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Implementation of the Nitric-Glycolic Acid Flowsheet at the Defense Waste Processing Facility – 23262

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ABSTRACT

The Defense Waste Processing Facility (DWPF) at the Savannah River Site (SRS) has transitioned to the Nitric-Glycolic Acid (NGA) flowsheet, replacing formic acid with glycolic acid as a chemical reductant. Under the previous Nitric-Formic Acid (NFA) flowsheet, catalytic hydrogen was generated during processing from the interaction of formic acid and trace quantities of noble metals, creating a continuous flammability control requirement for the Chemical Process Cell (CPC). In addition to virtually eliminating catalytic hydrogen generation, the NGA flowsheet reduces CPC cycle time, enhances mercury reduction, and supports the Salt Waste Processing Facility (SWPF) by allowing for receipt of higher volumes of waste. Furthermore, removal of 90% formic acid from the facility chemical inventory eliminated the potential for a chemical release resulting in a Site Area Emergency.

Implementation of the NGA flowsheet required a chemical transition period in the facility that ended when the Sludge Receipt and Adjustment Tank (SRAT) and Slurry Mix Evaporator (SME) vessel samples reported a low formate concentration. The NGA flowsheet has resulted in pH stabilization and favorable rheology in both the SRAT and SME. SRAT chemistry requirements, such as reduction of mercury compounds (to allow for removal via steam stripping) and nitrite destruction, have been demonstrated with a reduced acid stoichiometry. Increased weight percent (wt%) total dried solids in the SME were gradually achieved over several SME batches, and this material has been successfully fed to the melter.

The use of glycolic acid as a reductant in DWPF could result in carryover of glycolate into the recycle stream sent to the Concentration, Storage, and Transfer Facility (CSTF). Glycolate is a neutralization product of glycolic acid and may increase the thermolytic hydrogen generation rate at the CSTF in caustic conditions at elevated temperatures. To mitigate the impact of glycolate carryover in the DWPF recycle stream to the CSTF, sodium permanganate was used as an oxidant to decompose glycolate.

Implementation of the NGA flowsheet included reuse of existing tankage in DWPF to store and deliver sodium permanganate into the DWPF recycle stream prior to the recycle being sent to the CSTF. The glycolate destruction process has also been demonstrated to meet CSTF waste acceptance criteria.
Work is in progress to continue to quantify the process improvements gained by transitioning to the NGA flowsheet. This includes confirming the REDuction/OXidation (REDOX) equation, which controls the ratio of oxidizing and reducing acid (nitric acid and glycolic acid, respectively) added to a batch, via glass samples.

INTRODUCTION

SRS consists of several facilities to receive and store radioactive liquid waste, and to safely process and permanently dispose of waste to reduce risk to people and the environment. The two main types of radioactive waste are salt and sludge. Salt waste is processed through SWPF, producing monosodium titanate/sludge solids (MST/SS), strip effluent (SE), and decontaminated salt solution. The MST/SS stream contains concentrated sludge solids stream with strontium and other actinides adsorbed onto MST; SE is a cesium-laden, dilute acidic stream. Sludge, MST/SS, and SE are sent to DWPF for vitrification. During coupled operations with SWPF, sludge and MST/SS are transferred to the SRAT and chemically adjusted. An oxidizing acid is added to lower the pH of the caustic material and dissolve the solids to thin rheology. A reducing acid is added to reduce mercury (II) oxide to elemental mercury so that it may be steam stripped. Mercury removal is necessary because it can volatilize in the melter and form corrosive halides in the melter off-gas system. Control of the REDOX state of the material via additions of oxidizing and reducing acids allows for optimum melter operation. Following acid additions, SE is added to the SRAT and the material is concentrated. This material is sent to the SME where glass forming frit (from decontamination of canisters or process frit drops) is added. This mixture is concentrated through boiling. Condensate from both SRAT and SME processing is collected in the Slurry Mix Evaporator Condensate Tank (SMECT). Then, the frit-waste mixture is transferred to the Melter Feed Tank (MFT) and finally to the melter, which melts the waste and incorporates it into a glass matrix (vitrification) for final storage in canisters. DWPF has operated since 1996 using the NFA flowsheet.

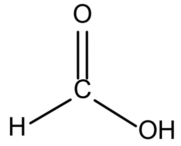
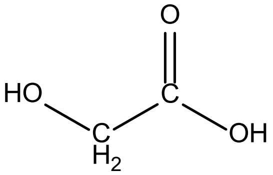
Although the NFA flowsheet converted approximately 18.7 million liters of radioactive slurry to about 7.5 million kilograms of glass, flammability control had been a processing limitation since start-up even with expansion of the original vessel vent design [1]. In addition, future sludge batches would be largely composed of waste with higher concentrations of noble metals and mercury, with little blending capability to reduce the impact of noble metal catalyzed hydrogen generation. In 2008, alternate reductants were evaluated with new evidence that mercury reduction and REDOX control may be sequenced [2]. The thought was that if mercury reduction could be achieved with smaller amounts of formic acid and REDOX adjustment accomplished with a different compatible material, like sugar or glycolic acid, then hydrogen generation could be significantly reduced. This change would allow flammability control below 25% composite lower flammability limit and eliminate the requirement for gas chromatographs. With this change, modifications to the vessel vent system would not be required for future difficult sludge batches.

From 2008 through early 2022 the NGA flowsheet was developed to meet the existing DWPF design criteria. Ultimately the NGA flowsheet as developed has been shown to effectively reduce mercury, significantly reduce hydrogen generation, improve rheology by reducing consistency and yield stress, provide pH stability throughout the CPC operation, eliminate the need for vessel vent expansion even with significantly higher radiolytic hydrogen generation, reduce antifoam requirements, and allow processing of significantly higher volumes of salt processing streams. Only minor physical facility modifications have been made to allow for destruction of residual glycolate prior to the recycle stream return to the waste storage tanks and to accommodate lower purge flows.

DEVELOPMENT OF THE NITRIC-GLYCOLIC ACID FLOWSHEET

Twenty acidic and non-acidic reducing agents were evaluated as alternatives to formic acid to reduce mercury, acidify the sludge, and to balance the melter REDOX. [3] A number of carboxylic acids, similar to formic acid, were evaluated and glycolic acid was selected as the most suitable replacement. Glycolic acid did not show the ability to reduce mercury in early screening studies with simple solutions of nitrite, nitrate, and mercury (II) oxide. [4] Therefore, early research focused on a blend of glycolic and formic acids which showed promise in reducing mercury with minimal hydrogen generation. Some key properties of both acids are provided in Table I. [5]

TABLE I. Properties of Formic and Glycolic Acids.

Reductant	Formula	Acid pKa	Molarity (mol/L)	Carbon Oxidation State	Structure
Formic Acid	CH_2O_2	3.75	23.6	+2	
Glycolic Acid	$C_2H_4O_3$	3.83	11.8	+1	

Laboratory scale SRAT and SME cycles were completed using non-radioactive simulants to determine the optimum ratio of formic to glycolic acid in the Nitric-Glycolic-Formic Acid flowsheet. Interestingly, it was found that mercury was successfully reduced using only glycolic acid, and all processing goals were achieved without the need for added formic acid. While the exact mechanism for mercury reduction is not known (i.e., glycolic acid by itself is probably incapable of directly reducing HgO), it is hypothesized that metal oxides (e.g., MnO_2) in the sludge matrix are converting a fraction of the glycolic acid to formic acid, which in turn acts as a reducing agent for mercury [6].

Over 120 experiments were performed using nitric and glycolic acid, with and without formic acid, including three radioactive demonstrations at various stages of process development. All testing using glycolic acid and representative waste significantly reduced mercury and met all other processing requirements. A comparison of the controlling reactions between the previous NFA flowsheet and the current NGA flowsheet is provided in Table II below.

TABLE II. Reactions of Nitrous Acid, Formic Acid, Glycolic Acid, Manganese, and Mercury.

Reaction	**NFA Flowsheet**	**NGA Flowsheet**
Nitrous Acid Disproportionation	$3HNO_2 = HNO_3 + 2NO + H_2O$	$3HNO_2 = HNO_3 + 2NO + H_2O$
Nitrous Acid Reduction to NO	$HCO_2H + 2HNO_2 = CO_2 + 2NO + H_2O$	$C_2H_4O_3 + 6HNO_2 = 2CO_2 + 6NO + 5H_2O$
Nitrous Acid Reduction to N_2O	$2HCO_2H + 2HNO_2 = N_2O + 2CO_2 + 3H_2O$	$2C_2H_4O_3 + 6HNO_2 = 3N_2O + 4CO_2 + 7H_2O$
Glycolic acid to Formic Acid	NA	$C_2H_4O_3 + 4HNO_2 = HCO_2H + CO_2 + 4NO + 3H_2O$

Reaction	NFA Flowsheet	NGA Flowsheet
Glycolic acid to Oxalic Acid	NA	$C_2H_4O_3 + 4HNO_2 = (COOH)_2 + 4NO + 3H_2O$
Reduction of HgO[a]	$HgO + HCO_2H = Hg + CO_2 + H_2O$	$HgO + HCO_2H = Hg + CO_2 + H_2O$
Reduction of MnO_2	$MnO_2 + HCO_2H + 2H^+ = Mn^{2+} + CO_2 + 2H_2O$	$3MnO_2 + C_2H_4O_3 + 6H^+ = 3Mn^{2+} + 2CO_2 + 5H_2O$

[a] Assumes formic acid is derived from glycolic acid in the NGA flowsheet.

The conversions of nitrite to nitrate, the decomposition of glycolate, and the conversion of glycolate to formate and oxalate were modeled for the NGA flowsheet using data from CPC simulant runs conducted by SRNL from 2011 to 2015. The waste sludge contains nitrite, nitrate, magnesium dioxide, and oxalate that participate in the above reactions with nitric and glycolic acid. Virtually all of the nitrite is converted to nitrate or N_yO_x gases in the CPC. Nitrite conversion varies for each sludge batch, with the portion of the nitrite converted to nitrate increasing the amount of nitrate in the sludge. The amount of glycolate in the final melter feed depends on the amount of oxalate and formate that is produced.

Acid and REDOX Equations

Rheology is the most important parameter in defining the CPC operating window and is a strong function of acid stoichiometry. Improvements in rheological properties of the alkaline waste streams are believed to be achieved through the dissolution of components in the waste and adjustment of electrostatic forces between slurry particles. The NGA flowsheet was found to be much better at dissolving metals compared to the baseline NFA flowsheet. This led to substantially lower yield stress SRAT and SME products. Higher weight percent total dried solids were achieved while staying within rheological limits. As a result, the use of glycolic acid allows for processing of slurries that could not be processed with the NFA flowsheet.

The Koopman Minimum Acid (KMA) [2] and Hsu Minimum Acid [7] equations were developed to define the total amount of nitric and formic acid required for processing the NFA flowsheet. Both equations are provided below on a mole basis (including soluble total inorganic carbon, or soluble TIC).

$$\mathbf{KMA_{mols} = 1.5*Mn_{mols} + 1*Hg_{mols} + 1*Nitrite_{mols} + 1*(soluble\ TIC_{mols}) + 1*OH^-_{mols} + 1.5*Ca_{mols} + 1.5*Mg_{mols}} \tag{1}$$

$$\mathbf{Hsu_{mols} = 1.2*Mn_{mols} + 1*Hg_{mols} + 0.75*Nitrite_{mols} + 2*TIC_{mols} + 1*OH^-_{mols}} \tag{2}$$

Acid calculations need to be performed for each individual SRAT batch as each batch is unique. Prior to transitioning to the NGA flowsheet, simulant experiments were performed to determine the operating window for CPC processing of Sludge Batch 9 (SB9) under the NGA flowsheet. Glycolic acid ranging from 52-64 mol percent of total acid, and acid stoichiometries (i.e., the ratio of mols added to the mols needed) ranging from 80.3% to 129% of the Hsu minimum acid were investigated. Results from these tests demonstrated the acid equations, originally developed for the NFA flowsheet, are sufficient to predict the composition of DWPF SRAT and SME products under the NGA flowsheet.

The REDOX of the melter feed is controlled by adjusting the ratio of nitric and glycolic acid used. For every mole of glycolic acid added, two moles of carbon are added as glycolic acid is a two carbon organic acid. The average oxidation state of each carbon in glycolic acid is +1, whereas the oxidation state of carbon in formic acid is +2, which means that glycolic acid is capable of reducing three times as much oxidant as formic acid upon full conversion to carbon dioxide.

An electron equivalents (EE) exchange REDOX model was developed to balance reductants and oxidants for melter feed processed in DWPF. [8] The model is represented by the number of electrons gained during reduction or lost during oxidation of various species. The overall relationship between the REDOX ratio of the final glass and the melter feed chemistry is given in terms of the transfer of molar EEs as defined in equations (3) and (4) below.

$$\mathbf{EE} = (\mathbf{2[F]} + \mathbf{4[C]} + \mathbf{4[Ox]} + (\mathbf{3.39} *.\mathbf{85})[\boldsymbol{A}] + \mathbf{6[G]} - \mathbf{5[N]} - \mathbf{0[Mn]}) * \left(\frac{\mathbf{45}}{\boldsymbol{T}}\right) \tag{3}$$

where [F] = formate (mol/kg feed), [C] = coal (carbon) (mol/kg feed), [Ox] = oxalate (mol/kg feed), [A] = antifoam (mol C/kg feed), [G] = glycolate (mol/kg feed), [N] = nitrate + nitrite (mol/kg feed), [Mn] = manganese (mol/kg feed), and T = total dried solids (wt%).

$$\mathbf{Glass\ Redox} = \mathbf{0.2358} + (\mathbf{0.1999} * \mathbf{EE}) \tag{4}$$

Scaling Studies

The majority of testing on the NGA flowsheet was performed on relatively small scales (e.g., 4-L kettles for nonradioactive simulants and 1-L or 4-L kettles for actual waste). To bridge the gap from laboratory to the facility scale, testing with non-radioactive simulants was completed using three experimental DWPF to laboratory volume scale factors (e.g., 12,000:1, 2,160:1, and 216:1). [9] Testing evaluated the impact of equipment scale on process chemistry, offgas composition, product rheology, and glass REDOX.
The chemistry and processing were virtually identical at the three scales tested. There were a few areas where a parameter did change with scale (such as nitrite to nitrate conversion and mercury collection) but nitrite to nitrate conversion is sensitive to internal reflux and was expected to change with scale. Hydrogen generation was reduced by several orders of magnitude when replacing formic acid with glycolic acid and this was not impacted by the testing scale [10].

Sludge Batch 9 Qualification Run

For each sludge batch that is processed in DWPF, SRNL performs qualification testing to demonstrate that the sludge batch is processable. In order to implement the new flowsheet, a 4-L scale test was conducted in the SRNL Shielded Cells using a SB9 slurry blend. CPC demonstrations utilizing the NGA flowsheet were performed at an acid stoichiometry of 78.0% KMA basis (87.1% Hsu basis) for the SRAT cycle. [11]

The total dried solids measurements of the SRAT and SME products matched the targets of 25 wt% and 48 wt% acceptably. The consistency and yield stress of the SRAT receipt material were within the DWPF design basis, while the SRAT and SME product yield stresses were below the DWPF design basis. Hydrogen was not detected above the detection limit of 0.0014 lb/hr in the SME. The final concentration of mercury in the SRAT product was below the target for mercury removal of 0.8 wt% of the total dried solids. Based on the results of the actual-waste qualification and previous simulant studies, SRNL recommended implementation of the NGA flowsheet in DWPF.

Permanganate Flowsheet Development/Chemistry

DWPF process condensates are collected and returned to the SRS CSTF. The Recycle Collection Tank (RCT) collects off-gas condensate during chemical processing, vitrification, and other unit operations performed in DWPF and is the singular return vessel delivering recycle effluent back to CSTF. Each batch of recycle may contain a small amount of glycolate from chemical processing and melter off-gas condensates. To avoid potential flammability issues due to thermolytic hydrogen generation from residual glycolate in the CSTF, methods to destroy glycolate in the RCT were investigated.

Tests using simulated and radioactive waste at caustic conditions demonstrated the use of a sodium permanganate strike to oxidize glycolate in the DWPF RCT prior to being returned to the CSTF. Tests at caustic conditions demonstrated sodium permanganate was effective in converting glycolate to oxalate, and permanganate (Mn^{7+}) is reduced to manganate (Mn^{6+}) with no significant formation of carbon dioxide or carbonate. Equation (5) was found to best describe the observed reaction of glycolate with permanganate under normal operating conditions. [12]

$$\mathbf{C_2H_3O_3^- + 4MnO_4^- + 5OH^- = C_2O_4^{2-} + 4MnO_4^{2-} + 4H_2O} \quad \mathbf{(5)}$$

Determination of the mechanistic chemical reaction confirmed the oxidant stoichiometry is effectively defined by the molar ratio of permanganate to glycolate (P/G). A kinetic model of the batch processing was developed by SRNL to describe the kinetics of glycolate destruction via chemical oxidation with sodium permanganate when RCT liquid is pre-adjusted with caustic and nitrite before permanganate addition. [13] The Post-Strike process strategy was found to be most effective for the nominal goal of reducing glycolate concentration to below 1 mg/L in 4 hours, well below the current waste acceptance criteria for DWPF streams returned to the CSTF.

INTERIM GLYCOLIC IMPLEMENTATION

Safety Basis Changes

Due to the extensive impacts on many different facility aspects, the project team developed a Safety Basis Strategy (SBS) to provide a common understanding of the management expectations, scope, roles and responsibilities, strategy, and methods to be used [14]. The SBS summarizes the methodology for hazard categorization and controls identification as well as identified key process inputs and assumptions. The SBS then highlights the documentation and analysis that has been developed to support final implementation.

Two separate revisions to the existing documented safety analysis were planned to support the use of glycolic acid at DWPF. The first revision considered an interim configuration in which both formic and glycolic acids were present within DWPF. A consolidated hazards analysis process was performed to document the controls needed for the safe handling and use of glycolic acid. This process included not only operation at DWPF but also downstream facilities as the potential exists for some amount of dissolved glycolate to be present in recycle stream from DWPF.

As the hazard controls for formic acid bounded the controls needed for glycolic acid, interim glycolic implementation did not significantly impact the facility operation or design. During transition, all NFA flowsheet controls remained in place. Calibrations and checks on instrumentation to measure glycolate were completed in the DWPF laboratory. Existing tanks were repurposed to provide storage and feeding of 20 wt% sodium permanganate to the RCT. Inspections, calibrations, and flushes were completed to ensure this system was operable for use to store and transfer sodium permanganate to the RCT. Physical equipment modifications for implementation of the NGA flowsheet and glycolate destruction process were documented in an implementation strategy [15].

One additional change to note was the total organic carbon (TOC) limit for the melter feed increased from 12,750 ppm to 14,000 ppm. The NGA flowsheet is higher in TOC due to the contribution from glycolate. Implementation of a new, more effective antifoam (Momentive™ Y-17112) allowed the facility to reduce the volume of antifoam used while processing, thus reducing its TOC contribution. This increased limit was also intended to allow for increasing the weight percent total dried solids in the SME product, resulting in a more favorable rheology.

Transition Plan

A transition plan was written to outline the suggested facility conditions prior to start of transition and proposed facility operating parameters during the transition period. This plan also described differences between the NFA flowsheet and the NGA flowsheet and provided guidance on determining when the flowsheet transition has been chemically completed. [16].

Specific processing parameter recommendations were made when transitioning to the new flowsheet during SB9 processing. Under the NFA flowsheet, the acid stoichiometry used during SB9 processing was 112% Hsu basis; under the NGA flowsheet acid stoichiometry would be gradually decreased to 87-90%. This was recommended to be consistent with the increasing percent of glycolic acid as formic acid was consumed. Acid stoichiometry was based on the calculated blend of formic and glycolic acid. The recommended REDOX target was 0.10 for bubbled operation and 0.20 for non-bubbled operation; bubbled argon removes available oxygen in the melt pool, resulting in the lower REDOX target for bubbled operations. The SRAT total dried solids target remained unchanged at 20-25 wt%. The recommended waste loading target (36%) was also not changed; this represents the percent by mass of waste in a canister. The SME total dried solids target was set at 40-50 wt%, as qualification of SB9 targeted 48 wt% solids to achieve favorable rheology. During SB9 processing under the NFA flowsheet, the total dried solids target was 40 wt%. Total dried solids were planned to be increased gradually up to 48 wt%, or as required to maintain effective melter feed rates. Antifoam additions of Momentive™ Y-17112 were recommended to be consistent with the SRNL addition strategy for the NGA flowsheet.

Per the transition plan, prior to interim glycolic implementation, the SRAT and SME should be brought to heel levels, along with the SMECT, Off Gas Condensate Tank, and Back-Up Off-Gas Condensate Tank. Following interim implementation, CPC vessels would be considered to be transitioned when a low formate concentration was achieved. This was estimated to be when the glycolate conversion to formate was about 10% or less at 90% or less acid stoichiometry. In the SRAT and SME, product samples would be used to demonstrate this. Since the SME is the point of compliance for the melter, MFT concentrations would be determined via calculation. Since the reductant is not present in the glass and REDOX is influenced by operating conditions, glass transition via REDOX measurements will be monitored over an extended period.

Demonstrating that the glycolate destruction process works at the DWPF scale is a key part of transition. Since the glycolate destruction requirement was less than measurement capability in the DWPF, SRNL developed the kinetic model discussed above. Initially, every RCT batch should be analyzed for the incoming glycolate concentration prior to the sodium permanganate addition. The glycolate concentration in the condensate recycle stream, at steady state, was expected to be close to the DWPF laboratory detection limit of approximately 20 mg/L. Therefore, glycolate was to be assumed to be at 20 mg/L unless quantifiable in the DWPF analysis. Until SRNL has verified that glycolate has been destroyed in DWPF consistent with the SRNL model, initially each RCT batch should be treated with sodium permanganate at twice the required amount at twice the required residence time (8 hours). If there was no detectable glycolate in the RCT sample, the glycolate concentration should be assumed to be at the detection limit. After three SRAT cycles, a set of samples was to be sent to SRNL to verify glycolate destruction. Based on the information provided, the processing strategy would be subject to change. Once the SRNL model has been verified, sodium permanganate was to be added at 50% excess calculated for a 4-hour residence time.

Transition of the Chemical Process Cell Vessels

Sludge Receipt and Adjustment Tank

Table III reports the acid calculation parameters for the SRAT batches processed to date. This table also includes the pH of the SRAT Product samples (i.e., samples of treated SRAT material), as well as the volumes of MST/SS and SE added during processing of each SRAT batch. Per the transition plan recommendation, SRAT 816 had an acid stoichiometry of approximately 100%. However, the SRAT 817 acid stoichiometry was 97.5%, rather than the 95% recommended for the second SRAT batch with glycolic acid. This was partly because the remaining formic acid in the facility upon transition was higher than anticipated, demonstrated by the percent of formic acid in the reducing acid additions. In addition, the MST/SS volume added to SRAT 817 was higher to maintain SWPF throughput; nominal MST/SS additions are approximately 10,600 L. MST/SS additions increase acid demand as the material is caustic. Thus, the acid stoichiometry was kept at 97.5% to reduce the final pH of the SRAT material to acidic to neutral conditions while still having a reducing acid addition less than approximately 1,500 L (a previous NFA flowsheet and interim glycolic control). Similarly, SRAT 818 had a higher acid stoichiometry (97.6%) and a lower REDOX target (0.07) to aid in further reducing the pH of the SRAT Product. After SRAT 818, the acid stoichiometry was able to be reduced to about 90% while still maintaining a REDOX target of 0.10. By SRAT 819, a negligible amount of formic acid remained.

The average pH of the 15 SRAT batches processed before transition was 7.7. Initially the pH of the SRAT Product samples was higher than anticipated. This was due to the amount of formic acid remaining in the facility. Larger SWPF stream additions can also contribute to a higher pH in the SRAT and downstream vessels. However, after SRAT 818, the pH fell within the expected range for NGA flowsheet. Despite significant differences between the MST/SS and SE volumes added to each SRAT batch, the pH steadily reduced to acidic to neutral conditions during transition. SRAT 821 in particular had a larger SE volume added and the pH remained below 7, demonstrating the stability of the NGA flowsheet.

TABLE III. SRAT Acid Calculation and Processing Parameters.

SRAT Batch No.	**816**	**817**	**818**	**819**	**820**	**821**	**822**	**823**	**824**
Percent Formic Acid of Reducing Acid (mol%)	66.7%	21.9%	6.3%	-	-	-	-	-	-
Acid Stoichiometry (%)	99.7%	97.5%	97.6%	90.4%	90.0%	90.0%	90.0%	90.0%	90.1%
REDOX Target	0.10	0.10	0.07	0.10	0.10	0.10	0.10	0.10	0.10
MST/SS Volume (L)	10,200	14,500	11,700	6,900	9,600	8,700	7,200	7,700	8,600
SE Volume (L)	78,000	53,600	103,100	51,700	25,600	76,100	28,000	65,800	61,600
pH	7.8	7.3	6.0	7.1	6.4	6.2	6.5	6.9	6.2

Table IV summarizes select SRAT Product sample results. Although the weight percent total dried solids were slightly higher than 25 wt% for some SRAT batches, this was not a concern. All material was successfully transferred to the SME without issue. Mercury sample results were reported starting with the second SRAT batch during interim glycolic transition. Mercury stripping was proven to be successful, as all SRAT batches had concentrations less than the target of 0.8 wt%. Both SRAT 820 and 822 had small volumes of SE added (and thus less steam stripping), therefore, slightly higher mercury concentrations were not a concern. Mercury results were not obtained for SRAT 821 as there was insufficient sample material remaining to perform the analysis. Formate and glycolate concentrations indicate the SRAT has fully transitioned. Since SRAT 819, sample results have indicated that less than 10% of glycolate is converted to formate. Figure 1 shows the change in the SRAT Product glycolate and formate concentrations over time.

TABLE IV. SRAT Product Sample Results.

SRAT Batch No.	**816**	**817**	**818**	**819**	**820**	**821**	**822**	**823**	**824**
Total Dried Solids (wt%)	22.73	25.73	25.32	25.53	23.79	23.87	24.04	24.61	23.09
Hg (wt%)	-	0.09	0.10	0.17	0.26	-	0.30	0.15	0.13
Formate (ppm)	20,981	6,751	1,625	1,055	1,234	733	773	988	795
Glycolate (ppm)	18,455	32,958	37,832	44,221	38,800	38,362	37,931	40,735	41,204

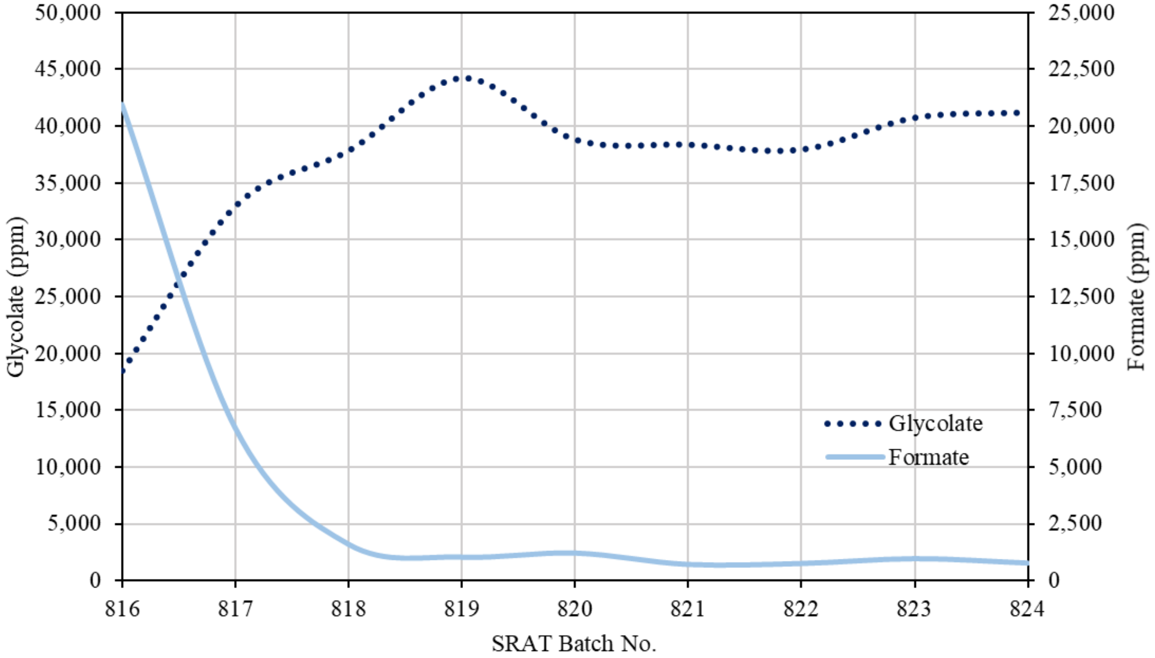


Fig. 1. SRAT Product Formate and Glycolate Concentrations.

Table V reports the SRAT Receipt (i.e., untreated material) and Product nitrite sample results. A less than symbol (<) indicates the result is below the reported detection limit. These results show nitrite continues to be converted to nitrate in the SRAT since transition to the NGA flowsheet.

TABLE V. Nitrite Concentrations of SRAT Receipt and Product Samples.

SRAT Batch No.	**816**	**817**	**818**	**819**	**820**	**821**	**822**	**823**	**824**
Receipt Nitrite (ppm)	10,269	10,770	10,782	10,954	10,195	10,296	10,145	11,115	10,794
Product Nitrite (ppm)	< 634	< 582	< 601	< 586	< 605	< 615	< 574	< 597	< 583

Slurry Mix Evaporator

Table VI displays the SME Product sample results, as well as the number of canisters decontaminated during the SME batch. Canister decontaminations result in the addition of frit and water to the SME. A higher number of "can blasts" corresponds to longer boiling times in the SME, which caused an increase in pH under the NFA flowsheet. The average pH of the 15 SME batches prior to transition was 10.4. As expected, the pH since transition to the NGA flowsheet has steadily decreased to a neutral range over time. The change in pH from the end of the SRAT cycle to the end of the SME cycle has also decreased for each SME batch, demonstrating the stability of the flowsheet.

While the recommended total dried solids target was 40-50 wt%, processing constraints limited the ability of the facility to achieve this target for some SME batches. The total dried solids in the SRAT 816 Product sample were 22.73 wt%, and the material could not be sufficiently concentrated in the SME to increase the total dried solids to 40 wt%. For SME 819, 823, and 824, the predicted TOC concentration exceeded 14,000 ppm at a higher weight percent total dried solids target and thus was limited to a target of 38-39 wt%. Sample pump issues resulted in additional water being added to SME 824, decreasing the total dried solids concentration. However, since SME 819, material sent to the melter has had minimal feeding issues, so targeting a higher weight percent total dried solids has not been necessary. Similarly, a 36% waste loading was generally targeted, however this was refined for each batch based on operational needs and processing constraints. TOC concentrations have remained below 14,000 ppm without needing to remediate.

TABLE VI. Can Blasts and SME Product Sample Results.

SME Batch No.	**816**	**817**	**818**	**819**	**820**	**821**	**822**	**823**	**824**
Number of Can Blasts	6	8	1	4	0	9	6	7	1
pH	10.2	9.8	7.6	7.6	7.0	7.3	7.4	7.3	7.1
Total Dried Solids (wt%)	38.37	40.71	41.19	37.13	41.26	40.70	40.07	38.53	36.87
Waste Loading (%)	39.13	31.75	34.13	33.37	34.45	32.53	37.71	38.29	32.62
Formate (ppm)	17,607	7,916	4,061	1,707	1,377	1,268	1,519	1,265	1,178
Glycolate (ppm)	11,136	20,815	28,655	30,829	31,111	30,990	28,532	30,940	28,869
TOC (ppm)	10,044	10,006	12,102	10,792	11,755	12,220	10,969	11,684	10,644

Formate and glycolate concentrations indicate that the SME has fully transitioned. Since SME 819, results have indicated that less than 10% of glycolate is converted to formate. Figure 2 shows the change in the SME Product glycolate and formate concentrations over time.

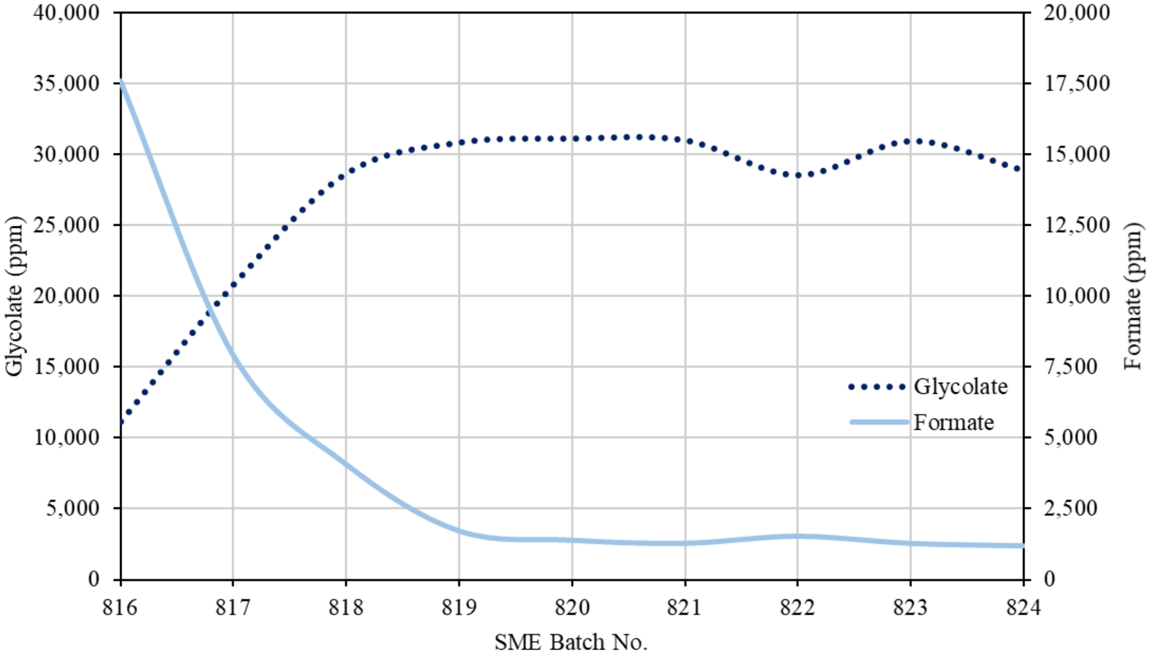


Fig. 2. SME Product Formate and Glycolate Concentrations.

Melter Feed Tank and Melter

Since the MFT cannot be sampled, formate and glycolate concentrations are determined via calculation using SME Product sample data, transfer volumes, and MFT heel volumes. Results are presented in Table VII.

TABLE VII. Calculated MFT Formate and Glycolate Concentrations.

MFT Batch No.	**816**	**817**	**818**	**819**	**820**	**821**	**822**	**823**	**824**
Formate (ppm)	24,888	14,415	7,731	3,580	2,171	1,629	1,573	1,393	1,266
Glycolate (ppm)	6,188	15,500	24,160	28,974	30,604	31,390	29,838	30,685	29,753

The results show that since MFT 821, less than 10% of glycolate is converted to formate, indicating the MFT has fully transitioned. Figure 3 shows the change in the predicted MFT glycolate and formate concentrations over time.

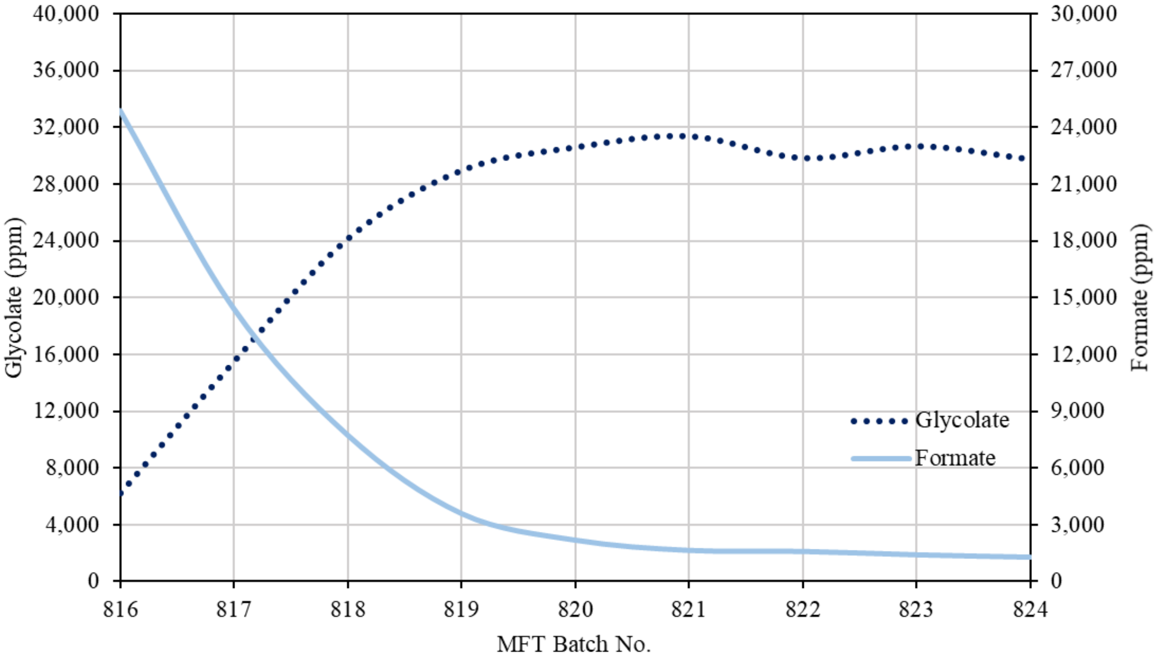


Fig. 3. Calculated MFT Formate and Glycolate Concentrations.

Feeding and pouring of glass canisters was successful throughout transition to the NGA flowsheet. As the MFT level approaches approximately 19,000 L, agitator blades in the vessel start to become exposed. This can cause air entrainment, resulting in melter feed pump trips. Previous batches processed under the NFA flowsheet could have over twenty feed pump trips in this regime, significantly extending processing time. Despite the total dried solids being lower than originally planned for SME batches, minimal to no feeding issues have been reported. From MFT 818 to 820, no feed pump trips occurred when the MFT level reached or decreased below 19,000 L. Only one feed pump trip occurred when processing MFT 821. Some feed pump trips occurred as the MFT reached its heel level (approximately 9,500 to 13,000 L), however there were still significantly fewer trips compared to when processing under the NFA flowsheet. This is likely because processing under the NGA flowsheet produces a thinner, more stable material that entrains less air.

Recycle Collection Tank

As described in the transition plan, RCT samples are taken pre-sodium permanganate strike and analyzed for glycolate. To date, all RCT batches have had pre-strike glycolate concentrations below detectible limits (approximately 20 mg/L). RCT sample results for iron have similarly been low or below detectible limits (approximately 42 mg/L), supporting that minimal entrainment has been present in the batches. These results illustrate the stability of the NGA flowsheet and the effectiveness of Momentive™ Y-17112 antifoam.

Due to glycolate concentrations consistently being less than approximately 20 mg/L in the RCT, the RCT processing strategy was adjusted to reduce cycle time. During transition initially, the RCT was sampled, struck with sodium permanganate based on the sample glycolate concentration, and transferred after an 8-hour residence time. This strategy was modified so that an RCT sample was still taken pre-strike, but the batch was struck with approximately 235 L of sodium permanganate (based on an assumed 20 mg/L glycolate concentration) prior to receipt of sample results. Sample results were used to confirm the batch contained 20 mg/L glycolate or less.

To confirm glycolate destruction in the RCT, two sets of three samples each were sent to SRNL for analysis during processing of SRAT batches 818 and 822. For SRAT 818, the first sample in the set was a SMECT sample, which was expected to provide the highest concentration of glycolate since no sodium permanganate is present in the SMECT. After the SMECT material was transferred to the RCT, an RCT sample was taken (pre-sodium permanganate strike). The third sample was taken from the RCT post-strike (after 8 hours) to provide information on glycolate returns to Tank 22 (recycle back to the high-level waste storage system) [17]. For SRAT 822, a pre-strike and two post-strike RCT samples (after 4 hours and 8 hours) were taken [18]. Ion chromatography (IC) and proton nuclear magnetic resonance (H-NMR) methods were used to determine the glycolate concentrations of the samples. Results are shown in the table below.

TABLE VIII. Measured Glycolate Concentrations Using IC and H-NMR.

Sample	**SRAT 818**		**SRAT 822**	
	IC (mg/L)	**H-NMR (mg/L)**	**IC (mg/L)**	**H-NMR (mg/L)**
SMECT	< 8	8	NM [a]	NM
RCT (pre-strike)	< 8	4.8	< 8	2.0
RCT (post-strike)	< 8	< 1.4	< 8 [b]	< 1[b]

[a] NM = Not Measured

[b] Both post-strike RCT samples (after 4 hours and 8 hours) had glycolate concentrations < 8 mg/L and < 1 mg/L for the IC and H-NMR methods, respectively.

These results demonstrate glycolate is destroyed in the RCT using sodium permanganate. Previously processed RCT batches were re-baselined to the post-strike glycolate concentrations reported by the H-NMR method. Receipt tanks of recycle waste have continued to meet waste acceptance criteria, remaining at or below a 3 mg/L glycolate concentration.

FINAL GLYCOLIC IMPLEMENTATION

Safety Basis Changes

After any residual formic acid was removed from the facility and MFT formate concentrations were less than 10% of the initial glycolate concentrations, the MFT was determined to be transitioned. After this, a second documented safety analysis change was implemented. Final glycolic implementation considered only glycolic acid as the primary chemical reductant and excluded the receipt and storage of formic acid. Removal of 90 wt% formic acid from the facility chemical inventory eliminated the potential for a chemical release resulting in a Site Area Emergency. The final glycolic configuration also included a modified control set that is specific to glycolic-only operation. Purge requirements for numerous process vessels were reduced due to the significant reduction in catalytic hydrogen generation. Required maintenance and operational activities were performed to ensure that the purge rates to the vessels could be adjusted and maintained at the lower rates.

In addition to a reduction in purge requirements, the TOC limit for the melter feed increased from 14,000 ppm to 17,000 ppm. Material Tracking Program limits (which determine the volumes of MST/SS and SE that can be added to a SRAT batch) also increased.

Process Improvements

The reduction in purge for the CPC vessels has aided in increasing steaming rates in the facility. While processing under the NGA flowsheet, steam was applied into the vessel process coils at a rate of approximately 1,500 kilograms per hour. Due to the drastic reduction in catalytic hydrogen generation, vessel temperatures can be increased more rapidly using higher steam rates without concern of carryover or overwhelming the off-gas system. Coupled with implementation of the Momentive™ Y-17112 antifoam, the facility is now able to approach operating at the original design basis maximum steam rate of approximately 2,250 kilograms per hour.

As previously noted, the increased TOC limit under final glycolic implementation was intended to allow for increasing the weight percent total dried solids in the SME product, resulting in a more favorable rheology. This will help ensure optimum melter operation with minimal feeding issues (as observed during transition). Due to the increased Material Tracking Program limits, larger MST/SS and SE volumes can be added to a SRAT batch. This supports increased SWPF throughput, decreasing the likelihood that DWPF will cause stoppages at SWPF.

FUTURE WORK

A glass sample was pulled prior to final glycolic implementation; work is currently ongoing to characterize this sample to verify the REDOX equation. Work is also in progress to complete validation of the SRNL glycolate destruction model under facility conditions for recycle. This will ensure conservative sodium permanganate additions and strike times can be credited for reduction of RCT glycolate concentrations below 3 mg/L.

DWPF intends to increase the feed rate of the SWPF streams to the SRAT and, thereby, maximize the benefit of the increased steam rate capability. Currently, the maximum steam rate is not utilized when feeding the two SWPF streams to the SRAT because the corresponding evaporation rate outpaces the addition rate. Increasing the feed rate of SWPF streams with the steam rate would decrease the SRAT cycle time. This would also support increased SWPF throughput.

Future sludge transfers to be sent from the Tank Farm are anticipated to have a higher mercury content. For SB9, approximately 34,000 kg of steam is required to reduce the mercury content below 0.8 wt% in the SRAT; future SRAT batches may require more than three times as much steam to be applied. When these future high mercury batches are processed, it is crucial the facility be able to steam faster to maintain pace with SWPF. Work is also in progress to improve mercury collection and recovery within the facility.

Due to the carryover susceptibility, formic acid addition rates were historically limited to approximately 4 lpm and split into four additions with 20 minutes between each addition. An anticipated improvement of the NGA flowsheet is to add glycolic acid at a rate of approximately 15 lpm as a single addition, which will significantly decrease the cycle time needed for glycolic acid additions.

CONCLUSIONS

Transition to the NGA flowsheet and final implementation has proven to be successful. Within seven processing cycles, the SRAT, SME, and MFT were transitioned with low formate concentrations in the vessels. Mercury stripping and nitrite destruction have both been successfully demonstrated in the SRAT at a reduced acid stoichiometry. The pH in both the SRAT and SME has been stable in an acidic to neutral range, validating the NGA flowsheet's stability at varying SWPF stream additions. Glycolate destruction chemistry in the RCT has been demonstrated. Following final glycolic implementation, the facility proceeded to begin processing Sludge Batch 10, which was qualified under the NGA flowsheet.

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