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Impact of Salt Waste Processing Facility Streams on the Nitric-Glycolic Flowsheet in the Chemical Processing Cell

C.J. Martino

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EXECUTIVE SUMMARY

An evaluation of the previous Chemical Processing Cell (CPC) testing was performed to determine whether the planned concurrent operation, or "coupled" operations, of the Defense Waste Processing Facility (DWPF) with the Salt Waste Processing Facility (SWPF) has been adequately covered. Tests with the nitric-glycolic acid flowsheet, which were both coupled and uncoupled with salt waste streams, included several tests that required extended boiling times. This report provides the evaluation of previous testing and the testing recommendation requested by Savannah River Remediation. The focus of the evaluation was impact on flammability in CPC vessels (i.e., hydrogen generation rate, SWPF solvent components, antifoam degradation products) and processing impacts (i.e., acid window, melter feed target, rheological properties, antifoam requirements, and chemical composition).

Previous testing did not cover the expected Precipitate Reactor Feed Tank (PRFT) volumes or composition, so minor risks remain regarding the impact of material transferred from SWPF to the PRFT on CPC processing (foaming) and product rheology. This impact is independent of the CPC flowsheet used. The risk of not investigating representative PRFT compositions and volumes related to Sludge Receipt and Adjustment Tank (SRAT) chemistry is relatively minor because the monosodium titanate (MST) is largely inert within the CPC operations and the PRFT is processed prior to SRAT acid addition. The PRFT adds soluble components that change the required acid addition, but the impact to processing with the nitric-glycolic flowsheet would be minor. The low hydrogen generation of the nitric-glycolic flowsheet is robust with respect to slurry salt content and excess acid addition.

Previous testing covered the expected batch volumes of Strip Effluent Feed Tank (SEFT) material. The successful testing of the nitric-glycolic flowsheet simulating 18,000 gallons of SEFT material exceeded the expected maximum batch volume of 15,600 gallons of SEFT material. Additionally, portions of the testing with high batch volumes of SEFT also simulated DWPF boiling times through periods of boiling and simmering. The risk of increasing boiling time is also lessened by use of the nitric-glycolic acid flowsheet because glycolate does not decompose to the same degree as formate during later stages of boiling. Although nitric-glycolic flowsheet testing used the Next Generation Solvent (NGS) feeds in coupled testing, the chemistry impacts of testing with NGS feeds should bound those of the baseline solvent system.

If SWPF integration takes place during Sludge Batch (SB) 9 and uses the nitric-glycolic flowsheet, no additional testing is necessary. The gaps in previous testing pertaining to PRFT volumes and composition, SEFT composition, and overall boiling time are relatively minor. The flowsheet testing already performed for SB9 is adequate technical process definition for integration with SWPF.

Coupled testing should continue to be performed as part of future nitric-glycolic flowsheet simulant testing. Coupled testing should use the PRFT volume and composition and the SEFT volume, composition and boiling time that are expected during SWPF operation. Test objectives should focus on pH trends, glycolate decomposition, foaming concerns, evidence of reactions late in processing, and product rheology. The expectation based on previous testing is that pH trends will be stable and there will be little evidence of glycolate decomposition and reactions late in the cycle.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ABBREVIATIONS

AR	Alpha Removal
ARP	Actinide Removal Process
CPC	Chemical Processing Cell
DWPF	Defense Waste Processing Facility
HGR	Hydrogen Generation Rate
KMA	Koopman Minimum Acid
LW	Liquid Waste
MAR	Measurement Acceptability Region
MCU	Modular Caustic-Side Solvent Extraction Unit
MST	Monosodium Titanate
NGS	Next Generation Solvent
PRFT	Precipitate Reactor Feed Tank
SB	Sludge Batch
SE	Strip Effluent
SEFT	Strip Effluent Feed Tank
SME	Slurry Mix Evaporator
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SWPF	Salt Waste Processing Facility
TAR	Technical Assistance Request
TiDG	N,N′,N″-tris (3,7-dimethyloctyl) guanidine
TOA	Tri-n-octylamine
WAC	Waste Acceptance Criteria

1.0 Introduction

Savannah River Remediation (SRR) requested that the Savannah River National Laboratory (SRNL) evaluate the impact of the boiling time increase for the Defense Waste Processing Facility (DWPF) Sludge Receipt and Adjustment Tank (SRAT) from running the Salt Waste Processing Facility (SWPF) design basis volumes of Alpha Removal (AR)/Precipitate Reactor Feed Tank (PRFT) and Strip Effluent (SE)/Strip Effluent Feed Tank (SEFT) streams.[1] The evaluation focuses on the BOBCalixC6[a] solvent system in SWPF and the nitric-glycolic flowsheet in DWPF. The evaluation includes impacts on chemistry and material properties (i.e., slurry physical properties) within DWPF. This report satisfies the requested deliverable of a report that either outlines the impact of the SWPF design basis volumes of AR and SE on the SRAT based on previous testing or a report that defines the testing needed to determine the impact.

For simplification in this evaluation, the AR stream containing Monosodium Titanate (MST)/sludge solids will be referred to as PRFT material regardless of its origin (either SWPF or the Actinide Removal Process (ARP)). Likewise, the SE stream will be referred to as SEFT material regardless of its origin (either SWPF or the Modular Caustic-side Solvent Extraction Unit (MCU)). PRFT and SEFT are the names generally used to identify the streams within DWPF.

Testing has been performed for the nitric-formic flowsheet using the SEFT from either the baseline (i.e., BOBCalixC6), the Next Generation Solvent (NGS) (i.e., MaxCalix[b]), and the blended solvent systems.[2]

Since Sludge Batch (SB) 3,[3] SRNL has performed testing specific to ARP as part of nitric-formic flowsheet testing with simulants. Simulated ARP streams typically added less monosodium titanate[c] (MST) to the slurry than the SWPF version of AR. The inclusion of these simulants did not adversely impact hydrogen generation. The risk from increased caustic boiling in the SRAT is potential carryover events in DWPF. DWPF has experienced these carryover events in the past while caustic boiling.

DWPF is preparing to make a flowsheet change to replace the use of formic acid in the Chemical Processing Cell (CPC) with glycolic acid. The switch to the nitric-glycolic acid flowsheet will reduce hydrogen generation, improve process rheology, and is expected to lead to more stable pH and reductant concentration over long boiling times in the SRAT.[4] Several sets of simulant CPC tests were run for the nitric-glycolic flowsheet that included NGS solvent system SE and ARP levels of AR material. An evaluation was performed on the integration of SWPF with DWPF running the nitric-glycolic flowsheet and concluded that more testing would be required for a complete understanding of the two facilities integration.[5] The rationale behind this conclusion is that the testing completed to date has not processed design basis volumes of PRFT and SEFT material needed to keep SWPF running continuously. Prototypic amounts of SWPF steams would lead to longer boiling times and increase the amount of antifoam added to vessels.

SRR issued a Technical Assistance Request (TAR) directing SRNL to evaluate running the DWPF SRAT under the nitric-glycolic flowsheet at the design basis volumes of SE and MST/sludge solids that will be required by DWPF to accommodate SWPF design basis volumes.[1] The TAR states that none of the nitric-glycolic testing completed to date has evaluated the SWPF (using BOBCalixC6) design basis volumes of PRFT and SEFT that will require processing by DWPF to keep SWPF running continuously. The TAR also states that the prototypic amount of material from SWPF will increase boiling times for the SRAT and has not yet been evaluated. These statements as well as the recommended path forward are evaluated in this report.

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[a] calix[4]arene-bis-(tertoctylbenzo-crown-6)
[b] 1,3-alt-25,27-bis(3,7-dimethyloctyl-1-oxy)calix[4]arenebenzocrown-6
[c] $NaHTi_2O_5$

2.0 Methodology

The TAR requests evaluation of the impact of "increased boiling time" from the SWPF volumes of PRFT and SEFT. This evaluation also considers other impacts of processing SWPF streams, primarily focusing on impacts to the CPC. Per the request, this analysis was limited to the nitric-glycolic flowsheet. The following list details which specific items are considered in this evaluation:

- Impact on flammability in CPC vessels
  - Hydrogen generation rate (HGR)
  - SWPF solvent, including Isopar® L and other solvent system components
  - Antifoam degradation product (ADP) production
- Processing impacts due to PRFT and SEFT additions
  - Acid stoichiometry window
  - Melter feed target balancing (the ability to attain a target concentration in the melter feed, which is important to achieving the target reduction/oxidation balance in the glass).
  - Rheological properties of slurry within the CPC vessels
  - Antifoam addition requirements in the CPC
  - Chemical composition of CPC materials

The following list details which specific items are outside of the scope of this evaluation and either have been or will be evaluated elsewhere:

- Impact on flammability in the melter
  - The impact of either solvent system on melter flammability was addressed elsewhere and is not included in this report.[6]
- Impact to glass and the Product Composition Control System model
  - Glass model revisions required to accommodate higher TiO_2 loading are being managed separately from this evaluation.[7]
  - Frit acceptability for both coupled and sludge-only processing and all other glass related tasks are managed separately from this evaluation.

3.0 Inputs and Assumptions

3.1 Inputs from TAR

Based on the Liquid Waste (LW) System Plan Revision 20A, the following inputs were provided by the TAR as inputs to this task:[1]

SWPF is to become operational December 3, 2018.

The SWPF nominal capacity is:

- First year of operation: 4,625,000 gal of salt solution
- Second twelve months: 7,200,000 gal of salt solution at nominal processing rate
- When SWPF exceeds 7,200,000 gal/yr of salt solution consumption, SEFT will be limited to 576,000 gal/yr

Nominally SWPF will produce:

- 0.08 gal of SEFT for DWPF for each gallon of salt solution processed (not to exceed 576,000 gal/yr)
- 0.02 gal of PRFT for DWPF for each gallon of salt solution processed

An SWPF outage is assumed after SWPF begins operation to perform NGS implementation to increase capacity to 9,000,000 gal/yr. NGS should not be considered for this evaluation.[1]

For this evaluation, one MST strike within SWPF is assumed as the baseline, but the current request is to evaluate the impact of multiple strikes on SRAT boiling time. SWPF will use MST and currently does not plan to use modified MST.

3.2 Other Inputs and Assumptions

The following inputs are copied or calculated from the SWPF material balance summary:[8,9]

- SWPF strip feed is 1 mM nitric acid, leading to SEFT composition of 10 mM Cs and 11 mM nitrate;
- PRFT stream has 28.3 g/L of MST for one strike, 39.2 g/L of MST for two strikes; and
- PRFT stream limit is 5 wt% insoluble solids.

The following additional assumptions were made for this evaluation without specific guidance:

- The DWPF availability is set to 70%. A low availability is used for conservatism in this analysis because decreasing availability increases volume of PRFT and SEFT per SRAT batch. Actual DWPF availability is expected to be 80%.
- Processing for a SRAT cycle or a SME cycle will be one per week.
- Thus, there are nominally 37 SRAT batches and 37 SME batches per year.
- The volume of PRFT and SEFT will be equally split amongst the batches processed.
- Multiple MST strikes will not impact boiling time as it is assumed not to impact the volume of PRFT processed.

Unless stated otherwise, the basis of scaling to a CPC batch is based on 6,000 gallons of SRAT receipt (sludge) and does not include the tank heel.

This evaluation is related to CPC testing. Other aspects of processing SWPF materials, such as whether such volumes would challenge batch or canister limits, were not considered as they fall outside of the realm of testing.

3.3 Calculated PRFT and SEFT Batch Volumes

Based on the inputs and assumptions above, 37 DWPF CPC batches per year and one SWPF MST strike would require that each DWPF CPC batch process 3,900 gallons of PRFT and 15,600 gallons of SEFT material.

4.0 Results and Discussion

4.1 Testing Background

Two types of CPC simulant testing were performed, sludge-only and coupled. Coupled testing includes various combinations of PRFT and SEFT material. Typically, coupled testing is only performed for one simulant flowsheet run and not performed with actual waste testing.

Table 4-1 contains details of the testing that is most pertinent to this evaluation. The pertinent testing includes coupled nitric-formic flowsheet testing with large SEFT volume additions and coupled and sludge only nitric-glycolic flowsheet testing with and without long boiling times.

Table 4-1. Key Testing Applicable to Evaluation

Test	PRFT Addition	SEFT Addition	Boiling Time
Nitric-Formic SEFT to SME Testing[2]	1,050 gal of ARP based on 0.2 g/L MST strike	8,000 gal to SRAT and 30,000 gal to SME, various solvent systems (baseline, NGS, and blend)	~20 hr in SRAT, ~80 hr total
Nitric-Glycolic Heel Study[10]	1,800 gal of ARP based on 0.2 g/L MST strike	8,920 gal to SRAT, 0.01 M boric acid with 87 mg/kg NGS solvent	~20 hr in SRAT, ~40 hr total
Nitric-Glycolic Scaled Demonstration[11]	none	None	~44 hr in SRAT, 69 to 75 hr total
Nitric-Glycolic Bounding Hydrogen Study[12]	none	18,000 gal to SRAT, 0.0125 M boric acid	~36 hr in SRAT, ~62 hr total, + simmer 0 to 32 hr
Nitric-Glycolic SB9 Testing[13] (only one test was coupled)	1,000 gal of ARP based on no MST strike	12,000 gal to SRAT, 0.015 M boric acid adjusted with NaOH to pH=8, 87 mg/kg of NGS solvent	~28 hr in SRAT, ~38 hr total, extended sludge-only run ~80 hr total

The first test listed is the evaluation performed for the nitric-formic flowsheet on the inclusion of SEFT material in the SME.[2] Processing difficulties were encountered with heat transfer rod fouling specific to the experimental system that ultimately led to increased hydrogen generation. Lab scale testing simulated a total of 38,000 gallons of SEFT material processed during these cycles split between the SRAT and the SME, for a respectable 80 hour boiling time. During this testing with design-basis boiling at a condensate production rate of 5,000 lb/hr, it was seen that formic acid decomposition was significant in the SME and would need to be accounted for during SRAT acid addition. DWPF operates at less than design-basis boiling (with an assumed condensate production rate of 2,500 lb/hr), which would increase the boiling time by a factor of two for the same SEFT addition volume. The results of the nitric-formic SEFT to SME testing support the need for additional testing if SWPF volumes are to be processed in DWPF using the nitric-formic flowsheet.

Tests with the new nitric-glycolic acid flowsheet included several tests that had extended boiling times, with and without coupled operation. Several coupled or long processing time tests have been performed with the nitric-glycolic flowsheet since 2012. The nitric-glycolic heel study, while coupled and representative of ARP and MCU processing, did not include large volumes of PRFT or SEFT and had a relatively short total processing time.[10] The scaled demonstration, which included similar tests at three scales up to ~1/200th scale, was not coupled.[11] However, the scaled demonstration tests included long boiling times, approximately three days combined between the SRAT and the SME. This roughly approximates the post-acid-addition boiling time required to process SWPF quantities of SEFT in the SRAT. No impacts were attributed to long boiling times in these studies and the pH remained stable during the later stages of processing.

The nitric-glycolic flowsheet testing performed for maximum HGR had intentionally large post-acid-addition boiling times.[12] This was accomplished, in part, by processing a relatively large 18,000 gallon scaled volume of SEFT material in the SRAT, which exceeds the per batch volume of SEFT material expected when SWPF is processing. Each of those tests had a total of 62 hours of boiling time plus an additional 0 to 32 hours of simmering at 100 °C. Of the testing performed, this test comes closest to boiling and standby times realistically encountered in DWPF. However, no PRFT was added in this testing. No impacts were attributed to long boiling and simmering time and the pH remained stable during the later stages of processing. This testing showed that even at DWPF representative boiling times, there are no significant chemistry impacts to the nitric-glycolic flowsheet from large SEFT additions.

One coupled test was performed for SB9 testing with the nitric-glycolic flowsheet.[13] Additionally, one extended sludge-only run was performed with lower boiling rates (2,500 lb/hr). The coupled test used a significantly lower volume of PRFT and a PRFT recipe that did not contain MST solids. An amount of SEFT was used that approached the levels representative of SWPF processing. The pH was stable late in the process for both the coupled and the extended runs, and no adverse impacts of long boiling time were noted.

4.2 Impacts of PRFT Material

There are differences between the PRFT contents to be received during SWPF operation and the PRFT material used in testing, which was based on ARP operation. Table 4-2 contains a comparison of the historic PRFT contents from ARP processing and the expected PRFT contents from SWPF processing. The two main differences in the PRFT sent from the two processes are the volume included and the amount of MST contained in the slurry. There may ultimately be differences in sludge content of the two streams, but the sludge concentration is unknown and strongly dependent on the Tank Farm feed method to SWPF.

Most of the testing has included less volume of PRFT and used a PRFT simulant that had less MST than the expected SWPF PRFT stream. This introduces a risk that is expected to be negligible. The previous nitric-glycolic flowsheet tests that included MST did not show the MST to impact the chemistry of the SRAT and SME reactions to an observable extent even though approximately 150 mg/L of titanium (corresponding to approximately 0.25% of the MST) was soluble in the SRAT product.[10] Also, the function of MST as an adsorbent of strontium and actinides is no longer necessary once the PRFT material has been transferred to the SRAT. For either flowsheet, MST has been thought to remain largely chemically inert during the CPC processing and not promote catalytic hydrogen generation. However, there are several other risks associated with introducing greater volumes of PRFT and PRFT composition having more MST.

Table 4-2. Comparison of PRFT Feeds from ARP and SWPF

PRFT from ARP	PRFT from SWPF
MST: Additions evolved from 0.4 g/L to 0.2 g/L to 0 g/L of MST used. 0.2 g/L has historically led to less than 8 g/L of MST in PRFT.[14,15,16]	MST: Baseline additions of 0.4 g/L, one strike or two strikes. An additional polishing strike possible 1 strike leads to 28.3 g/L of MST in PRFT stream. 2 strikes leads to 39.2 g/L of MST in PRFT stream. Limit is 5 wt% insoluble solids (~63 g/L).
Sludge solids: Based on sampling, very little sludge solids contained in PRFT slurry, estimated as less than 200 mg/L.[17]	Sludge solids: This concentration is largely unknown and dependent on the Tank Farm salt processing. Allowable level of sludge is up to 1,200 mg/L, but may not differ significantly from the ARP levels.
Volume: DWPF has received a maximum of 50,000 gal/yr of PRFT (in 2013) but now receives much less due to processing without MST (see Appendix).	Volume: 144,000 gal/yr of PRFT based on 7,200,000 gal/yr of salt solution processed. Up to 188,000 gal/yr at design throughput.
Soluble solids: Sodium content often ~1M, sodium is the primary calcined solids component from ARP stream. Sodium nitrate is the major soluble solids component. Oxalate in stream due to filter cleaning.	Soluble solids: Considerably lower soluble solids content. Sodium is limited to 0.7 M including the sodium in MST, with soluble sodium closer to 0.5 M. Sodium nitrate is the major soluble solids component (with smaller quantities of sodium nitrate, sodium hydroxide, and other sodium salts).
Cleaning: Oxalic acid used for washing, increases oxalate sent to DWPF in PRFT stream.	Cleaning: Nitric acid used for filter cleaning, with negligible oxalate content in PRFT stream.

First, due to the increased caustic boiling time and the reduced effectiveness of IIT Antifoam 747 during caustic boiling, there is a greater risk of foaming prior to acid addition. The risk of foaming during caustic boiling in the SRAT is potential carryover events and the potential need for additional antifoam addition. This risk has the same impact on the nitric-glycolic flowsheet as it does for the nitric-formic flowsheet.

Second, the PRFT adds soluble components that change the acid addition requirement. While the soluble PRFT components are the same components typical of the sludge batch, the quantities and ratios of soluble components will be impacted by large PRFT additions. From a chemistry standpoint, processing with more PRFT is roughly equivalent to processing with a less-washed sludge feed. Thus, the amount of acid addition and the balance between nitric and glycolic acid are impacted by the volume and soluble component composition of the PRFT stream. Thus, there will be some impacts to the optimal acid addition, but previous testing has demonstrated that this factor is not expected to impact hydrogen generation, antifoam degradation, and other properties considered when processing with the nitric-glycolic flowsheet. The low hydrogen generation from the nitric-glycolic flowsheet is relatively robust and would not be as dependent on the potential increase in soluble components in the SRAT. The differences noted between the previous nitric-glycolic flowsheet tests with and without PRFT material appeared to be due to processing the salt components in the PRFT, such as increased acid demand and nitrous oxide production.[13,10] Because the magnitudes of the observed impacts were minor, the increase in PRFT volume and MST content of PRFT are not expected to significantly impact the chemistry of the SRAT and SME reactions. Salts from the additional volume of PRFT material are expected to impact the quantity of other offgas components within the nominal range seen during flowsheet testing.

Third, there is a slight risk for an impact to the rheological properties of the SRAT and SME products. When acid is added optimally, yield stresses of the SRAT and SME products are expected to be relatively low with the nitric-glycolic flowsheet. Thus, the risk is low that a rheological property change due to increased PRFT volumes and MST concentration would have a negative impact on processing. There is a possibility that the inclusion of SWPF representative PRFT material may have positive impacts on the SME product rheology.

Fourth, the additional sodium and titanium to be processed into the glass may require greater batch-to-batch consistency in processing or processing using multiple frits. The glass chemistry is not the focus of this analysis and is typically addressed during the sludge batch qualification efforts.

For the nitric-glycolic flowsheet, the gap between the testing performed and the expected PRFT after SWPF pose little impact. Due to the relative robustness of the nitric-glycolic flowsheet toward low hydrogen production and pH stability, there is little risk toward hydrogen production and product end-point chemistry from increasing PRFT. Processability impacts from additional foaming or unexpected rheology are handled by processing adjustments at DWPF. Thus, additional nitric-glycolic flowsheet testing is not required for SB9 prior to SWPF integration. For future sludge batches, however, the risks should be investigated by including coupled runs during simulant testing that have SWPF representative quantities and composition of PRFT material.

4.3 Impacts of SEFT Material

Table 4-3 is a comparison of the SEFT material coming from MCU with that expected initially from SWPF. Apart from the different solvent system used, the major difference is the volume of SEFT material processed. A review of the previous testing with the nitric-glycolic flowsheet shows that previous tests covered the expected batch volumes of SEFT for SWPF integration. Testing typically included SEFT containing the maximum solvent carryover, which is limited by the WAC and is not expected to increase with SWPF integration.

The coupled testing of SEFT material for the nitric-glycolic flowsheet has used the NGS. Based on previous evaluations, it is not expected that any results of the nitric-glycolic CPC tests would have greatly differed if the baseline solvent system would have been used rather than NGS.[18] The impacts of the NGS boric acid SEFT additions would be similar and likely bound the potential chemistry impacts of the baseline nitric acid SEFT additions. The baseline nitric acid SEFT material tends to be more similar in pH to the SRAT during processing than the NGS boric acid SEFT material. In addition to the Isopar® L solvent, both solvent systems contain an extractant, a modifier, and a suppressor. The modifier is identical between the two solvent systems and the extractants are chemically similar. The suppressor, however, differs between the two solvent systems, with baseline solvent using tri-n-octylamine (TOA) and NGS using N,N′,N″-tris (3,7-dimethyloctyl) guanidine (TiDG). The SEFT material from either solvent system will likely contain small amounts of the suppressor component and breakdown products from the suppressor. However, these components are expected to have a similar and minimal impact on processing due to their low concentration in the slurry. Thus, nitric-glycolic CPC flowsheet test results showing little or no impact when using the NGS SEFT would be expected to extend to processing with the baseline SEFT.

Table 4-3. Comparison of SEFT Feeds from MCU and SWPF

SEFT from MCU	SEFT from SWPF
Currently uses NGS system (MaxCalix), nominally 10 mM boric acid plus additional $CsNO_3$. Previously used the baseline system (BOBCalixC6), nominally 1 mM nitric acid with $CsNO_3$. Coupled CPC testing with the baseline system typically used 33 mM nitric acid. Boric acid has minor impact on calcined solids. SEFT stream may contain some of the TOA suppressor or TOA breakdown products. SEFT material will contain Isopar® L up to 87 mg/L and smaller amounts of extractant, and modifier.	Will startup using the baseline system (BOBCalixC6), nominally 1 mM nitric acid and 10 mM $CsNO_3$. Nitric acid does not impact the calcined solids. SEFT stream may contain TiDG suppressor or TiDG breakdown products. SEFT material will contain Isopar® L up to 87 mg/L and smaller amounts of extractant, and modifier.
Volume has been 107,000 gal/yr or less (see Appendix).	Volume is a maximum 576,000 gal/yr.
Cesium levels limited by only processing the lower activity salt feeds.	Cesium levels will contribute to alkaline content of glass.

This analysis leads to a similar conclusion as the previous assessment that future testing should be prototypic of the final flowsheet for SWPF.[5] However, this analysis disagrees with the conclusion of the prior report that testing with the nitric-glycolic flowsheet did not include design basis volume of SEFT material.[5] In line with the stated assumptions, this evaluation has demonstrated that the volume of 18,000 gallons of SEFT processed during a portion of the nitric-glycolic testing exceeded the expected 15,600 gallons of SEFT per CPC batch expected during SWPF operation. Thus, no additional testing is required for addition of SEFT from SWPF into the SRAT for processing SB9 with the nitric-glycolic flowsheet.

4.4 SWPF Stream Volume versus Boiling Time

The specific gap identified in the TAR is related to an extended boiling time required to process SWPF. However, DWPF is still expected to maintain a one week SRAT cycle after SWPF integration. This configuration will require a larger volume of PRFT and SEFT material to be processed during the week. Thus, a larger portion of the overall SRAT cycle might now be needed to achieve the targeted volume reduction from boiling. The amount of PRFT that can be processed per batch will be determined by the range analyzed in the Measurement Acceptability Region (MAR) analysis for glass properties. The maximum amount of SEFT per batch will be determined by the limits on cesium-137 and the range analyzed in the MAR analysis. As long as processing does not exceed these limits for PRFT and SEFT, it may be possible for DWPF to extend the cycle times to longer than one week thereby reducing the impact of time required for once-per-batch activities, such as SRAT product analysis. If DWPF processes in this manner, even larger volumes and longer boiling times would be encountered than those assumed in this analysis.

The boiling time could be considered separately from the volume of PRFT and SEFT material processed per batch. Caustic boiling and PRFT boiling occur prior to acid addition and thus have little impact on the post-acid addition chemical reactions. However, processing the PRFT will take a portion of the overall SRAT cycle time.

Based on a relatively low 2,000 lb/hr of condensate production (at the low end of what DWPF would process), processing 15,600 gallons of SEFT would take about 2.7 days. Thus, the acid addition and post-acid boiling for the SRAT can easily take less than 4 days. Mercury stripping also impacts SRAT boiling time. Processing batches with very high mercury could add additional constraints that increase the SRAT boiling time.

Routine CPC flowsheet testing for either flowsheet has not been designed to match the precise boiling times and idle times involved with the current DWPF processing. Most CPC flowsheet testing seeks to maximize hydrogen generation by processing at high boiling rates. Testing higher boiling rates leads to shorter overall boiling times than used in DWPF. With the nitric-formic flowsheet, testing shorter boiling times likely leads to overall lesser formic acid decomposition evident in the SRNL testing than would be encountered in the facility. Testing without matching the precise boiling time has been acceptable in simulant flowsheet testing with the nitric-formic flowsheet. The risk of not performing tests at DWPF-representative boiling and idling times is even lower for the nitric-glycolic acid flowsheet. Unlike the nitric-formic flowsheet, the nitric-glycolic flowsheet has lower conversion of the reductants to carbon dioxide with extended processing.[19] As seen from the nitric-glycolic flowsheet testing performed for maximum hydrogen generation, a portion of the testing with high batch volumes of SEFT (18,000 gal) have also simulated DWPF boiling times through periods of boiling and simmering (up to 94 hr in total). This testing may approximate the expected boiling time with SWPF representative SEFT volumes.

4.5 Considerations Outside of Evaluation Scope

Outside of the scope of this evaluation, there has been no evaluation of how SWPF quantities and compositions of PRFT would impact the glass quality in the current sludge batch (SB9). See the recommendation in Section 5.0 for additional MAR analyses and frit selection/evaluation.

The TAR requested that this evaluation to consider the baseline solvent system and not the NGS solvent system. The coupled testing that has been completed for the nitric-glycolic flowsheet has been with the NGS solvent system. The evaluation for NGS and the baseline is the same for all considerations except for the glass MAR (due to the additional boron in NGS).

The SB9 flowsheet testing and qualification have been performed for both the nitric-formic flowsheet and the nitric-glycolic flowsheet. This evaluation is for the nitric-glycolic flowsheet in DWPF. If SWPF were to be integrated with DWPF under the nitric-formic flowsheet with the volumes and concentrations of PRFT and SEFT assumed in this evaluation, further evaluation of testing would be required.

5.0 Testing Recommendations

If SWPF integration takes place during SB9 and uses the nitric-glycolic flowsheet, no additional testing is necessary. The gaps in previous testing pertaining to PRFT volumes and composition, SEFT composition, and overall boiling time are relatively minor. The low hydrogen generation of the nitric-glycolic flowsheet is robust with respect to slurry salt content and excess acid addition. Additionally, the pH, other chemistry, and material properties of the products have not been noted to change after extended periods of boiling and simmering with the nitric-glycolic flowsheet. Thus, the flowsheet testing already performed for SB9 is adequate to allow for integration with SWPF.

With the exception of the testing to support sending SEFT material to the SME,[2] previous coupled testing with the nitric-formic flowsheet was based on processing ARP and MCU quantities and compositions of PRFT and SEFT material. If SWPF quantities and compositions of PRFT and SEFT material are to be processed during SB9 using the nitric-formic flowsheet, additional simulant testing should be considered to reduce the risk of exceeding the HGR if planned operation involves acid addition outside of the previously tested regime.

Coupled testing should continue as part of future flowsheet simulant testing. Coupled testing that simulate start of SWPF radioactive operations should use the PRFT volume and composition and the SEFT volume, composition and boiling time that are expected to be encountered during those operations. The recommended testing in Table 5-1 corresponds to two tests that are designed to determine the impact of larger PRFT volumes and extended boiling times. The two tests involve high and low excess acid at maximum PRFT and SEFT volumes at a relatively low boiling rate. Objectives of the test should focus on pH, glycolate decomposition, unexpected reactions late in the SRAT processing, and impacts of PRFT on rheological properties and foaming. The initial recommendation of PRFT and SEFT volumes and compositions Table 5-1 should be revised for future flowsheet testing after actual historical SWPF information becomes available.

Consideration should be given toward testing coupled operation in the shielded cells as part of the qualification. While not strictly required by the DWPF WAC, including PRFT and SEFT material in the qualification of a blend could provide valuable processability information if DWPF employs coupled-only operation.

This report does not include an evaluation of how SWPF quantities and compositions of PRFT and SEFT would impact the glass quality. Regardless of which flowsheet is used, additional MAR analyses and frit selection/evaluation will be necessary if the SWPF is to start up during the current sludge batch (SB9). This analysis would also be necessary for future sludge batches. Since coupled operations will be necessary, high and low bounds on the SEFT and PRFT quantities and compositions should be considered during MAR analyses and frit evaluation/selection. The previous gap analysis identified that even under the condition of consistent feeds from SWPF into DWPF, it is possible that the frits available for some future sludge batches may be phase separated frits.[20]

Table 5-1. Recommendations for Future Sludge Batch Testing

Parameter	Recommendation
Flowsheet	Nitric-Glycolic Acid
Acid Stoichiometry	80 to 110% Koopman Minimum Acid (KMA) based on rheology and gas production considerations.[13] If initial testing is performed for other flowsheet testing objectives, a single acid stoichiometry or revised maximum and minimum acid stoichiometries can be used for the extended boiling time test.
Percent Reducing Acid	Adequate to reach target REDOX based on additional PRFT and SEFT components added and glycolate reaction.
PRFT	Use SWPF volume and chemistry. 3,900 gallons of PRFT per 6,000 gallon SRAT feed, prior to SRAT acid addition. PRFT should contain at least 28.3 g/L of MST (if anticipating single strike), up to 39.2 g/L of MST (if anticipating double strike). PRFT need not contain sludge solids, although part of SWPF design. No more than 0.5 M soluble sodium with nitrite as the primary anion, plus nitrate, hydroxide, and carbonate. Oxalate should not be a major component of the stream.
SEFT	Use SWPF volume and chemistry. 15,600 gal of SEFT per 6,000 gal SRAT feed, after initial SRAT dewater. SEFT should contain dilute nitric acid (1 mM) based on the BOBCalixC6 solvent extraction system plus 10 mM of non-radioactive $CsNO_3$. Entrained Isopar® L or entrained baseline solvent system should be included in testing.
Boiling Time	For a portion of coupled testing, boiling time post-acid-addition should be extended by using the typical DWPF boiling rate rather than the design basis boiling rate.
SME	SME will nominally have a shorter boiling time than the SRAT. Testing should include multiple canister decontamination water additions and standard frit additions.

6.0 Conclusions

An evaluation of the previous CPC testing was performed to determine whether the planned concurrent operation, or "coupled" operations, of DWPF with SWPF has been adequately covered. Tests with the nitric-glycolic acid flowsheet, which were both coupled and uncoupled with salt waste streams, included several tests that required extended boiling times. This report provides the evaluation of previous testing and the testing recommendation requested by Savannah River Remediation. The focus of the evaluation was impact on flammability in CPC vessels (i.e., HGR, SWPF solvent components, ADPs) and processing impacts (i.e., acid window, melter feed target, rheological properties, antifoam requirements, and chemical composition).

Previous testing did not cover the expected PRFT volumes or composition, so minor risks remain regarding the impact of material transferred from SWPF to the PRFT on CPC processing (foaming) and product rheology. This impact is independent of the CPC flowsheet used. The risk of not investigating representative PRFT compositions and volumes related to SRAT chemistry is relatively minor because the MST is largely inert within the CPC operations and the PRFT is processed prior to SRAT acid addition. The PRFT adds soluble components that change the required acid addition, but the impact to processing with the nitric-glycolic flowsheet would be minor. The low hydrogen generation of the nitric-glycolic flowsheet is robust with respect to slurry salt content and excess acid addition.

Previous testing covered the expected batch volumes of SEFT material. The successful testing of the nitric-glycolic flowsheet simulating 18,000 gallons of SEFT material exceeded the expected maximum batch volume of 15,600 gallons of SEFT material. Additionally, portions of the testing with high batch volumes of SEFT also simulated DWPF boiling times through periods of boiling and simmering. The risk of increasing boiling time is also lessened by use of the nitric-glycolic acid flowsheet because glycolate does not decompose to the same degree as formate at later stages of boiling. Although nitric-glycolic flowsheet testing used the NGS feeds in coupled testing, the chemistry impacts of testing with NGS feeds should bound those of the baseline solvent system.

If SWPF integration takes place during SB9 and uses the nitric-glycolic flowsheet, no additional testing is necessary. The gaps in previous testing pertaining to PRFT volumes and composition, SEFT composition, and overall boiling time are relatively minor. The flowsheet testing already performed for SB9 is adequate technical process definition for integration with SWPF.

Coupled testing should continue to be performed as part of future nitric-glycolic flowsheet simulant testing. Coupled testing should use the PRFT volume and composition and the SEFT volume, composition and boiling time that are expected during SWPF operation. Test objectives should focus on pH trends, glycolate decomposition, foaming concerns, evidence of reactions late in processing, and product rheology. The expectation based on previous testing is that pH trends will be stable and there will be little evidence of glycolate decomposition and reactions late in the cycle.

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Appendix A. Letter on Historic PRFT and SEFT Volumes from ARP and MCU

Re: historic PRFT and SEFT volumes
Jeremiah Ledbetter to: Chris Martino 01/12/2017 12:22 PM
Cc: Victoria Kmiec, Austin Chandler, Lauryn Jamison

History: This message has been replied to.

A PRFT batch is about 4000-4500 gallons. We did 11 batches in 2013 and 5 batches in 2014. We had an outage for a long period of 2015 and only did 3 batches.
Now we are on the no-MST flowsheet and have to perform batch washing about once every 6 months and thus get PRFT about twice per year. We batch washed once in July and expect to do the next one in the next couple weeks.

2015 we added 46,501 gallons of SEFT
2016 we added 106,611 gallons of SEFT
I don't have exact data available for further back but can pull if you need. Just ball parking while looking at the year long trend, 2014 looks to be about 50k and 2013 is about 65k.

Jeremiah Ledbetter
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8-7985