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An Evaluation of the Impact of Glycolate and Glycolate Mitigation on the Defense Waste Processing Facility Recycle Diversion Project Flowsheet

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EXECUTIVE SUMMARY

The impact of thermolytic hydrogen generation from glycolate in Defense Waste Processing Facility (DWPF) recycle was evaluated in support of the DWPF Recycle Diversion Project. The evaluation and identification of gaps in knowledge considered the range of conditions anticipated in the process including the addition of sodium permanganate, the range of Recycle Collection Tank (RCT) pH values (i.e., 9 to >13), and species concentrations during wiped film evaporator (WFE) processing. All species that have measurable influence on thermolytic hydrogen generation rate (HGR) are soluble in the aqueous waste stream and thus crossflow filtration is not anticipated to have an impact on HGR. Model-predicted HGRs for the evaporator bottoms using both atmospheric and WFE evaporator options with and without glycolate mitigation (assuming 1 and 125 ml/L glycolate in the RCT) are provided in the table below.

Model-Predicted Thermolytic HGR from Glycolate in the DWPF Recycle Evaporator System

Evaporator	Permanganate Strike in RCT	Max Temp.	Glycolate (mg/L)	Model-Predicted HGR ($ft^3\ hr^{-1}\ gal^{-1}$)
WFE (vacuum)	No	60 °C	2540	2.70E-07
Atmospheric	No	120 °C	2540	2.51E-05
WFE (vacuum)	Yes	60 °C	20.3	2.16E-09
Atmospheric	Yes	120 °C	20.3	2.01E-07

Two streams from the Recycle Diversion process, the concentrated solids stream from the filter and the bottoms from the WFE, will likely be sent to the Concentration Storage and Transfer Facilities (CSTF). In order to meet an expected CSTF Waste Acceptance Criteria (WAC) for glycolate to limit HGR, the Glycolate Mitigation process and the inputs and assumptions for Glycolate Mitigation were also evaluated.

Results from Savannah River National Laboratory (SRNL) testing and published reports demonstrated nitrite is unreactive towards permanganate in highly caustic solutions (i.e., pH >13) and permanganate (Mn^{7+}) is reduced to manganate (Mn^{6+}). Changes to RCT chemistry may occur at pH <13 and affect parameters required for the glycolate mitigation process. At lower pH, nitrite oxidation becomes more favorable and may compete with glycolate in the permanganate oxidation reaction. Also, manganate is likely to further reduce to manganese dioxide (MnO_2) and reduce the required permanganate to glycolate molar ratio (P/G) for glycolate destruction. Additional experiments are recommended to understand the effect of a permanganate strike on RCT chemistry in the pH range of 9 to 13 if the process continues to consider running in this range.

The kinetic model used to predict necessary P/G ratios and reaction durations was primarily based on data where the nominal condition of the RCT after chemical additions was considered with pH >13. Since the nitrite reaction may consume a portion of the permanganate that is needed for the oxidation of glycolate, the model may be impacted in a non-conservative manner below pH 13. Due to the use of this model, it is recommended that further investigation of the glycolic mitigation be performed below pH 13 if those conditions will be encountered in the RCT.

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LIST OF ABBREVIATIONS

BUOGCT	Backup Off-Gas Condensate Tank
CCP	Corrosion Control Program
CPC	Chemical Processing Cell
CSTF	Concentration, Storage, and Transfer Facilities
DWPF	Defense Waste Processing Facility
DWTT	Decontamination Waste Treatment Tank
ETF	Effluent Treatment Facility
HGR	Hydrogen Generation Rate
HLW	High Level Waste
MST	Monosodium Titanate
NGA	Nitric-Glycolic Acid
OGCT	Off-Gas Condensate Tank
P/G	Permanganate to Glycolate Molar Ratio
PISA	Potential Inadequacy in the Safety Analysis
RCT	Recycle Collection Tank
SEE	Systems Engineering Evaluation
SMECT	Slurry Mix Evaporator Condensate Tank
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
SWPF	Salt Waste Processing Facility
WAC	Waste Acceptance Criteria
WFE	Wiped Film Evaporator

1.0 Introduction

The Savannah River Site (SRS) Defense Waste Processing Facility (DWPF) processes radioactive High Level Waste (HLW) sludge solids from the Concentration, Storage, and Transfer Facilities (CSTF); which includes the SRS Tank Farm and Evaporator facilities, and a concentrated Cs-137 laden stream and a Monosodium Titanate (MST) and sludge solids stream from the SRS Salt Waste Processing Facility (SWPF). The waste is chemically adjusted with acids and reductant (currently with 50 wt.% nitric acid and ~90 wt.% formic acid, but eventually formic acid will be substituted with ~70 wt.% glycolic acid), and frit is added so that a durable, borosilicate glass waste form can be produced when the material is vitrified in the melter. As a result of the evaporation of water during both the melter feed preparation and the melter feed vitrification steps in DWPF, a recycle waste stream is generated, neutralized, and sent back to the CSTF. The recycle waste is a dilute aqueous stream originating from the collection of condensate liquids containing some minor sludge, MST, and frit solids and other waste components resulting from melter feed entrainment during foamover events and transfer of volatile species into the condensate. The recycle stream volume is significant and is expected to approach 3 million gallons per year once SWPF reaches full operation, requiring the use of multiple large CSTF tanks for storage. The recycle waste is currently collected in the SRS Tank Farm and periodically evaporated in the 242-16H (2H) Evaporator to conserve storage space.

Diverting the bulk of the recycle waste stream from the Tank Farm is essential for the eventual closure of the waste tanks, and hence the completion of the SRS liquid waste mission. Savannah River Remediation (SRR) recently performed a Systems Engineering Evaluation (SEE) for diverting the DWPF recycle stream.[1] Crossflow filtration (at the 512-S and 96H facilities) and wiped-film evaporation (adjacent to SRS Modular Caustic Extraction facility) were selected as the preferred methods for processing the diverted recycle. The final streams produced from these unit operations, including filter solids, evaporator bottoms, and evaporator overheads, will be transferred to the sludge batch preparation tank, the salt batch preparation tank, and the Effluent Treatment Facility (ETF), respectively, with the ETF receiving the bulk of the recycle volume.[2] Transfer of much of the water from the DWPF recycle to ETF accomplishes the primary goal of diverting the bulk of the material from the CSTF.

The Recycle Collection Tank (RCT) in the DWPF Chemical Processing Cell (CPC) is the starting point for evaluating the process chemistry for the Recycle Diversion Project. OLI calculations recently conducted by SRR evaluated the composition of the DWPF recycle stream under various processing scenarios and conditions.[3] The RCT mainly receives transfers from the Slurry Mix Evaporator Condensate Tank (SMECT), the Off-Gas Condensate Tank (OGCT), the Backup Off-Gas Condensate Tank (BUOGCT), the Decontamination Waste Treatment Tank (DWTT), and from laboratory drains. The SMECT and OGCT sources represent the largest volume contributors to the RCT and are acidic, primarily due to the scrubbing of nitrogen oxides generated during processing as well as acid additions to the SMECT. The other streams that are transferred to the RCT can be acidic or caustic. Currently, the recycle condensate is adjusted in the RCT using sodium hydroxide and sodium nitrite additions to give a pH ≥13 and a nitrite concentration sufficiently high to meet Corrosion Control Program (CCP) criteria for the CSTF carbon steel tanks.

For this analysis, it was requested that cases with minimal chemical additions for streams internal to the DWPF Recycle Diversion process be included. Previous investigations of evaporation of the recycle stream under acidic conditions were shown to be problematic due to foaming, iodine volatility, and other issues.[4,5] To ensure that the Recycle Condensate is not acidic when evaporated, the RCT may be adjusted by the addition of sodium hydroxide to a pH of 9 or greater for internal processing within the DWPF Recycle Diversion process, versus the current requirement of ≥13 for direct transfer to CSTF. The streams transferred to CSTF (the concentrated solids stream from filtration and the concentrated bottoms stream from evaporation) will still be required to meet CSTF CCP.

Additionally, under the Nitric-Glycolic Acid Flowsheet, sodium permanganate will be added to the RCT to reduce the concentration of glycolate in the recycle stream to low levels (near 1 mg/L) in the CSTF.[6]

SRR Engineering requested that Savannah River National Laboratory (SRNL) evaluate the impact of thermolytic hydrogen generation from glycolate in the diverted DWPF Recycle stream, with and without Glycolate Mitigation.[7-9] The HGR evaluation and identification of gaps in knowledge will take into account the range of conditions anticipated in the process including the addition of sodium permanganate, the range of RCT pH values considered (9 to ≥13), and the species concentrations during Wiped Film Evaporator (WFE) processing.

Two streams from the Recycle Diversion process, the concentrated solids stream from the filter and the bottoms from the WFE, will likely be sent to the CSTF (sludge and salt batch preparation tanks, respectively). Thus, in order to meet an expected CSTF Waste Acceptance Criteria (WAC) for glycolate to limit HGR, the Glycolate Mitigation process (addition of sodium permanganate to the RCT) will still be necessary.[6] Additionally, the Glycolate Mitigation process and the inputs and assumptions in the kinetic model for Glycolate Mitigation will need to be evaluated for the proposed adjustments to the chemistry in the RCT, with pH as low as 9. While the Glycolate Mitigation process has been investigated and determined to function from acidic to caustic conditions, the majority of the data and the kinetics analysis were performed with RCT material containing current DWPF levels of sodium hydroxide and sodium nitrite additions.

2.0 Background

With the startup of Salt Waste Processing Facility, DWPF is planning to transition to the Nitric-Glycolic Acid (NGA) Flowsheet. Switching the reducing acid from formic acid to glycolic acid will significantly decrease flammability concerns within the DWPF.[10] The 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 to the SRS CSTF. Each batch of recycle may contain a small amount of glycolate from chemical processing and melter off-gas condensates.

The expected impact of glycolate on hydrogen generation rate (HGR) in the DWPF recycle has been previously studied by SRNL.[11] Testing was performed with actual Tank 22 waste samples with and without added glycolate. Tank 22 is the current receipt tank for DWPF recycle and has a similar salt concentration as the RCT. The HGR testing was performed at a glycolate loading of 120 mg/L and at a temperature range of 30 °C to boiling (~101.5 °C). All Tank 22 supernate tests gave results below the limit of quantification for HGR of 5.6×10^{-8} ft^3 h^{-1} gal^{-1}. Thermolytic HGR appears to be somewhat lower in the presence of sludge solids.[12] Thus, supernate tests would be conservative with respect to thermolytic HGR. However, the overall HGR would be affected by an increase in radiolytic HGR induced by the sludge solids.

To support resolution of the Potential Inadequacy in the Safety Analysis (PISA) for the SRS CSTF, SRNL personnel have performed tests with simulants and radioactive waste to measure the thermolytic production of hydrogen gas from organics including glycolate dissolved in caustic tank waste media. These HGR measurements led to the generation of model expressions for the thermolytic production of hydrogen from glycolate and non-glycolate organics.[12] The HGR expression for glycolate thermolysis shown below in Equation (**1**) is derived from simulant testing and confirmed with radioactive waste testing with added glycolate.

$$\boldsymbol{HGR_{GLY} = 6.262 \times 10^{5}([NO_3]^{0.282}\ [OH]^{1.441}\ [Na]^{1.520}\ [C_{GLY}])e^{\frac{-82{,}300}{RT}}} \qquad (1)$$

where,

HGR_{GLY} is the hydrogen production rate from the thermolysis of glycolate in $ft^3\ h^{-1}\ gal^{-1}$,
$[OH]$ is the concentration of hydroxide in $mol\ L^{-1}$,
$[Na]$ is the concentration of sodium in $mol\ L^{-1}$,
$[C_{GLY}]$ is the concentration of carbon from glycolate in $mol\ L^{-1}$,
$[NO_3]$ is the concentration of nitrate in $mol\ L^{-1}$,
R is the ideal gas constant, 8.314 $J\ mol^{-1}\ K^{-1}$, and
T is the temperature in K.

The model expression given in Equation (**1**) was generated from testing within a specific range of salt concentrations and temperatures;[12] the current applicable range for the model expression is given in Table 2.1.

Table 2-1. Limits of Applicability for Glycolate Thermolysis Model Expression.

Parameter	Minimum	Maximum
Aluminum (M)	9.64E-04	2.49E+00
Nitrite (M)	2.21E-01	2.78E+00
Nitrate (M)	6.55E-02	6.34E+00
Hydroxide (M)	4.66E-02	2.30E+01
Sulfate (M)	4.94E-04	2.50E-01
Carbonate (M)	2.38E-03	6.54E-01
Sodium (M)	3.40E-01	2.56E+01
Temperature (°C)	60	170

To avoid potential flammability issues due to thermolysis of glycolate in the CSTF, SRNL was tasked to quantify and mitigate glycolate returns from DWPF's recycle stream.[13] Laboratory scale studies using chemical simulants and radioactive waste samples were completed to evaluate the feasibility of using sodium permanganate to destroy glycolate in the RCT. The results from these laboratory studies were summarized in a series of reports.[14-18]

Tests at caustic conditions demonstrated sodium permanganate was effective in converting glycolate to oxalate, and permanganate (Mn^{7+}) was reduced to manganate (Mn^{6+}) with no significant formation of carbon dioxide or carbonate. Equation (**2**) was found to best describe the observed reaction of glycolate with permanganate under nominal and low glycolate entrainment conditions.[16]

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

The oxidant stoichiometry is effectively defined by the molar ratio of permanganate to glycolate (P/G). Testing confirmed that glycolate at starting concentrations ranging from 68 to 5100 mg/L, can be reduced below reportable limits of 10 to 100 mg/L respectively.[a]

A kinetic model was developed to predict P/G ratios and reaction durations required to reduce initial glycolate concentrations to a desired value in the RCT.[19] This model assumes current RCT processing conditions with a pre-strike with caustic (NaOH) and sodium nitrite for corrosion control concerns. The model assumes an initial fixed glycolate concentration, but is presently being extended to incorporate a permanganate pre-strike to the caustic heel prior to glycolate carryover.[20] For the purpose of this analysis,

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[a] Note: Subsequent development of NMR methodology has decreases quantitation limits to lower levels.

it is assumed that the glycolate mitigation process is performed within the RCT and with chemicals and fresh recycle material added prior to the permanganate strike.

3.0 Methodology

3.1 Conditions and Assumptions

The Block Flow Diagram Revision A issued in March 2021 is the basis for the flowsheet.[2] The process contains two major unit operations, crossflow filtration and evaporation. The concentrated solids stream from the crossflow filter is sent to a CSTF sludge batch preparation tank and the filtrate is fed to the evaporator. The evaporator condensate is sent to ETF and the concentrate is sent to a CSTF salt batch preparation tank.

The RCT material composition is based on process history and the feed basis considered varies. At one extreme, the current addition of sodium hydroxide and sodium nitrite is considered, with pH >13 and nitrite:nitrate of at least 1.66:1. At the other extreme, the RCT is adjusted by addition of the full amount of sodium nitrite but only the amount of sodium hydroxide to bring the pH to 9. There are unknowns for future process changes, including the NGA flowsheet implementation and the replacement of Antifoam 747 with Momentive™ Y-17112 antifoam, that are not fully reflected in the RCT composition based on DWPF process history.

The following chemical and process assumptions applied for the evaluations of the DWPF Recycle Diversion Process:

- Nitric-Glycolic Acid Flowsheet implemented
- New DWPF antifoam Momentive™ Y-17112 implemented with no new degradation species observed in the SMECT and OGCT condensate streams (due to the high stability of the new antifoam and the expectation that lower antifoam addition rates are expected relative to the current antifoam)
- Only SMECT, OGCT, and chemical addition contributions to the RCT considered for baseline case
- RCT volume: 9,000 gallons (including NaOH and $NaNO_2$ additions to heel)
- RCT volume with added permanganate: 9,100 gallons
- Nominal Hydroxide: 0.16 M (assuming 75 gallons of 19.1 M NaOH added to heel, current addition amount). Lower hydroxide addition also considered.
- Nitrite: 0.16 M (due to addition of 215 gallons of 6.6 M $NaNO_2$ to heel) [3]
- Permanganate: 0.018 M (assuming no reaction with glycolate, 135 gallons[b] of 1.64 M (20 wt%) $NaMnO_4$ to 9,000 gallons of RCT)[3]
- Total Na^+: 0.34 M
- Assumed liquid density: 1.0 g/mL
- 0.12 wt. % Frit 803 (due to addition of 41 kg frit per 9100-gallon RCT batch; partial dissolution expected)
- Frit 803 composition: SiO_2 – 78.0 wt. %, Na_2O – 8.0 wt. %, B_2O_3 – 8.0 wt. %, Li_2O – 6.0 wt. %
- pH: 9 to $\geq$13 (due to addition of 50 wt. % NaOH to tank heel)
- The glycolate mitigation process is that outlined in the modeling report.[19]
- Permanganate reaction time before filtration: 4-48 hours
- In the absence of a major foamover, the initial glycolate concentration in the RCT without glycolate mitigation would be 125 mg/L or less.
- Final glycolate (following permanganate strike): 1 mg/L
- RCT temperature: 30 °C

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[b] 135 gallons is the working volume of the permanganate tank and is considered the maximum amount for a single addition unless there is a special evolution to address a carryover event. The expected nominal amount is closer to 60 gallons.

- Filtration temperature: <50 °C
- Evaporator temperature: 60-120 °C (based on vacuum or atmospheric operations, respectively)
- Evaporator concentrate Na^+: 5.6 to 7.0 M
- Evaporator concentration factor: 16.3 to 20.3[c]

3.2 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60.[21] This document, including all calculations, was reviewed by Design Verification by Document Review. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.[22] Calculations are recorded in the electronic laboratory notebook system. All work, analysis, and documentation were performed with quality assurance methods commensurate with the Safety Class data requirements.[8]

4.0 Results and Discussion

4.1 Glycolate Thermolytic HGR

4.1.1 HGR in RCT and crossflow filter

At the low temperatures (≤50 °C) in the DWPF recycle stream, the radiolytic HGR would be expected to be dominant in comparison to the thermolytic HGR.[11] Changing the amount of sodium hydroxide added to the RCT heel to target a pH of 9 would result in sodium and hydroxide concentrations below the applicable range, shown in Table 2-1, for the Glycolate Thermolytic HGR expression. While this gap exists, a significant reduction in the HGR would be expected at the lower hydroxide and sodium concentration when compared to the current RCT conditions. Additionally, extrapolation of the model to temperatures <60 °C is predicted to give a larger HGR than what the actual real waste tests suggest.[12] While extrapolations may be performed with minimal risk to the conservative assumptions made in model generation, a bounding HGR for the recycle stream is given below that is within the current minimal limits of the model. Any permanganate strikes for glycolate mitigation in the RCT would further lead to similar reduction in the HGR. All species that have a positive influence on thermolytic HGR are soluble in the aqueous waste stream and as such, the crossflow filtration is not anticipated to have an impact on HGR.

The model-predicted thermolytic HGR for glycolate can be given with current RCT chemistry (pH ≥13) without glycolate mitigation as a bounding rate, assuming a glycolate concentration of 125 mg/L in the RCT, a bounding temperature of 60 °C, and sodium and anion concentrations that meet minimum model limits. The model-predicted HGR is 1.67E-12 $ft^3\ gal^{-1}\ hr^{-1}$, which is insignificant in comparison to the current limits on radiolytic HGR in the recycle stream. The DWPF recycle stream is currently limited to an HGR of 4.5E-06 $ft^3\ gal^{-1}\ hr^{-1}$ at 25 °C for transfers to CSTF.[23] Additionally, previous testing with a Tank 22 slurry sample gave a measurable HGR of 1-2E-07 $ft^3\ gal^{-1}\ hr^{-1}$ at all temperatures, which is consistent with radiolytic hydrogen generation from sludge solids.[11]

4.1.2 *HGR in Evaporator*

The assumed concentration factor range in the DWPF recycle stream evaporator system is 16.3 to 20.3. Salt concentrations in the evaporator bottoms within the assumed concentration factor range fall within the applicable model limits shown in Table 2-1 for the Glycolate Thermolytic HGR expression. Assuming an initial glycolate concentration of 125 mg/L in the RCT, the maximum glycolate concentration in evaporator bottoms would be 2,540 mg/L. Similarly, the assumed initial glycolate concentration would be 1 mg/L with

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[c] This is calculated from the concentration of RCT material with 0.34 M of Na^+ to an evaporator bottoms concentration of 5.6 to 7.0 M Na^+. These are being considered as maximum values, and this analysis does not evaluate whether these concentration factors are attainable within the process.

a permanganate strike in the RCT; this would give a maximum concentration of 20.3 mg/L in the evaporator bottoms. It is assumed that the anticipated operating temperature for the wiped-film evaporator is 60 °C, and if an atmospheric evaporator is used instead, then the anticipated maximum operating temperature would be 120 °C. Table 4.1 gives the model predicted HGR in the concentrated evaporator bottoms using both evaporator options with and without glycolate mitigation.

Table 4-1. Model-Predicted Thermolytic HGR from Glycolate in the DWPF Recycle Evaporator System.

Evaporator	Permanganate Strike in RCT	Max Temp.	Glycolate (mg/L)	Model-Predicted HGR ($ft^3\ hr^{-1}\ gal^{-1}$)
WFE (vacuum)	No	60 °C	2540	2.70E-07
Atmospheric	No	120 °C	2540	2.51E-05
WFE (vacuum)	Yes	60 °C	20.3	2.16E-09
Atmospheric	Yes	120 °C	20.3	2.01E-07

4.1.3 Other Potential Flammability Program Impacts

There are two other potential impacts to flammability programs within DWPF Recycle Diversion and downstream facilities that are not directly related to HGR calculations.

First, the release of dissolved flammable gasses during heating and boiling may be more relatively significant for a vacuum evaporator. Hydrogen from radiolysis and other volatile components can be dissolved at small concentrations in the aqueous phase. Upon heating, the solubility of hydrogen and other gases in the aqueous phase decreases, and the components are released into the vapor phase. This mechanism is still applicable to vacuum evaporation, where the lower gas phase pressure facilitates release of dissolved gases at lower temperatures. In addition to radiolytic and thermolytic hydrogen generation, the release of previously generated hydrogen and other dissolved gases should be considered during evaporator ventilation design.

Second, the assumptions for the CSTF evaporator modeling reports used to define 2H and 3H evaporator concentration factors are predicated on the recycle stream not significantly changing.[19,24] The DWPF Recycle Diversion process will change the recycle stream to CSTF to the extent that model assumptions should be reevaluated. However, when the DWPF Recycle Diversion process is implemented, the use of the 3H evaporator may be phased out, making the concentration factor analysis no longer applicable. If the CSTF evaporator models are still applicable at the time of DWPF Recycle Diversion implementation, we recommend that a follow-up evaluation be performed to assess the extent of the impact on concentration factor model assumptions.

4.2 Glycolate Mitigation Process

4.2.1 Experimental Test Coverage

Studies were designed to simulate an RCT containing glycolate at low (65 mg/kg), nominal (125 mg/L), and high (~4500 mg/L) concentrations to encompass routine operations and foamover conditions in DWPF. Prototypical experiments were conducted in alkaline conditions at pH ~13, but no experimental data exists for the oxidation of glycolate using sodium permanganate between pH 9 and 13. Particular gaps exist in the kinetics of glycolate oxidation, the fate of permanganate, and the destruction of nitrite.

The molar ratio of nitrite to nitrate in DWPF returns is kept above 1.66 for corrosion control concerns.[25] In the Formic-Acid flowsheet, nitrite and caustic are added to the RCT heel before the addition of condensate to eliminate the need for chemical addition steps prior to transfer out of the RCT. Results from SRNL testing and published reports demonstrated nitrite is unreactive towards permanganate in highly caustic solutions[17,18,26] and the addition of permanganate prior to nitrite had little effect on the overall reaction. The reaction of permanganate with nitrite was reported to be much more significant at pH 11 and below.[27] Experiments would need to be performed in RCT simulants at pH <13 to understand the kinetics of the permanganate-nitrite reaction in the range of pH 9-13 and to evaluate off-gas generation in this range.

A number of experiments were performed at pH <12 in down-select and protocol tests for glycolate destruction.[15,16] In these experiments, nitrite was added *after* condensate addition to avoid the potential for oxidation of nitrite to nitrate or NO_x by the permanganate intended for glycolate destruction. However, the initial RCT simulant contained a small amount of nitrite to simulate residual from the RCT heel. While not the focus of the scoping reports, the oxidation of nitrite was monitored in RCT simulants at pH 3, 4, and 8 after the addition of permanganate.[15,16] These measured nitrite concentrations significantly decreased after the addition of permanganate.[d]

Tests at caustic conditions demonstrated sodium permanganate was effective in converting glycolate to oxalate, while permanganate (Mn^{7+}) is reduced to manganate (Mn^{6+}). Manganate is known to disproportionate to manganese (Mn^{4+}) and permanganate in all but highly alkaline solutions. The formed manganese typically precipitates as MnO_2 and the permanganate is available for additional oxidation reactions. It was noted that manganate appeared to persist in the highly alkaline RCT simulants for several weeks.[16]

It is likely that at pH <13 a different reaction mechanism would dominate, where permanganate is reduced to manganese dioxide as seen in Equation (**3**) below. This reaction requires less permanganate and glycolate is fully oxidized to carbon dioxide.

$$\mathbf{C_2H_3O_3^- + 2MnO_4^- = 2CO_2(g) + 2MnO_2(s) + 3OH^-} \qquad (3)$$

4.2.2 Potential impacts of glycolate on filtration and/or evaporation within Recycle Diversion

Post precipitation of MnO_2 from soluble manganate may be a downstream impact in the WFE if the recycle stream is highly caustic but may have little impact at pH < 12 as the precipitation reaction is expected to occur in the adjustment tank. The formation of MnO_2 solids may increase filtration times, but no evidence of corrosion from permanganate oxidation was observed in experiments simulating the DWPF RCT, transfer-lines and waste tank materials of construction in highly alkaline solutions.[28]

4.2.3 Other Potential Recycle Diversion Impacts

Without the DWPF Recycle Diversion process, the RCT material is transferred to CSTF and stored in Tank 22. The Tank 22 material is sent to Tank 38 or 43 and processed in the 2H evaporator system. Ultimately, material from Tanks 38 and 43 is sent to a salt batch preparation tank, either directly or through other CSTF waste tanks. With the DWPF Recycle Diversion process, the evaporator bottoms may be sent directly to a salt batch preparation tank.

Based on the more direct route to SWPF, the amount of time between the Glycolate Mitigation permanganate strike and processing the evaporator bottoms in SWPF could be shortened to just over six weeks. Thus, there is a slight risk that a higher level of manganate would be transferred and processed in SWPF with the DWPF Recycle Diversion process than would be encountered for the Tank 22 to 2H-

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[d] Nitrite measurements in these experiments were performed after samples were quenched with sodium sulfite, which is known to interfere with the nitrite measurement.

evaporator system processing. Manganate can potentially react with organic components of the SWPF solvent system. It may be prudent to gather additional data to determine if this could result in precipitation of MnO_2 solids in the SWPF solvent extraction process, which could lead to accumulation of MnO_2 solids in the SWPF contactors or fouling of coalescers.

4.2.4 Recommendations

Additional experiments are required to understand the effect of a permanganate strike on RCT chemistry below pH 13. Studies should focus on quantifying the rate and extent of nitrite destruction as a function of pH and the effect of nitrite destruction on glycolate oxidation. Additional experiments are also needed to study possible changes to the glycolate-permanganate reaction mechanism between pH 9 and 13.

4.3 Glycolate Mitigation Model

A kinetic model was developed to predict P/G ratios and reaction durations required to reduce initial glycolate concentrations to a desired value in the RCT in highly alkaline conditions.[19] This model assumes current RCT processing conditions with a pre-strike with caustic (NaOH) and sodium nitrite for corrosion control concerns.

The model was primarily based on the data in three reports where the nominal condition of the RCT after chemical additions was considered, with pH just above 13.[16-18] The model is being relied upon as part of a control to assure that the CSTF WAC is being met and CSTF flammability assumptions are protected. It is expected that glycolate going to CSTF will be limited to less than or equal to 1 mg/L.[6]

Since the nitrite reaction consumes a portion of the permanganate needed for the oxidation of glycolate, the model may be impacted in a non-conservative manner below pH 13. Due to the use of this model, it is recommended that further investigation of the glycolic mitigation be performed at pH 12 and below if those conditions will be encountered in the RCT.

5.0 Conclusions

The impact of thermolytic hydrogen generation from glycolate in DWPF recycle was evaluated in support of the DWPF Recycle Diversion Project. The evaluation and identification of gaps in knowledge considered the range of conditions anticipated in the process including the addition of sodium permanganate, the range of RCT pH values considered (i.e., 9 to >13), and the species concentrations during WFE processing. All species that have measurable influence on thermolytic HGR are soluble in the aqueous waste stream and thus crossflow filtration is not anticipated to have an impact on HGR. The HGR expression for glycolate thermolysis predicts the highest HGR of 2.51E-05 $ft^3\ hr^{-1}\ gal^{-1}$ in the atmospheric evaporator with no glycolate mitigation. The lowest predicted HGR of 2.16E-09 $ft^3\ hr^{-1}\ gal^{-1}$ is in the WFE evaporator under vacuum with glycolate mitigation.

The persistence of manganate will be greatly reduced at pH <13 likely resulting in the rapid formation of MnO_2 solids in the RCT. The presence of MnO_2 solids may increase filtration times, but little impact from the permanganate oxidation process is expected on the effectiveness of crossflow filtration or evaporation. However, two streams from the Recycle Diversion process (i.e., the concentrated solids stream from the filter and the bottoms from the WFE) will likely be sent to the CSTF. In order to meet an expected CSTF WAC for glycolate to limit HGR, the Glycolate Mitigation process and the inputs and assumptions for Glycolate Mitigation were also evaluated.

Results from SRNL testing demonstrated nitrite is unreactive towards permanganate in highly caustic solutions (i.e., pH >13) and permanganate (Mn^{7+}) is reduced to manganate (Mn^{6+}). Changes to RCT chemistry may occur at pH <13 and affect parameters required for the glycolate mitigation process. At lower pH, nitrite oxidation becomes more favorable and may compete with glycolate in the permanganate oxidation reaction. This may reduce the effectiveness of the permanganate strike and also require the chemical addition strategy for the RCT to be modified to incorporate the addition of nitrite after glycolate destruction. Also, manganate is likely to further reduce to manganese dioxide (MnO_2) and reduce the required P/G ratio for glycolate destruction. Additional experiments are recommended to understand the effect of a permanganate strike on RCT chemistry in the range of pH 9-13.

The kinetic model used to predict the P/G ratios and reaction durations required to reduce initial glycolate concentrations to a desired value in the RCT was primarily based on data where the nominal condition of the RCT after chemical additions was considered with pH >13. Since the nitrite reaction may consume a portion of the permanganate, and the permanganate is needed for the oxidation of glycolate, the model may be impacted in a non-conservative manner below pH 13. Due to the use of this model, it is recommended that further investigation of the glycolic mitigation be performed below pH 13 if those conditions will be encountered in the RCT.

6.0 Recommendations, Path Forward or Future Work

Additional experiments are required to understand the effect of a permanganate strike on RCT chemistry below pH 13. Studies should focus on quantifying the rate and extent of nitrite destruction as a function of pH and the effect of nitrite destruction on glycolate oxidation. Additional experiments are also needed to study possible changes to the glycolate-permanganate reaction mechanism between pH 9 and 13 and potential downstream impacts from soluble manganate.

Since the nitrite reaction consumes a portion of the permanganate needed for the oxidation of glycolate, the model may be impacted in a non-conservative manner below pH 13. Due to the use of this model, it is recommended that further investigation of the glycolic mitigation be performed at pH 12 and below if those conditions will be encountered in the RCT.

If the CSTF evaporator models are still applicable at the time of DWPF Recycle Diversion implementation, we recommend that an evaluation be performed at that time to assess the extent of the impact on concentration factor model assumptions.

7.0 References

1. G. Winship, “Diversion of DWPF Recycle from HLW Tank Farms Systems Engineering Alternatives Analysis,” Savannah River Remediation, Aiken, SC, G-AES-S-00005, Rev. 0, 2019.
2. “Defense Waste Processing Facility Block Flow Diagram,” M-M5-G-00683, Rev. A, 2021.
3. D.B. Henley and S.T. Isom, “Initial OLI Runs in Support of the DWPF Recycle Diversion Project,” Savannah River Remediation, Aiken, SC, SRR-LWE-2021-00016, Rev. 0, 2021.
4. T.L. Fellinger, D.T. Herman, and M.E. Stone, “DWPF Recycle Evaporator Shielded Cells Testing,” WSRC-TR-2005-00309, Rev. 0, 2005.
5. M.E. Stone, W.E. Daniel, and D.K. Peeler, “DWPF Recycle Evaporator Flowsheet Evaluation (U),” Savannah River National Laboratory, Aiken, SC, WSRC-TR-2005-00226, Rev. 0, 2005.
6. E.W. Holtzscheiter, “Qualitative Assessment of the Risks and Benefits of the Implementation of the Nitric-Glycolic Acid (NGA) Flowsheet in the Defense Waste Processing Facility (DWPF),” Savannah River Remediation, Aiken, SC, SRR-WSE-2020-00020, Rev. 0, 2020.
7. A.W. Wiggins Jr., “DWPF Recycle Diversion - Glycolate Destruction,” Savannah River Remediation, Aiken, SC, X-TTR-H-00108, Rev. 1, 2021.
8. W.D. King, C.J. Martino, and B.J. Wiersma, “Task Technical and Quality Assurance Plan for DWPF Recycle Diversion: Glycolate Hydrogen Generation and Mitigation, Recycle Chemistry, and Evaporator Corrosion and Erosion Evaluations; and Recycle Simulant Formulation,” Savannah River National Laboratory, Aiken, SC, SRNL-RP-2021-00538, Rev. 0, 2021.
9. A.W. Wiggins Jr., “Technology Development Roadmap for DWPF Recycle Diversion Project Flowsheet,” Savannah River Remediation, Aiken, SC, G-ESR-H-00255, Rev. 0, 2021.
10. D.P. Lambert, M.S. Williams, C.H. Brandenburg, M.C. Luther, J.D. Newell, and W.H. Woodham, "Sludge Batch 9 Simulant Runs Using the Nitric-Glycolic Acid Flowsheet," Savannah River National Laboratory, SRNL-STI-2016-00319, Rev. 0, 2016.
11. C.J. Martino, J.M. Pareizs, and J.D. Newell, “Thermolytic Hydrogen Generation Testing of Tank 22 Material ” Savannah River National Laboratory, Aiken, SC, SRNL-STI-2018-00385, Rev. 0, 2018.
12. W.H. Woodham and C.J. Martino, “Evaluation of Thermolytic Production of Hydrogen from Glycolate and Common Tank Farm Organics in Simulated Waste,” Savannah River National Laboratory, Aiken, SC, SRNL-STI-2019-00605, Rev. 1, 2020.
13. G. Chen and M. Clark, "Evaluation of Chemical Additives for Glycolate Mitigation," Savannah River Remediation, LLC, Aiken, SC, X-TTR-S-00068, Rev. 0, 2018.
14. T.B. Peters and C.A. Nash, "Defense Waste Processing Facility (DWPF) Glycolate Mitigation: Scoping Test Results," Savannah River National Laboratory, Aiken, SC, SRNL-L3100-2018-00043, Rev. 0, 2018.
15. D.P. Lambert, A.M. Howe, M.S. Williams, C.L. Trivelpiece, and R.G. William, "Evaluation of Chemical Additives for Glycolate Destruction in the Recycle Collection Tank," Savannah River National Laboratory, Aiken, SC, SRNL-STI-2018-00585, Rev. 1, 2019.
16. J.R. Zamecnik, D.P. Lambert, W.T. Riley, and W.G. Ramsey, "Permanganate Oxidation of Defense Waste Processing Facility (DWPF) Recycle Collection Tank (RCT) Simulants – Protocol Runs for Nominal and Chemical Process Cell (CPC) Foamover Conditions," Savannah River National Laboratory, Aiken, SC, SRNL-STI-2019-00292, Rev. 0, 2019.
17. M.J. Siegfried, W.G. Ramsey, and M.S. Williams, "Permanganate Oxidation of Defense Waste Processing Facility (DWPF) Recycle Collection Tank (RCT) Simulants Larger Scale Protocol Runs - Chemical Process Cell (CPC) Nominal and Foamover Conditions," Savannah River National Laboratory, Aiken, SC, SRNL-STI-2019-00588, Rev. 0, 2019.
18. C.A. Nash and M.J. Siegfried, "Permanganate Oxidation of Actual Defense Waste Processing Facility (DWPF) Slurry Mix Evaporator Concensate Tank (SMECT) and Offgas Condensate Tank (OGCT) Samples to Remediate Glycolate," Savannah River National Laboratory, Aiken, SC, SRNL-STI-2020-00012, Rev 0, 2020.

19. M.J. Siegfried, C.A. Nash, S.P. Harris, W.H. Woodham, and T.L. White, "Modeling the Destruction of Glycolate in the Defense Waste Processing Facility (DWPF) Recycle Stream and Concentration Factors for Glycolate in the 2H Evaporator," Savannah River National Laboratory, Aiken, SC, SRNL-STI-2020-00247, 2020.
20. E.W. Holtzscheiter, "Models for the Destruction of Glycolate in the RCT," Savannah River Remediation, Aiken, SC, X-TTR-S-00083, Rev. 1, 2021.
21. Conduct of Engineering Technical Reviews, Manual E7, Procedure 2.60, Rev, 18. Savannah River Site, Aiken, SC, 2019.
22. "Savannah River National Laboratory Technical Report Design Check Guidelines," WSRC-IM-2002-00011, Rev. 2, 2004.
23. W.B. Dean, "Waste Compliance Plan for Radioactive Liquid Waste Transfers From the DWPF to 241-H Tank Farm (U)," Savannah River Remediation, Aiken, SC, X-WCP-S-00001 Rev. 2, 2020.
24. W.H. Woodham, "Calculation of Glycolate Concentration Factors Across the 242-25H (3H) Evaporator System," Savannah River National Laboratory, Aiken, SC, SRNL-STI-2020-00385, 2020.
25. K. Martin, "CSTF Corrosion Control Program," Westinghouse Savannah River Company, Aiken, SC, WSRC-TR-2002-00327 Rev. 9, 2015.
26. D.L. Halgren, "Peroxide Deconstruction Testing for the 200 Area Effluent Treatment Facility," Hanford Site, HNF-45613, 2010.
27. A. Obuchi, A. Okuwari, and T. Okabe, "The Rate of Oxidation Reaction of Nitrite in an Alkaline Permanganate Solution," *Nippon Kagaku Kaishi,* 1974 [8] 5 (1974).
28. R.E. Fuentes, "Impact of Permanganate Oxidation of Glycolate on Corrosion of the Defense Waste Processing Facility (DWPF) Recycle Collection Tank (RCT), Transfer-line and Waste Tank Materials of Construction (MoC)," Savanna River National Laboratory, SRNL-STI-2019-00742, Rev. 0, 2020.

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