the scale factor, the acid addition more closely matched 150% stoichiometry. In either case, a redox target of $0.2 \text{ Fe}^{+2}/\Sigma\text{Fe}$ was used. The redox calculation spreadsheets for Run 1LC are shown in Table XI.
- 6) Run 2LC simulates a baseline case for the new Tank 42 sludge simulant and typical operating conditions. The redox calculation spreadsheets for Run 2LC are shown in Table XII.
- 7) A review, as required by the Conduct of Research and Development was completed and is contained in an earlier document, Conduct of R&D for Hydrogen Study for Tank 42 Sludge and Loaded CST DWPF Bench Scale Runs (U), SRT-PTD-99-0024.
- 8) The experiments were completed the week of June 7, 1999.

Table IX. Batching Summary for Variability Runs 1LC and 2LC

Batching Summary	Run 1LC	Run 2LC
Sludge Mass	2270.0 g	2270.0 g
Nitric Acid Volume, ml	46.68 ml	46.68 ml
Formic Acid Volume, ml	93.18 ml	93.18 ml
CST (Air Dry) Solids Addition #1, g	69.44 g	0.00 g
CST Water Addition #1, g	624.92 g	0.00 g
CST (Air Dry) Solids Addition #2, g	69.44 g	0.00 g
CST Water Addition #2, g	624.92 g	0.00 g
SRAT Product Sample, ml	125	125
Frit Addition #1, g	343.25 g	396.89 g
	Frit 202	Frit 200
SME Water Addition #1, g	630.48 g	728.99 g
SME 90 wt% Formic Acid Addition #1, g	6.99 g	8.09 g
Frit Addition #2, g	343.25 g	396.89 g
	Frit 202	Frit 200
SME Water Addition #2, g	630.48 g	728.99 g
SME 90 wt% Formic Acid Addition #2, g	6.99 g	8.09 g
SRAT Air Purge ¹ , scc/min	529.5	529.5
SRAT Helium purge, scc/min	2.66	2.66
SME Air Purge ¹ , scc/min	185.9	185.9
SME Helium purge, scc/min	0.93	0.93

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

Table X. Scaling Calculations for Large Batch Variability Runs 1LC and 2LC

	DWPF	TNX 1LC	Time	DWPF	TNX 2LC	Time
Scale factor		10,004*			10,004*	
Sludge Added Volume	6,000 gal	2045 ml		6,000 gal	2045 ml	
Sludge Heel Volume	0 gal	0 ml		0 gal	0 ml	
Sludge Added Density	1.11	1.11		1.11	1.11	
Sludge Heel Density	0.0	0.0		0.0	1.13	
Sludge Added Mass	25210 kg	2270.0 g		25210 kg	2270.0 g	
Sludge Heel Mass	0 kg	0.0 g		0 kg	0.0 g	
SRAT Added Water	1,000 gal	340.8 ml	2.1 hrs	1,000 gal	340.8 ml	2.1 hrs
SRAT purge air*	188 scfm	529.5 scc/min		188 scfm	529.5 scc/min	
SRAT He purge	0.50 vol %	2.66 scc/min		0.50 vol %	2.66 scc/min	
SME purge air*	66 scfm	186.8 scc/min		66 scfm	186.8 scc/min	
SME He purge	0.50 vol %	0.93 scc/min		0.50 vol %	0.93 scc/min	
Antifoam (100 ppm in Total Sludge)	5.56 lbs	0.23 g		5.56 lbs	0.23 g	
Antifoam Solution (20 to 1 solution)	111.16 lbs	4.54 g		111.16 lbs	4.54 g	
Elemental Hg to Reduce						
nitric acid feedrate	2 gpm	0.760 ml/min	0.9 hrs	2 gpm	0.760 ml/min	0.9 hrs
formic acid feedrate	2 gpm	0.837 ml/min	2.0 hrs	2 gpm	0.837 ml/min	2.0 hrs
boilup rate	5,000 lb/hr	3.78 g/min		5,000 lb/hr	3.78 g/min	
Formic Molarity	23.55 M	21.30 M		23.55 M	21.30 M	
Nitric Molarity	10.35 M	10.30 M		10.35 M	10.30 M	
Formic Volume	222.7 gal	93.18 ml		222.7 gal	93.18 ml	
Formic Mass		112.23 g			112.23 g	
Nitric Volume	122.8 gal	46.68 ml		122.8 gal	46.68 ml	
Nitric Mass		61.06 g			61.06 g	
formic feed time	111.4 min	111.4 min		111.4 min	111.4 min	
Nitric feed time	61.4 min	61.4 min		61.4 min	61.4 min	
Total Vol		2525.75 ml			2525.75 ml	

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

*The listed volumes give a scale factor of 1/11,105th but due to an improper density correction, a scaling factor of 1/10,004th was used in these experiments.

Table X. Scaling Calculations for Large Batch Variability Runs 1LC and 2LC Continued

	DWPF	TNX 1LC	Time	DWPF	TNX 2LC	Time
Frit Volume, gallons	2,016 gal	762.788 g		2,331 gal	881.973 g	
Frit Density	1.5			1.5		
Frit wt % solids	60%			60%		
Frit Solids	15,141.6 lbs	686.509 g		17,507.4 lbs	793.776 g	
Formic Acid	277.6 lbs	12.586 g		321.0 lbs	14.553 g	
Water	18,228.8 lbs	826.480 g		21,077.0 lbs	955.618 g	
Transfer Water	9,613.7 lbs	435.879 g		11,115.8 lbs	503.985 g	
Total Water	27,842.5 lbs	1262.359 g		32,192.9 lbs	1459.603 g	
Total	43,261.7 lbs	1961.454 g		50,021.3 lbs	2267.931 g	
CST Solids in Solution	3,062.9 lbs	138.871 g		0.0 lbs	0.000 g	
CST Water in Solution	27,566.3 lbs	1249.838 g		0.0 lbs	0.000 g	
CST Solution Total	30,629.2 lbs	1388.709 g		0.0 lbs	0.000 g	
CST Solids Addition 1	1,531.5 lbs	69.435 g		0.0 lbs	0.000 g	
CST Water Addition 1	13,783.2 lbs	624.919 g		0.0 lbs	0.000 g	
CST Solids Addition 2	1,531.5 lbs	69.435 g		0.0 lbs	0.000 g	
CST Water Addition 2	13,783.2 lbs	624.919 g		0.0 lbs	0.000 g	
frit*	15,141.6 lbs	686.509 g		17,507.4 lbs	793.776 g	
90 wt % formic acid	308.4 lbs	13.984 g		356.6 lbs	16.170 g	
water	27,811.6 lbs	1260.961 g		32,157.2 lbs	1457.986 g	
Total	43,261.7 lbs	1961.454 g		50,021.3 lbs	2267.931 g	
frit Addition 1*	7,570.8 lbs	343.254 g		8,753.7 lbs	396.888 g	
90 wt % formic addition 1	154.2 lbs	6.992 g		178.3 lbs	8.085 g	
water addition 1	13,905.8 lbs	630.480 g	2.8 hrs	16,078.6 lbs	728.993 g	3.2 hrs
frit Addition 2*	7,570.8 lbs	343.254 g		8,753.7 lbs	396.888 g	
90 wt % formic addition 2	154.2 lbs	6.992 g		178.3 lbs	8.085 g	
water addition 2	13,905.8 lbs	630.480 g	2.8 hrs	16,078.6 lbs	728.993 g	3.2 hrs

*Frit 202 added to Run 1LC, Frit 200 added to Run 2LC

Table XI. Loaded CST Tank 42 Sludge Run 1LC Redox Calculation

Stream	PHA	Sludge	Frit		SME	
Oxide Contribution (%) (in SME)	0.0%	26.0%	64.0%		13054.4	kg Calc. Basis
Density (kg/L)	1.0355	1.110	n/a		137.0%	
Total Solids (%)	10.00%	16.98%	n/a		48.0%	
Calcine Factor (ox/sol)	1.00	0.79	n/a		n/a	
Hydroxide (M)	n/a	0.511	n/a		n/a	
Mercury (ppm)	n/a	1763.1	n/a		n/a	
Total Mn (wt% solids)	n/a	3.74	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	6342.0	0.0	(kg/100kg frit)		
NO2 Destruction	0.0%	100.0%	0.0%			
Nitrate (ppm)	1012.1	2640.0	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		101.54				
Factor for total formate destruction		15.0%				
Total formate destruction, kg		15.23				
Oxide Mass (kg)	0.0	3394.2	8354.8		11749.0	
Solids Mass (kg)	0.00	4280.83	8354.84		12635.68	
Total Mass (kg)	0.00	25211.04	n/a		26324.33	
Volume (L)	0.00	22,712.65	n/a		19214.84	
% Stoichiometry	n/a	137.5%*	n/a		n/a	
Volume HNO3@50% (L)	n/a	2,383.54	n/a		n/a	
NO2 Contribution (kg)	0.000	159.888	0.000		159.888	
NO2 Remaining (kg)	0.000	0.000	0.000		0.000	
NO3 Contribution (kg)	0.000	1652.080	0.000		1652.080	
COOH Contribution (kg)	0.000	(101.54)	93.843		(7).697	
NO2 (Molar@45%)					0.000	
NO3 (Molar@45%)					1.130	
COOH (Molar@45%)					-0.007	
Predicted Fe(II)/ΣFe			0.09	≤	BDL@0.03	≤ 0.1
Volume HCOOH@90% (L)			2885.44		2672.24	2921.02
% Stoichiometry	n/a	137.5%	n/a		n/a	
Volume HCOOH@90% (L)	n/a	1,047.44	n/a		n/a	
NO2 Contribution (kg)	0.000	159.888	0.000		159.888	
NO2 Remaining (kg)	0.000	0.000	0.000		0.000	
NO3 Contribution (kg)	0.000	122.518	0.000		122.518	
COOH Contribution (kg)	0.000	1095.285	93.843		1189.128	
NO2 (Molar@45%)					0.000	
NO3 (Molar@45%)					0.084	
COOH (Molar@45%)					1.120	
Predicted Fe(II)/ΣFe			0.09	≤	0.443	≤ 0.1
Volume HNO3@50% (L)			1035.29			1008.37

*The target stoichiometry was to be 137.5% but due to scaling factor error the actual stoichiometry closer to 150%.

Table XI. Loaded CST Tank 42 Sludge Run 1LC Redox Calculation Continued

mol% Nitric	n/a	19.5%	n/a		n/a	
Volume HCOOH@90% (L)	n/a	843.19	n/a		n/a	
Volume HNO3@50% (L)		464.79				
NO2 Contribution (kg)	0.000	159.888	0.000		159.888	
NO2 Remaining (kg)	0.000	0.000	0.000		0.000	
NO3 Contribution (kg)	0.000	420.783	0.000		420.783	
COOH Contribution (kg)	0.000	792.425	0.000		792.425	
NO2 (Molar@45%)					0.000	
NO3 (Molar@45%)					0.288	
COOH (Molar@45%)					0.746	
Predicted Fe(II)/ΣFe			0.09	≤	0.200	≤ 0.1

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Table XII. Loaded CST Tank 42 Sludge Run 2LC Redox Calculation

Stream	PHA	Sludge	Frit		SME	
Oxide Contribution (%) (in SME)	0.0%	26.0%	74.0%		13195.1	kg Calc. Basis
Density (kg/L)	1.0355	1.110	n/a		137.0%	
Total Solids (%)	10.00%	16.98%	n/a		48.0%	
Calcine Factor (ox/sol)	1.00	0.80	n/a		n/a	
Hydroxide (M)	n/a	0.511	n/a		n/a	
Mercury (ppm)	n/a	1763.1	n/a		n/a	
Total Mn (wt% solids)	n/a	3.74	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	6342.0	0.0	(kg/100kg frit)		
NO2 Destruction	0.0%	100.0%	0.0%			
Nitrate (ppm)	1012.1	2640.0	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		101.54				
Factor for total formate destruction		15.0%				
Total formate destruction, kg		15.23				
Oxide Mass (kg)	0.0	3430.7	9764.4		13195.1	
Solids Mass (kg)	0.00	4280.83	9764.40		14045.23	
Total Mass (kg)	0.00	25211.04	n/a		29260.91	
Volume (L)	0.00	22,712.65	n/a		21358.33	
% Stoichiometry	n/a	137.5%*	n/a		n/a	
Volume HNO3@50% (L)	n/a	2,383.54	n/a		n/a	
NO2 Contribution (kg)	0.000	159.888	0.000		159.888	
NO2 Remaining (kg)	0.000	0.000	0.000		0.000	
NO3 Contribution (kg)	0.000	1652.080	0.000		1652.080	
COOH Contribution (kg)	0.000	(101.54)	93.843		(7).697	
NO2 (Molar@45%)					0.000	
NO3 (Molar@45%)					1.130	
COOH (Molar@45%)					-0.007	
Predicted Fe(II)/ΣFe			0.09	≤	BDL@0.03	≤ 0.1
Volume HCOOH@90% (L)			2831.85		2595.28	2871.33
% Stoichiometry	n/a	137.5%	n/a		n/a	
Volume HCOOH@90% (L)	n/a	1,047.44	n/a		n/a	
NO2 Contribution (kg)	0.000	159.888	0.000		159.888	
NO2 Remaining (kg)	0.000	0.000	0.000		0.000	
NO3 Contribution (kg)	0.000	122.518	0.000		122.518	
COOH Contribution (kg)	0.000	1095.285	93.843		1189.128	
NO2 (Molar@45%)					0.000	
NO3 (Molar@45%)					0.084	
COOH (Molar@45%)					1.120	
Predicted Fe(II)/ΣFe			0.09	≤	0.443	≤ 0.1
Volume HNO3@50% (L)			1076.34			1046.42

*The target stoichiometry was to be 137.5% but due to scaling factor error the actual stoichiometry closer to 150%.

Table XII. Loaded CST Tank 42 Sludge Run 2LC Redox Calculation Continued

mol% Nitric	n/a	19.5%	n/a		n/a	
Volume HCOOH@90% (L)	n/a	843.19	n/a		n/a	
Volume HNO3@50% (L)		464.79				
NO2 Contribution (kg)	0.000	159.888	0.000		159.888	
NO2 Remaining (kg)	0.000	0.000	0.000		0.000	
NO3 Contribution (kg)	0.000	420.783	0.000		420.783	
COOH Contribution (kg)	0.000	792.425	0.000		792.425	
NO2 (Molar@45%)					0.000	
NO3 (Molar@45%)					0.288	
COOH (Molar@45%)					0.746	
Predicted Fe(II)/ΣFe			0.09	≤	0.200	≤ 0.1

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Run # 1LC & 2LC

Date: 6/9/99

PREREQUISITES

1. ☒ Signed TAR requesting work.
2. ☒ Issued Testing scope and task assignment.
3. ☒ Prepare and analyze sludge for density, total base (pH 5.5), nitrate, manganese, nitrite, density, solids.
4. ☒ Prepare loaded CST as directed by task plan.
5. ☒ Calibrate GC. Calibrate for nitrogen, oxygen, N_2O , hydrogen, and carbon dioxide.
6. ☒ Prepare sufficient 90% formic acid and 50% nitric acid.
7. ☒ Prepare sufficient antifoam solution or make sure sufficient solution is available.
8. ☒ Calculate batching and scaling for experiment based on DWPF parameters.
9. ☒ Calculate redox for experiment based on DWPF parameters.
10. ☒ Setup 2 experimental rigs per sketch below.
11. ☒ Complete leak checks and water runs.

Run # 1LC

Date: 6/9/99

PREPARATION FOR SRAT CYCLE

Note: Do not insulate kettle until acid addition is complete or cannot reach desired temperature.

1. ☒ Add 2270 g of Tank 42 Sludge to kettle using 2-liter transfer bottle or beaker.
2. ☒ Turn on kettle agitator. Setpoint = 200 rpm. Mark Sludge Level in Kettle as De-water Level for later de-watering and concentration.
3. ☒ Add trim chemicals (from Table VII) directly to the kettle.
4. ☒ Transfer 340.8 g of distilled water to the kettle (use to rinse all containers used for adding sludge, noble metals, mercury, etc.).
5. ☒ Calibrate pH probe with pH 4 and 10 buffer. Record measured pH of pH 7 buffer 7.163.
6. ☒ Install pH probe in kettle. Record initial pH of sludge 11.996.
7. ☒ 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.
8. ☒ Disconnect outlet flowmeter.
9. ☒ Set the air flow to kettle at 529.5 sccm. Set the He flow to 2.66 sccm.
10. ☒ Turn on cooling water to SRAT condenser. Setpoint = 40°C.
11. ☒ Turn on cooling water to Chilled (FAVC) condenser. Setpoint = 10°C.
12. ☒ Make sure the GC computer has enough memory space for the run (at least 40 Mbyte). (957 mb free)
13. ☒ Set the GC computer time equal to the clock time. Record the time in the log book. (1:23 pm)
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 # 1LC

Date: 6/9/99

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 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 **46.68 ml of 50-wt% nitric acid at 0.760 ml/min** (reference Table X) to the kettle. Should take about 1 hour.
5. ✓ Now add **93.18 ml of 90-wt% formic acid at 0.837 ml/min** (reference Table X) to the kettle. Should take about 2 hours.
6. ✓ Add **2.3 g 1:10 antifoam solution** and **2.3 g water** directly to the kettle (100 ppm antifoam).
7. ✓ Add first addition of CST of **69.44 g** (dry basis or as-received) from Table IX.
8. ✓ Add first addition of CST water of **624.92 g** from Table IX.
9. ✓ 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 **3.78 g/min boil-up rate** and bring the kettle contents to boiling.
10. ✓ Dewater until remove **1115 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 5 hours.
11. ✓ Add second addition of CST of **69.44 g** (dry basis or as-received) from Table IX.
12. ✓ Add second addition of CST water of **624.92 g** from Table IX.
13. ✓ Dewater until remove **624.9 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 2.8 hours.

Run # 1LC

Date: 6/10/99

SRAT CYCLE (continued)

14. ☒ **Reflux the slurry for a total of 8 hours** (including the dewater times in steps 10 and 13) at **3.78 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. (*Refluxed over 12 hours*)
15. ☒ Pull a **125** ml sample from the kettle, record the weight on the run sheet. Label as **Loaded CST SRAT 1LC** and send to lab for analyses.
16. ☒ Remove Sampler and insert rubber stopper in port.

Run # 1LC

Date: 6/10/99

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 343.25 g frit 202 to the kettle (1st frit addition - Table IX). Actual amount of frit to add: 343.03 g⁶
3. ☒ Add about 6.99 g of 90-wt% formic acid to the kettle (1st formic addition - Table IX). Actual amount of formic to add: 6.99 g⁶
4. ☒ Add about 630.48 g of water to the kettle (1st water addition - Table IX). Actual amount of water to add: 630.07 g⁶
5. ☒ Bring kettle contents to boiling. Record the run data every 20 minutes on the data sheet.
6. ☒ Remove about 808 g of water (about 3.6 hours). Actual amount of water to remove: 812.9 g⁶
7. ☒ When dewatering is complete, turn off the heat to cool the kettle to sub-boiling.
8. ☒ Add about 343.25 g frit 202 to the kettle (2nd frit addition - Table IX). Actual amount of frit to add: 343.03 g⁶
9. ☒ Add about 6.99 g of 90-wt% formic acid to the kettle (2nd formic addition - Table IX). Actual amount of formic to add: 6.99 g⁶
10. ☒ Add about 630.48 g of water to the kettle (2nd water addition - Table IX). Actual amount of water to add: 630.07 g⁶
11. ☒ Bring kettle contents to boiling. Record the run data every 20 minutes on the data sheet.
12. ☒ Remove about 808 g of water (about 3.6 hours). Actual amount of water to remove: 812.4 g⁶
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 Loaded CST SME 1LC 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. 2368.6 g
18. ☒ Complete pH meter post calibration check. Record measured pH in pH 7 buffer 7.455.
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).
21. ☒ Turn off all instruments.

⁶ Actual amounts calculated after account for SRAT samples pulled and other losses.

Run # 2LC

Date: 6/9/99

PREPARATION FOR SRAT CYCLE

Note: Do not insulate kettle until acid addition is complete or cannot reach desired temperature

1. ☒ Add 2270 g of Tank 42 Sludge to kettle using 2-liter transfer bottle or beaker.
2. ☒ Turn on kettle agitator. Setpoint = 200 rpm. Mark Sludge Level in Kettle as De-water Level for later de-watering and concentration.
3. ☒ Add trim chemicals (from Table VIII) directly to the kettle.
4. ☒ Transfer 340.8 g of distilled water to the kettle (use to rinse all containers used for adding sludge, noble metals, mercury, etc.). (346.8 g actually added)
5. ☒ Calibrate pH probe with pH 4 and 10 buffer. Record measured pH of pH 7 buffer 7.173.
6. ☒ Install pH probe in kettle. Record initial pH of sludge 12.099.
7. ☒ 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.
8. ☒ Disconnect outlet flowmeter.
9. ☒ Set the air flow to kettle at 529.5 sccm. Set the He flow to 2.66 sccm.
10. ☒ Turn on cooling water to SRAT condenser. Setpoint = 40°C.
11. ☒ Turn on cooling water to Chilled (FAVC) condenser. Setpoint = 10°C.
12. ☒ Make sure the GC computer has enough memory space for the run (at least 40 Mbyte). (1.07 GB)
13. ☒ Set the GC computer time equal to the clock time. Record the time in the log book. (9:29 am)
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 # 2LC

Date: 6/9/99

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 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 **46.68 ml of 50-wt% nitric acid at 0.760 ml/min** (reference Table X) to the kettle. Should take about 1 hour.
5. ☒ Add **93.18 ml of 90-wt% formic acid at 0.837 ml/min** (reference Table X) to the kettle. Should take about 2 hours.
6. ☒ Add **2.3 g 1:10 antifoam solution** and **2.3 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 give desired boil-up rate and bring the kettle contents to boiling.
8. ☒ Dewater until remove **490 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. (496 g removed)
9. ☒ Add **2.3 g 1:10 antifoam solution** and **2.3 g water** directly to the kettle (100 ppm antifoam).
10. ☒ Reflux the slurry for 8 hours (including the dewater time in step 8) at **3.78 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.
11. ☒ Pull a **125 ml** sample from the kettle, record the weight on the run sheet. Label as **Loaded CST SRAT 2LC** and send to lab for analyses.
12. ☒ Remove Sampler and insert rubber stopper in port.

Run # 2LC

Date: 6/10/99

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 396.89 g of frit 200 to the kettle (1st frit addition - Table IX). Actual amount of frit to add: 397.91 g⁷
3. ☒ Add about 8.09 g of 90-wt% formic acid to the kettle (1st formic addition - Table IX). Actual amount of formic to add: 8.11 g⁷
4. ☒ Add about 728.99 g of water to the kettle (1st water addition - Table IX). Actual amount of water to remove: 730.87 g⁷
5. ☒ Bring kettle contents to boiling. Record the run data every 20 minutes on the data sheet.
6. ☒ Remove about 930 g of water (about 4.1 hours). Actual amount of water to remove: 932.0 g⁷
7. ☒ When dewatering is complete, turn off the heat to cool the kettle to sub-boiling.
8. ☒ Add about 396.89 g of frit 200 to the kettle (1st frit addition - Table IX). Actual amount of frit to add: 397.91 g⁷
9. ☒ Add about 8.09 g of 90-wt% formic acid to the kettle (1st formic addition - Table IX). Actual amount of formic to add: 8.11 g⁷
10. ☒ Add about 728.99 g of water to the kettle (1st water addition - Table IX). Actual amount of water to remove: 730.87 g⁷
11. ☒ Bring kettle contents to boiling. Record the run data every 20 minutes on the data sheet.
12. ☒ Remove about 930 g of water (about 4.1 hours). Actual amount of water to remove: 932.0 g⁷
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 Loaded CST SME 2LC 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 7.477.
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).
21. ☒ Turn off all instruments.

⁷ Actual amounts calculated after account for SRAT samples pulled and other losses.

SRT-PTD-99-0030, Rev. 0

CC: E. W. Holtzscheiter, 773-A
J. E. Occhipinti, 704-27S
S. L. Marra, 704-T
R. E. Edwards, 704-25S
R. E. Eibling, 704-1T
P. R. Monson, 704-1T
D. P. Lambert, 704-1T
M. F. Williams, 704-1T
J. W. Duvall, 704-1T
M. L. Moss, 772-T
S. O. King, 677-T
V. J. Williams, 677-T
T. O. Burckhalter, 677-T
D. C. Koopman, 704-T

June 15, 1999

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

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

Run Plan For Hydrogen Study of Melter Feed Preparation of Tank 42 Sludge and Reduced-Sized Loaded CST In The Defense Waste Processing Facility (DWPF) (U)

This run plan documents the run with Tank 42 sludge and size-reduced loaded CST to support the CST Homogeneity and DWPF Chemistry activities for impact of CST on hydrogen evolution and foaming (SDT-TTR-99-13). 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 trimming, 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) One Bench Scale run will be completed. Run 3LC will refer to the size-reduced loaded CST and Tank 42 sludge run.
- 2) The sludge used for these experiments is a Tank 42-sludge simulant prepared by Dave Koopman from several barrels of the Optima Tank 51 simulant.
 - a) Dave's recipe targets a 17.26 weight percent solids sludge after the trim chemicals (noble metals and mercury) are added. This sludge will be referred to as Loaded CST Tank 42 Sludge and its pre-trim measured as well as post-trim predicted elemental weight percent analyses are shown in Table VI.
 - b) 110% of Tank 42 levels of noble metals and 100% of Tank 42 levels of mercury will be added to the sludge batch as shown in Table VII. These levels will require approximately 8 hours of refluxing in the SRAT to steam strip mercury and meet the DWPF constraint of 0.45 wt % mercury.

Table XIII. Elemental Analyses of Loaded CST Tank 42 Sludge

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	9.08%	8.98%	Al		0.00%
*Ag		0.04%	C2O4	0.15%	0.14%
Ca	2.69%	2.66%	Cl		0.00%
Cd		0.00%	CO3	2.20%	2.18%
Cl		0.02%	Cr		0.00%
Cr		0.19%	F	0.03%	0.03%
Cu	0.03%	0.03%	K		0.00%
F		0.00%	Li		0.00%
Fe	27.12%	26.83%	Na		0.00%
*Hg		1.05%	NO2	3.40%	3.36%
K	0.13%	0.13%	NO3	1.41%	1.43%
Li	0.00%	0.00%	OH	1.78%	1.76%
Mg	1.37%	1.35%	PO4	1.65%	1.64%
Mn	3.83%	3.79%	SO4	0.20%	0.20%
Na	6.63%	6.56%			
Ni	0.37%	0.37%			
P		0.31%			
*Pd		0.0023%			
Pu		0.00%			
*Rh		0.0056%			
*Ru		0.023%			
Se		0.00%			
Si	0.90%	0.89%			
Te		0.00%			
Ti	0.04%	0.04%			
U		0.00%			
Zn	0.14%	0.14%			

*These materials added in the Post-Trim

Table XIV. Trim Chemical Addition for Sludge for Run 3LC

		Target Addition, g	Actual Addition, g	Wt% Solids w/o Trim	Target Solids w/Trim, g ⁵	Actual Solids added, g ⁵
<i>Tank 42 Sludge</i>		2270.0	2270.0	16.8%	385.7	385.7
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%	0.244	0.245	0.6349	0.155	0.155
<i>HgO</i>	100.00%	4.373	4.373	0.9261	4.050	4.050
<i>Pd(NO₃)₂*H₂O</i>	15.27% ⁸	0.058	0.058	0.1527	0.0090	0.0090
<i>Rh(NO₃)₃*2H₂O</i>	4.93% ⁴	0.438	0.438	0.0493	0.0216	0.0216
<i>RuCl₃</i>	41.74% ⁴	0.213	0.213	0.4174	0.0890	0.0890

Element		Target Wt% Solids ⁹	Actual Wt% Solids
Ag		0.04%	0.04%
Hg		1.05%	1.05%
Pd		0.0023%	0.0023%
Rh		0.0056%	0.0056%
Ru		0.023%	0.023%

- 3) The batching of the materials for Run 3LC is designed to produce a glass containing 26-wt % calcined sludge solids, 10-wt % CST, and 64-wt % frit 202. A batching summary is shown in Table IX.
- 4) Calculated acid addition rates, boilup rates, purge rates, antifoam addition, etc. were based on scaling from DWPF settings as shown in Table X.
- 5) Run 3LC simulates a processing case with a 17 weight percent solids sludge and a reduced-sized loaded CST. A nominal acid addition of 137.5% of stoichiometry was targeted but due to an error in the scale factor, the acid addition more closely matched 150% stoichiometry. In either case, a redox target of $0.2 \text{ Fe}^{+2}/\Sigma\text{Fe}$ was used. The redox calculation spreadsheets for Run 3LC are shown in Table XI.
- 6) A review, as required by the Conduct of Research and Development was completed and is contained in an earlier document, Conduct of R&D for Hydrogen Study for Tank 42 Sludge and Loaded CST DWPF Bench Scale Runs (U), SRT-PTD-99-0024.
- 7) The experiments were completed the week of June 14, 1999.

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

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

Table XV. Batching Summary for Variability Runs 3LC

Batching Summary	Run 3LC
Sludge Mass	2270.0 g
Nitric Acid Volume, ml	46.68 ml
Formic Acid Volume, ml	93.18 ml
CST 10-wt% Solution Addition #1, g ²	700.0 g
CST 10-wt% Solution Addition #2, g ²	700.0 g
SRAT Product Sample, ml	125
Frit 202 Addition #1, g	343.25 g
SME Water Addition #1, g	630.48 g
SME 90 wt% Formic Acid Addition #1, g	6.99 g
Frit 202 Addition #2, g	343.25 g
SME Water Addition #2, g	630.48 g
SME 90 wt% Formic Acid Addition #2, g	6.99 g
SRAT Air Purge ¹ , scc/min	529.5
SRAT Helium purge, scc/min	2.66
SME Air Purge ¹ , scc/min	185.9
SME Helium purge, scc/min	0.93

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

²Actual 10-wt% solution should be 694.36 g. 700 g is half of prepared 10-wt% solution.

Table XVI. Scaling Calculations for Large Batch Variability Run 3LC

	DWPF	TNX 3LC	Time
Scale factor		10,004*	
Sludge Added Volume	6,000 gal	2045 ml	
Sludge Heel Volume	0 gal	0 ml	
Sludge Added Density	1.11	1.11	
Sludge Heel Density	0.0	0.0	
Sludge Added Mass	25210 kg	2270.0 g	
Sludge Heel Mass	0 kg	0.0 g	
SRAT Added Water	1,000 gal	340.8 ml	2.1 hrs
SRAT purge air*	188 scfm	529.5 scc/min	
SRAT He purge	0.50 vol %	2.66 scc/min	
SME purge air*	66 scfm	186.8 scc/min	
SME He purge	0.50 vol %	0.93 scc/min	
Antifoam (100 ppm in Total Sludge)	5.56 lbs	0.23 g	
Antifoam Solution (20 to 1 solution)	111.16 lbs	4.54 g	
Elemental Hg to Reduce			
nitric acid feedrate	2 gpm	0.760 ml/min	0.9 hrs
formic acid feedrate	2 gpm	0.837 ml/min	2.0 hrs
boilup rate	5,000 lb/hr	3.78 g/min	
Formic Molarity	23.55 M	21.30 M	
Nitric Molarity	10.35 M	10.30 M	
Formic Volume	222.7 gal	93.18 ml	
Formic Mass		112.23 g	
Nitric Volume	122.8 gal	46.68 ml	
Nitric Mass		61.06 g	
formic feed time	111.4 min	111.4 min	
Nitric feed time	61.4 min	61.4 min	
Total Vol		2525.75 ml	

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

*The listed volumes give a scale factor of $1/11,105^{\text{th}}$ but due to an improper density correction, a scaling factor of $1/10,004^{\text{th}}$ was used in these experiments.

Table X. Scaling Calculations for Large Batch Variability Run 3LC Continued

	DWPF	TNX 1LC	Time
Frit Volume, gallons	2,016 gal	762.788 g	
Frit Density	1.5		
Frit wt % solids	60%		
Frit Solids	15,141.6 lbs	686.509 g	
Formic Acid	277.6 lbs	12.586 g	
Water	18,228.8 lbs	826.480 g	
Transfer Water	9,613.7 lbs	435.879 g	
Total Water	27,842.5 lbs	1262.359 g	
Total	43,261.7 lbs	1961.454 g	
CST Solids in Solution	3,062.9 lbs	138.871 g	
CST Water in Solution	27,566.3 lbs	1249.838 g	
CST Solution Total	30,629.2 lbs	1388.709 g	
CST Solids Addition 1	1,531.5 lbs	69.435 g	
CST Water Addition 1	13,783.2 lbs	624.919 g	
CST Solids Addition 2	1,531.5 lbs	69.435 g	
CST Water Addition 2	13,783.2 lbs	624.919 g	
frit 202	15,141.6 lbs	686.509 g	
90 wt % formic acid	308.4 lbs	13.984 g	
water	27,811.6 lbs	1260.961 g	
Total	43,261.7 lbs	1961.454 g	
frit 202 Addition 1	7,570.8 lbs	343.254 g	
90 wt % formic addition 1	154.2 lbs	6.992 g	
water addition 1	13,905.8 lbs	630.480 g	2.8 hrs
frit 202 Addition 2	7,570.8 lbs	343.254 g	
90 wt % formic addition 2	154.2 lbs	6.992 g	
water addition 2	13,905.8 lbs	630.480 g	2.8 hrs

Table XVII. Loaded CST Tank 42 Sludge Run 3LC Redox Calculation

Stream	PHA	Sludge	Frit		SME	
Oxide Contribution (%) (in SME)	0.0%	26.0%	64.0%		13054.4	kg Calc. Basis
Density (kg/L)	1.0355	1.110	n/a		137.0%	
Total Solids (%)	10.00%	16.98%	n/a		48.0%	
Calcine Factor (ox/sol)	1.00	0.79	n/a		n/a	
Hydroxide (M)	n/a	0.511	n/a		n/a	
Mercury (ppm)	n/a	1763.1	n/a		n/a	
Total Mn (wt% solids)	n/a	3.74	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	6342.0	0.0	(kg/100kg frit)		
NO2 Destruction	0.0%	100.0%	0.0%			
Nitrate (ppm)	1012.1	2640.0	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		101.54				
Factor for total formate destruction		15.0%				
Total formate destruction, kg		15.23				
Oxide Mass (kg)	0.0	3394.2	8354.8		11749.0	
Solids Mass (kg)	0.00	4280.83	8354.84		12635.68	
Total Mass (kg)	0.00	25211.04	n/a		26324.33	
Volume (L)	0.00	22,712.65	n/a		19214.84	
% Stoichiometry	n/a	137.5%*	n/a		n/a	
Volume HNO3@50% (L)	n/a	2,383.54	n/a		n/a	
NO2 Contribution (kg)	0.000	159.888	0.000		159.888	
NO2 Remaining (kg)	0.000	0.000	0.000		0.000	
NO3 Contribution (kg)	0.000	1652.080	0.000		1652.080	
COOH Contribution (kg)	0.000	(101.54)	93.843		(7).697	
NO2 (Molar@45%)					0.000	
NO3 (Molar@45%)					1.130	
COOH (Molar@45%)					-0.007	
Predicted Fe(II)/ΣFe			0.09	≤	BDL@0.03	≤ 0.1
Volume HCOOH@90% (L)			2885.44		2672.24	2921.02
% Stoichiometry	n/a	137.5%	n/a		n/a	
Volume HCOOH@90% (L)	n/a	1,047.44	n/a		n/a	
NO2 Contribution (kg)	0.000	159.888	0.000		159.888	
NO2 Remaining (kg)	0.000	0.000	0.000		0.000	
NO3 Contribution (kg)	0.000	122.518	0.000		122.518	
COOH Contribution (kg)	0.000	1095.285	93.843		1189.128	
NO2 (Molar@45%)					0.000	
NO3 (Molar@45%)					0.084	
COOH (Molar@45%)					1.120	
Predicted Fe(II)/ΣFe			0.09	≤	0.443	≤ 0.1
Volume HNO3@50% (L)			1035.29			1008.37

*The target stoichiometry was to be 137.5% but due to scaling factor error the actual stoichiometry closer to 150%.

Table XI. Loaded CST Tank 42 Sludge Run 3LC Redox Calculation Continued

mol% Nitric	n/a	19.5%	n/a		n/a	
Volume HCOOH@90% (L)	n/a	843.19	n/a		n/a	
Volume HNO3@50% (L)		464.79				
NO2 Contribution (kg)	0.000	159.888	0.000		159.888	
NO2 Remaining (kg)	0.000	0.000	0.000		0.000	
NO3 Contribution (kg)	0.000	420.783	0.000		420.783	
COOH Contribution (kg)	0.000	792.425	0.000		792.425	
NO2 (Molar@45%)					0.000	
NO3 (Molar@45%)					0.288	
COOH (Molar@45%)					0.746	
Predicted Fe(II)/ΣFe			0.09	≤	0.200	≤ 0.1

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Run # 3LC

Date: 6/15/99

PREREQUISITES

1. ☒ Signed TAR requesting work.
2. ☒ Issued Testing scope and task assignment.
3. ☒ Prepare and analyze sludge for density, total base (pH 5.5), nitrate, manganese, nitrite, density, solids.
4. ☒ Prepare loaded CST as directed by task plan.
5. ☒ Calibrate GC. Calibrate for nitrogen, oxygen, N_2O , hydrogen, and carbon dioxide.
6. ☒ Prepare sufficient 90% formic acid and 50% nitric acid.
7. ☒ Prepare sufficient antifoam solution or make sure sufficient solution is available.
8. ☒ Calculate batching and scaling for experiment based on DWPF parameters.
9. ☒ Calculate redox for experiment based on DWPF parameters.
10. ☒ Setup experimental rig per sketch below.
11. ☒ Complete leak checks and water runs.

Run # 3LC

Date: 6/15/99

PREPARATION FOR SRAT CYCLE

Note: Do not insulate kettle until acid addition is complete or cannot reach desired temperature.

1. ☒ Add **2270 g** of **Tank 42 Sludge** to kettle using 2-liter transfer bottle or beaker.
2. ☒ Turn on kettle agitator. **Setpoint = 200 rpm. Mark Sludge Level in Kettle as De-water Level for later de-watering and concentration.**
3. ☒ Add trim chemicals (from **Table VII**) directly to the kettle.
4. ☒ Transfer **340.8 g** of distilled water to the kettle (use to rinse all containers used for adding sludge, noble metals, mercury, etc.).
5. ☒ Calibrate pH probe with pH 4 and 10 buffer. Record measured pH of pH 7 buffer 7.123.
6. ☒ Install pH probe in kettle. Record initial pH of sludge 12.116.
7. ☒ 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.
8. ☒ Disconnect outlet flowmeter.
9. ☒ Set the air flow to kettle at **529.5 sccm**. Set the He flow to **2.66 sccm**.
10. ☒ Turn on cooling water to SRAT condenser. **Setpoint = 40°C**.
11. ☒ Turn on cooling water to Chilled (FAVC) condenser. **Setpoint = 10°C**.
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 # 3LC

Date: 6/16/99

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 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 46.68 ml of 50-wt% nitric acid at 0.760 ml/min (reference Table X) to the kettle. Should take about 1 hour.
5. ✓ Now add 93.18 ml of 90-wt% formic acid at 0.837 ml/min (reference Table X) to the kettle. Should take about 2 hours. (94.53 ml actually added)
6. ✓ Add 2.3 g 1:10 antifoam solution and 2.3 g water directly to the kettle (100 ppm antifoam).
7. ✓ Add first addition of 700 g of 10-wt% size-reduced CST solution (half of prepared bottle contents) from Table IX. (455.5 g 9.1-wt% solution actually added with 50 g wash water)
8. ✓ 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 3.78 g/min boil-up rate and bring the kettle contents to boiling.
9. ✓ Dewater until remove 1120 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 5 hours. (955.0 g water actually removed)
10. ✓ Add second addition of 700 g of 10-wt% size-reduced CST solution (half of prepared bottle contents) from Table IX. Use 100 g of de-ionized water to wash bottle contents. (1085.8 g 9.1-wt% solution actually added with 50 g wash water)
11. ✓ Dewater until remove 730 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 3.2 hours. (1037 g water actually removed)

Run # 3LC

Date: 6/16/99

SRAT CYCLE (continued)

12. ☒ Reflux the slurry for a total of 8 hours (including the dewater times in steps 10 and 13) at 3.78 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. (*Refluxed for over 12 hours*)
13. ☒ Pull a 125 ml sample from the kettle, record the weight on the run sheet. Label as **Loaded CST SRAT 3LC** and send to lab for analyses.
14. ☒ Remove Sampler and insert rubber stopper in port.

Run # 3LC

Date: 6/16/99

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 343.25 g frit 202 to the kettle (1st frit addition - Table IX). Actual amount of frit to add: 342.47 g¹⁰
3. ☒ Add about 6.99 g of 90-wt% formic acid to the kettle (1st formic addition - Table IX). Actual amount of formic to add: 6.98 g⁶
4. ☒ Add about 630.48 g of water to the kettle (1st water addition - Table IX). Actual amount of water to add: 629.04 g⁶
5. ☒ Bring kettle contents to boiling. Record the run data every 20 minutes on the data sheet.
6. ☒ Remove about 808 g of water (about 3.6 hours). Actual amount of water to remove: 811.6 g⁶
7. ☒ When dewatering is complete, turn off the heat to cool the kettle to sub-boiling.
8. ☒ Add about 343.25 g frit 202 to the kettle (2nd frit addition - Table IX). Actual amount of frit to add: 342.47 g⁶
9. ☒ Add about 6.99 g of 90-wt% formic acid to the kettle (2nd formic addition - Table IX). Actual amount of formic to add: 6.98 g⁶
10. ☒ Add about 630.48 g of water to the kettle (2nd water addition - Table IX). Actual amount of water to add: 629.04 g⁶
11. ☒ Bring kettle contents to boiling. Record the run data every 20 minutes on the data sheet.
12. ☒ Remove about 808 g of water (about 3.6 hours). Actual amount of water to remove: 811.6 g⁶
(actually removed 812.4 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 Loaded CST SME 3LC 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 7.122.
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).
21. ☒ Turn off all instruments.

¹⁰ Actual amounts calculated after account for SRAT samples pulled and other losses.

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Revision 0

August 26, 1999

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