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Analysis of Defense Waste Processing Facility (DWPF) Condensate Samples and Evaluation of the Glycolate Destruction Process during Nitric-Glycolic Flowsheet Transition

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EXECUTIVE SUMMARY

Glycolate concentrations were measured by the Savannah River National Laboratory (SRNL) in Slurry Mix Evaporator Condensate Tank (SMECT) and Recycle Collection Tank (RCT) samples retrieved after implementation of the Nitric-Glycolic Acid flowsheet at the Defense Waste Processing Facility (DWPF). No glycolate has been detected in any sample using Ion Chromatography (IC) with a detection limit of 8 mg/L, and no glycolate has been detected using either IC or Proton Nuclear Magnetic Resonance Spectroscopy (^{1}HNMR) after a permanganate strike was performed in the RCT.

Measured Glycolate Concentrations and Uncertainty (%U) in DWPF, SMECT, and RCT Samples

Sample ID	Batch No.	Retrieval Date	IC mg/L	^{1}HNMR mg/L (%U)	Sample Notes
RCT 29968	5123	9/4/2022	< 8	4.8 (8)	Pre Permanganate Strike
RCT 29985	5123	9/5/2022	< 8	< 1.4	9 hours Post Permanganate
SMECT 29946	4846A	9/4/2022	< 8	8 (8)	--
RCT 30283	5153	11/10/2022	< 8	2.0 (6)	Pre Permanganate Strike
RCT 30286	5153	11/10/2022	< 8	< 1.0	4 hours Post Permanganate
RCT 30287	5153	11/10/2022	< 8	< 1.0	8 hours Post Permanganate
SMECT 30455	4896	12/8/2022	< 8	3.1	*Average Value 0.50 %RSD*

Duplicate tests were performed at approximately 17 °C on SMECT sample 30455 to demonstrate nominal operation of the permanganate oxidation process under protocols similar to those used in the DWPF RCT. The sample was pre-adjusted with corrosion control chemicals sodium nitrite and sodium hydroxide. Sodium glycolate was added to the SMECT sample and permanganate concentrations were selected to obtain measurable values after 4 hours of reaction. Results were compared with a kinetic model developed by SRNL to predict the mass of sodium permanganate and reaction times required to achieve a targeted glycolate concentration in a SMECT sample at 17 °C. The model adequately predicted glycolate concentration with one hour reaction times. After four hours, the model underpredicted glycolate concentration for the first test and adequately predicted glycolate for the duplicate test.

A discussion of the glycolate measurements in this study and their relation to processing conditions at DWPF is provided.

- The majority of data used to determine the form of the kinetic model was acquired within one hour after the addition of permanganate. Additionally, glycolate was not detected below 10 mg/L for the majority of previous experiments, including the previous radioactive waste demonstration.

- Sludge solids were previously observed to enhance the glycolate destruction process. The experiments described in this report were on a SMECT sample with no observed solids.

- Experiments with radioactive waste were performed in the SRNL shielded cells at 17 °C, which is lower than the 20-30 °C typical for DWPF RCT operating conditions. Higher reaction temperatures will increase glycolate destruction rates.

- The RCT contains a heel that likely includes unreacted permanganate from prior batches. Any unreacted permanganate was unaccounted for in this study, and would lead to higher P/G ratios and faster glycolate destruction rates.

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LIST OF ABBREVIATIONS

ACSM	Analytical Characterization and Sample Management
CST	Crystalline Silicotitanate
CSTF	Concentration, Storage and Transfer Facilities
DMA	Direct Mercury Analysis
DWPF	Defense Waste Processing Facility
HDPE	High Density Polyethylene
^{1}HNMR	Proton Nuclear Magnetic Resonance Spectroscopy
IC	Ion Chromatography
ICPES	Inductively Couples Plasma Emission Spectroscopy
IS	Internal Standard
MST	Monosodium Titanate
NGA	Nitric-Glycolic Acid
OGCT	Offgas Condensate Tank
P/G	Molar Ratio of Permanganate to Glycolate
RCT	Recycle Collection Tank
RSD	Relative Standard Deviation
SAM	Standard Addition Method
SMECT	Slurry Mix Evaporator Condensate Tank
SRMC	Savannah River Mission Completion
SRNL	Savannah River National Laboratory
TMSP	Trimethylsilylpropanoic Acid
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
WAC	Waste Acceptance Criteria

1.0 Introduction

The Savannah River Site's Defense Waste Processing Facility (DWPF) has transitioned to the Nitric-Glycolic Acid (NGA) Flowsheet, replacing formic acid with glycolic acid as the reducing acid.[1] To avoid flammability concerns due to thermolysis of residual glycolate in returns to the Concentration, Storage and Transfer Facilities (CSTF), Savannah River Mission Completion (SRMC) destroys glycolate in DWPF's Recycle Collection Tank (RCT) via chemical oxidation using 20 wt% sodium permanganate.

Tests with simulated and radioactive waste 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.[2,3] Equation (1) was found to best describe the observed reaction of glycolate with permanganate under nominal and low glycolate entrainment conditions.[4]

$$\mathbf{C_2H_3O_3^- + 4MnO_4^- + 5OH^- = C_2O_4^{2-} + 4MnO_4^{2-} + 4H_2O} \tag{1}$$

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 was developed by Savannah River National Laboratory (SRNL) to describe the destruction of glycolate via chemical oxidation with sodium permanganate when RCT liquid is pre-adjusted with caustic and nitrite before permanganate addition.[5] 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 four hours, but the model is more broadly applicable.[6]

The model is composed of Equations (2) and (3) below. The equations together do not have an analytical solution that can be written out and numerical integration is required to obtain results. For the present study, the model used an instantaneous initial charge of permanganate which negates the feed term $a*P_a$. A follow-on memo provides model results for 30 cases of glycolate destruction in the RCT with varying initial glycolate concentrations and P/G ratios.[7]

$$\mathbf{d[P]/dt = -K_1 * 4 * [G] * [P] - K_x * [P] + a * P_a} \tag{2}$$

$$\mathbf{d[G]/dt = -K_1 * [G] * [P] + a * G_a} \tag{3}$$

Where,

[G] = glycolate concentration in mmol,
[P] = permanganate concentration in mmol,
t = time in minutes,
K_1 = kinetic rate constant in $mmol^{-1}$ min^{-1},
K_x = loss term for permanganate in min^{-1}
a = feed rate in L min^{-1}
P_a = concentration of permanganate in the incoming flow in mmol
G_a = concentration of glycolate in the incoming flow in mmol

The model has a kinetic rate constant, K_1, and additional loss term for permanganate, K_x, to account for reactions with species other than glycolate. Values for $K_1 = 0.00286$ min^{-1} $mmol^{-1}$ and $K_x = 0.00276$ min^{-1} were derived using data from the radioactive demonstration of glycolate destruction using SMECT material from DWPF at 17 °C.[2,5] This run was selected for determination of rate constants since kinetics were slower than the OGCT demonstration and the resulting kinetic model was shown to bound at least 84% of previous data with 95% confidence.[5]

The transition plan to the NGA flowsheet states sodium permanganate will be added with at least 50% excess and the molar ratio of permanganate to glycolate (P/G) will be based on a residence time of 4 hours to ensure excess reaction time (actual reaction times will vary from ~8 to 24 hours).[1] The transition plan assumes the initial glycolate concentration for influents to the RCT is 30 to 65 mg/L and the amount of sodium permanganate required to be added to each RCT batch to destroy glycolate to ~1 mg/L is 31 to 76 gallons. This corresponds to P/G ratios of 11 to 29 and does not account for additional permanganate that is added for conservatism. The radioactive demonstration of glycolate destruction was aimed at minimizing sodium permanganate additions while achieving an endpoint glycolate concentration of about 10 mg/L, and 10 mg/L was expected to be sufficient to minimize the impact on CSTF.[2] More recently, the CSTF WAC set a limit for glycolate to less than or equal to 3 mg/L glycolate.[8]

SRMC requested that SRNL perform experiments to destroy glycolate in samples retrieved from the Slurry Mix Evaporator Condensate Tank (SMECT) at DWPF and demonstrate the kinetic model adequately predicts the mass of sodium permanganate and the reaction time required to achieve a targeted glycolate concentration (currently ~1 mg/L), or a value consistent with the CSTF Waste Acceptance Criteria (WAC). SMECT samples were used in place of RCT samples to remove uncertainty associated with residual oxidant in the RCT from previous permanganate strikes.

To compare measured glycolate results with model predictions, glycolate concentrations need to be measured at known times after the addition of sodium permanganate. During previous testing with actual waste, the SRNL detection limit for glycolate by Ion Chromatography (IC) was approximately 10 mg/L. Recent method development activities have demonstrated a detection limit for glycolate of approximately 1 mg/L and a limit of quantification of 3 mg/L using Proton Nuclear Magnetic Resonance Spectroscopy (^{1}HNMR).[9]

SRNL support was requested in a Technical Task Request (TTR).[10] A Task Technical and Quality Assurance Plan (TTQAP)[11] and run plan describing experiments to be performed were issued.[12]

2.0 Experimental Procedure

2.1 Sample Receipt and Initial Characterization

2.1.1 SMECT Sample 29946 and RCT Samples 29968 and 29985

Three 200 mL samples were received at SRNL on September 7, 2022 and sent directly to Analytical Characterization and Sample Management (ACSM) for analysis. Samples were labeled as SMECT 29946, RCT 29968 and RCT 29985.[13]

Both RCT samples were quenched by DWPF at the point of sample retrieval with sodium sulfite, reducing residual permanganate and terminating the glycolate destruction reaction. Sample RCT 29968 was retrieved prior to permanganate addition (9/4/22 at 1658). Sample RCT 29985 was retrieved approximately nine hours after 62.6 gallons of sodium permanganate was supplied to the RCT (9/5/22 at 1349). Sodium permanganate addition time began on 9/5/2022 at 0424 and finishing at 0429. The RCT volume was approximately 8690 gallons with a pH of 13.1 at the time of retrieval. The RCT volume was ~8840 gallons before the post-permanganate sample RCT 29985 was retrieved.

2.1.2 RCT Samples 30283, 30286 and 30287

Three 200 mL samples were received at SRNL on November 14, 2022 at the SRNL shielded cells. All three samples were quenched by DWPF at the point of sample retrieval with sodium sulfite to terminate the glycolate destruction reaction. Samples labeled as RCT 30283, RCT 30286 and RCT 30287 were respectively retrieved before the addition of permanganate, and 4 and 8 hours after the addition of permanganate. The as-received samples needed to be subdivided to ensure ACSM hood limits were not exceeded. Three 15 mL aliquots from each of the three samples (i.e., 45 mL per sample) were submitted to ACSM for analysis.[14]

2.1.3 SMECT Sample 30455

SRNL received SMECT 30455 in three stainless steel dip vials. The as-received samples were composited into one container for a combined volume of 465 mL. Figure 1 shows photographs of the as-received samples and the samples composited in a 1 liter Teflon bottle. A subsample of the composited SMECT material was submitted to ACSM for glycolate analysis by IC and ^{1}HNMR prior to initiation of the glycolate destruction study. After conclusion of the study, the remaining composited SMECT material was submitted for mercury, IC and Inductively Coupled Plasma Emission Spectroscopy (ICPES) analysis.

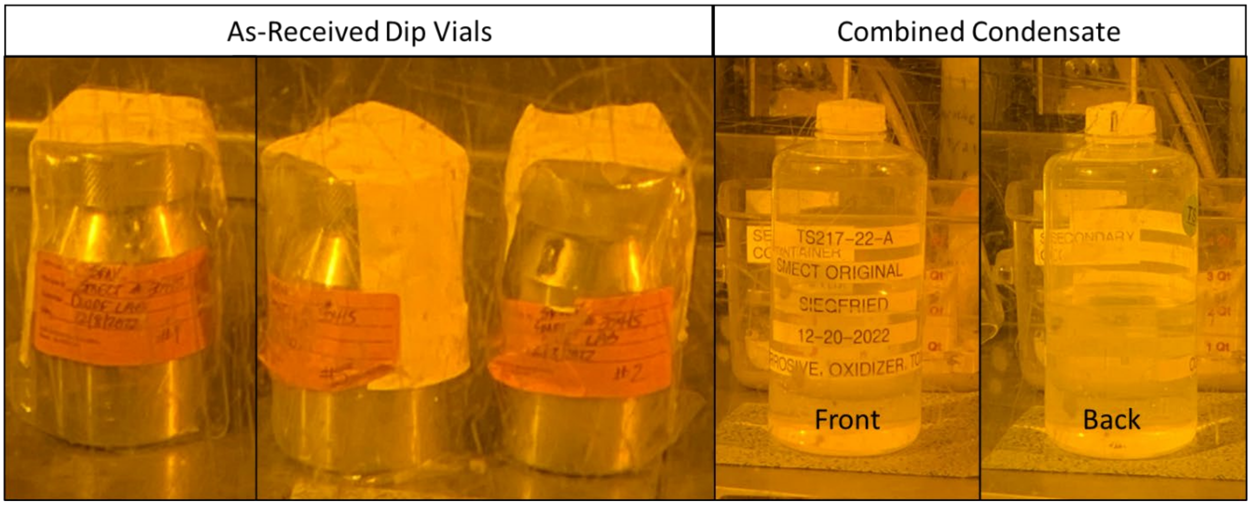


Figure 1: Photographs of as-received and composited SMECT samples

2.2 <u>Glycolate Destruction Test Protocol</u>

Duplicate tests were performed on SMECT sample 30455 to demonstrate nominal operation of the permanganate oxidation process under protocols similar to those used in DWPF. Sodium permanganate was added at a reduced amount to obtain measurable glycolate concentrations after 4 hours of reaction time. Both tests were performed in a clean 500 mL Erlenmeyer flask with a magnetic stir-bar. Mixing rate was set visually such that a vortex was observed with no air entrainment.

Glycolate in the composited SMECT sample was below the IC detection limit of 8 mg/L. The glycolate concentration was therefore assumed to be 8 mg/L and adjusted by adding sodium glycolate to obtain a final concentration of approximately 35 mg/L. Aqueous solutions of 50% sodium hydroxide and 6.6 M sodium nitrite were added to the SMECT sample to mimic DWPF processing of RCT condensate pre-adjusted with corrosion control chemicals.

Note that while volumes are given in the discussions here, masses were recorded during feed and reagent additions to batches. The following steps were performed for each of the duplicate tests:

1. Add ~210 mL of SMECT feed to the designated Erlenmeyer flask with mixing.
2. Add the pre-measured mass of 50% sodium hydroxide to the flask with mixing.
3. Add the pre-measured mass of 6.6 M sodium nitrite to the flask with mixing.
4. Add the pre-measured mass of sodium glycolate to the flask to obtain the desired glycolate concentration.
5. Mix for approximately 5 minutes, then pull a 50 mL slurry sample. This was the "Time 0" sample.
6. Add the pre-measured amount of 20 wt% sodium permanganate to obtain a P/G ratio of ~10. Start a timer to coincide with the sodium permanganate addition.
   Note: the P/G ratio was adjusted to account for the ~50 mL "Time 0" sample
7. Take and quench 50 mL samples for IC and ^{1}HNMR analysis at 1 and 4 hours after permanganate addition. These were the "Time 1" and "Time 2" samples, respectively.

Each sub-sample was approximately 50 mL in volume. Sample bottles were pre-loaded with sodium sulfite at three times the stoichiometric ratio to quench unreacted sodium permanganate at the time of sampling. Dose rates for all samples were below 5 mrem/hr whole body.

Table 2-1 provides a summary of the samples and analytical measurements performed and if a sample was quenched at the time of retrieval. Glycolate concentrations were measured on both the as-received and Time 0 samples using IC with a detection limit of 8 mg/L. All samples were measured using ^{1}HNMR with a limit of quantification of 3 mg/L and a limit of detection as low as 1 mg/L.

Table 2-1. Sample Frequency, Quench, and Analyses Performed on SMECT 30455

Sample	Quench	Analytical Method
As-Received SMECT Sample	None	IC-Glycolate, IC, ^{1}HNMR, ICPES, DMA
Pre-Permanganate Addition (i.e., "Time 0")	3x Sulfite	IC-Glycolate, ^{1}HNMR
One hour (i.e., "Time 1")	3x Sulfite	IC-Glycolate, ^{1}HNMR
Four Hours (i.e., "Time 2")	3x Sulfite	IC-Glycolate, ^{1}HNMR

2.3 Glycolate Measurements by ^{1}HNMR

Sample preparation for ^{1}HNMR analysis followed the previously established method.[15] Samples (~6 mL) were prepared in high density polyethylene (HDPE) bottles with aliquots of D_2O (~1.2 mL), trimethylsilylpropanoic acid (TMSP) as an internal standard (0.15 mL of 100 mg/L stock solution), and glycolate spikes. The sample cocktail was then treated with two strikes of 3 g crystalline silicotitanate (CST) and 1 g monosodium titanate (MST) at 10 seconds each and filtered through glass wool and 0.7 micron Whatman Puradisc glass microfiber syringe filters. A 0.5 M NaOH blank with D_2O and a control with D_2O, TMSP and glycolate were similarly treated with CST and MST strikes. Approximately 1.5 mL of sample is pipetted into 5 mm NMR tubes for analysis. Glycolate concentrations were calculated using both the internal standard (IS) and the standard addition method (SAM).

2.4 Scaling

A comparison between DWPF and laboratory scale volumes are provided in Table 2-2. The experiments were performed at 1/130,000 fraction of the RCT volume assuming 7310 gallons of DWPF condensate. Despite the small size, the chemistry is not expected to be scale dependent. The experiments did not include material representing the heel from the previous RCT batch. The volumes shown for additions to the experiments are shown before the removal of the approximately 50 mL Time 0 samples.

Table 2-2. Comparison of DWPF and Laboratory Scales

	DWPF (gal)	Run 1 (mL)	Run 2 (mL)
RCT Heel	1400	0	0
Condensate	7310	211	205
50% NaOH	75	2.39	2.39
6.6 M $NaNO_2$	215	6.84	6.84

2.5 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.[16] To match the requested Safety Class functional classification, this report has received a Design Verification by document review per Manual E7, Procedure 2.60, Section 5.3.[17] Data and observations for the experiments and the design checklists for this report are stored in electronic laboratory notebook experiment C8102-00273-10.

3.0 Results and Discussion

3.1 Initial SMECT Sample Characterization

Glycolate concentrations and 2 sigma uncertainty (%U) in the composited SMECT sample (i.e., SMECT 30455), as well as information on previous condensate samples obtained after implementation of the Nitric-Glycolic flowsheet at DWPF, are provided in Table 3-1. No glycolate has been detected by SRNL in any sample using IC, and no glycolate has been detected using either IC or ^{1}HNMR after a permanganate strike was performed in the RCT.

Table 3-1. Measured Glycolate Concentrations in DWPF SMECT and RCT Samples

Sample ID	Batch No.	Retrieval Date	IC mg/L	^{1}HNMR mg/L (%U)	Sample Notes
RCT 29968	5123	9/4/2022	< 8	4.8 (8)	Pre Permanganate Strike
RCT 29985	5123	9/5/2022	< 8	< 1.4	9 hours Post Permanganate
SMECT 29946	4846A	9/4/2022	< 8	8 (8)	--
RCT 30283	5153	11/10/2022	< 8	2.0 (6)	Pre Permanganate Strike
RCT 30286	5153	11/10/2022	< 8	< 1.0	4 hours Post Permanganate
RCT 30287	5153	11/10/2022	< 8	< 1.0	8 hours Post Permanganate
SMECT 30455	4896	12/8/2022	< 8	3.1*	--

**0.50 %RSD – average value of IS and SAM methods. Uncertainty is represented as %RSD because IS measurements were below 3 mg/L limit of quantitation.*

The glycolate concentration reported in Table 3-1 for SMECT 30455 was measured via ^{1}HNMR using both IS and SAM methods.[15] The concentration of 3.1 is an average of the two measurements with a relative standard deviation (RSD) of 0.50%.

Table 3-2 provides ICPES data, Table 3-3 measured anion concentrations, and Table 3-4 lists results from mercury analyses performed on the as-received SMECT sample (SMECT 30455). Based on these results, the highest concentration of metals detected in the SMECT is mercury (40 mg/L), followed by sodium (8.1 mg/L) and iron (2.8 mg/L). The forms of mercury detected were nearly equal parts inorganic (i.e., ionic), purgeable (i.e., elemental), and methyl (i.e., organic). The measured mercury species accounted for 74% of the measured total mercury.

Table 3-2. ICPES Results from the Composited SMECT Sample

Measured		Below Detection Limit			
Element	**mg/L (10% RSD)**	**Element**	**mg/L**	**Element**	**mg/L**
Al	0.365	Ba	< 0.009	P	< 0.115
B	0.389	Be	< 0.001	Pb	< 0.234
Cr	0.229	Ca	< 0.554	S	< 0.393
Cu	0.339	Cd	< 0.009	Sb	< 0.029
Fe	2.78	Ce	< 0.026	Sn	< 0.084
Mn	1.34	Co	< 0.021	Sr	< 0.017
Na	8.09	Gd	< 0.006	Th	< 0.119
Ni	0.21	K	< 0.557	Ti	< 0.052
Si	1.54	La	< 0.003	U	< 0.116
Zn	0.311	Li	< 0.324	V	< 0.017
		Mg	< 0.091	Zr	< 0.017
		Mo	< 0.038		

Table 3-3. Measured Anion Concentrations in the Composite SMECT Sample

Anion	mg/L (% U)	Anion	mg/L (% U)
Fluoride	< 10	Phosphate	< 10
Formate	< 10	Sulfate	< 10
Chloride	< 10	Oxalate	< 10
Nitrite	< 10	Bromide	< 50
Nitrate	4340 (10)		

Table 3-4. Concentration and Speciation of Mercury in the Composite SMECT Sample

Method	mg/L (% U)
Direct Mercury Analysis	39.6 (10)
Purgeable Mercury	10.3 (40)
Inorganic Mercury	9.94 (40)
Ethyl Mercury	< 1 (20)
Methyl Mercury	9.07 (20)

3.2 Glycolate Destruction Runs

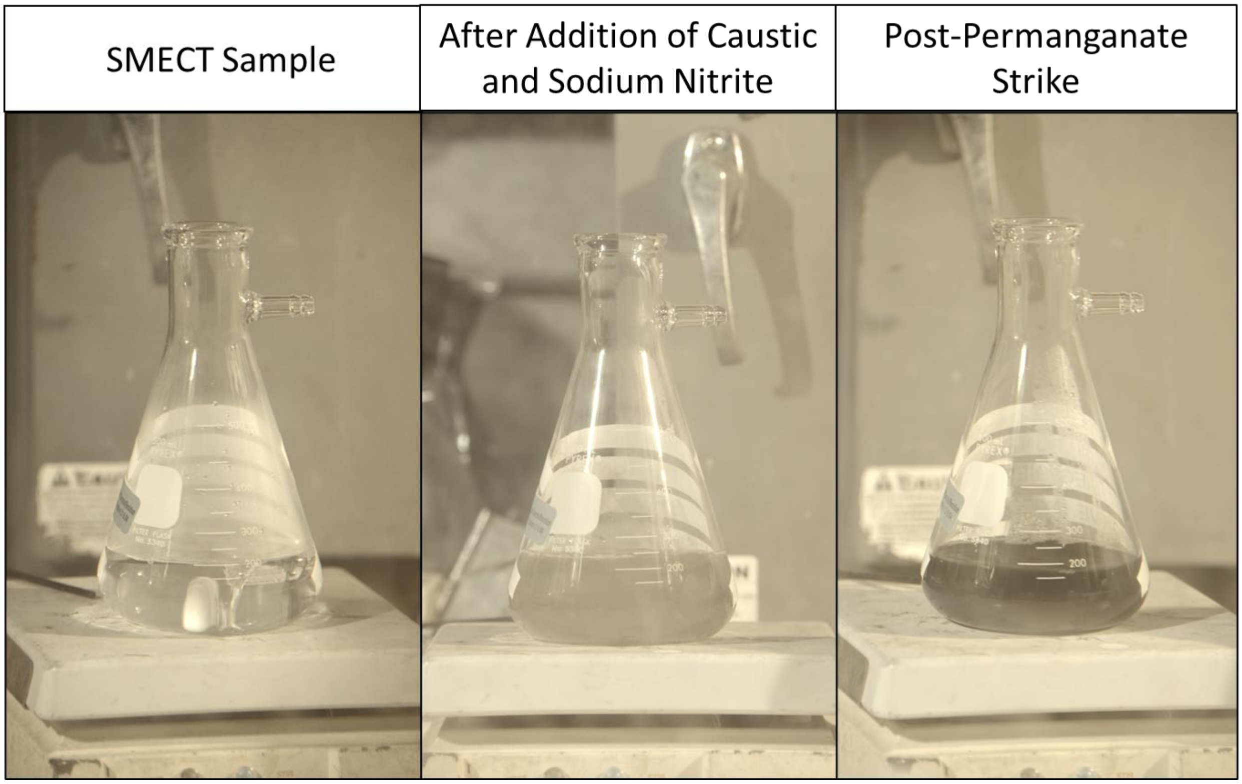
A list of parameters for the duplicate runs are found in Table 3-5. The temperature for both runs was measured to be approximately 17 °C using a thermocouple placed next to the reaction vessel. The temperature was assumed to be the ambient temperature inside the shielded cells during both runs. 17 °C is the lowest temperature agreed to in the run plan and lower than the typical RCT operational temperature of 20-30 °C.

Table 3-5. Reaction Conditions

	Initial Temp (°C)	Added Glycolate (mg/L)	Initial Reaction Volume (mL)	Time 0 Glycolate (mmol/L)	Time 0 Permanganate (mmol/L)	P/G Ratio
Run 1	17	32.0	170.8	0.492	4.84	9.8
Run 2	17	31.4	168.9	0.458	4.90	10.7

The initial reaction volume for both tests was approximately 170 mL. Included in this volume is the added 50% sodium hydroxide, 6.6 M sodium nitrite, additional sodium glycolate, and 20% sodium permanganate. It also accounts for material removed by the Time 0 sample obtained prior to the addition of sodium permanganate. Time 0 glycolate values were measured using IC. Time 0 permanganate values were measured gravimetrically. Units for Time 0 permanganate and glycolate are provided in mmol/L to be consistent with the model and the resulting P/G ratios are provided. P/G ratios were selected to allow sufficiently slow reaction kinetics to obtain measurable glycolate concentrations throughout the reaction.

Photographs of notable steps in the glycolate destruction runs are provided in Figure 2. Both runs were visually similar. The initial SMECT sample was clear with no visible solids. Immediately after the addition of 50% sodium hydroxide, which is also a clear solution, the sample became cloudy. Minutes after mixing was stopped, dark/grey solids were observed that settled in the Erlenmeyer flask. The solids readily resuspended upon resumption of mixing. No visual changes appeared after addition of the 6.6 M sodium nitrite or sodium glycolate. The solution turned a dark purple color after addition of 20% sodium permanganate, and no color change was observed in the flask throughout the remainder of the experiment. Upon being quenched with sodium sulfite, brown solids were observed which settled to reveal a clear supernate.



SMECT Sample

After Addition of Caustic and Sodium Nitrite

Post-Permanganate Strike

Figure 2: Photographs of the initial SMECT sample (left), the SMECT sample after addition of corrosion control chemicals (middle), and after addition of glycolate and sodium permanganate (right).

Glycolate concentrations measured during Runs 1 and 2 are provided in Table 3-6 and Table 3-7. Results using both IC and ^{1}HNMR are provided. In some cases, results using two ^{1}HNMR methods, the IS and SAM, are reported. Some results using the SAM were inconclusive and are not included in the tables below.

Table 3-6. Run 1 (P/G = 9.8) - Measured and Predicted Glycolate Concentrations in mg/L

Method	Initial SMECT mg/L (%U)	Time 0 mg/L (%U)	Time 1 - 63 min mg/L (%U)	Time 2 - 241 min mg/L (%U)
IC	< 8 (20)	36.9 (20)	13.6 (20)	10.7 (20)
^{1}HNMR (IS)	4.4 (14)	28 (44)	20 (18)	11 (18)
^{1}HNMR (SAM)	2.0†	*	*	*
Model	--	36.9	18.3	6.2

* Measurement inconclusive
† Below quantitation limit

Table 3-7. Run 2 (P/G = 10.7) - Measured and Predicted Glycolate Concentrations in mg/L

Method	Initial SMECT mg/L (%U)	Time 0 mg/L (%U)	Time 1 – 60 min mg/L (%U)	Time 2 - 240 min mg/L (%U)
IC	< 8 (20)	34.4 (20)	10.0 (20)	< 8 (NA)
^{1}HNMR (IS)	4.4 (14)	28 (29)	13 (32)	6.0 (51)
^{1}HNMR (SAM)	2.0†	*	14 (53)	5.2 (105)
Model	--	34.4	17.4	5.44

* Measurement inconclusive
† Below quantitation limit

Also included in Table 3-6 and Table 3-7 are the kinetic model predictions for glycolate concentrations at Time 1 and Time 2. IC data for Time 0 were used as the inputs for the initial glycolate concentrations. These values closely matched the glycolate concentration measured in the as-received SMECT sample combined with the added sodium glycolate. The measured mass of permanganate and the Time 0 volumes were used to calculate initial permanganate concentrations. A plot showing the model predictions for glycolate concentration as a function of time are shown in Figure 3 and Figure 4. Measured IC and IS ^{1}HNMR data are also shown with error bars depicting 2 sigma uncertainty.

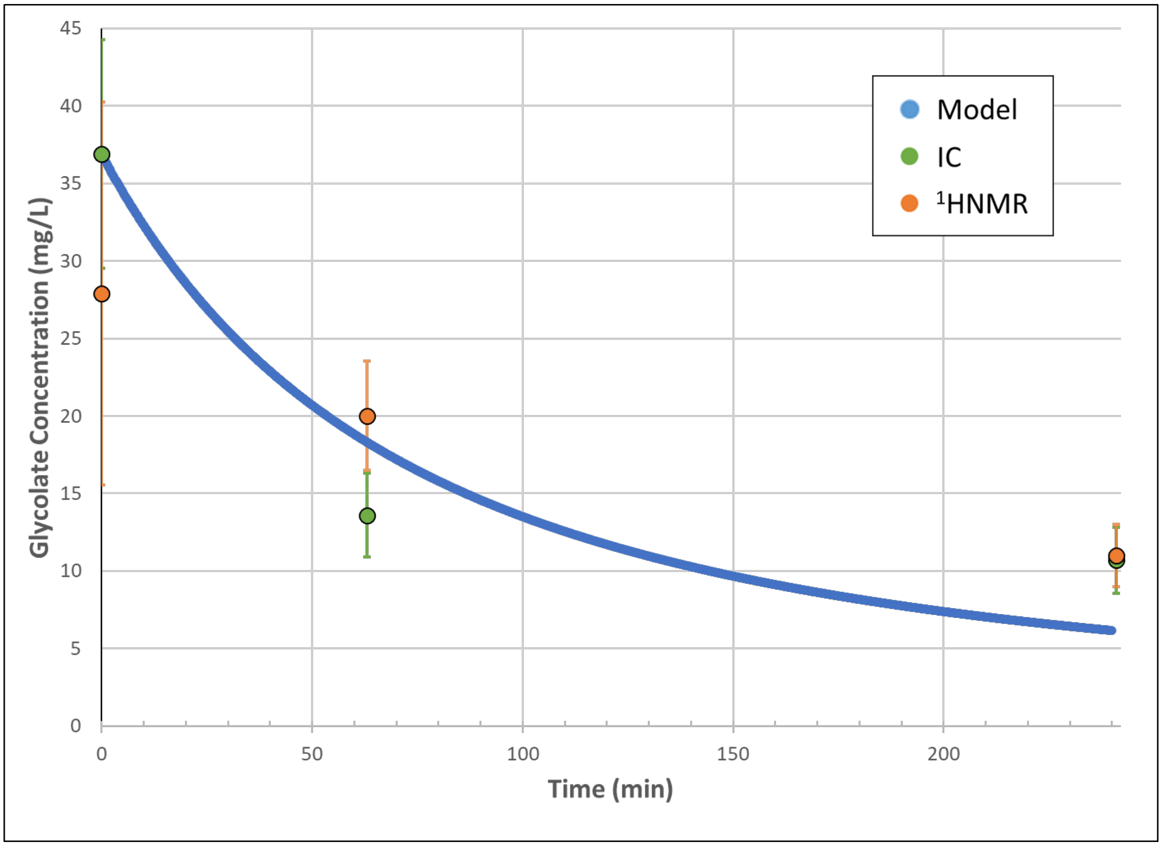


Figure 3: Plot of measured and predicted glycolate concentrations for Run 1

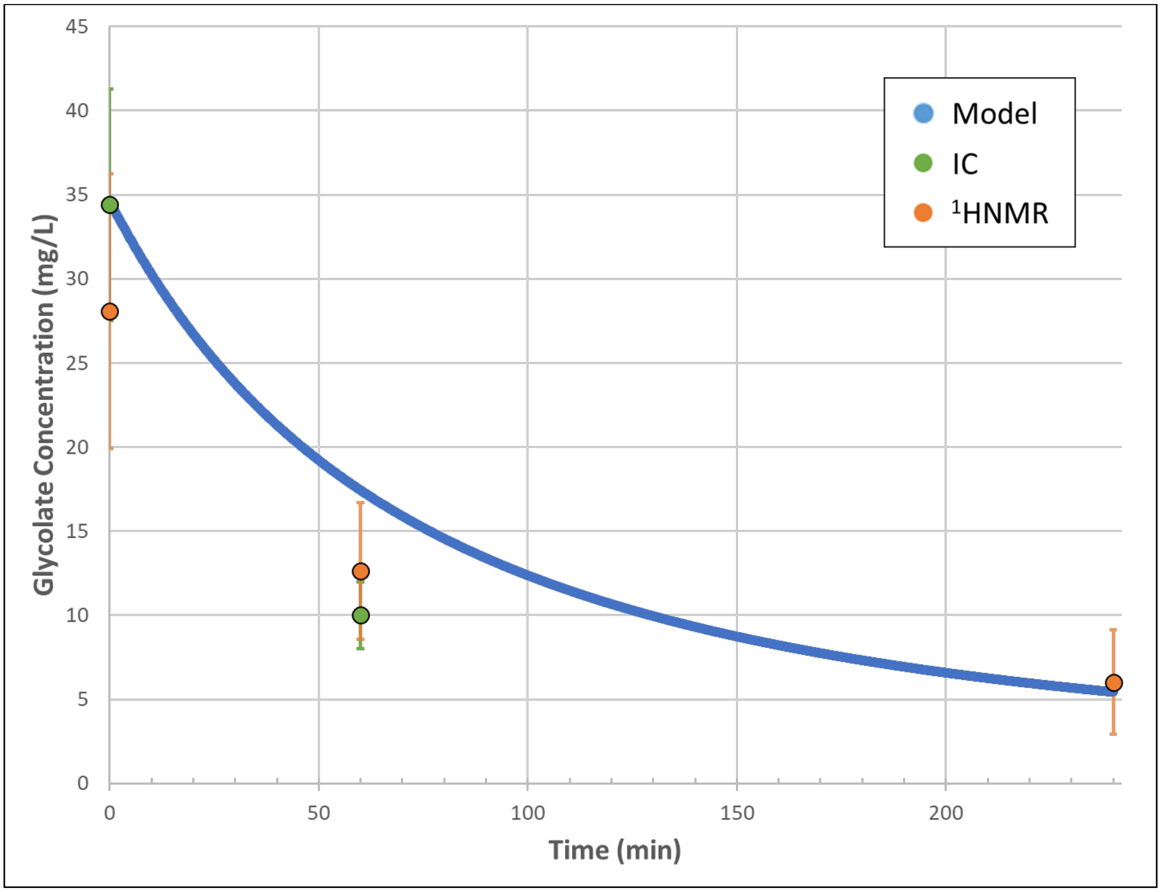


Figure 4: Plot of measured and predicted glycolate concentrations for Run 2

3.3 <u>Discussion of Measured Results vs. Model Predictions</u>

For both runs, glycolate decreased as a function of time throughout the experiment and, for both runs, glycolate concentrations were below or within measurement uncertainty of the model-predicted value at 1 hour. For Run 1, the glycolate concentration in the Time 2 sample was higher than the 6.2 mg/L predicted by the model. The measured glycolate concentration in the Run 2 Time 2 sample was nearly identical to the model prediction.

The theoretical model was shown to bound at least 84% of past simulant and radioactive waste studies with 95% confidence.[5] There are a number of possible explanations that address inconsistencies in the model with reaction durations longer than one hour and/or concentrations below 10 mg/L. For example, the majority of data used to determine the form of the kinetic model was acquired within one hour after the addition of permanganate. This is because a majority of the prior experiments, including the prior real waste demonstration, the limit of detection for glycolate was 10 mg/L or greater.[9]

Prior to implementation of the NGA flowsheet at DWPF, the source of glycolate for simulant studies was simulated SRAT product containing solids. The source of glycolate in the radioactive waste demonstration was a SME product with solids. Zamecnik et. al. noted that sludge solids enhanced the glycolate destruction process.[4] Solids-enhanced glycolate destruction was also suggested as an explanation in the radioactive-waste demonstration of glycolate destruction for the reaction being quicker in an OGCT sample with visible solids compared to an analogous reaction using a SMECT sample.[2]

A comparison of ICPES measurements between the 2020 SMECT sample[2] and the SMECT sample used in this study reveals there is less material carried over to the SMECT, likely due to implementation of the Momentive Y17112 antifoam. The radioactive SMECT test data was used to fit the kinetic model because that data set was found to have slow glycolate destruction kinetics relative to the body of nonradioactive data and also the radioactive OGCT test.[18] In the present study, the glycolate source was reagent grade chemical with no added solids. With fewer solids in the SMECT, it is therefore reasonable to assume slower glycolate destruction reaction kinetics. It is also reasonable to assume a faster glycolate destruction reaction rate in the RCT which has solids (e.g., MnO_2 solids from prior permanganate strikes) and potentially unreacted permanganate in the heel.

During early testing of the glycolate destruction methods, the statistically designed experimental approach included temperature as a variable.[19] Focusing on the four tests that used sodium permanganate with a starting pH of 13, tests 1b and 5a were performed at 15 °C and tests 6a and 7 were performed at 50 °C. The experimental design of the test also varied initial glycolate concentration, permanganate addition time, and permanganate stoichiometric excess, complicating the direct comparison of the results from the four tests points. The results also cannot be directly compared with the models of Equations (2) and (3) because the testing included other organics that potentially consumed permanganate, leading to a very different K_X. Also complicating matters, two of the tests (Tests 1b and 6a) had a relatively long permanganate addition time of 2 hours.

The report included a statistical analysis showing that glycolate destruction was statistically correlated with temperature and permanganate stoichiometric excess.[19] The analysis used the final (6 hour) glycolate measurement, showing the two tests at 15 °C had conversions (glycolate destruction) of 64% and 79% and the two tests at 50 °C had conversions of 92% and 87%. While temperature clearly correlated with higher conversions as measured at 6 hours, an hour after permanganate addition was complete the glycolate concentrations may have been below limit of quantification as the IC-glycolate method was still being refined. For the two tests with short permanganate addition times of 10 minutes (Tests 5a and 7), the solutions appeared to reach a final glycolate concentration within about 90 minutes. Thus, for a kinetic study, it would be best to look at only the first glycolate measurements after permanganate addition.

Of the two tests with 10-minute permanganate addition times, test 5a was performed at 15 °C and had glycolate concentrations of 122 and 32 mg/L after 0 and 30 minutes, respectively, and test 7 was performed at 50 °C and had glycolate concentrations of 273 and 42 mg/L after 0 and 30 minutes, respectively. [19] Test 7 also only had about 50% of the amount of permanganate added to Test 5a. Assuming a simple kinetic model for the initial decomposition of glycolate, where the rate has a first order relationship with initial glycolate and permanganate concentrations, tests 5a and 7 show that the initial glycolate destruction reaction has a strong temperature dependence, with an activation energy of greater than 100 kJ/mol. In summary, based on both the initial and overall glycolate destruction results for permanganate tests at pH 13, the glycolate destruction rate was seen to have a direct correlation with temperature.

All glycolate destruction experiments using real waste were performed at 17 ºC, which was the ambient temperature of SRNL's shielded cells, but lower than typical in the RCT. Figure 5 shows a PI plot of the RCT liquid temperature (DTI5841) from June 2021 to June 2023. Over the past two years, the RCT typically operated in the range of 20-30 ºC. RCT temperatures below 20 ºC often coincide with an outage period where negligible condensate is generated. Considering the known dependence of reaction rate on temperature, faster reaction kinetics are anticipated in the RCT during typical operating conditions.

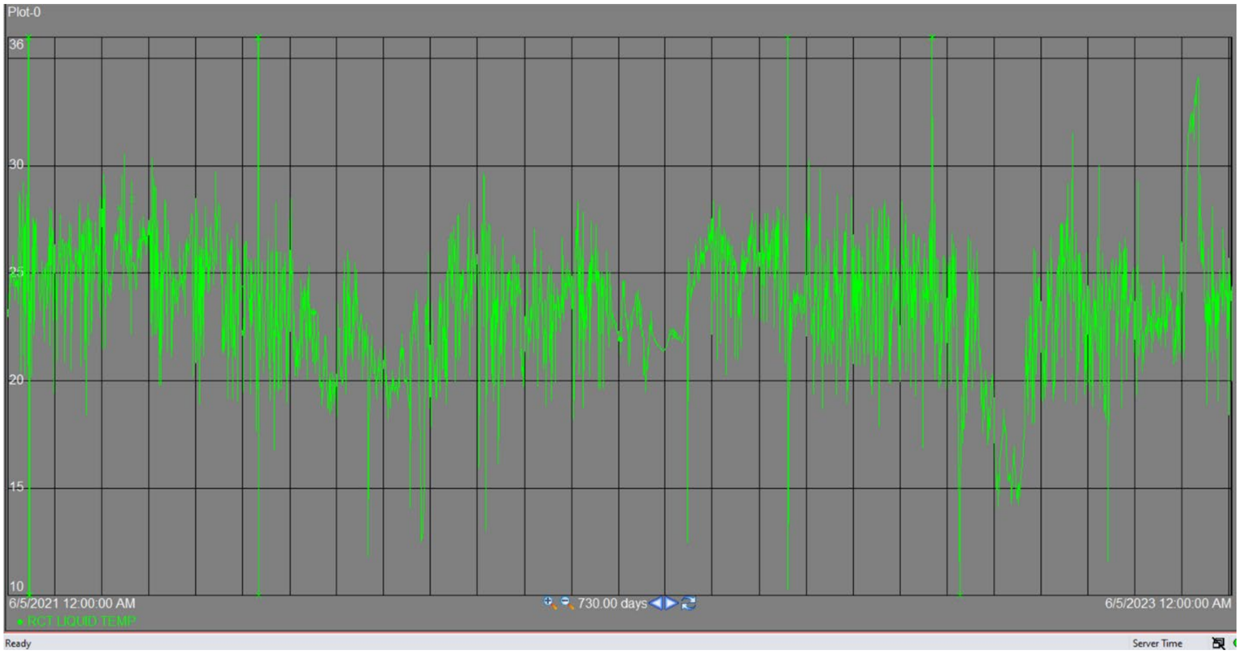


Figure 5: PI plot of RCT liquid temperature (DTI5841) showing temperature from 6/2021 to 6/2023

The 2020 radioactive-waste demonstration of glycolate destruction provided glycolate and oxalate concentrations as a function of time for one month after the addition of permanganate.[2] While glycolate concentrations were below the limit of detection of 10 mg/L, oxalate ingrowth was observed in samples 31 days after initiation of the glycolate destruction reaction. Studies with simulants at caustic conditions demonstrated sodium permanganate converts glycolate to oxalate.[3] The continued ingrowth of oxalate is an indication the glycolate destruction reaction continued well beyond the addition of permanganate.

4.0 Conclusions

Glycolate concentrations were measured by SRNL in SMECT and RCT samples retrieved after implementation of the NGA flowsheet at DWPF. No glycolate has been detected in any sample using IC with a detection limit of 8 mg/L, and no reportable glycolate has been detected using either IC or ^{1}HNMR after a permanganate strike was performed in the RCT.

Duplicate tests were performed on SMECT sample 30455 to demonstrate nominal operation of the permanganate oxidation process under protocols similar to those used in the DWPF RCT. Sodium glycolate was added to the SMECT sample and permanganate concentrations were selected to obtain measurable results after 4 hours of reaction. Results were compared with a kinetic model developed by SRNL to predict the mass of sodium permanganate and reaction times required to achieve a targeted glycolate concentration.

In both tests, measured glycolate concentrations were within uncertainty or below the model-predicted value after one hour. However, for samples measured at four hours, data from the first experiment was approximately 4 mg/L higher than predicted while the second test matched the model prediction.

To ensure that the DWPF always decomposes glycolate to less than the current 3 mg/L WAC limit, DWPF currently targets a model predicted decomposition to 1 mg/L at 4 hours reaction time. The glycolate destruction model was shown to be consistent with the known uncertainty of bounding 84% of the previous data with 95% confidence.

The following four points provide insight to relate glycolate destruction test data to the facility:

1) The majority of data used to determine the form of the kinetic model was acquired within one hour after the addition of permanganate. Additionally, glycolate was not detected below 10 mg/L for the majority of previous experiments, including the previous real waste demonstration.

2) A SMECT sample was used in place of an RCT sample to remove uncertainty associated with unreacted permanganate in the RCT heel. The SMECT sample used in this study contained notably fewer solids than the previous radioactive waste demonstration. Since sludge solids were observed to enhance the glycolate destruction process, it is reasonable to assume the current study had slower glycolate destruction rates than the previous SMECT experiment from which the rate constants were derived. The DWPF RCT slurries would be expected to contain more sludge, glass, and/or manganese dioxide solids than the SMECT samples used in this testing.

3) Experiments with radioactive waste were performed in the SRNL shielded cells at 17 ºC, which is lower than the 20-30 ºC typical for DWPF RCT operating conditions. Faster glycolate destruction rates are expected at the higher temperatures typical of DWPF RCT operations.

4) The RCT contains a heel that likely includes unreacted permanganate from prior batches. Any unreacted permanganate is unaccounted for in this study, and would lead to higher P/G ratios with faster glycolate destruction rates.

5.0 Recommendations

Based on the conclusions from this report and prior investigations, SRNL recommends that DWPF continue to implement the glycolate destruction process based on the model in SRNL-STI-2021-00190. Based on the measured initial glycolate concentration, implementation should target a final glycolate concentration of 1 mg/L to ensure the 3 mg/L WAC requirement is not exceeded. Addition of sodium permanganate in excess of the amount predicted by the model is at the discretion of DWPF Engineering.

Any carryover event should be evaluated based on the conditions resulting from the carryover as a special evolution consistent with current operational plans.

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