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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

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EXECUTIVE SUMMARY

The Savannah River Site's Defense Waste Processing Facility (DWPF) flowsheet is being upgraded with the introduction of the Nitric-Glycolic Flowsheet. The new flowsheet improves or maintains necessary parameters such as 1) reduction of mercury, 2) adjustment of feed rheology, and 3) adjustment of melter oxidation/reduction potential. Further, the potential for catalytic hydrogen generation in DWPF processing is virtually eliminated.

The Nitric-Glycolic flowsheet significantly improves DWPF's ability to address one of the Savannah River Site's key challenges - the incorporation of effluent received from the Salt Waste Processing Facility (SWPF). SWPF will deliver significant effluent volume to DWPF, resulting in a concurrent increase in DWPF effluent returned to the Concentration, Storage, and Transfer Facilities (CSTF). To avoid potential flammability issues due to thermolysis of glycolate in the CSTF, Savannah River Remediation (SRR) tasked Savannah River National Laboratory (SRNL) to quantify and mitigate glycolate returns via DWPF's recycle stream. A joint SRR/SRNL workshop and a series of scoping studies identified chemical oxidation of glycolate within the DWPF Recycle Collection Tank (RCT) as the most promising process option. A series of down-select experimental tests was then performed. Ultimately, sodium permanganate was selected as the most effective oxidant.

Larger scale-testing (22 L reaction vessel) has been performed to validate the results of previous testing (performed with a 2 L reaction vessel). Larger scale testing with simulants was requested to address technology readiness level criteria and provide confidence that adverse extensive effects are not manifested with increased reaction volumes. This testing was performed with a non-radioactive RCT simulant doped with 68, 140, and 5100 mg/kg glycolate. Glycolate was introduced via a sludge simulant to mimic both nominal entrainment and abnormal process foamover conditions.

One additional DWPF operational aspect of this testing was to evaluate the addition of sodium nitrite to the RCT. Sodium nitrite is added as a CSTF corrosion control chemical. Subsequently, work was performed to determine if the sodium nitrite added prior to the permanganate strike would impact mitigation efficiency.

All tests have been concluded safely with the following results.

1) RCT glycolate content can be reduced to below the ion chromatography (IC) detection limit within 90 minutes for all concentrations investigated using the permanganate to glycolate (P/G) ratios described below,
2) Glycolate is oxidized to oxalate in caustic with no significant formation of carbon dioxide or carbonate,
3) Permanganate (Mn^{7+}) is reduced to manganate (Mn^{6+}), and
4) Nitrite is not oxidized to nitrate.

Determination of the mechanistic chemical reaction (per items 2 and 3, above) confirms the oxidant stoichiometry is effectively defined by the initial P/G molar ratio. This allows the required amount of permanganate to be more accurately predicted and minimizes the recommended DWPF operational permanganate strike. At low initial glycolate concentration (68 and 140 mg/kg), the minimum required initial P/G molar ratio was found to be in the range of 5-6. At foamover conditions (5100 mg/kg glycolate) a lower P/G molar ratio of approximately 2.2 was needed.

This scale-test effort was designed in conjunction with additional SRNL tests to be performed with fully radioactive DWPF condensates, as described herein.

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LIST OF ABBREVIATIONS

CPC	Chemical Process Cell
CSTF	Concentration, Storage, and Transfer Facilities
DWPF	Defense Waste Processing Facility
FTIR	Fourier Transform InfraRed (Spectroscopy)
GC	Gas Chromatography
IC	Ion Chromatography
ICP-ES	Inductively Coupled Plasma Emission Spectroscopy
OGCT	Off-gas Condensate Tank
P/G	Permanganate to glycolate (initial molar ratio)
PSAL	Process Science Analytical Laboratory
RCT	Recycle Collection Tank
sccm	standard cubic centimeters per minute
SMECT	Slurry Mix Evaporator Condensate Tank
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SWPF	Salt Waste Processing Facility
TAR	Technical Assistance Request
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
UV-Vis	Ultraviolet-visible

1.0 Introduction

Testing to develop a process to oxidize glycolate and other organic species in non-radioactive waste simulants was requested by Savannah River Remediation (SRR).[1] A Task Technical and Quality Assurance Plan (TTQAP) was written to describe the testing requested by SRR in the development of a process to oxidize glycolate and other organic species that are responsible for hydrogen generation from thermolysis.[2] Scoping studies have been completed as requested by a Technical Assistance Request (TAR)[3] to evaluate the feasibility of using sodium permanganate and Fenton's Reagent (iron catalyzed hydrogen peroxide) for destroying glycolate.[4] The results from these scoping studies were summarized in a report.[5]

Six phases of tests with simulants have been planned in developing an oxidation flowsheet for the Recycle Collection Tank (RCT), as shown in Table 1. The first three phases have been completed. The first phase comprised of scoping tests of permanganate and Fenton's reagent.[5] The second phase was a matrix of 23 tests completed to inform a down-select decision by SRR and to complete testing needed to understand the influence of various factors in defining the optimum processing conditions for oxidation of organics.[6] From the results of this testing, oxidation by permanganate was chosen over Fenton's reagent with hydrogen peroxide. The third phase of testing was to demonstrate nominal operation of the permanganate oxidation process under protocols similar to those used in the Defense Waste Processing Facility (DWPF).[7]

Table 1. Test phase status and TTQAP task activities

Phase	Description	Status	TTQAP Task Activity
1	Scoping Tests	Complete	1 e
2	Down Select Testing	Complete	1 a-g
3	Protocol Testing – Nominal and CPC Foamover Conditions	Complete	Parts 1 and 3
4	Actual Waste Testing	In progress, included in a separate Run Plan	2
5	Larger Scale Testing	Described in this document	1 h
6	Corrosion Testing	In progress, included in a separate Run Plan	4

(Phases 4-6 not in order of actual testing.)

This report describes experiments to determine the effect of scaling on the oxidation of glycolate using sodium permanganate in a typical RCT simulant. In addition to the scaled experiments, supplemental experiments were performed to investigate the impact of the order of addition of the nitrite corrosion inhibitor, to investigate the influence of varied glycolate concentrations from Chemical Process Cell (CPC) carryover, and to further refine the suggested permanganate to glycolate (P/G) molar ratio as per recommendations from the protocol testing phase.[7]

2.0 Background

2.1 Scaled Testing

Earlier phases of testing on glycolate destruction were performed in 2 L reaction vessels at 16800:1 RCT scale or less by volume. Larger scale testing with simulants was requested to address technology readiness level criteria and provide confidence that adverse extensive effects are not manifested with increased reaction volumes. Since the chemistry occurs in the liquid phase, no expected scale-up factor beyond the 20 L selected is recommended to predict the anion destruction.

Off-gas analysis on 1.8 L experiments required a 10x scale air purge rate for adequate sample turnover. Using similar purge rates with larger sample volumes allows for the measurement of more concentrated off-gas samples with a corresponding increased sensitivity. 20 L testing will allow for a scaled prototypical flowrate (i.e., not 10x scale increased flowrate used in prior experiments); off-gas analysis will have improved sensitivity for previously undetected toxic or flammable gases requested in the Technical Task Request (TTR).

2.2 Basis for Supplemental 1.8 L Experiments

Previous studies on the destruction of glycolate using permanganate in RCT simulants initially assumed the reduction of manganate (MnO_4^-) to manganese dioxide (MnO_2) and the complete oxidation of organic species (e.g., formate, oxalate, antifoam) and nitrite. Tests at caustic conditions demonstrated permanganate was effective in converting glycolate to oxalate but showed negligible reactivity for other species in the simulant solution (e.g., formate, nitrite, etc.).[6,7] In addition, equation (1) was found to best describe the observed reaction of glycolate with permanganate under nominal and low glycolate entrainment conditions.[7]

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

Due to the unexpected specificity for glycolate, the amount of permanganate utilized during many of the tests to destroy glycolate was found to be excessive resulting in final glycolate concentrations below the limits of detection. Figure 1 is reproduced from the protocol testing report[7] and shows glycolate destruction versus the P/G molar ratio in RCT simulants containing 125 mg/kg glycolate. Linear extrapolation of the measured glycolate data suggests a P/G ratio of 5.2 is required for complete destruction of glycolate. With most of the previous experiments performed with a P/G ratio greater than 6, additional tests with lower P/G ratios were recommended to improve data fidelity.

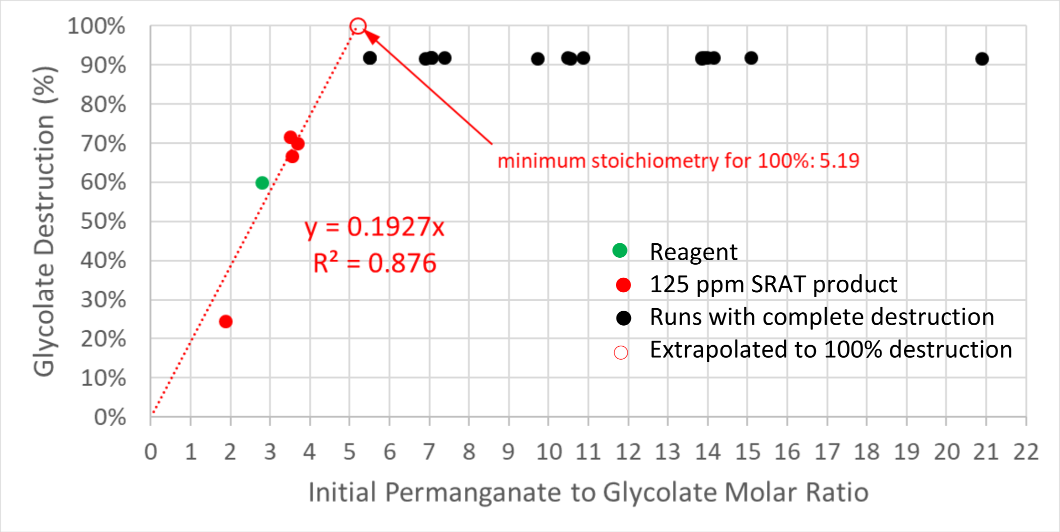

Figure 1. Glycolate destruction versus initial permanganate to glycolate molar ratio for 125 mg/kg glycolate[7]

Glycolate destruction results for the large 500 gallon foamover runs with 5000 mg/kg glycolate did not appear to follow equation (1). Greater than 99% of glycolate was destroyed using a P/G of 2.03. Although the destruction percentage was >99%, the actual concentration of glycolate was still above the detection limit of 100 mg/kg and further testing of 500 gallon foamover conditions was recommended. In addition, multiple permanganate strikes were suggested to minimize the total permanganate needed.

The molar ratio of nitrite to nitrate in the Concentration, Storage, and Transfer Facilities (CSTF) returns is kept above 1.66 for corrosion control concerns.[8] 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. In down-select and protocol tests, 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. Results from protocol tests and published reports[9] found nitrite is unreactive towards permanganate in caustic solutions. It was recommended that tests be performed with nitrite and caustic added before permanganate to demonstrate that added nitrite will not be oxidized.

3.0 Experimental Procedure and Operations

Testing was designed to mimic and expand upon previous protocol runs with similants.[7] Test planning assumed a starting point immediately after transfer of the RCT to the Low Point Pump Pit Recycle Tank, with a 1,400 gallon heel left in the RCT and 5,600 gallons of Slurry Mix Evaporator Condensate Tank (SMECT) or Off-Gas Condensate Tank (OGCT) material. At this point in the process cycle, the RCT has a high concentration of free hydroxide and nitrite compared to the SMECT and the OGCT but low compared to the RCT with condensate or CSTF, assuming it has not been preconditioned with sodium hydroxide and sodium nitrite. Three scenarios of glycolate carryover from the SMECT to the RCT were considered for this study: 1) low glycolate, 2) nominal (i.e., expected) entrainment, and 3) a large 500 gallon foamover event.

3.1 Experimental Design and Test Protocols

Four experimental parameters were investigated in the present study: reaction volume (i.e., scale), the order of nitrite addition, glycolate concentration, and the P/G molar ratio. The conditions for all runs performed in this series are shown in Table 2, with run numbers corresponding to the numbers listed in the plan.[10] Letters “a” and “b” denote experiments performed in addition to those listed in the initial plan. The P/G ratios and glycolate concentrations listed in Table 2 were derived from measured values and differ slightly from the target values in the run plan due to a higher than expected glycolate concentration in the foamover simulant. Experiments 6 and 11 were not performed due to negligible observed reactivity of nitrite. The liquid volumes for Experiments 8-10 were reduced from 1.8 to 1.6 L due to the larger volumes of permanganate solution required for glycolate mitigation.

Table 2: Summary of test conditions

Run #	Scale	6.6 M Nitrite Addition	Foamover Conditions	Glycolate	Permanganate to Glycolate
-	Liter	(B)efore or (A)fter	Gallon	mg/kg	Molar Ratio
1	1.8	B	14	140	3.3
2	1.8	B	14	140	4.5
3	1.8	B	14	140	5.7
4	1.8	A	14	140	3.5
5	1.8	A	14	140	4.6
7	1.8	B	6.7	68	3.6
7a	1.8	B	6.7	68	5.7
8	1.6	B	500	5100	2.6
8a	1.6	B	500	5100	1.3
8b	1.6	B	500	5100	1.3 (x2)*
9	1.6	B	500	5100	2.2
10	1.6	A	500	5100	2.6
12	20	B	14	140	3.5
13	20	B	14	140	4.5
14	20	B	14	140	5.6

*Permanganate was added twice with each strike contributing 1.3 moles of permanganate per mole of initial glycolate

Three transfer events were simulated to investigate a wide range of carryovers from the SMECT and/or OGCT to the RCT contributing 6.7, 14, and 500 gallons of sludge. The 14 gallon transfer represents a "nominal entrainment" of sludge and is similar to the expected future glycolate concentration in the RCT[11] contributing 140 mg/kg glycolate. The 6.7 gallon transfer contributes 68 mg/kg glycolate and was chosen to simulate "low" entrainment. The 68 mg/kg concentration was selected as a lower boundary to provide measurable data above the 10 mg/kg chromatographic detection limits for glycolate. The 500 gallon transfer represents a large foamover event contributing ≈5100 mg/kg glycolate to the RCT.

3.2 Simulant Compositions

The simulant composition represents the transfer from the SMECT or OGCT onto the heel in the RCT and approximates the expected compositions of these tanks on a routine basis. The condensate simulants were made from reagent chemicals and from a characterized Sludge Receipt and Adjustment Tank (SRAT) product sludge simulant sample.[7] Formate and oxalate were added to increase their concentrations to about 20 mg/kg each. This value was based on the typical ratio of oxalate to glycolate in SRAT products. Formate was added at the higher than expected concentration of 20 mg/kg so that its destruction could be evaluated since the ion chromatography (IC) detection limit is about 10 mg/kg. For experiments with a post-reaction nitrite addition (i.e., experiments 4, 5, and 10 in Table 2), nitrate and nitrite were added to match the concentrations for a heel nitrite/nitrate molar ratio of

4.4, which was found to be an approximate average of typical RCT samples. For all other experiments, nitrite and nitrate were added to match concentrations for a combined heel and condensate molar ratio of 4.4.

SRAT product simulant was used to simulate sludge carryover contributing 68, 140, and 5100 mg/kg glycolate in the RCT. The SRAT product simulant was the same simulant used in Phase 3 testing and a complete description can be found in the protocol report.[7] The IC analysis performed in this work provided slightly higher glycolate concentrations for the SRAT product than assumed for prior protocol runs (65000 vs 57100 mg/kg), but within the range of glycolate concentrations measured previously. The concentrations of glycolate, formate, oxalate, nitrite, nitrate, and hydroxide in the SRAT product simulant, and in the combined SRAT product/RCT simulant with and without added nitrite are shown in Table 3. Antifoam was present at SRAT product levels in the SRAT product simulant.

Table 3. Composition of SRAT product and combined SRAT product and RCT simulants

Simulant	Glycolate mg/kg	Formate mg/kg	Oxalate mg/kg	Nitrate mg/kg	Nitrite mg/kg	Sodium Hydroxide mol/L
SRAT Product	57100	773	8390	58200	<100	--
Simulant for Post-Nitrite Strike						
Combined RCT Simulant (14 gal)	140	20	20	3100	1760	0.2
Combined RCT Simulant (500 gal)	5100	61*	662*	4588*	1760	0.2
RCT Simulant Precharged with Nitrite						
Combined RCT Simulant (6.7 gal)	68	20	20	3100	10100	0.2
Combined RCT Simulant (14 gal)	140	20	20	3100	10100	0.2
Combined RCT Simulant (500 gal)	5100	61*	662*	4588*	14980*	0.2

*Values higher due to excess provided by the SRAT product simulant

3.3 Oxidation Stoichiometry – Molar Ratios

Previous protocol runs initially assumed complete oxidation of the organic species and nitrite by sodium permanganate. Phase 3 protocol tests with simulants at high pH showed negligible oxidation of formate, oxalate, and nitrite.[7] For these scaled protocol runs the stoichiometry is defined on a glycolate-only basis with oxidant addition being defined using a P/G molar ratio.

For the experiments simulating low and nominal entrainment (i.e., 68 and 140 mg/kg glycolate), P/G molar ratios ranging from 3.3 to 5.7 were used to generate a range of final concentrations near the lower detection limits for glycolate of 10 mg/kg. Results from Phase 3 testing simulating 500 gallon foamover conditions (i.e., 5100 mg/kg glycolate) determined a lower molar ratio of approximately 2.0 was sufficient to destroy glycolate by about 99%, but not below detection limits. Experiments in this report were performed using a P/G molar ratio of 1.3, 2.2 and 2.6. An additional experiment with a final P/G ratio of 2.6 was performed with the permanganate subdivided into two 1.3 P/G additions spaced 90 minutes apart.

3.4 Experimental Scaling

Experiments simulating nominal and low glycolate entrainment were performed at 16800:1 and 1530:1 scale on a volume basis. The material volumes will be discussed below on a DWPF basis. These volumes were then scaled to the laboratory tests by the RCT volume ratio of 8000 gal to 1.8 L (4.44 gal/mL scale factor) and 19.8 L (0.404 gal/mL scale factor). The volume of the simulated condensate transfers was the scaled amount that would fill the RCT to 8000 gallons minus the amounts of NaOH to be added.

The volumes of chemicals are shown in Table 4 for DWPF and laboratory scales. The volumes shown are based on reasonable values for the operation of the RCT. Note that the actual historical condensate addition volumes vary significantly, so there is no one correct volume to simulate. The condensate volume assumed was that which brings the total RCT volume to 8000 gallons before permanganate addition and without foamover. The permanganate volumes assume a 14 gallon foamover and a P/G ratio of 5.7.

Table 4. Chemical scaling of nominal glycolate laboratory experiments vs. DWPF operations

Step	DWPF (gal)	Large-Scale Laboratory (mL)	Small-Scale Laboratory (mL)
RCT Heel	1400	3,470	315
50 wt% NaOH	75	186	16.9
Condensate	6310	15,600	1420
Sludge[1]	14	34.6	3.15
20 wt% Permanganate[1,2]	53	132	12
6.6M $NaNO_2$ Solution	215	532	48.4

1) *Volumes assume the total RCT volume of 8000 gal before permanganate addition and with no sludge foamover*
2) *Assuming a P/G ratio of 5.7*

Experiments simulating 500 gallon foamovers contributing approximately 5100 mg/kg glycolate were performed at a slightly smaller 18900:1 scale on a volume basis (5.00 gal/mL scale factor). All small-scale experiments were performed using a 2 L volume reaction vessel. The liquid volumes for foamover studies were reduced from 1.8 to 1.6 L due to the larger volumes of permanganate solution (e.g., 150-200 mL) required for glycolate mitigation.

3.5 Experimental Apparatus and Parameters

Two liter experiments were performed in an apparatus similar to the apparatus used for protocol testing with no off-gas or on-line pH measurements.[7] Testing was performed using a 2.0 L borosilicate glass jacketed reactor. A 20 wt% sodium permanganate solution was added to the reaction vessel using a syringe pump. Addition durations were consistent with previous protocol runs at 20 minutes for the low and nominal entrainment and 65 minutes for 500 gallon foamover conditions. Reaction times for nominal and foamover conditions were respectively 3 and 6 hours from the start of permanganate addition unless otherwise noted. An agitator was used throughout testing to ensure the solution was well mixed. A sampler allowed on-line removal of contents as needed. A more detailed list of test parameters and conditions follows.

- Vessel construction: Borosilicate glass, water jacketed
- Total available volume in vessel: approximately 2.0 L
- Liquid volume: approximately 1.8 L
- Headspace volume: approximately 0.2 L
- Reaction temperature: 20 ± 2 °C (maintained by water jacket)
- Mixer rate: 250 rpm

Large scale tests were completed in a 22 L borosilicate glass reaction vessel with approximately 19.8L RCT simulant (2.2 L headspace). A dry air purge was used to dilute the off-gas and the off-gas was analyzed using Gas Chromatography (GC) and Fourier Transform Infrared Spectroscopy (FTIR). A temperature probe was utilized in all testing. An agitator was used to mix the solution at 250 rpm. A sketch of the equipment is shown in Figure 2.

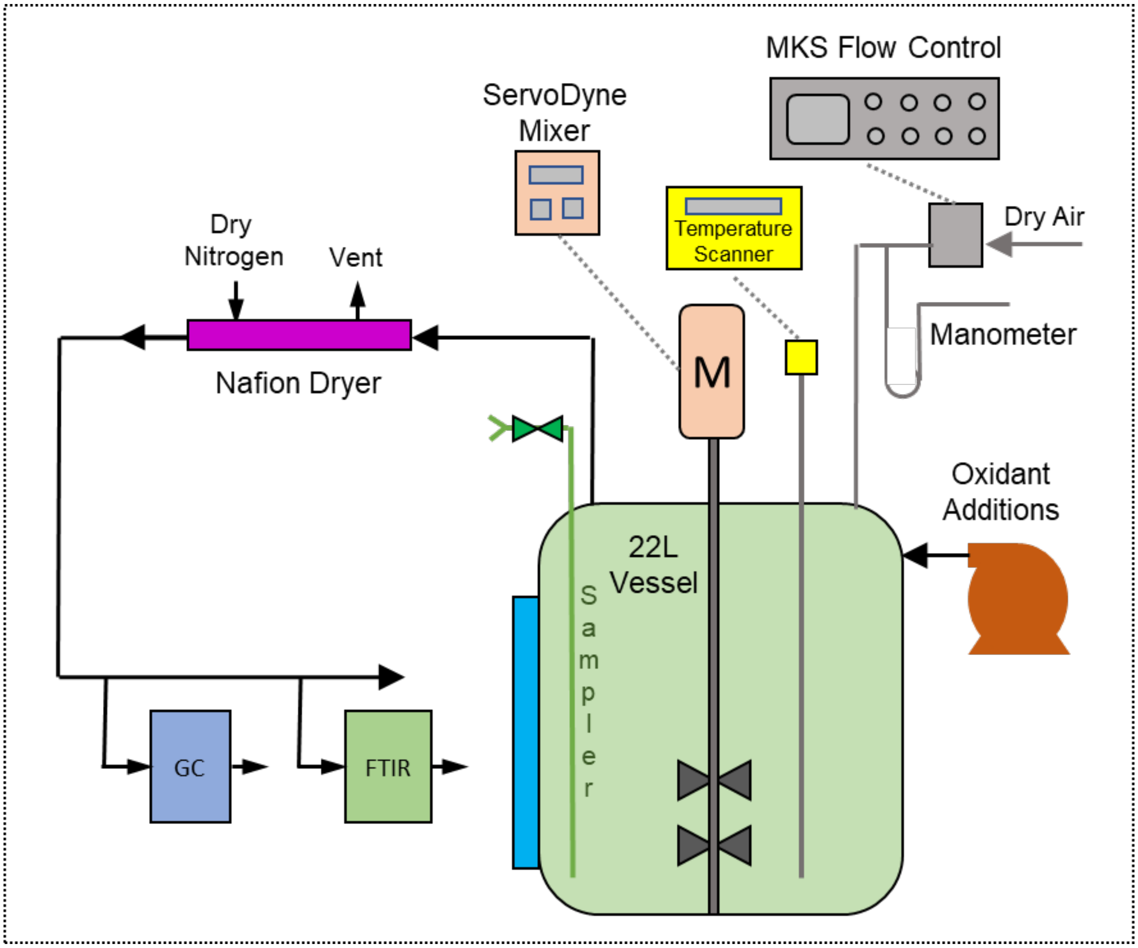

Figure 2 – Equipment apparatus sketch

The testing parameters for all 20 L tests were as follows:

- Vessel construction: borosilicate glass
- Total available volume in vessel: 22 L
- Liquid volume: approximately 19.8 L
- Headspace volume: approximately 2.2 L
- Target purge rate: 81 sccm (21 °C, 1 atm) with no tracer
- Purge gas composition: air (dried, CO_2-free)
- Individual test duration (nominal and low glycolate): 3 h from start of permanganate addition
- Individual test duration (foamover): 6 h from start of permanganate addition
- Reaction temperature: room temperature (≈20 °C), non-insulated
- Mixer rate: 250 rpm

3.6 Liquid Analysis

Liquid samples were pulled throughout testing and analyzed to track the decomposition of the organics and nitrite. Analytical protocols were similar to those developed during the protocol runs.[7] Samples were analyzed by the

Process Science Analytical Laboratory (PSAL) for anions (glycolate, formate, oxalate) by IC. These samples were quenched with sodium sulfite to stop oxidation of the organics by converting the permanganate to unreactive MnO_2 or Mn(II). PSAL used a Dionex OnGuard II H cartridge to minimize matrix effects and improve peak shape. The typical linear IC calibration range is 1-10 mg/L, so samples must be diluted into this range. Samples from runs starting at 68 and 140 mg/kg glycolate were diluted 10X by mass to be in the calibration range of the IC, while the runs starting at 5100 mg/kg were diluted by 100X to be in range.

For nitrite and nitrate measurements, samples in each test were diluted 1000X to bring concentrations in the calibration range for IC analysis. The 1000X dilution also reduced the pH and potentially allowed nitrite to be oxidized by unreacted permanganate. To minimize unwanted pH induced reactions, analyses were performed within 2 hours of sample collection and preparation.

Density and total solids measurements were acquired by PSAL for sludge and supernatant samples. The pH was derived from total free hydroxide concentration determined by total base titration. Inductively coupled plasma emission spectroscopy (ICP-ES) was used to measure total Mn. A fiber optic ultraviolet-visible (UV-Vis) spectrometer equipped with a transmission dip probe with a variable length optical path (0.5-20 mm) scanning in the range of 400 to 800 nm was used to qualitatively follow the relative amounts of manganese species in-situ for runs with low and nominal glycolate. The large amount of sludge required to contribute 5100 mg/kg glycolate for foamover studies resulted in opaque simulants providing insufficient signal for qualitative measurements by UV-Vis spectroscopy.

3.7 Off-gas Analysis

Off-gas analysis was performed on the three 19.8 L scale runs. Off-gas analysis was not performed for the 1.8 L experiments which would have required a 10x scale air purge rate for adequate sample turnover. The simulant volumes used in 1530:1 scale testing allowed for 1530:1 scale purge rates providing improved sensitivity due to higher expected off-gas concentrations. The off-gas samples were analyzed using an FTIR and a GC. The TTR requested analysis for toxic and flammable gases along with H_2, CO_2, and NO_x. It should be noted that during down select testing using smaller volumes (e.g., 1.8 L) with 10x scale purge rates, no H_2 attributed to process was ever detected and CO_2 is not expected in caustic conditions.[6] The analysis frequency for the FTIR and GC were <10 seconds and four minutes respectively.

3.8 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in Manual E7, Procedure 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist[12] contained in WSRC-IM-2002-00011, Rev. 2. Data from the experiments was posted in Electronic Laboratory Notebooks C8102-00274-04 through 17.

The TTR for this work specified the testing has a functional class of Safety Class. The planning, test protocols, and data review per WSRC-IM-2002-00011 Rev. 2 are compliant with the requirements for Safety Class data collection.

4.0 Results

Results from each experiment are summarized in Table 5 and subdivided by initial glycolate concentrations and ranked in order of P/G ratio. Rows highlighted in green denote experiments where the sodium nitrite corrosion inhibitor was added to the reaction vessel at the end of the experiment. The nitrite/nitrate values were calculated prior to the post-reaction nitrite strike as no nitrite oxidation is expected post-reaction. The percent of initial glycolate destroyed 90 and 180 minutes after the start of permanganate addition are shown. For all tests, greater than 80% of the reaction occurred within 90 minutes of the start of permanganate addition. P/G ratios were found that reduced glycolate concentrations below IC detection limits for all initial glycolate concentrations investigated.

Table 5: Experimental results – glycolate destruction and the after/before ratio of nitrite and nitrate

Run #	Scale (Liter)	P/G Molar Ratio	Glycolate Destruction (%) 90 min	Glycolate Destruction (%) 180 min	Glycolate Concentration (mg/L) 180 min	Nitrite Ratio After/Before Reaction	Nitrate Ratio After/Before Reaction
68 mg/kg Glycolate							
7	1.8	3.6	49	60	27	1.10	1.09
7a	1.8	5.7	85	≥85	≤10	0.97	0.93
140 mg/kg Glycolate							
1	1.8	3.3	70	82	26	0.99	0.91
4	1.8	3.5	46	50	70	1.00	0.96
12	20	3.5	75	88	15	1.00	0.97
13	20	4.5	91	92	12	1.01	0.95
2	1.8	4.5	82	87	19	0.98	0.97
5	1.8	4.6	67	83	24	1.06	1.01
14	20	5.6	91	≥92	≤10	0.97	0.93
3	1.8	5.7	85	89	15	1.00	1.00
5100 mg/kg Glycolate							
9	1.6	2.2	98	≥98	≤100	0.86**	1.29**
8	1.6	2.6	95	96	121	0.79	1.03
10	1.6	2.6	≥98	≥98	≤100	0.66	0.92
8b	1.6	1.3 (x2)*	84	≥98	≤100	0.84	0.93

*A second permanganate addition was started at 90 minutes with both additions contributing 1.3 moles of permanganate per moles of initial glycolate

**Results acquired 4 days after 1000x dilution

4.1 Impact of Permanganate to Glycolate Molar Ratio

4.1.1 *Nominal Entrainment Conditions: 140 mg/kg Glycolate*

The glycolate and oxalate concentrations as a function of time are plotted in Figure 3 for each experiment with 140 mg/kg initial glycolate pre-charged with nitrite. For the 1.8 L experiments, the starting glycolate and oxalate concentrations were assumed from sample masses of the simulant prior to permanganate addition; all other values were obtained from IC analysis. Results are presented for both 1.8 L (16800:1) and 20 L (1530:1) scales using three molar ratios of initial P/G.

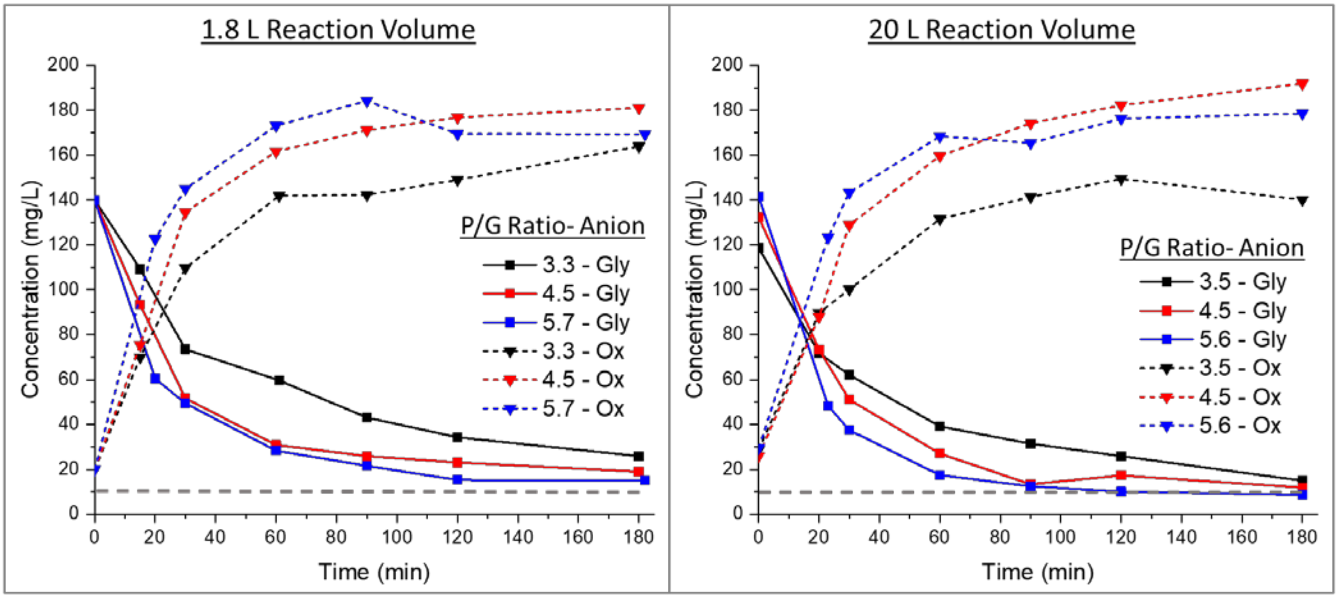

Figure 3: Glycolate and oxalate as a function of time and P/G ratio for *(left)* 1.8 L and *(right)* 20 L reaction volumes. IC detection limit = 10 mg/L as shown.

The glycolate destruction and oxalate generation rates were similar for both reaction volumes with all three P/G ratios investigated. For all reactions, the glycolate concentration decreased as a function of time and oxalate concentrations increased by approximately the same molar amount. The extent and rate of glycolate destruction and oxalate generation increased as the ratio of permanganate to glycolate increased from 3.3 to 5.7. A P/G molar ratio of 5.7 was found to reduce glycolate concentrations near or below the IC detection limits of 10 mg/L in 180 minutes with approximately 90% destroyed within 90 minutes of the start of permanganate addition.

The RCT simulant solutions used for all runs shown in Figure 3 were pre-charged with nitrite to provide a nitrite to nitrate molar ratio of 4.4. Figure 4 shows the 20 L scale glycolate data shown in Figure 3 and includes the measured nitrite to nitrate molar ratios before and after glycolate destruction by permanganate. No measurable loss of nitrite was observed with any of the permanganate runs using low or nominal glycolate simulants.

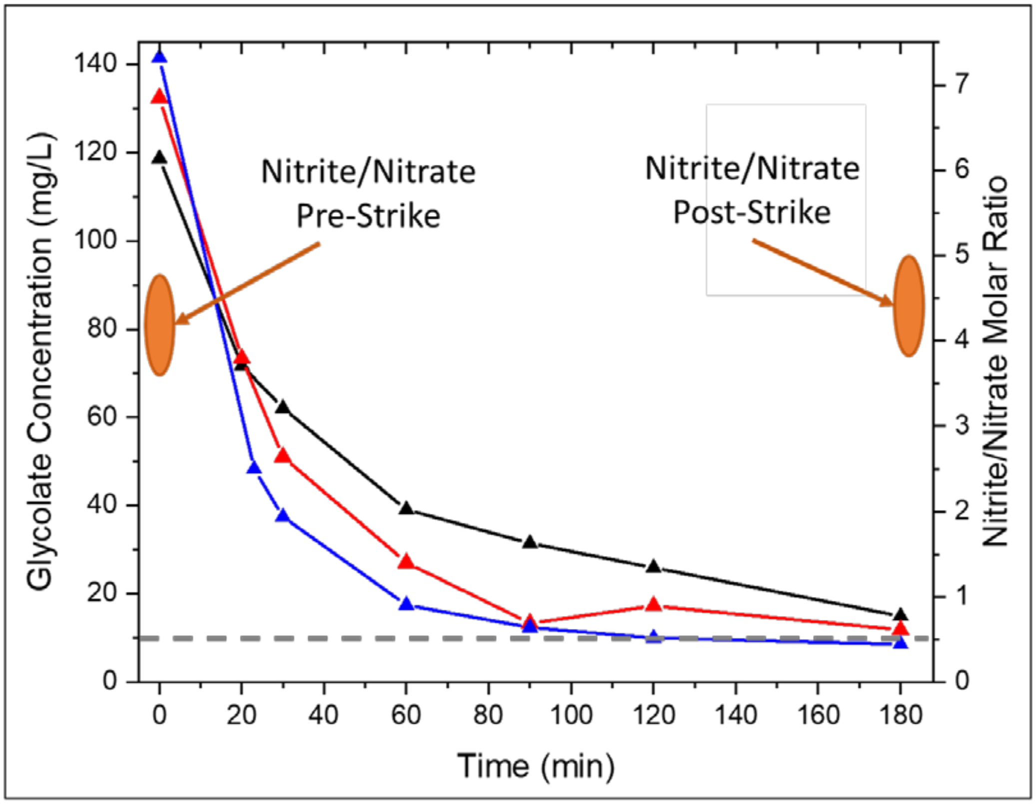

Figure 4: Glycolate concentration and nitrite/nitrate ratio as a function of time and P/G ratio

Less glycolate was destroyed as a function of time with comparable P/G ratios in runs with the nitrite corrosion inhibitor added at the end of the experiment as shown in Table 5 with green highlighted rows signifying post nitrite strike runs. Though inconclusive, it is possible higher concentrations of nitrite aid in the destruction of glycolate. Further discussion on the effect of the order of nitrite addition is found in section 4.2.

4.1.2 *500 Gallon Foamover Conditions: 5100 mg/kg Glycolate*

Sodium permanganate was added to 1.6 L solutions simulating a 500 gallon foamover from the SMECT to the RCT. Measured concentrations of glycolate and oxalate as a function of time are shown in Figure 5 for P/G ratios of 2.2 and 2.6, and for a P/G ratio of 2.6 with the nitrite corrosion inhibitor added before and after the permanganate oxidation reaction. For all runs, glycolate concentrations were reduced to near the IC detection limit within 90 minutes of the start of permanganate addition. The addition of nitrite prior to permanganate did not appear to have any effect on the glycolate destruction reaction. Results are consistent with data from the protocol report in that, on a molar basis, less permanganate is required to destroy glycolate in the presence of relatively large amounts of sludge simulant.

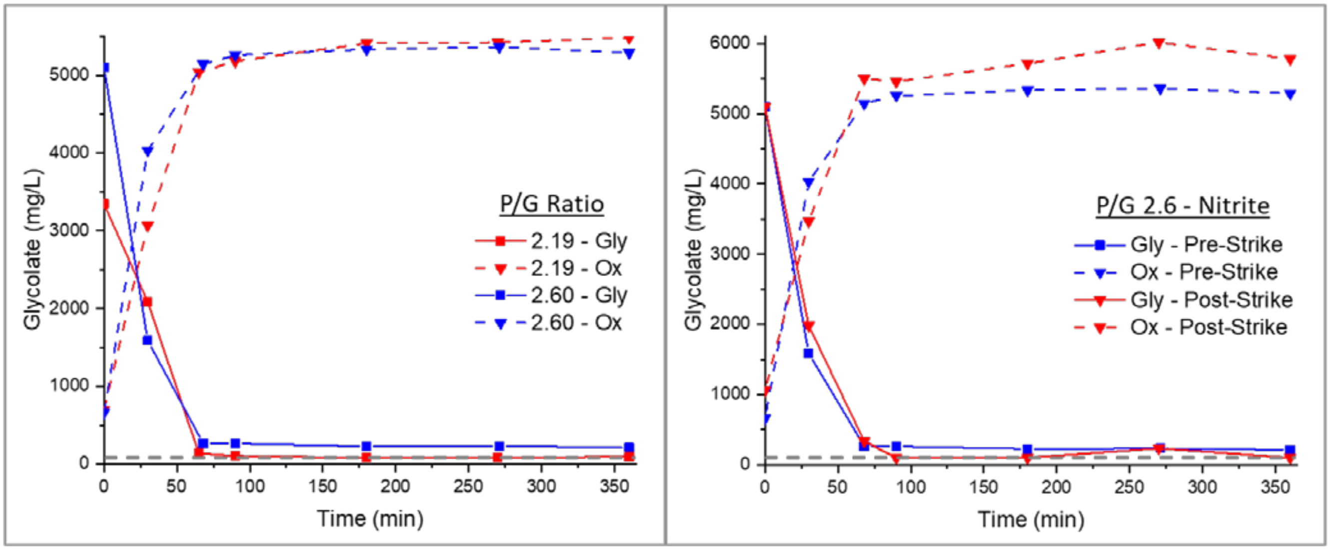

Figure 5: Glycolate and oxalate concentrations for foamover runs comparing *(left)* P/G ratio and *(right)* the order of nitrite addition.

It should be noted the IC detection limit for glycolate in this study was 1 mg/L. The 500 gallon foamover RCT simulant samples required a 100x dilution to be within the calibration range for IC analysis. A difference of 1 or 2 mg/L in the IC corresponds to a dilution corrected value of 100-200 mg/L. A difference of 100 mg/L near the limit of detection should be considered within the noise and virtually identical.

Figure 6 shows results from glycolate destruction experiments with a final permanganate to initial glycolate molar ratio of 2.6 using two oxidant addition strategies. In the first, permanganate was added in one continuous 60 minute injection. In the second, permanganate additions were subdivided into two aliquots of 1.3 mols of permanganate to initial glycolate. The two permanganate injections were performed for 30 minutes with 90 minutes between injection start times.

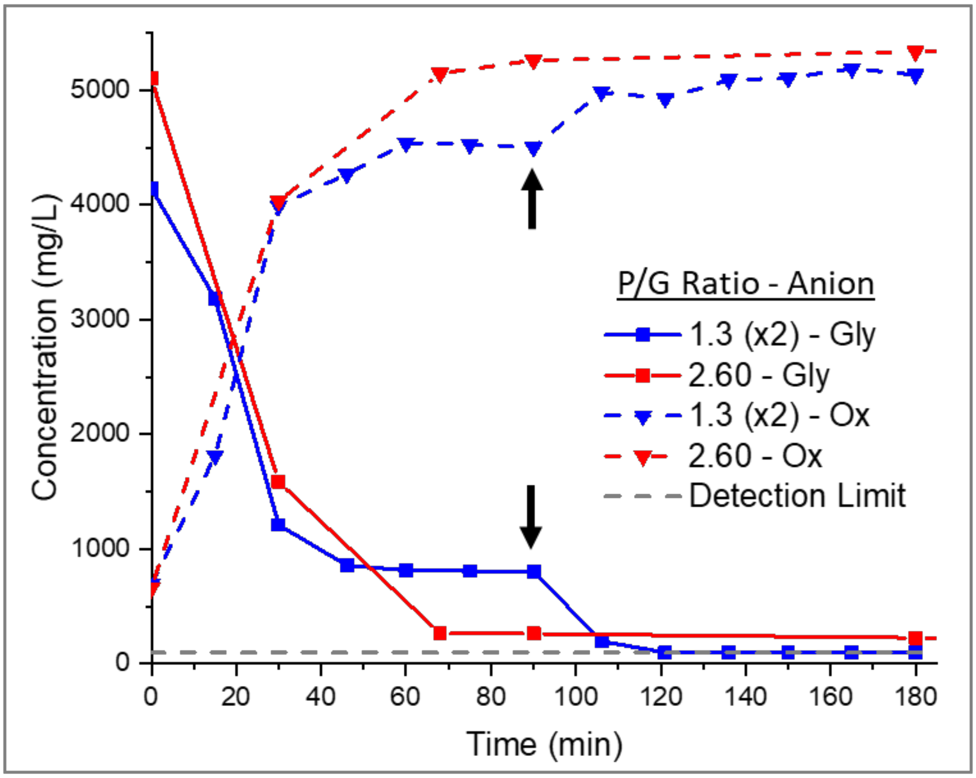

Figure 6: Glycolate and oxalate concentrations as a function of time in foamover runs with a total P/G ratio of 2.6. Arrows note the initiation of a second 1.3 P/G permanganate strike.

Both addition scenarios were demonstrated to reduce glycolate concentrations below detection limits. The glycolate concentration for the continuous 60-minute addition scenario dropped to near the 100 mg/L IC detection limit (i.e., 98% destruction) within 70 minutes of the start of permanganate addition. Addition of 1.3 P/G saw the glycolate reduction plateau at 800 mg/L after 60 minutes from the start of addition. The follow-on addition reduced the glycolate concentration to below 100 mg/L at the end of the second 30-minute addition.

4.1.3 *Lower Glycolate RCT Conditions: 68 mg/kg Glycolate*

Figure 7 shows measured glycolate and oxalate concentrations in experiments using “low” glycolate simulants. Results with 68 mg/kg starting glycolate were very similar to results from the nominal entrainment and appear to follow reaction (1). The glycolate concentration decreased as a function of time and oxalate concentrations increased by approximately the same molar amount in both runs. Similar to simulants with nominal glycolate, a P/G ratio of 5.7 reduced glycolate to below detection limits within 90 minutes.

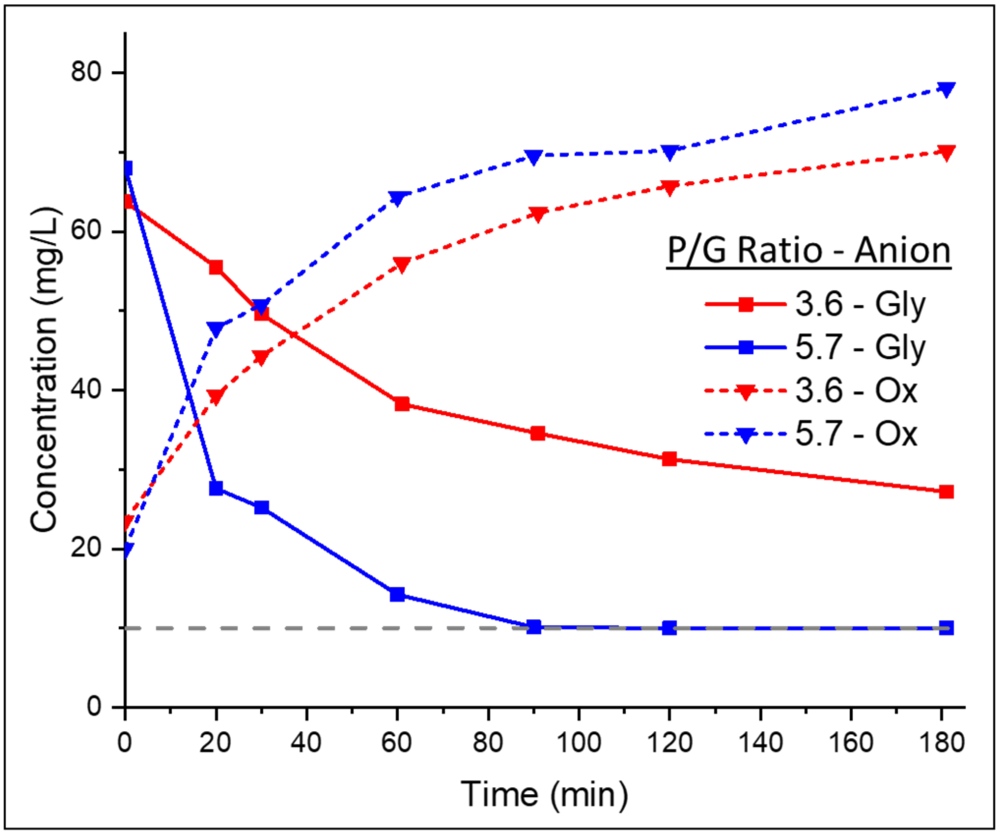

Figure 7: Glycolate and oxalate as a function of time and initial permanganate to glycolate molar ratio. Initial glycolate concentration: 68 mg/kg.

4.2 Order of Chemical Addition

All tests were conducted with a nitrite/nitrate molar ratio of 4.4, which was found to be an approximate average of typical RCT samples. The shaded rows in Table 5 denote experiments where the sodium nitrite corrosion inhibitor was added to the reaction vessel at the end of the experiment. The nitrite/nitrate values reported in Table 5 were calculated prior to the post-reaction nitrite strike as no nitrite oxidation was expected post-reaction. A complete listing of measured nitrite and nitrate concentrations for each run can be found in Table 6 and Table 7.

Table 6 shows the nitrite and nitrate concentrations for the low and nominal glycolate runs with the nitrite corrosion inhibitor added to the RCT simulant prior to permanganate addition. For experiments simulating low and nominal glycolate entrainment, the measured nitrite concentrations before the oxidation reaction are within 10% of the values measured at the end of the run; indicating nitrite destruction is negligible under protocol conditions.

Table 6: Nitrite and nitrate concentrations in low and nominal glycolate RCT simulants

	1.8-Liter Low		**1.8-Liter Nominal**			**20-Liter Nominal**		
Run #	7	7a	1	2	3	12	13	14
P/G Ratio	3.6	5.8	3.4	4.6	5.7	3.5	4.6	5.6
Before Permanganate Addition								
Nitrite (mol/L)	0.206	0.238	0.238	0.238	0.238	0.216	0.228	0.269
Nitrate (mol/L)	0.045	0.051	0.052	0.052	0.052	0.053	0.050	0.069
After Permanganate Addition								
Nitrite (mol/L)	0.227	0.232	0.235	0.233	0.237	0.216	0.229	0.260
Nitrate (mol/L)	0.048	0.047	0.047	0.051	0.052	0.051	0.047	0.065

Table 7 lists the measured nitrite and nitrate concentrations from foamover runs before and after permanganate addition. The measured nitrite concentrations were lower post-reaction for all foamover runs suggesting nitrite destruction may be occurring. The final nitrate concentrations were within 10% of their starting value suggesting the oxidation of nitrite to nitrate is unlikely. The unaccounted nitrite may have formed a NO_x species, but no off-gas measurements were performed for 1.8 L experiments. However, it should be noted that all nitrite to nitrate molar ratios were well above the minimum of 1.66 required for waste tank corrosion control.

Table 7: Nitrite and nitrate concentrations in post-nitrite strike and simulated foamover RCT simulants

	Nominal		**Foamover**			
Run #	4	5	8	8b	9	10
P/G Ratio	3.5	4.6	2.6	2.6	2.2	2.6
Before Permanganate Addition						
Nitrite (mol/L)	0.042	0.042	0.346	0.346	0.320*	0.047
Nitrate (mol/L)	0.048	0.048	0.082	0.071	0.061*	0.082
After Permanganate Addition						
Nitrite (mol/L)	0.042	0.044	0.274	0.292	0.275*	0.031
Nitrate (mol/L)	0.046	0.048	0.084	0.066	0.078*	0.075
After Post-Strike Nitrite Addition						
Nitrite (mol/L)	0.233	0.227				0.284
Nitrate (mol/L)	0.062	0.060				0.072

*Measurement acquired 4 days after dilution

Also found in Table 7 are nitrite and nitrate concentrations from runs with the nitrite corrosion inhibitor added at the end of the run. Measurements from oxidation experiments with nominal glycolate, regardless of the order of nitrite addition, yielded similar nitrite and nitrate concentrations before and after permanganate addition. The slight increase in nitrate measured after the post-nitrite addition is likely due to measurement uncertainty or an artifact of sample dilution during preparation for IC analysis.

Similar to previous protocol testing, samples analyzed for nitrite were diluted with water and then quickly analyzed. Results confirm that nitrite was not destroyed by permanganate at high pH (i.e., pH > 13). Except for Run 9, nitrate and nitrite concentrations in foamover simulants decreased from their initial values prior to permanganate addition. In Run 9, the diluted sample was unintentionally stored at pH ≈10 for 4 days with residual unquenched manganate resulting in nitrite being partially oxidized to nitrate. The sample dilution and subsequent drop in pH was performed in preparation for IC analysis and is not typical or expected for RCT operations.

4.3 Off-gas Analysis of 20 L Scale Runs

Off-gas generation from the three large scale tests was monitored by GC and FTIR. The relevant FTIR results from the experiment with the highest P/G ratio of 5.6 are shown in Figure 8 and the relevant GC results for all three tests are shown in Figure 9. The results from the first two experiments with lower P/G ratios of 3.5 and 4.5 showed the same trends (all component concentrations at or below detection limits) with the run with a P/G of 5.6 being the only one to provide detectable levels of off-gas components during testing.

From the FTIR data, observable off-gas generation began just after the completion of the permanganate addition to the vessel. The highest detectable level of CO_2 was approximately 22 ppm (the ≈40 ppm CO_2 observed in Figure 9 during vessel loading and cleanout is consistent with ambient air) while that of the NO_x species were observed below 10 ppm. From the GC data, the H_2 concentrations were observed to trend around the detection limit throughout testing. The only indication of reactivity from an off-gas perspective was observed in the highest P/G ratio test (Run 14) where H_2 was observed just above detection limit, reaching a value of only ≈16ppm, 2-3 orders of magnitude below the safe operating limit set at 1.0 vol.% (10000 ppm), one quarter of the Lower Flammability Limit (LFL). As these tests were all performed at high pH (>13), the majority of off-gas species being monitored (CO_2 and NO_x) were likely adsorbed by the solution as they were generated and, therefore, were not present in the off-gas stream to any significantly quantifiable levels.

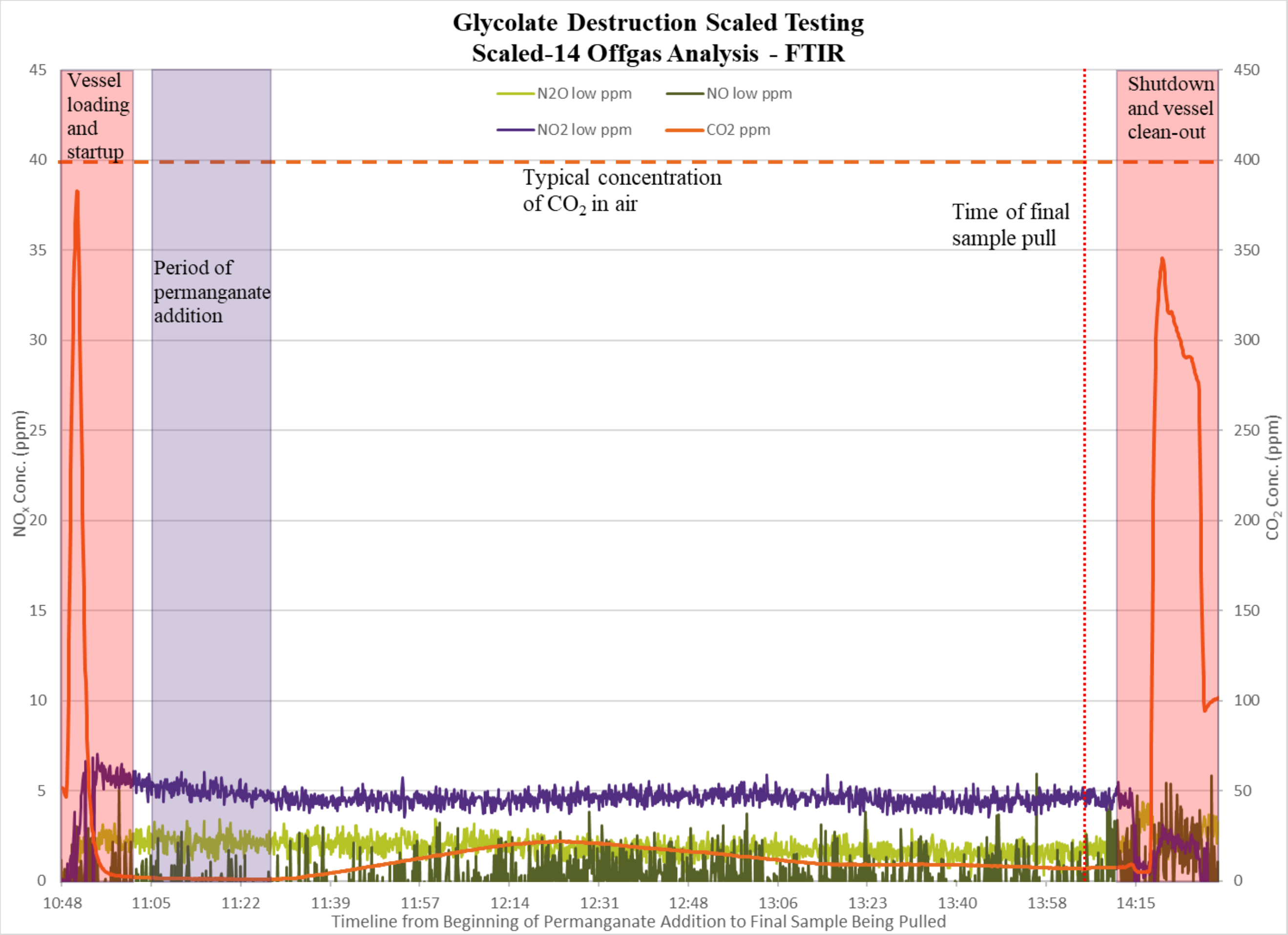

Figure 8: Off-gas concentrations from FTIR data during scaled run 14 from equipment setup to shutdown; regions highlighted in red correspond to the vessel being opened.

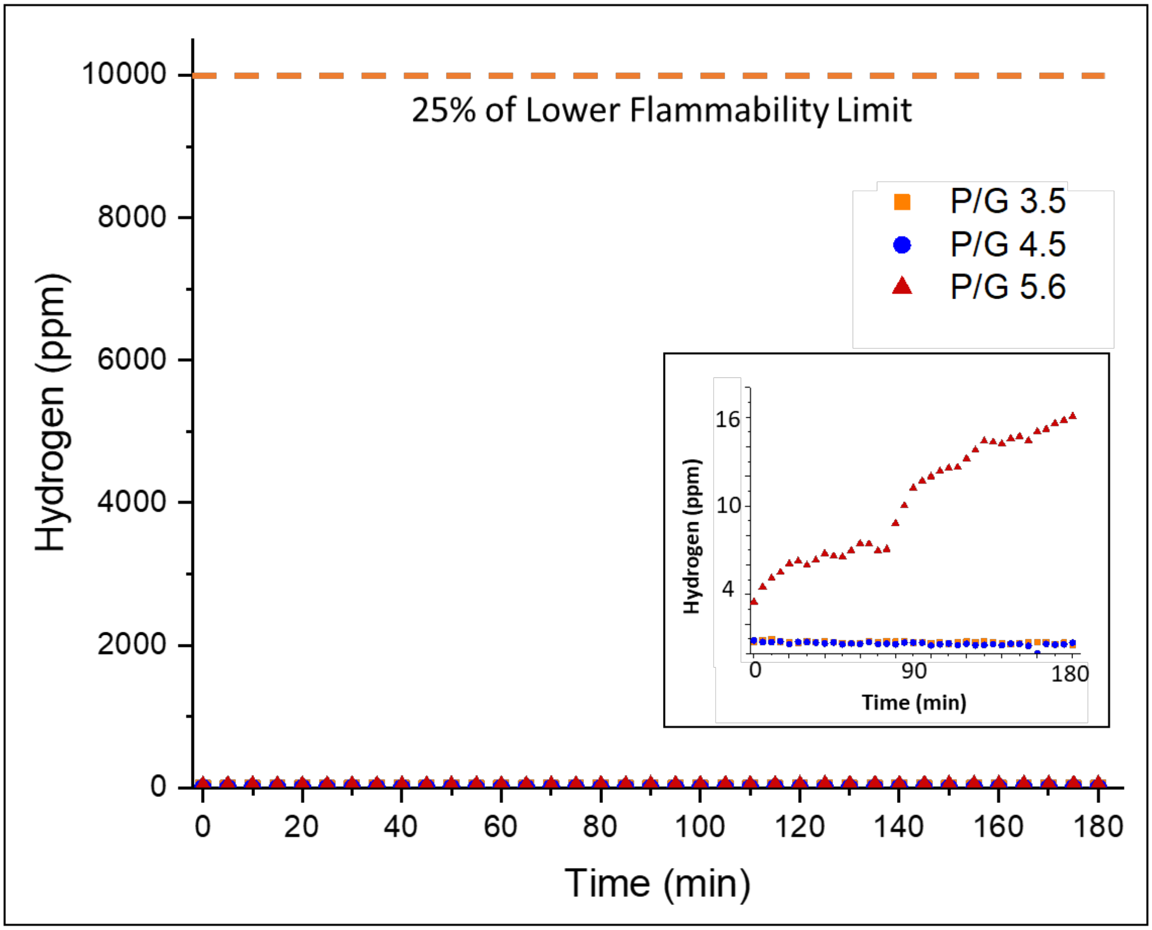

Figure 9. Off-gas H_2 concentrations from GC data during all three scaled runs from equipment setup to shutdown with respect to 25% of the Lower Flammability Limit (LFL) for H_2. Inset shows magnified view for comparison.

4.4 Manganese Speciation: In-Situ UV-Vis Measurements and Analysis

The oxidation states of manganese have distinct colors that can be monitored using UV-Vis spectroscopy.[13] UV-Vis measurements were acquired in-situ for the 1.8 L experiments simulating low and nominal entrainment of glycolate. Collecting UV-Vis measurements was not feasible for foamover studies due to the large concentration of SRAT product simulant allowing insufficient transmission of light.

Figure 10 shows the fractions of permanganate and manganate to the final total manganese concentration measured by UV-Vis for Run 2 with a starting glycolate concentration of 140 mg/kg and a P/G ratio of 4.5. The fraction of permanganate grows for the first 20 minutes as permanganate is added to the reaction vessel. As the reaction progresses, the fraction of manganate increases by approximately the same amount as the reduction of permanganate.

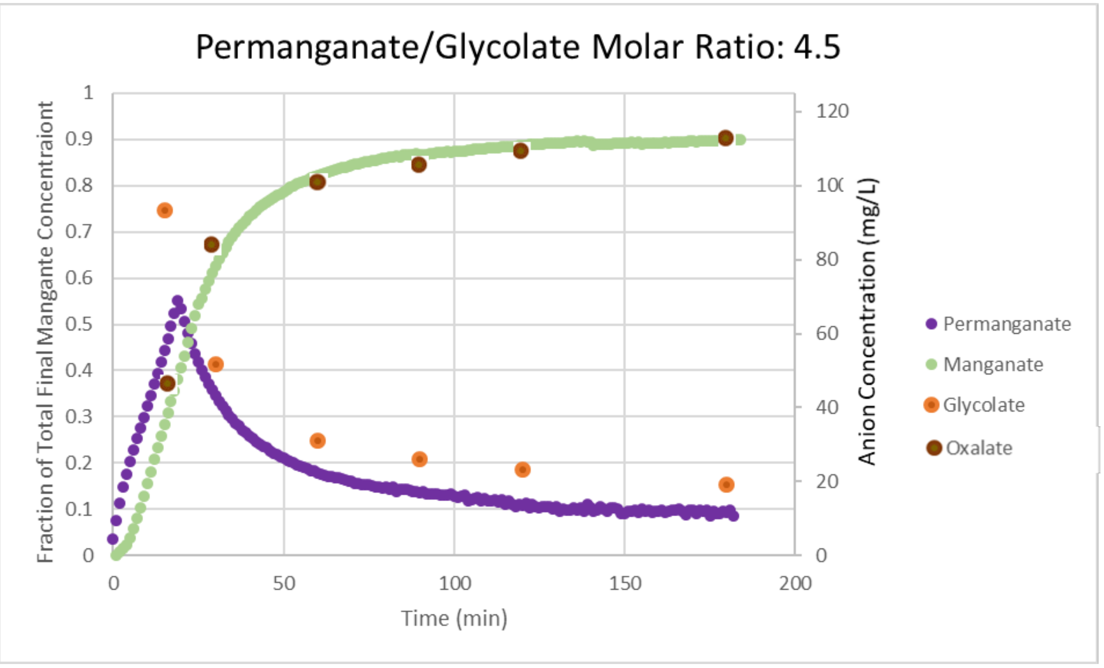

Figure 10: Permanganate and manganate as a fraction of the total manganese concentration overlaid with glycolate and oxalate concentrations as a function of time.

Also included in Figure 10 are concentrations of glycolate and oxalate measured by IC throughout the run. Previous efforts to understand the permanganate/glycolate interaction found equation (1) best describes the observed reaction of glycolate with permanganate under nominal and low glycolate entrainment conditions.[7]

$$C_2H_3O_3^- + 4MnO_4^- + 5OH^- = C_2O_4^{2-} + 4MnO_4^{2-} + 4H_2O \qquad (1)$$

This mechanism is supported by IC analysis showing that glycolate is oxidized to oxalate and UV-Vis measurements that confirm permanganate (Mn^{7+}) is reduced to manganate (Mn^{6+}).

5.0 Conclusions and Recommendations

The 20 L scale protocol test series has been completed. The following conclusions are drawn.

1) Glycolate, at starting concentrations ranging from 68 to 5100 mg/kg can be reduced below detectable limits of 10 to 100 mg/L respectively. From an operational basis, nominal SMECT/OGCT to excessive SMECT foamover conditions can be mitigated by a permanganate strike within DWPF specified time and conditions.
2) The larger (20 L) scale experimental results are consistent with the 1.8 L experiment, indicating no loss of process efficiency.
3) The molar ratio of permanganate to glycolate (P/G) required to mitigate glycolate to below detectable levels is dependent on the initial glycolate concentration.
    a. A P/G ratio of ≈5.7 is sufficient for low and nominal glycolate entrainment conditions, and
    b. A P/G ratio of ≈2.2 is sufficient for foamover conditions

4) In all experiments, > 80% of the glycolate destruction reaction was complete within 90 minutes of the start of permanganate addition.
5) Nitrite destruction was negligible for low and nominal glycolate entrainment scenarios. A small amount of nitrite destruction may occur in foamover conditions.
6) IC analysis confirms that glycolate is oxidized to oxalate.
7) In-situ UV-Vis measurements of low and nominal glycolate runs confirm permanganate (Mn^{7+}) is reduced to manganate (Mn^{6+}). UV-Vis analysis of foamover simulants was inconclusive due to insufficient transmission through the higher concentration SRAT product simulant.

The following recommendation for upcoming real waste verification testing is made.

1) Target a molar ratio of permanganate to glycolate of 5.7 for low and nominal glycolate concentrations.
2) Nitrite should be added prior to oxidant addition consistent with DWPF operational practice.

6.0 References

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