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Permanganate Oxidation of Defense Waste Processing Facility (DWPF) Recycle Collection Tank (RCT) Simulants – Protocol Runs for Nominal and Chemical Process Cell (CPC) Foamover Conditions

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EXECUTIVE SUMMARY

Savannah River National Laboratory (SRNL) has completed a work scope in support of the Savannah River Remediation (SRR) Nitric-Glycolic flowsheet. Glycolic acid will replace formic acid as a reducing agent in the pre-processing of High-Level Waste sludge performed at the Defense Waste Processing Facility (DWPF). Glycolic acid will perform the same function as formic acid, namely reduction of mercury and adjustment of feed rheology and melter oxidation/reduction potential, while significantly reducing the potential for hydrogen generation in DWPF processing. Development testing has demonstrated glycolic acid virtually eliminates hydrogen production in the pre-processing steps.

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). This work scope demonstrates that glycolate can be destroyed under the Nitric-Glycolic flowsheet prior to returning the DWPF recycle stream to CSTF.

To avoid potential flammability issues due to thermolysis of glycolate in CSTF, SRR tasked SRNL to quantify and mitigate glycolate returns via DWPF's recycle stream. The development of a strategy for glycolic mitigation was initiated with a system's engineering workshop. Various chemical and/or physical solutions for how and where to destroy glycolate were considered – consistent with DWPF's operational capabilities and process requirements. The workshop identified chemical oxidation of glycolate within the DWPF Recycle Collection Tank (RCT) as the most promising option. (The RCT collects offgas condensate from pre-processing, vitrification, and other unit operations performed in DWPF and is the singular return vessel delivering recycle effluent back to CSTF.) A series of down-select experimental tests were performed that showed sodium permanganate was the most effective oxidant.

This work was performed to identify an appropriate operational protocol for DWPF implementation. Building upon the downselect experiments, the work targeted an improved description of suitable RCT conditions prior to the strike (pH, etc.), permanganate addition rate, and destruction reaction kinetics. Data collected were also used to determine the best expression of reaction stoichiometry and the effective minimum permanganate addition required.

The most optimal protocol conditions (as per DWPF requirements) are consistent with a permanganate strike at or near pH 12. The most significant results (at high pH) include the following:

Nitrite is not oxidized to nitrate by permanganate. Therefore, nitrite can be added to the RCT prior to permanganate.

Glycolate is oxidized to oxalate with no significant formation of CO_2 or carbonate.

At low initial glycolate (125 mg/kg), it is estimated that the minimum initial permanganate to glycolate (P/G) molar ratio is 4.0, with an additional 1-2 (5-6 total) required to achieve complete oxidation to below 10 mg/kg (detection limit). During testing, permanganate (Mn^{7+}) is reduced to manganate (Mn^{6+}) and not to MnO_2 (Mn^{4+}), as is evident by looking at the color of the products. But since the solutions are so strongly colored, the development of an analytical technique to quantify the concentration of the manganese species is needed. The residual manganate is less than 1% by mass of the resulting RCT product. Additional testing is in progress to determine the final oxidation state in Tank 22.

Formate and oxalate are not oxidized, formate does not appear to be generated from glycolate; the nitrite to nitrate ratio does not affect the oxidation of glycolate; added mercuric ion at 200 mg/kg does not affect the oxidation of glycolate; and at low glycolate; the presence of SRAT product sludge does not affect the oxidation of glycolate.

For a simulated 500 gal DWPF-scale carryover of SRAT product contributing 4500 mg/kg glycolate, the permanganate required per mole of glycolate is less than for simulated 14.5 gallon carryover contributing 125 mg/kg glycolate. The presence of sludge components at these conditions does affect the course of the oxidation reaction. Permanganate is likely reduced at least partially to MnO_2 rather than to only manganate, so relatively less is required.

Greater than 99% of the glycolate in the foamover tests was destroyed (to 40 mg/kg) with a permanganate to glycolate molar ratio of 2.0, but the target <10 mg/kg glycolate was not reached.

The antifoam straight-chain analog PEG was not significantly oxidized by permanganate at pH 12-13.

Larger scale tests to be performed by SRNL are based on the complete list of recommendations as described in Section 5 of this document.

TABLE OF CONTENTS

1.0 Introduction 1

2.0 Background 2

2.1 Quality Assurance 4

3.0 Experimental Procedure and Operations 4

3.1 Experimental Design and Test Protocols 4

3.1.1 Test Strategies 4

3.1.2 Test Temperatures 6

3.2 Test Duration 6

3.3 Simulant Compositions 6

3.3.1 RCT Heel Composition 6

3.3.2 Condensate Simulants (SMECT or OGCT) 7

3.3.3 Antifoam Simulant 12

3.4 Oxidant Stoichiometry and Experimental Design 12

3.5 Experimental Apparatus and Parameters 15

3.6 Scaling 17

3.7 Offgas Analysis 17

3.8 Liquid Analyses 18

3.8.1 pH 18

3.8.2 Sampling and Analysis 18

3.9 Test Chronology 19

4.0 Results and Discussion 19

4.1 Glycolate and Nitrite Destruction 20

4.1.1 Offgas Results for Runs Starting at Acidic pH 23

4.2 Glycolate Destruction, Stoichiometric Reactions, and Effects of Nitrite to Nitrate Ratio, Added Mercury, and Sludge 24

4.3 Qualitative Residual Manganese Species Results 30
4.4 Reaction Kinetics: Proposed Rate Equations for Glycolate Oxidation 31
4.4.1 First Order in Glycolate Only 32
4.4.2 First Order in Both Glycolate and Permanganate (Second Order Overall) 32
4.4.3 Rate Constants for Oxidation of Glycolate 33
4.4.4 Possible Reactions in the Presence of Sludge 39
4.4.5 Oxidation of Antifoam Analog PEG 40
5.0 Conclusions 40
6.0 Recommendations 41
7.0 References 42
8.0 Appendixes A-1

LIST OF TABLES

Table 1. Test Phase Status and TTQAP Task Activities 2
Table 2. Target and Approximate Actual Permanganate Oxidant Stoichiometries in Down-select Testing 3
Table 3. Chemical Addition Order and Scaling 5
Table 4. RCT Heel Simulant Composition Targets (pH ~13) 7
Table 5. SRAT Product Anion Composition 9
Table 6. SRAT Product Elemental Analysis and Physical Properties 10
Table 7. Target Acidity, pH, and Nitrate for Reagent Condensate Simulant 10
Table 8. Simulant Compositions 11
Table 9. Determination of Sludge for 125 mg/kg Glycolate 12
Table 10. Antifoam and PEO Simulant 12
Table 11. Initially Assumed Stoichiometric Reactions for Complete Oxidation of Organics to CO_2 13
Table 12. Summary of Test Conditions 14
Table 13. Modified Stoichiometric Reactions for Glycolate Oxidation 15
Table 14. Properties of Reaction Products 20
Table 15. Experimental Results: Glycolate Destruction and Carbon Balance 21
Table 16. Experimental Results: Nitrite Destruction and Nitrogen Balances 22
Table 17. Kinetics of Oxidation Reactions 34

LIST OF FIGURES

Figure 1. RCT Cycle Steady-State Heel Composition 7

Figure 2. Equipment Apparatus Sketch 16

Figure 3. Photo of Apparatus 17

Figure 4. Offgas and pH During Acidic Starting Runs 1 & 2 24

Figure 5. Glycolate Destruction versus Initial Permanganate to Glycolate Molar Ratio for 125 mg/kg Glycolate 25

Figure 6. Example Glycolate and Oxalate Concentrations versus Time 26

Figure 7. Glycolate Concentration Comparison versus Nitrite to Nitrate Ratio 26

Figure 8. Glycolate Concentration Comparison versus Reagent and SRAT Product Simulants 27

Figure 9. Effect of Added Mercuric Nitrate on Glycolate Oxidation 27

Figure 10. Glycolate and Oxalate for Foamover Runs 28

Figure 11. Glycolate and Oxalate for Foamover Runs at Longer Time 28

Figure 12. Comparison of Foamover and 125 mg/kg Glycolate Test Glycolate Concentrations 29

Figure 13. Glycolate at 6 Hours versus P/G 30

Figure 14. Comparison of Product Solution Colors 31

Figure 15. Correlation of First Order Rate Constants with P/G Ratio 35

Figure 16. Second Order Rate Constants versus P/G Ratio 35

Figure 17. Example Fits of 125 mg/kg Glycolate Rate Data 36

Figure 18. First Order Rate Constants for Foamover Runs versus P/G 37

Figure 19. Second Order Rate Constants for Foamover Runs versus P/G 37

Figure 20. Foamover Runs Data Fits 38

LIST OF ABBREVIATIONS

AD	Analytical Development
CPC	Chemical Process Cell
CSTF	Concentration, Storage and Transfer Facilities
DWPF	Defense Waste Processing Facility
FTIR	Fourier Transform InfraRed (Spectroscopy)
HMDSO	Hexamethyldisiloxane
IC	Ion Chromatography
ICP-ES	Inductively Coupled Plasma Emission Spectroscopy
mmol	millimole
N/N	nitrite to nitrate molar ratio
NG	Nitric-Glycolic (Flowsheet)
OGCT	Offgas Condensate Tank
P/G	Permanganate to glycolate initial molar ratio
PEG	Polyethylene glycol
PEO	Polyethylene oxide
ppm	parts per million by volume or moles
PSAL	Process Science Analytical Laboratory
RCT	Recycle Collection Tank
REDOX	REDuction/OXidation
sccm	standard cubic centimeters per minute
scfm	standard cubic feet per minute
SMECT	Slurry Mix Evaporator Condensate Tank
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
TC	Total Carbon
TIC	Total Inorganic Carbon
TMS	Trimethylsilanol
TOC	Total Organic Carbon
TTQAP	Task Technical and Quality Assurance Plan
TTR	Task Technical Request
UV/VIS	ultraviolet / visible

1.0 Introduction

The chemical process flowsheet used to convert Savannah River Site (SRS) high-level waste into borosilicate glass is being modified. Glycolic acid will replace formic acid as a reducing agent in the pre-processing of sludge.[1] Glycolic acid will perform the same function as formic acid, namely reduction of mercury, adjustment of feed rheology and oxidation/reduction potential of glass. Glycolic acid has been shown superior to formic acid during chemical processing in the Sludge Receipt and Adjustment Tank (SRAT) with regards to the reduced production of hydrogen gas, the primary flammability concern, and the stability of pH during the concentration of melter feed.

This change is being implemented to improve operations within the Defense Waste Processing Facility (DWPF) and better support one of the Site's key challenges: the incorporation of strip effluent and monosodium titanate streams received from SWPF with sludge and subsequent feed preparation. DWPF operations include the receipt of High-Level Waste sludge and intensely radioactive process effluents, feed preparation and vitrification, and process condensate collection and return to Concentration, Storage and Transfer Facilities (CSTF). As the volume of strip effluent requiring processing significantly increases as SWPF comes on line, DWPF condensate returns to the CSTF will increase. A small concentration of glycolate, ≤120 mg/L[2] is anticipated to return to the CSTF with each batch (typical entrainment from CPC or melter) of DWPF recycle. To avoid the generation of hydrogen through thermolysis in the CSTF, SRNL has been tasked to mitigate the concentration of glycolate returned via DWPF recycle stream through chemical destruction of glycolate.

The approach employed by Savannah River Remediation (SRR) to direct this flowsheet change evaluates mission-level DWPF operations/impacts and potential impacts to the CSTF. SRR and SRNL initiated the glycolic mitigation activity in November 2017. A systems engineering workshop[3] was held to establish potential mitigation options. These possible solutions were intended to address how to and where to destroy glycolate – consistent with DWPF operational capability and process requirements. The workshop identified chemical oxidation of glycolate within the DWPF RCT as the most promising option.

Testing to develop a process to oxidize glycolate and other organic species in non-radioactive waste simulants has been requested by Savannah River Remediation (SRR).[4] 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.[5] Scoping studies have been completed as requested by a Technical Assistance Request (TAR)[6] to evaluate the feasibility of using sodium permanganate and Fenton's Reagent (iron catalyzed hydrogen peroxide) for destroying glycolate.[7] The results from these scoping studies were summarized in a report.[8]

Seven phases of tests with simulant have been planned in developing an oxidation flowsheet for the Recycle Collection Tank (RCT), as shown in Table 1. The first two phases have been completed. The first phase was additional scoping tests of permanganate and Fenton's reagent.[8] 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 impact of various factors in defining the optimum processing conditions for oxidation of organics.[9] From the results of this testing, oxidation by permanganate was chosen over Fenton's reagent with hydrogen peroxide.[10]

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	Described in this document	Parts of 1 and of 3
4	Off-Normal Conditions (other than Foamover)	Future	Parts of 1 and of 3
5	Actual Waste Testing	Future	2
6	Larger Scale Testing	Future	1 h
7	Corrosion Testing	Stand-alone	4

(Phases 4-7 not necessarily in order of actual testing.)

The third phase of testing, described in this document, demonstrated nominal operation of the permanganate oxidation process under protocols similar to those used in the Defense Waste Processing Facility (DWPF). The specific off-normal condition of a CPC foamover into the Slurry Mix Evaporator Condensate Tank (SMECT) was performed in this phase. In addition, a test of permanganate oxidation of Antifoam 747 or the poly(ethylene)oxide chain portion of Antifoam 747 was requested.

A fourth phase of testing will study off-normal conditions such as excessive melter offgas entrainment, sump transfers, (Decontamination Waste Treatment Tank) DWTT transfers, products of DWPF tank cleaning, etc.; this phase will be covered in a future plan. Phases 5 and 6 will be to continue these protocol tests with actual waste testing and larger scale testing. Phase 7 covers corrosion testing and monitoring under simulated RCT operating conditions and chemical compositions. This phase will be performed as stand-alone testing.

2.0 Background

The following is a brief list of the results of the high pH down-select testing that are pertinent to the definition of conditions for the protocol testing.

Glycolate Destruction

- Glycolate destruction is improved by using higher oxidant stoichiometries.
- Glycolate destruction is improved slightly by higher temperature, slower addition rate, and lower pH, but none of these trends are particularly strong.

Oxidant Stoichiometry

- Previous testing based the oxidant stoichiometry on 100% conversion of organic carbon to carbon dioxide or carbonate.
- The oxidant stoichiometry calculations did not account for permanganate destroyed by nitrite. Nitrite appeared to be significantly destroyed in every test. If the nitrite is included in the oxidant stoichiometry calculations, the actual stoichiometries were sometimes lower and sometimes higher. (The initial nitrite varied significantly based on the amount that decomposed prior to test initiating.) The sample prep used in the down-select test resulted in nitrite destruction in the high pH tests that was not attributed to permanganate. In the protocol testing reported here, samples analyzed for nitrite were diluted with water and then quickly analyzed. The results demonstrated that the nitrite was not destroyed by permanganate in in the high pH protocol tests.

- Excluding methyl mercury, propanal, and trimethylsilanol, and adding nitrite to the stoichiometry gives the stoichiometry values shown in Table 2.

Table 2. Target and Approximate Actual Permanganate Oxidant Stoichiometries in Down-select Testing

Target Stoichiometry	Actual Stoichiometry
1X	1.02-1.24X
1.25X	0.96-1.70X
1.5X	1.16-1.86X

For these reasons, the oxidant stoichiometry for the Protocol Tests was defined to include nitrite and exclude organic species that were either unreactive or for which the results were inconclusive.

Fate of Organic Species

- Methyl mercury was not destroyed by permanganate.
- The results for propanal are inconclusive, but it appears that destruction was small. Some propanal volatilized during simulant preparation before the oxidant addition. At low pH, some propanal appears to have been partially oxidized by nitrite to what, based on the infrared spectrum, was possibly propenyl nitrite.
- Trimethylsilanol was mostly released as hexamethyldisiloxane (HMDSO). The evidence for oxidation is inconclusive. (Two trimethylsilanol $\rightarrow$ HMDSO + H_2O)
- Glyoxylate appears to be completely oxidized to form more oxalate at high pH and more CO_2 at low pH.
- Due to the presence of glyoxylate in the tests, it was not possible to determine if glycolate was oxidized to oxalate.
- Glycolate and glyoxylate may also be oxidized to formate.
- Formate destruction was greater than 92% at pH 8 and 13, but was negligible at pH 3 (formate appears to have been generated from formaldehyde or glyoxylate).
- The oxidation of formaldehyde to formic acid may affect the formate destruction values.

The results indicated that, to within the ability to measure individual organics and the Total Organic Carbon, methyl mercury, propanal, and trimethylsilanol are mostly unreactive towards oxidation by permanganate. The ability to measure trimethylsilanol and propanal in the feed and product is insufficient to determine if oxidation has occurred.

Offgas Generation

- At pH 3 and 8, nitrite appeared to be mostly oxidized to nitrate. At pH 13, the results were ambiguous, indicating both nitrite and nitrate destruction. For both to be destroyed, there would need to be another nitrogen containing product. Insufficient N_yO_x gases were detected to account for the amounts of nitrite and nitrate destroyed.
- Carbon dioxide was measured throughout pH 3 runs, with less at pH 8 and almost none at pH 13 since CO_2 would form soluble carbonate.
- Various gases were emitted during the preparation of the simulant in the vessel. Some propanal, and methanol from the formaldehyde solution, were emitted, while trimethylsilanol was evolved as HMDSO. Upon nitrite addition, NO, NO_2, and N_2O were generated. As previously noted, some propenyl nitrite may have been emitted in some tests.

2.1 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60[11]. 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 T7909-00035-25 through T7909-00035-42.

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.

3.0 Experimental Procedure and Operations

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 Offgas Condensate Tank (OGCT) material. At this point in the process cycle, the RCT is high in free hydroxide and nitrite compared to the SMECT and the OGCT but low compared to the RCT or CSTF, assuming it has not been preconditioned with sodium hydroxide and sodium nitrite. The RCT is primarily fed by the SMECT and OGCT. During typical processing, the SMECT and the OGCT condensates are pH 1-3 nitric acid solutions.

3.1 Experimental Design and Test Protocols

The conditions for the experimental tests were specified in a Run Plan.[13] The material volumes will be discussed below on a DWPF basis. These volumes were scaled in the laboratory tests by the RCT volume ratio of 8000 gal to 1.8 L (16,800 L/L, or 4440 gal/L, 4.44 gal/mL scale factor).

3.1.1 *Test Strategies*

To test actual operational protocols, the test program was conducted to mimic actual operation of the RCT irrespective of the purge. Currently the RCT heel is typically pre-charged with a minimum of 75 gal of 50 wt% sodium hydroxide and 215 gal of 6.6 M sodium nitrite to meet the corrosion control requirements for transfer to Tank 22. The RCT heel volume is usually 1400 gal.[14] Permanganate destruction of glycolate was expected to also destroy nitrite, so nitrite was added after oxidation was complete. Addition of the NaOH prior to condensate addition was done with the expectation that offgas generation that occurs at low pH would be alleviated at high pH.

NOTE: *Condensate* will be used to describe either a SMECT or OGCT condensate.

The SMECT condensate contains mostly HNO_3 added to maintain the pH around 2 with some HNO_3 from scrubbing of NO_x gases in the SRAT condenser and scrubber. Note that DWPF has been reducing the amount of HNO_3 added[15] to the SMECT to reduce oxidation and dissolution of elemental mercury. The condensate will also contain some sludge components (solids and liquid) carried over from the SRAT and Slurry Mix Evaporator (SME). The amount of carryover will vary. Similarly, the OGCT condensate will contain mostly HNO_3 from NO_x scrubbing and melter feed carryover. The composition of this carryover will be very similar to the SMECT composition, so for this work, the same Condensate simulants will be assumed to apply to the SMECT and OGCT.

The following two addition strategies, Cases A and B, were tested:

A. To the caustic RCT heel which also contains nitrite, the acidic condensate was added. (In actual operation in DWPF in this scenario, the combined contents could have a pH from acidic to neutral to slightly caustic.) Sodium hydroxide and sodium nitrite were then added after permanganate oxidation. Two tests were performed under these conditions.

B. The RCT heel was adjusted with NaOH before condensate transfer such that no additional NaOH is needed after permanganate oxidation. The combined RCT contents remained caustic. Sodium nitrite was then added after completion of permanganate oxidation. All but two tests were conducted under these conditions.

At a meeting of SRNL and SRR personnel, SRR indicated that the preferred mode of operation would be Case B.[14]

In Case A, the RCT contents reached a pH of about 3 prior to permanganate addition. The condensate simulant was designed to reach about this pH upon addition to the heel simulant. The tests used an RCT heel simulant and a simulant for Condensate. The volume of the simulated Condensate transfers was scaled to the amount that would fill the RCT to 8000 gal minus the amounts of NaOH and $NaNO_2$ to be added.

The Case A tests with no prior addition of NaOH to the heel were used to determine how much CO_2 and NO_x gases are emitted upon acidification of the heel and during the beginning part of permanganate addition. Offgas monitoring by FTIR was performed for the Case A tests. In these tests, the condensate was added at the highest prototypic rate of less than 100 gpm[14] (22.5 mL/min).

In the Case B tests, the RCT remained caustic throughout operation. These tests with prior addition of NaOH remained at high pH and evolved little offgas. Although these tests should not require offgas monitoring, monitoring was performed during the first several tests to confirm this assumption. The Condensate simulant was added either to the heel at a high flowrate or pre-mixed with the heel and placed directly into the test vessel. The scaled addition rate (~22.5 mL/min) was not necessary since the pH will remain high.

The chemical addition orders for the two heel conditions are shown in Table 3 for DWPF and laboratory scale. 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 is that which brings the total RCT volume to 8000 gal before permanganate addition. The permanganate volumes are approximate values for illustration only here. The quantities used for foamover testing are also shown in Table 3. See section 3.3 for explanation of dilute condensates and foamover. The 500 gal amount of sludge for the foamover case was provided by SRR.[14]

Table 3. Chemical Addition Order and Scaling

			NaOH Before Condensate*			
	NaOH After Condensate		Dilute Condensates		Foamover	
Step	**DWPF (gal)**	**Laboratory (mL)**	**DWPF (gal)**	**Laboratory (mL)**	**DWPF (gal)**	**Laboratory (mL)**
RCT Heel	1400	315	1400	315	1400	315
50 wt% NaOH	NA	NA	75	16.9	75	16.9
Condensate	6310	1420	6310	1420	5810	1308
Sludge	NA	NA	NA	NA	500	112.5
20 wt% sodium permanganate	~90	~20	~90	~20	~90	~20
50 wt% NaOH	75	16.9	NA	NA	NA	NA
6.6M $NaNO_2$ Solution	215	48.4	215	48.4	215	48.4

* Heel, NaOH and Condensate may be pre-mixed before test.

3.1.2 *Test Temperatures*

The temperature of the RCT for the past 10 years has varied between 20 to 30 °C. Tests were conducted at 20 °C because the reaction rates should be lower at this temperature. Several tests may be repeated at 30 °C in future testing.

3.2 Test Duration

For the NaOH addition after condensate cases, the addition of the Condensate simulant to the Heel simulant took about 1 hour at the prototypic flowrate. As previously noted, this duration could have been decreased if it had been found that the reactions at the lower pH are not affected by the addition rate. For the NaOH addition Before condensate cases, the addition rate was much higher and took 15 minutes or less.

Because the permanganate was added over 20 minutes for the 125 mg/kg glycolate tests, the total duration only needed to be as long as necessary for the glycolate oxidation to be near completion. The duration of the oxidation portion of each test was about 3 hours. The duration was adjusted to six hours for the larger foamover tests.

The final addition of NaOH for the After condensate case and the sodium nitrite solution took a few minutes.

The maximum overall duration per 125 mg/kg glycolate test was about 4.5 hours from start of Condensate addition to sodium nitrite addition.

The permanganate addition duration was 20 minutes for the 125 mg/kg glycolate tests and 65 minutes for the foamover tests (4500 mg/kg glycolate). The longer time used for the foamover tests assumed the DWPF addition pump had a maximum flowrate of 10 gallons per minute. The 20 minute duration assumes that the pump used in DWPF will have the necessary range of setpoint flowrates that will accommodate this duration. The DWPF and equivalent lab-scale flowrates were approximately 4.5 gpm and 1.0 mL/min, respectively for the 125 mg/kg glycolate tests; the exact values depended on actual quantities added.

3.3 Simulant Compositions

3.3.1 *RCT Heel Composition*

The RCT is operated with a normal heel volume of about 1400 gal after transfer to Tank 22.[14] The RCT heel composition simulated the major components of the RCT based on typical historical data. Minor components such as sludge and residual glycolate were not included. Rather, these species were introduced in the Condensate simulants. Some MnO_2, manganate, or unreacted permanganate from previous permanganate oxidations could also be present in the heel, but were not simulated.

The two compositions used for the RCT Heel simulant are given in Table 4. Most tests were conducted with a nitrite/nitrate molar ratio of 4.4, which was found to be an approximate average of typical RCT samples. Some tests were performed with a heel simulant that contained a nitrite/nitrate ratio of 2.0 that is closer to the minimum of 1.66 required for waste tank corrosion control. These simulants were made from reagent chemicals.

The compositions shown in Table 4 were adjusted from the values shown in the Run Plan Table 4[13] so that repeated RCT cycles would give same nitrite and nitrate composition, excluding changes due to permanganate. This repeated cycle is shown in Figure 1; the new heel composition after condensate addition was calculated to be slightly different than the heel simulant, but well within experimental uncertainties. The molar ratio of 4.4 simulates typical ratios in the RCT. The molar ratio of 2.0 is that required for corrosion control in Tank 22.

Table 4. RCT Heel Simulant Composition Targets (pH ~13)

Nitrite/Nitrate	Molar Ratio 4.4			Molar Ratio 2.0		
Species	Conc. (M)	Conc. (mg/L)	Conc. (mg/kg)	Conc. (M)	Conc. (mg/L)	Conc. (mg/kg)
Nitrite	0.214	9840	9772	0.0973	4474	4443
Nitrate	0.0486	3015	2994	0.0486	3015	2994
Nitrite/Nitrate Ratio	4.4	-	-	2.0	-	-
Hydroxide	~0.18	-	-	~0.18	-	-
pH	~13.3	-	-	~13.3	-	-

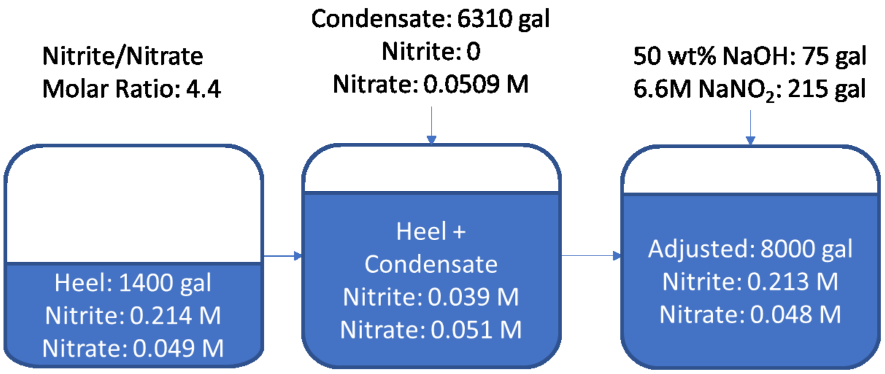


Figure 1. RCT Cycle Steady-State Heel Composition

3.3.2 *Condensate Simulants (SMECT or OGCT)*

The Condensate simulants represent the transfer from the SMECT or OGCT onto the Heel simulant in the RCT. The Condensate simulants were made from several reagent chemicals or from reagent chemicals and a characterized SRAT product sludge sample. A single simulant composition was used to simulate both the SMECT and OGCT.

The 'Reagent' simulant contained reagent chemicals with no sludge solids. The chemicals used were sodium salts of glycolate, formate, oxalate, and nitrate, with the pH adjusted with HNO_3. This simulant was used only for the first two tests were done at low starting pH. For the remaining tests with Reagent simulant, a simulant composition was used that combined the condensate, heel, and NaOH addition in the proportions shown in Table 3.

Tests with dilute SRAT product ('SRAT Prod') as the source of glycolate were all done at high pH, using a combined condensate including SRAT product, heel, and NaOH simulant. This simulant was made from reagent chemicals to adjust the nitrite, nitrate, formate, and oxalate concentrations while the SRAT product supplied all the glycolate. The 'Foamover' tests used SRAT product at a much higher concentration and was generated similarly from the sludge and reagent chemicals.

The target concentration of glycolate in the Reagent and SRAT product simulants was 125 mg/kg in the combined condensate, heel, and NaOH addition. The 125 mg/kg target is significantly higher than expected but was chosen to be high enough to determine the kinetics of glycolate destruction. The targets for formate and oxalate were both 20 mg/kg. The 20 mg/kg oxalate value is based on a somewhat typical ratio of oxalate to glycolate in SRAT products. The relative amount of oxalate varies from about 10-20% of the glycolate. The formate concentration by ratio would be only 1-2 mg/kg, so formate was added at the higher concentration of 20 mg/kg so that its destruction could be evaluated since the ion chromatography (IC) detection limit is about 10 mg/kg.

Antifoam will be present at SRAT product levels in the SRAT Product simulant. No organics other than glycolate, formate, and oxalate were added to any of the simulants. The down-select testing showed no evidence that methyl mercury, propanal, and trimethylsilanol were oxidized. Moreover, the concentrations of propanal and trimethylsilanol have been shown to be in the tens of ppm range in condensate in simulant testing and are not found in SRAT product since they are volatile. Glyoxylate has not been detected in NG flowsheet testing so was not be added. Formaldehyde was not added because it cannot be measured by currently available techniques. However, note that formaldehyde is a minor impurity in glycolic acid (<1000 ppm in 70 wt% glycolic acid).[16]

Because the SRAT product diluted to 125 mg/kg glycolate did not have enough formate and oxalate, both were trimmed in to meet these targets. The SRAT product used was from a well-characterized mixture of product material from simulant tests SB9-NG 52, 55, and 57 (from 2016; NG is Nitric-Glycolic), which had Koopman Minimum Acid (KMA) acid stoichiometries of 100-115%.[17] These SRAT products contained unmeasured amounts of Antifoam 747 or its degradation products. In these tests, the residual amount of antifoam added was minimal, since the antifoam likely completely degraded during the CPC testing that produced them.

The anion composition of the SRAT product mixture is shown in Table 5. The results from AD had less variation than the SRNL Process Science Analytical Laboratory (PSAL) results, and the Dionex prepared samples had slightly higher glycolate values; these are the values that were chosen to represent the composition of the SRAT product mixture. The amount of SRAT product added to produce 125 mg/kg glycolate in the RCT simulant was based on the 57100 mg/kg average measured value. The elemental analyses and physical property analyses are given in Table 6. The elemental composition was determined by Inductively Coupled Plasma Emission Spectroscopy (ICP-ES). The soluble concentrations and fractions of Mn, Fe, and Ni in the SB9-NG 52, 55, 57 SRAT products are also listed in Table 6.[17]

Table 5. SRAT Product Anion Composition

Laboratory:		PSAL					
Preparation Method:		**Dionex OnGuard H transition metals cartridge**					
Anion	**Sample:**	**1**	**2**	**3**	**4**	**Mean**	**Std. Dev.**
glycolate	mg/kg	61200	60400	61200	62900	61425	1053
formate	mg/kg	889	934	889	913	906	22
nitrate	mg/kg	64000	53600	64400	50500	58125	7130
oxalate	mg/kg	6080	5100	6140	7080	6100	809
sulfate	mg/kg	2430	2850	2560	2770	2653	192
nitrite	mg/kg	<100	<100	<100	<100		
Preparation Method:		**Versapor 0.5 micron filter**					
glycolate	mg/kg	58300	69700	71200	64900	66000	5810
formate	mg/kg	865	841	864	753	831	53
nitrate	mg/kg	53300	49900	49200	53500	51500	2240
oxalate	mg/kg	10800	11000	11200	9910	10700	569
sulfate	mg/kg	1660	1520	1610	1750	1640	96
nitrite	mg/kg	<100	<100	<100	<100		
	Laboratory:	**AD**					
Preparation Method:		**Dionex OnGuard H transition metals cartridge**					
Anion	**Sample:**	**5**	**6**	**7**	**8**	**Mean**	**Std. Dev.**
glycolate	mg/kg	58300	56400	56600	57000	57100	854
formate	mg/kg	720	780	785	804	773	34
nitrate	mg/kg	56800	58200	59100	58700	58200	1010
oxalate	mg/kg	8510	8370	8330	8350	8390	83
sulfate	mg/kg	1980	1870	1880	1890	1900	48
nitrite	mg/kg	<100	<100	<100	<100		
Preparation Method:		**Pall Acrodisc 0.5 micron filter**					
glycolate	mg/kg	56700	55400	55700	56700	56100	675
formate	mg/kg	650	656	638	663	652	10
nitrate	mg/kg	55100	55800	56400	56200	55900	559
oxalate	mg/kg	9590	9030	9930	9770	9580	392
sulfate	mg/kg	1740	1720	1750	1790	1750	29
nitrite	mg/kg	<100	<100	<100	<100		

Table 6. SRAT Product Elemental Analysis and Physical Properties

Elements mg/kg slurry			
Ag	**Al**	**Ca**	**Cr**
21.4	15700	2285	306
Cu	**Fe**	**K**	**Mg**
107	38800	115	503
Mn	**Na**	**Ni**	**S**
13450	26800	3185	725
Si	**Zn**	**Zr**	**Hg**
69.3	82.7	220	1405

	Soluble Fraction (%)			Concentration in Supernate (mg/L)		
Run	**Mn**	**Fe**	**Ni**	**Mn**	**Fe**	**Ni**
52	49	11	26	6910	4390	790
55	53	3	31	11050	1760	1410
57	50	6	29	9160	3170	1145

Total Solids	wt%	28.87%
Insoluble Solids	wt%	16.42%
TIC	mg/kg	273
TOC	mg/kg	28775
Slurry Density	g/mL	1.224
Supernate Density	g/mL	1.100
pH		5.61

The Reagent simulant was also adjusted for typical acidity (pH) and total nitrate in the SMECT. The Reagent simulant runs were done with condensate (alone) at about pH 1.3, which is similar to typical values for the SMECT and OGCT (Table 7). The desired RCT pH values after condensate addition are ~3.0 and ~13.3 for NaOH addition after and before condensate addition, respectively. Note that the initial pH of the condensate simulant does not have much effect on the pH of the heel plus condensate mixture when NaOH is added before the condensate. The pH and nitrate concentrations of the SRAT Product simulant were used as-is.

Table 7. Target Acidity, pH, and Nitrate for Reagent Condensate Simulant

Variable	Units	Value
pH		~1.3
Acidity	M	~0.041
Nitrate from Acid	mg/L	~2540
Total Nitrate	mg/L M	3170 ~0.051

The anion, Hg, and Mn concentrations for the simulants used are shown in Table 8. The foamover and SRAT product simulant compositions were calculated from the dilution of the SRAT product sludge and the added reagent chemicals.

Table 8. Simulant Compositions

		SMECT or OGCT	RCT Simulant Reagent and SRAT Product		RCT Simulant Foamover	
Species		**Simulant: Reagent Condensate [a]**	**Condensate + Heel 4.4 + NaOH**	**Condensate + Heel 2.0 + NaOH**	**Condensate + Heel 4.4 + NaOH**	**Condensate + Heel 2.0 + NaOH**
Glycolate	mg/kg	153	125	125	125	125
Formate	mg/kg	24.4	20	20	20	20
Oxalate	mg/kg	24.4	20	20	20	20
Nitrite	mg/kg	0	1760	800	1760	800
Nitrate	mg/kg	3170	3100	3100	4540[c]	4540
Nitrite/Nitrate Molar Ratio of Heel		NA	4.4	2.0	4.4	2.0
Total Hydroxide	M	NA	~0.2	~0.2	~0.2	~0.2
pH		~1.3	~13	~13	~13	~13
			Reagent	**SRAT Product**		
Total Hg[b]	mg/kg	0	0 or 200	~3 or 203	~110	
Total Mn[b]	mg/kg	0	0	~30	~1050	

[a] concentrations increased so condensate + heel + NaOH meet targets

[b] added or actual from SRAT Product

[c] higher due to more nitrate in foamover than typically in condensate

The foamover simulant was produced to target 125 mg/kg glycolate by adding approximately 14.5 gallons of the SRAT product as shown in Tables 5 and 6. The value of 14.5 gallons is calculated from the density and the concentration of glycolate in the sludge to make the RCT concentration 125 mg/kg, as shown in Table 9. Note that the amount of sludge would be different for different glycolate concentrations and sludge densities.

Table 9. Determination of Sludge for 125 mg/kg Glycolate

Quantity	Units	Value
RCT Volume	gal	8000
RCT Mass ($\rho \approx 1.01$)	kg	30600
Glycolate Target	mg/kg	125
Glycolate in RCT	kg	3.82
Glycolate in Sludge	mg/kg	57100
Sludge Density	kg/L	1.224
Sludge for 3.82 kg Glycolate	kg L gal	67.0 54.7 14.5

Several runs with added or spiked mercuric ion Hg^{2+} as $Hg(NO_3)_2$ were performed. The concentration of dissolved Hg in RCT samples has ranged from around 50 to as high as 2600 mg/L, with typical values being about 200-300 mg/kg. Some of this dissolved Hg is Hg^{2+} ion and some is methyl mercury. To determine any effect of Hg^{2+}, about 200 mg/kg of Hg^{2+} was added to the Reagent Condensate simulant, and the SRAT Product simulant was also spiked with 200 mg/kg. No methyl mercury was added since the down-select testing showed that no oxidation of methyl mercury appeared to occur. Spiking of Hg^{2+} was done after adjustments to pH and nitrate concentration, so it is expected that it formed HgO solids.

3.3.3 *Antifoam Simulant*

A single test of the oxidation of the straight chain portion of the Antifoam 747 molecule was requested. The straight chain portion of the antifoam is a poly(ethylene oxide) (PEO) chain ($-CH_2CH_2O-$); note PEO is often also called poly(ethylene glycol), or PEG. The PEO simulant will be the polyethylene glycol dimethyl ester shown in Table 10. The PEO chain length is about 10 and the molecular weight is approximately 500; the carbon chain length in Antifoam 747 is approximately 10 wt % 12 ethylene oxide units and 90 wt % 8 ethylene oxide units. The oxidation of this PEO simulant will be monitored by measuring the loss of Total Organic Carbon (TOC), gain of Total Inorganic Carbon (TIC) and of oxalate. The TIC measures CO_2 generated that would be retained as carbonate in the caustic simulant.

Table 10. Antifoam and PEO Simulant

Chemical Species	Approximate Chemical Formula
Antifoam 747	$C_{25.4}H_{57.5}O_{10.5}Si_{2.5}$
Polyethylene Glycol Dimethyl Ester (PEG)	$C_{22}H_{46}O_{11}$ $[CH_3-O-(CH_2CH_2-O-)_{10}CH_3]$ (ethylene oxide is $-CH_2CH_2-O-$)

3.4 Oxidant Stoichiometry and Experimental Design

The stoichiometry for the complete oxidation of the organic species and nitrite that was initially assumed is given in Table 11. A stoichiometry of 100% for any species implies it is totally oxidized per the assumed reaction. In the down-select tests, greater than 80% destruction of glycolate was seen in most tests with actual stoichiometry (including nitrite and excluding species not actually oxidized) of 1.0 and greater (see Appendix D). The down-select tests did not conclusively identify the final oxidized product of glycolate or determine the extents of formate, oxalate, and nitrite oxidation. The down-select test results suggested that oxalate might be the primary oxidized product from glycolate at high pH and that oxalate would not be further oxidized.

Initially, all tests were planned to be done at stoichiometries of α = 0.8, 1.0, and 1.2 per the reactions in Table 11. The stoichiometries in Table 11, including any excess, can be represented by the following equation:

$$\mathrm{NaMnO_4\ (mol)} = \alpha * \left(\frac{2\ \mathrm{mol\ P}}{3\ \mathrm{mol\ NO_2^-}} + \frac{2\ \mathrm{mol\ P}}{\mathrm{mol\ G}} + \frac{2\ \mathrm{mol\ P}}{3\ \mathrm{mol}\ (\mathrm{F}+\mathrm{X})} + \frac{1.697\ \mathrm{mol\ P}}{\mathrm{mol\ PEG\ carbon}} \right) \tag{1}$$

where P is sodium permanganate, G is glycolate, F is formate, X is oxalate, and PEG is as defined previously.

Table 11. Initially Assumed Stoichiometric Reactions for Complete Oxidation of Organics to CO_2

Chemical Species	Reaction with Sodium Permanganate
Glycolate	$C_2H_3O_3^- + 2\ MnO_4^- = 2\ CO_2(g) + 2\ MnO_2(s) + 3\ OH^-$
Formate	$HCO_2^- + \frac{2}{3}\ MnO_4^- + \frac{1}{3} H_2O = CO_2(g) + \frac{2}{3}\ MnO_2(s) + \frac{5}{3}\ OH^-$
Oxalate	$C_2O_4^{2-} + \frac{2}{3}\ MnO_4^- + \frac{4}{3} H_2O = 2\ CO_2(g) + \frac{2}{3}\ MnO_2(s) + \frac{8}{3}\ OH^-$
Nitrite	$NO_2^- + \frac{2}{3}\ MnO_4^- + \frac{1}{3}\ H_2O = NO_3^- + \frac{2}{3}\ MnO_2(s) + \frac{2}{3}\ OH^-$
PEG simulant of Antifoam chain	$C_{22}H_{46}O_{11} + \frac{112}{3} NaMnO_4 \rightarrow 22CO_2 + \frac{112}{3} NaOH + \frac{112}{3} MnO_2 + \frac{13}{3} H_2O$

It quickly became evident that the amount of permanganate was excessive and much lower amounts needed to be tested. The initial results showed that glycolate was oxidized to oxalate and not to CO_2 at high pH and that oxalate was not further oxidized to CO_2. The results for formate were inconclusive, suggesting it was probably neither oxidized nor generated.

The tests performed are summarized in Table 12. The run numbers, shown in column 1, in non-italics are originally planned runs (1-20) with the letter ‘a’ appended to the number if the oxidant stoichiometry was changed from the original amount as listed in the Run Plan (Run 17 should have been 17a since conditions were changed). Run numbers in *italics* are supplemental runs that were added during the testing program. Blue highlighted rows are runs using SRAT product as source of glycolate. Note that there is no Run 24 and that the original Run 21 (PEG) was renamed Run 31. The target stoichiometry on the original basis of Table 11 is shown in column 6. Modified stoichiometry bases, to be discussed later, are given in columns 7-9. The runs are ordered by the values in column 7.

As experimental data was analyzed, it became apparent that the stoichiometries in Table 11 did not match the results of the oxidations in caustic conditions. The modified reactions in Table 13 more closely matched the experimental data, with MnO_2 as the final Mn product for the foamover tests, and manganate (MnO_4^{2-})as the final Mn product for the Reagent simulant and SRAT product tests. No oxidation of formate or oxalate was then assumed. Nitrite oxidation appeared to be at most partial, so a completion factor β was proposed. The evolution of the stoichiometric assumptions will be described in the Experimental Results section. The permanganate requirement equation is then given by equation 2 where the lack of oxidation of PEG (described later) is anticipated.

$$\mathrm{NaMnO_4\ (mol)} = \alpha * \left(\beta \times \frac{2\ \mathrm{mol\ P}}{3\ \mathrm{mol\ NO_2^-}} + \frac{\left(4\!/\!3\ \mathrm{or}\ 4\right)\ \mathrm{mol\ P}}{\mathrm{mol\ G}} \right) \tag{2}$$

Table 12. Summary of Test Conditions

1	2	3	4	5	6	7	8	9
Run	**Run Order**	**Simulant Type**	**Nitrite to Nitrate Ratio in Heel**	**Mercuric Ion Added @ 200 mg/kg**	**Stoichiometry Target Original Basis**	**Initial Permanganate to Glycolate Molar Ratio**	**Stoichiometry Based on Oxalate and MnO_2 Products**	**Stoichiometry Based on Oxalate and Manganate Mn(VI) Products**
Starting pH ~3, 125 mg/kg Glycolate, NaOH and $NaNO_2$ Added After Permanganate								
1	1	Reagent	4.4	No	1.0	18.0	13.5	4.50
2	2	Reagent	4.4	No	1.2	21.7	16.3	5.43
Starting pH >12, 125 mg/kg Glycolate*, NaOH Added Before Permanganate, $NaNO_2$ After								
15a	22	SRAT Prod	2.0	No	0.2	1.88	1.41	0.47
25	*13*	*Reagent*	*4.4*	*No*	*0.2*	*2.80*	*2.10*	*0.70*
7a	16	SRAT Prod	4.4	No	0.2	3.49	2.62	0.87
12a	21	SRAT Prod	4.4	Yes	0.2	3.55	2.66	0.89
30	*24*	*SRAT Prod*	*2.0*	*No*	*0.4*	*3.69*	*2.77*	*0.92*
26	*14*	*Reagent*	*4.4*	*No*	*0.4*	*5.50*	*4.13*	*1.38*
16a	25	SRAT Prod	2.0	No	0.6	5.49	4.12	1.37
21	*10*	*Reagent*	*4.4*	*No*	*0.4*	*6.89*	*5.17*	*1.72*
23	*12*	*Reagent*	*4.4*	*No*	*0.4*	*7.04*	*5.28*	*1.76*
28	*17*	*SRAT Prod*	*4.4*	*No*	*0.4*	*7.04*	*5.28*	*1.76*
11a	20	SRAT Prod	4.4	Yes	0.4	7.06	5.29	1.76
14a	9	Reagent	2.0	No	0.8	7.38	5.54	1.85
13	8	Reagent	2.0	No	1.0	9.72	7.29	2.43
22	*11*	*Reagent*	*4.4*	*No*	*0.6*	*10.5*	*7.90*	*2.63*
29	*23*	*SRAT Prod*	*4.4*	*Yes*	*0.6*	*10.5*	*7.86*	*2.62*
8a	18	SRAT Prod	4.4	No	0.6	10.9	8.15	2.72
4	4	Reagent	4.4	No	1.0	13.8	10.4	3.46
3	3	Reagent	4.4	No	0.8	13.8	10.4	3.46
10a	7	Reagent	4.4	Yes	0.8	13.9	10.4	3.48
27	*15*	*Reagent*	*4.4*	*No*	*0.8*	*14.0*	*10.5*	*3.50*
6	19	SRAT Prod	4.4	No	0.8	14.1	10.6	3.54
9	6	Reagent	4.4	Yes	1.0	15.1	11.3	3.77
5	5	Reagent	4.4	No	1.2	20.9	15.7	5.22
Starting pH >12, ~4450 mg/kg Glycolate, NaOH Added Before Permanganate, $NaNO_2$ After								
18a	26	Foamover	4.4	No	0.6	1.53	1.15	0.38
20a	29	Foamover	2.0	No	0.7	1.60	1.20	0.40
19a	27	Foamover	4.4	No	0.8	2.03	1.52	0.51
17(a)	28	Foamover	4.4	No	0.9	2.31	1.73	0.58
Polyethylene Glycol								
31	31	PEG	4.4	No	1.0	NA	NA	NA

Table 13. Modified Stoichiometric Reactions for Glycolate Oxidation

Chemical Species	Partial Oxidation with Permanganate (to MnO_2 or Manganate)	
Glycolate	MnO_2 product: $C_2H_3O_3^- + \frac{4}{3}\ MnO_4^- = C_2O_4^{2-} + \frac{4}{3}\ MnO_2(s) + \frac{4}{3}\ H_2O + OH^-$	(3)
Glycolate	Manganate product: $C_2H_3O_3^- + 4\ MnO_4^- + 5\ OH^- = C_2O_4^{2-} + 4\ MnO_4^{2-} + 4\ H_2O$	(4)
Formate	No oxidation	
Oxalate	No oxidation	
Nitrite	$(\ NO_2^- + \frac{2}{3}\ MnO_4^- + \frac{1}{3}\ H_2O = NO_3^- + \frac{2}{3}\ MnO_2(s) + \frac{2}{3}\ OH^-\ )$ x (β % Complete)	

3.5 Experimental Apparatus and Parameters

Testing was performed using a 2.0-L borosilicate glass jacketed reactor. The reactor design provided for temperature-controlled operations of approximately 1.8 L of RCT simulant. Either nitric acid or sodium hydroxide was added to reach the initial pH target. The oxidants were added to the vessel via a syringe pump. An agitator was used throughout testing to ensure the solution was well mixed.

A sampler allowed on-line removal of contents as needed. An in situ pH probe was utilized in all experiments to monitor reaction progress. An air purge of 81 sccm was selected to provide enough turnover in the gas to enable measurement with FTIR and MS. However, this increased purge rate (10 times higher than the scaled DWPF airflow) dilutes the off-gas more than would be seen during processing. As a result, absolute concentrations need scaled to the actual purge rate. A reflux condenser was present to prevent dewatering and to cool the offgas prior to analysis. Offgas analysis was performed with a MS and a FTIR. A gas chromatograph (GC) was used when the MS was not available.

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 0.25 L including condenser
- Target purge rate: 81 sccm (standard conditions of 21.11 °C, 1 atm)
- Purge gas composition: Air
- Reaction temperature: 20 ± 2 °C (maintained by water jacket)
- Condenser cooling water setpoint: 10 ± 2 °C
- Condenser gas outlet temperature target: ~10 °C
- Mixer rate: 100 to 300 rpm

A sketch of the equipment is shown in Figure 2. A photo of the equipment is shown in Figure 3.

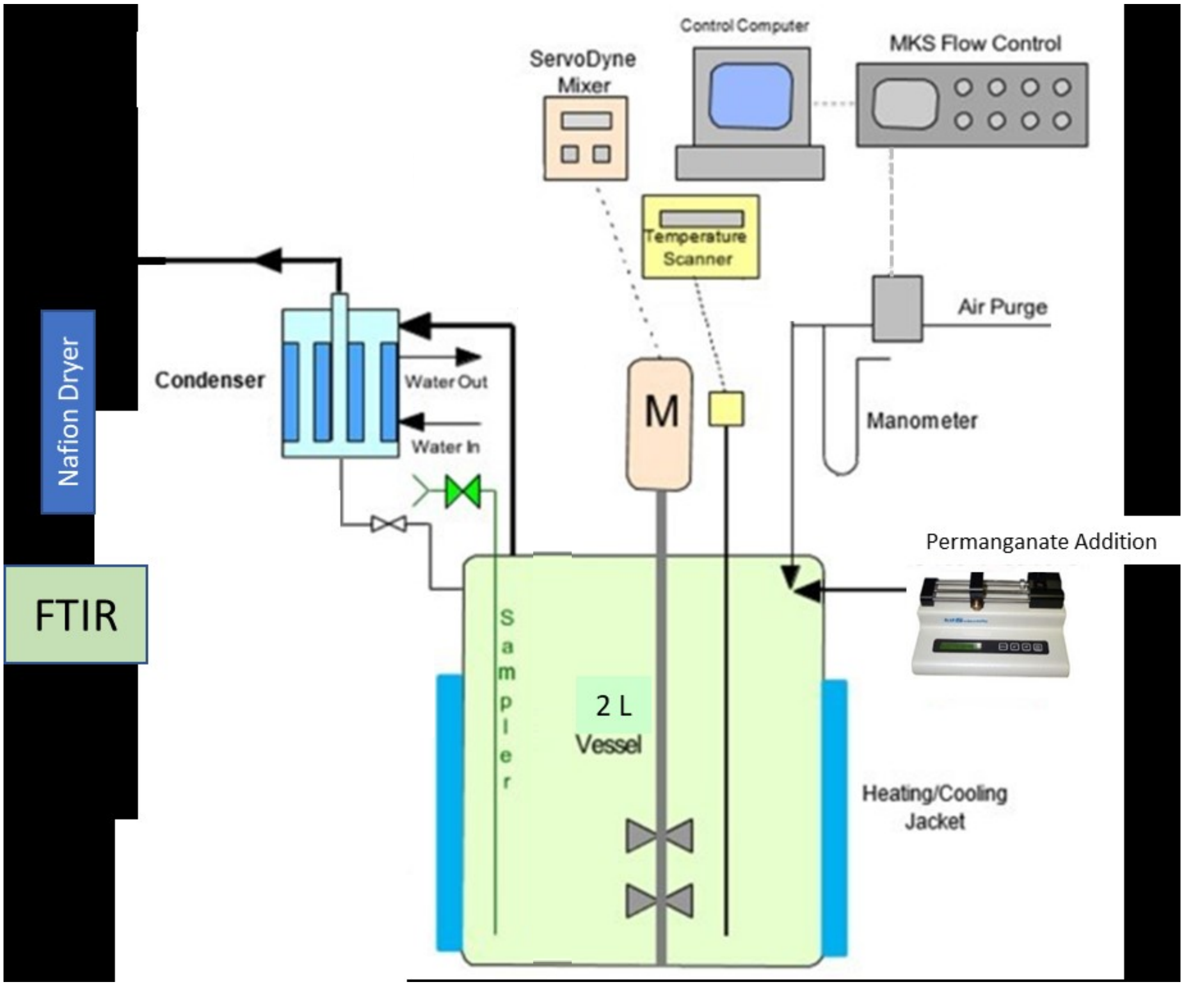


Figure 2. Equipment Apparatus Sketch

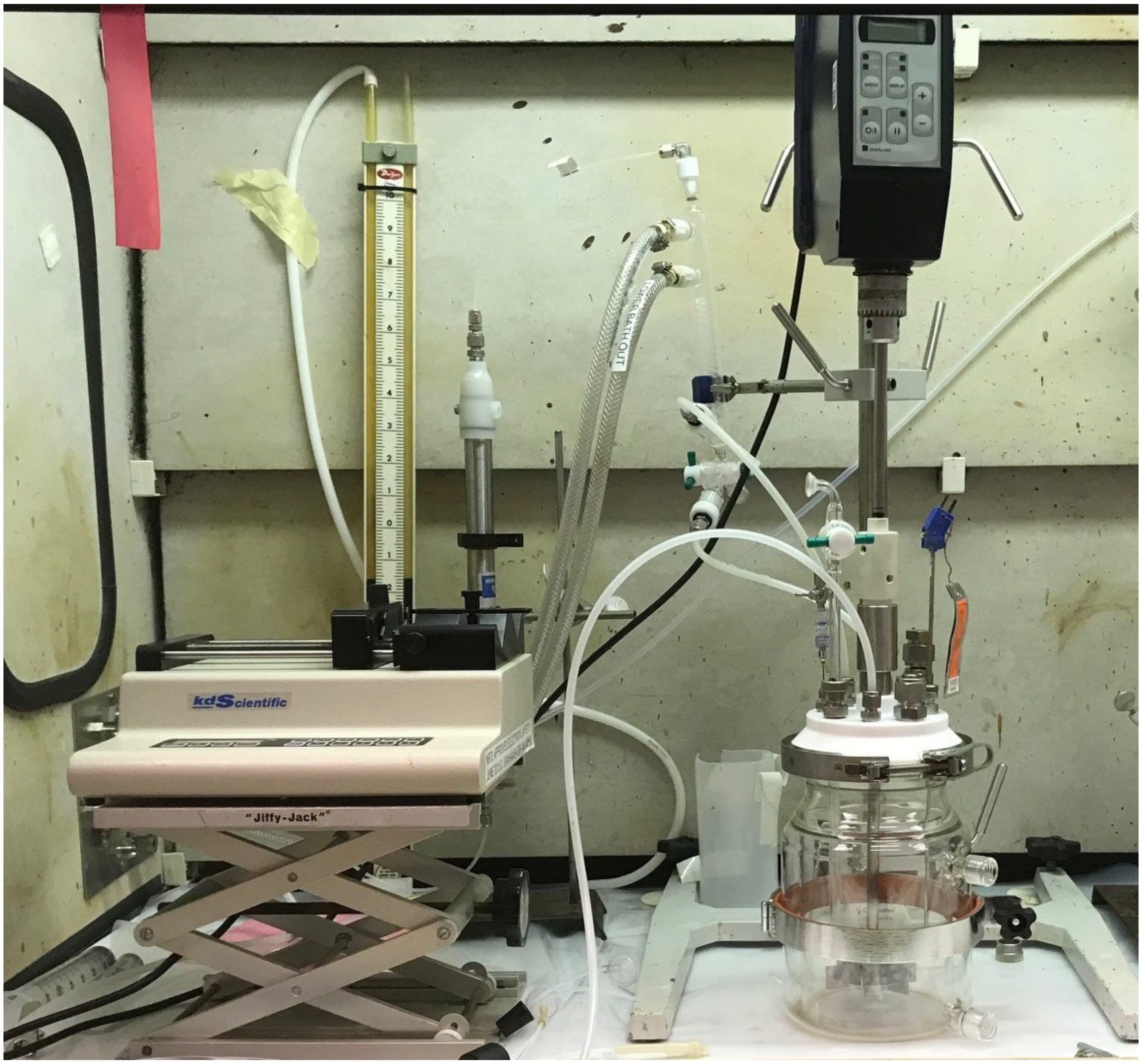


Figure 3. Photo of Apparatus

3.6 Scaling

The experimental reactor was 2 L in volume. The RCT is 12,000 gallons and has a working volume of 8,000 gallons. Instead of geometrically scaling the RCT, the working volume of the experimental reactor was set at 1.8 L, to minimize the offgas volume and turnover the offgas more frequently.

The RCT has an air purge of 4.8 standard cubic feet per minute (scfm).[18] The purge in the experiments, when used, was set at 81 standard cubic centimeters per minute (sccm at 21.11 °C, 1 atm), which is 10X compared to geometric scaling to increase the turnover in the vapor space during the experiments.

3.7 Offgas Analysis

Offgas samples in the tests starting with acidic conditions (Runs 1, 2) and the first three caustic runs were analyzed using an FTIR. An MKS MultiGas™ 2030 FTIR spectrometer was connected to the offgas system and was able to quantitatively measure CO, CO_2, NO, NO_2, N_2O, and H_2O, and many organics (but none were seen). Because the chilled offgas leaving the Nafion® drier was dried well below the dew point, this composition was not representative of the gas entering or exiting the condenser. The FTIR obtained data roughly every 15 seconds.

3.8 Liquid Analyses

3.8.1 *pH*

A pH probe was used during the tests starting at low pH; but was not used when starting at high pH where the pH was and remained about 13. The pH meter was calibrated prior to each test and a check was performed after each test by measuring the pH of 4, 7 and 10 buffer solutions.[19]

3.8.2 *Sampling and Analysis*

Liquid samples were pulled throughout testing (at 30, 90, and 180 minutes after the start of permanganate addition) and analyzed to track the decomposition of the organics and nitrite. For the low pH tests, the samples were quenched with sodium hydroxide to stop the destruction of nitrite. In all tests, the samples were quenched with sodium sulfite to stop the oxidation of the organics by converting the permanganate to unreactive MnO_2 or Mn(II). Both sodium hydroxide and sodium sulfite were added by mass. These samples were then analyzed by PSAL for anions (glycolate, formate, oxalate) by IC. PSAL used a new anion IC preparation method using a Dionex OnGuard II H cartridge (cation exchange cartridge containing sulfonic acid functional groups that exchange H ions for transition metal ions (e.g., Mn)) to minimize matrix effects and improve peak shape. Samples from runs starting at 125 mg/kg glycolate were diluted 10X by mass to be in the calibration range of the IC, while the runs starting at 4450 mg/kg were diluted from 10X to 1000X as needed to be in range.

The typical linear IC calibration range is 1-10 mg/L, so samples must be diluted into this range. For this work, calibration standards at higher concentrations (up to about 60 mg/L) were added and polynomial fitting of the calibration data done to extend the range of concentrations that could be analyzed without performing additional dilutions. For some samples where nitrite in the dilution was found to be <1 mg/L, a 0.5 mg/L standard was added to the calibration.

The suitability of using sodium sulfite to quench the permanganate oxidation reactions was questioned during the beginning of this work. No literature references had been cited showing that the quenching would be complete and that no additional reactions could occur between the time of quenching and analysis by IC. A reference was found that showed that the hydrate sulfite bisulfite (HSO_3^-) could react with permanganate to stabilize the formation of the strong oxidizer Mn^{3+}.[20] These reactions were studied at neutral to acidic pH where bisulfite can be formed from sulfite, so there should not be any effect on quenching highly caustic samples. Nonetheless, the stability of quenched samples was examined to rule out any unwanted effects.

A study of quenching agents for permanganate oxidation showed that for the oxidation of phenol, sulfite at 10-40X excess at pH 11 did not completely quench the oxidation.[21] These authors did not perform any tests at higher pH. The use of thiosulfate, or hyposulfite ($S_2O_3^{2-}$) was shown to be superior to sulfite, so this method of quenching was tested. Thiosulfate was found to be incompatible with the OnGuard II H cartridge treatment. Excess thiosulfate was decomposed to sulfite or sulfate and elemental sulfur solids; these solids could not be filtered with a 0.45μ filter and so could be analyzed by the IC. It was shown that sulfite quenched samples are not stable after 100 days (shorter durations were not tested). The glycolate concentrations of test samples were found to drop by a factor of ten. Because this instability was suspected, most samples were then analyzed within 2 days of quenching.

Part way into testing, it was determined that the sulfite quench method was probably reacting with nitrite. Solutions treated with sulfite showed unexpected conversion of nitrite to nitrate and overall nitrogen loss, evidently to a gaseous product such as N_2, N_2O, or NH_3. Sulfite is a strong enough reducing agent to potentially cause such reactions, although most references suggest that nitrite should not react with sulfite at pH>7.[22] No further testing was done to determine the fate of nitrite in the sulfite quenched samples. Rather, only the final sample in each test was diluted 1000X in water and analyzed by IC within 2 hours to minimize any further reaction of the nitrite. The pH of these 1000X diluted samples was about 10. Based on the observed long-term instability of these diluted samples, it is recommended that the diluted samples be pH adjusted with 50 wt% NaOH to a pH of 12 or greater prior to analysis to reduce the likelihood of nitrite oxidation.

No analysis for manganese compounds was performed. Some of the product solutions were examined qualitatively for color and intensity. After completion of the experimental program, it was demonstrated that an ultraviolet visible (UV/VIS) spectrometer could be used to qualitatively follow the relative amounts of manganese species permanganate and manganate.

3.9 Test Chronology

The first two tests were performed starting with a normal heel with a nitrite/nitrate ratio of 4.4. To this 315 mL heel, 1420 mL of acidic condensate simulant at pH 1.3 was metered in at a rate of 40 mL/min for about 36 minutes. The permanganate was then metered in over 20 minutes and allowed to continue mixing until 3 hours. The required sodium hydroxide and sodium nitrite solutions were then added. The offgas generation was monitored by the FTIR during these phases.

The remaining tests were done with the starting pH at about 13. The starting solutions, whose compositions were given in section 3.3, were added as described below.

Reagent Simulant Tests

About 1765 g of combined simulant for the heel, acidic condensate, and NaOH was used. The entire amount was added to the vessel, followed by permanganate addition over 20 minutes, followed by further reaction until 3 hours. Sodium nitrite solution was then added. Different combined simulants were used for the two nitrite/nitrate ratios used.

Note: Test 23 was a duplication of test 21, but the permanganate was added in small amounts over the course of 2.5 hours rather than all at the beginning. This was done to more closely examine the color changes occurring at lower permanganate addition amounts (more dilute) where the solution colors were less intense and less opaque.

SRAT Product Tests

About 1761 g of combined simulant for the heel, NaOH, and additional species not present in the SRAT product (nitrate, formate, oxalate) were added to the vessel. The small quantity of SRAT product (~3.8 g) was then added. The permanganate addition and further reaction were done as in the Reagent simulant tests. Sodium nitrite solution was then added. Different combined simulants were used for the two nitrite/nitrate ratios used.

Foamover Tests

For these tests, the combined simulant was made in the vessel rather than prior to the tests. About 1694 g of water, 29 g 50 wt% NaOH, 138 g SRAT product sludge, and sodium nitrite solution (different amounts depending on the nitrite/nitrate ratio) were combined in the vessel. The permanganate addition was done over 65 minutes, and further reaction over 6 hours was completed. Sodium nitrite solution was then added.

4.0 Results and Discussion

The total solids, insoluble solids, slurry density, and total hydroxide of the reaction products are summarized in Table 14. The total insoluble solids for the Reagent and SRAT Product runs are mostly the manganese species. The Reagent results are higher because more permanganate was used in most of these runs. The Foamover total solids are higher due to the additional sludge present; similarly, the insoluble solids are also higher. The insoluble solids in the Reagent runs would be totally due to manganese, probably as MnO_2; however, these samples were analyzed several months after they were taken, and it was observed that insoluble solids increased while standing due to decomposition of the manganate species. The total hydroxide, which was targeted at 0.20-0.21 M was achieved in the Reagent and SRAT Product runs, but the values in the Foamover runs were lower. Although lower, they are still within the expected RCT range of 0.1 to about 0.2 M.

Table 14. Properties of Reaction Products

Measurement		Simulant Type Reagent	 SRAT Product	 Foamover
Total Solids	wt%	3.17%	3.03%	5.38%
Insoluble Solids	wt%	0.41%	NM	2.28%
Slurry Density	kg/L	1.020	1.021	1.041
Total Hydroxide	M	0.206	0.205	0.155

NM=Not measured

4.1 Glycolate and Nitrite Destruction

The final glycolate destruction results of each test are summarized in Table 15. Runs that were performed early in the test program did not have samples analyzed until 60-90 days later, which could result in greater oxidation of glycolate than the actual at the end of the test. These tests are marked by an asterisk. Fortunately, these tests were at high permanganate additions where the oxidation was expected to be high anyway.

The first two rows summarize the two tests done starting at low pH. The next set of rows show the results starting at 125 mg/kg glycolate for both Reagent and SRAT product simulant tests. The last four rows show the foamover test results. Each subset is ordered by the increasing initial permanganate to glycolate molar ratio. The glycolate concentrations at 3 h (and 6 h for foamover), the final glycolate destruction percentages, and the start-to-finish carbon balance are also shown. The results for the nitrite to nitrate conversion, overall start-to-finish nitrogen balance, and the ratio of the actual measured to expected nitrite in the final product after the corrosion control nitrite addition are shown in Table 16.

Table 15. Experimental Results: Glycolate Destruction and Carbon Balance

Run	Simulant Type	Nitrite to Nitrate Ratio in Heel	Initial Permanganate to Glycolate Molar Ratio	Glycolate Destruction (≥%) @ 3 h	Glycolate Concen-tration (mg/kg) @ 3 h	Glycolate Concen-tration (mg/kg) @ 6 h	Carbon Balance Closure (%)
Starting pH ~4, 125 mg/kg Glycolate, NaOH and $NaNO_2$ Added After Permanganate							
1*	Reagent	4.4	18.0	83%	19		87%
2*	Reagent	4.4	21.7	>90%	<10		99%
Starting pH >12, 125 mg/kg Glycolate*, NaOH Added Before Permanganate, $NaNO_2$ After							
15a	SRAT Prod	2.0	1.88	25%	88		120%
25	Reagent	4.4	2.80	60%	50		118%
7a	SRAT Prod	4.4	3.49	72%	34		112%
12a	SRAT Prod	4.4	3.55	67%	41		114%
30	SRAT Prod	2.0	3.69	70%	37		128%
26	Reagent	4.4	5.50	>92%	<10		107%
16a	SRAT Prod	2.0	5.49	>92%	<10		117%
21	Reagent	4.4	6.89	>92%	<10		103%
23*	Reagent	4.4	7.04	>92%	<10		96%
28	SRAT Prod	4.4	7.04	>92%	<10		116%
11a	SRAT Prod	4.4	7.06	>92%	<10		118%
14a*	Reagent	2.0	7.38	>92%	<10		114%
13*	Reagent	2.0	9.72	>92%	<10		105%
22	Reagent	4.4	10.5	>92%	<10		105%
29	SRAT Prod	4.4	10.5	>92%	<10		121%
8a	SRAT Prod	4.4	10.9	>92%	<10		136%
4*	Reagent	4.4	13.8	>92%	<10		126%
3*	Reagent	4.4	13.8	>92%	<10		122%
10a*	Reagent	4.4	13.9	>92%	<10		112%
27	Reagent	4.4	14.0	>92%	<10		115%
6	SRAT Prod	4.4	14.1	>92%	<10		123%
9*	Reagent	4.4	15.1	>92%	<10		98%
5*	Reagent	4.4	20.9	>92%	<10		122%
Starting pH >12, ~4450 mg/kg Glycolate, NaOH Added Before Permanganate, NaNO2 After							
18a	Foamover	4.4	1.53	81%	860	804	84%
20a	Foamover	2.0	1.60	85%	681	633	105%
19a	Foamover	4.4	2.03	99.0%	78	38-47	96%
17	Foamover	4.4	2.31	99.1%	65	34-41	102%
						Mean	111%
						Std. Dev.	12%

* samples analyzed 60 days or more after run performed

Table 16. Experimental Results: Nitrite Destruction and Nitrogen Balances

Run	Simulant Type	Nitrite to Nitrate Ratio in Heel	Initial Permanganate to Glycolate Molar Ratio	Nitrite to Nitrate Conversion (based on Nitrate) (%)	Nitrite to Nitrate Conversion (based on Nitrite) (%)	Nitrogen Balance Closure (%)	Nitrite After Nitrite Addition Actual/Expected
Starting pH ~3, 125 mg/kg Glycolate, NaOH and NaNO2 Added After Permanganate							
1	Reagent	4.4	18.0	87%	48%	85%	NA
2	Reagent	4.4	21.7	82%	51%	91%	NA
Starting pH >12, 125 mg/kg Glycolate*, NaOH Added Before Permanganate, NaNO2 After							
15a	SRAT Prod	2.0	1.88	-8%	-12%	99%	110%
25	Reagent	4.4	2.80	-25%	57%	135%	101%
7a	SRAT Prod	4.4	3.49	-7%	-10%	99%	108%
12a	SRAT Prod	4.4	3.55	31%	-50%	65%	115%
30	SRAT Prod	2.0	3.69	-5%	-6%	100%	111%
26	Reagent	4.4	5.50	-20%	40%	126%	106%
16a	SRAT Prod	2.0	5.49	-15%	0%	104%	107%
21	Reagent	4.4	6.89	42%	30%	95%	102%
23	Reagent	4.4	7.04	46%	32%	94%	104%
28	SRAT Prod	4.4	7.04	33%	-56%	61%	110%
11a	SRAT Prod	4.4	7.06	-20%	5%	111%	97%
14a	Reagent	2.0	7.38	77%	31%	88%	NA
13	Reagent	2.0	9.72	80%	36%	88%	NA
22	Reagent	4.4	10.5	78%	68%	96%	105%
29	SRAT Prod	4.4	10.5	-7%	0%	103%	106%
8a	SRAT Prod	4.4	10.9	-14%	-10%	102%	102%
4	Reagent	4.4	13.8	91%	35%	72%	NA
3	Reagent	4.4	13.8	83%	4%	66%	NA
10a	Reagent	4.4	13.9	89%	40%	78%	NA
27	Reagent	4.4	14.0	-14%	36%	122%	106%
6	SRAT Prod	4.4	14.1	-10%	2%	105%	105%
9	Reagent	4.4	15.1	20%	41%	109%	NA
5	Reagent	4.4	20.9	92%	52%	83%	NA
Starting pH >12, ~4450 mg/kg Glycolate, NaOH Added Before Permanganate, NaNO2 After							
18a	Foamover	4.4	1.53	-9%	-29%	93%	98%
20a	Foamover	2.0	1.60	-15%	-23%	98%	109%
19a	Foamover	4.4	2.03	-6%	-17%	96%	103%
17	Foamover	4.4	2.31	1%	-2%	99%	101%
			Mean	3%	3%	100%	105%
			Std. Deviation	28%	33%	17%	5%

Shaded cells based on unreliable sulfite quenched samples; mean & std. deviation exclude these values.

The carbon balance closures in Table 15 were fairly good overall with a mean of 111% and a standard deviation of 12%. The balances are based on oxalate as the only carbon-containing product for the high pH runs. The amount of oxalate, especially in the SRAT product runs, was higher than expected from the amount of glycolate reacted, suggesting that the initial oxalate in the SRAT product was higher than expected (by about 20 mg/kg).

The nitrogen balances were also very good on average at 100%, with a standard deviation of 17%. Note that the runs shown highlighted in red were not included in the overall nitrogen values because these sample results are from the analysis of sulfite quenched samples where the nitrite and nitrate analyses are known to be incorrect.

The nitrite to nitrate conversion values differed significantly between whether the loss of nitrite or the gain of nitrate was used, but on average were 3% (essentially zero). The significant scatter in the results shown by the standard deviations shows that the nitrite and nitrate IC analyses of the permanganate oxidized solutions was less reliable than normally expected for these anions. The presence of permanganate appears to interfere with the chromatographic baseline making quantitation difficult. However, on average, both bases for the nitrite to nitrate conversion indicate that there was probably no significant oxidation of nitrite. Upon discovering this result, two literature references were found that indicate nitrite should not be oxidized by permanganate in caustic (>12) solutions.[23]

4.1.1 *Offgas Results for Runs Starting at Acidic pH*

The offgas generation during the acidic starting tests was monitored. The offgases and pH are shown in Figure 4 for runs 1 and 2. The results for these runs were almost identical. As the pH 1.3 condensate was added to the pH 13 heel, which contained nitrite, evolution of CO_2, NO, and NO_2 began. Once the pH dropped to 4, the evolution of these gases increased quickly but not to high rates. The CO_2 then started to drop while the NO_x gases continued to rise. Upon permanganate addition, the NO_x evolution dropped quickly as the pH rose, while the CO_2 briefly increased until the pH was about 7 where it the decreased to near zero due to reaction of CO_2 with caustic in solution to form carbonate. At the caustic conditions, the oxidation of glycolate also changed from generating CO_2 and maybe oxalate to generating only oxalate. The total CO_2 emitted including that generated before permanganate addition accounted for only 1.2-1.7% of the glycolate. This CO_2 could have been due to dissolved carbonate in the caustic heel. The total NO_x was about 0.1% of the nitrite. The oxalate generated in runs 1 and 2 accounted for 50-75% and 70-90% of the glycolate carbon, respectively, and the carbon balance closures were 87 and 80%, respectively. The unaccounted remainder is presumed to have been carbonate. (Because of the very low levels of carbonate, the TIC analytical method was not attempted.)

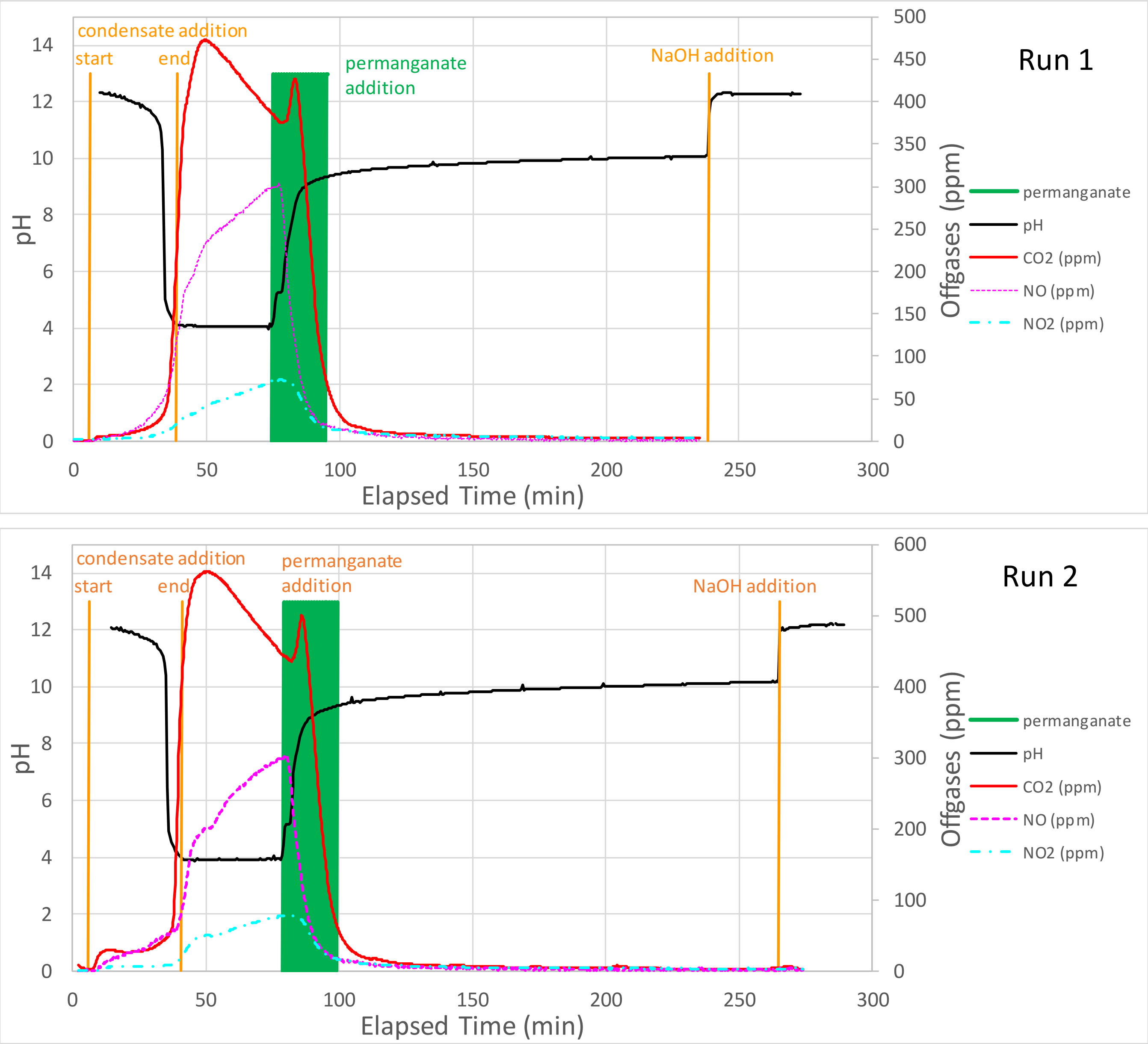


Figure 4. Offgas and pH During Acidic Starting Runs 1 & 2

4.2 Glycolate Destruction, Stoichiometric Reactions, and Effects of Nitrite to Nitrate Ratio, Added Mercury, and Sludge

The results in Table 15 show that at high pH, above somewhere between an initial permanganate to glycolate ratio of 3.7 and 5.5, the oxidation becomes complete within the detection limit of glycolate. Note that the highest glycolate destruction value that can be reported is based on the detection limit of 10 mg/kg, so starting with 125 mg/kg glycolate, <10 mg/kg gives a percent destruction of >92% [(125-10)/125]. The glycolate destruction data from Table 15 are plotted in Figure 5.

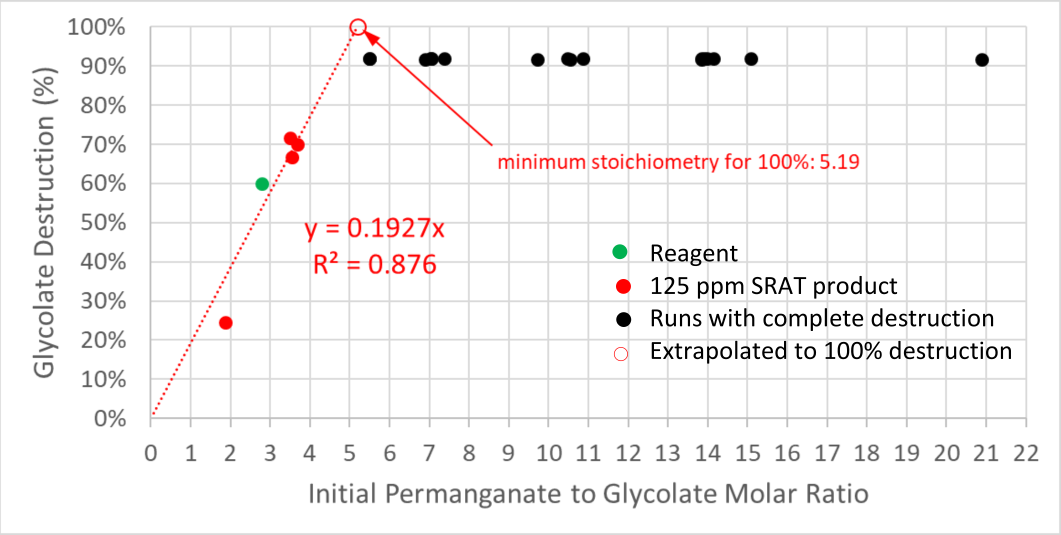


Figure 5. Glycolate Destruction versus Initial Permanganate to Glycolate Molar Ratio for 125 mg/kg Glycolate

Figure 5 is a plot of % glycolate destruction versus the permanganate to glycolate molar ratio (P/G). The graph is linear over the P/G testing range of 2-4, with a y-intercept of 0%. Extrapolating the data to 100% destruction results in an estimated requirement for the permanganate to glycolate molar ratio (P/G) of about 5.2. Since the glycolate isn't oxidized to CO2 and permanganate isn't reduced to MnO2, equation (4) , reproduced below, best describes the reaction chemistry The stoichiometry of equation (4) implies that the minimum P/G should be 4.0. Several references support a P/G>4 for high pH conditions.[23b, 24] A modest excess requirement for complete reaction is reasonable.

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

Comparison of Run 1 starting at low pH to runs starting at high pH shows that at high pH the oxidation was essentially complete at P/G greater than 5.5, while at low pH the oxidation was only 83% complete at P/G of 18.0. These results suggest that the oxidation of glycolate is significantly faster at high pH than a low pH. One reference states "many organic permanganate oxidations proceed faster or requires more oxidant under alkaline than under neutral or weakly acidic conditions".[23b]

The glycolate destruction results for the large foamover runs (Table 15) do not appear to follow reaction (4). Greater than 80% glycolate destruction was seen at P/G of only 1.53 and almost complete (>99%) destruction was seen at P/G of 2.03. Although the destruction percentage was >99%, the actual concentration of glycolate was still above 10 mg/kg. With P/G less than 4, reaction (4) would imply at best about 50% destruction. Therefore, it appears that with the foamover quantity of sludge, the oxidation reaction is closer to reaction (3) reproduced below, where the stoichiometric requirement is P/G 4/3.

$$C_2H_3O_3^- + \tfrac{4}{3}\,MnO_4^- = C_2O_4^{2-} + \tfrac{4}{3}\,MnO_2(s) + \tfrac{4}{3}\,H_2O + OH^- \qquad (3)$$

The measured glycolate and oxalate concentrations for several runs are shown in Figure 6. (Note in the graphs the run numbers from Table 12 or Table 15 are shown at the bottom right.) The runs are labeled by the P/G ratio. The initial concentration of oxalate was about 93 mg/kg (SRAT Prod) or about 20 mg/kg (Reagent). The increase in oxalate was approximately equal to the decrease in glycolate on a molar basis; on a mass basis oxalate equals about 1.17 times glycolate. Note that the lowest glycolate concentration value is the detection limit of 10 mg/kg. For many runs, the actual values would drop to zero.

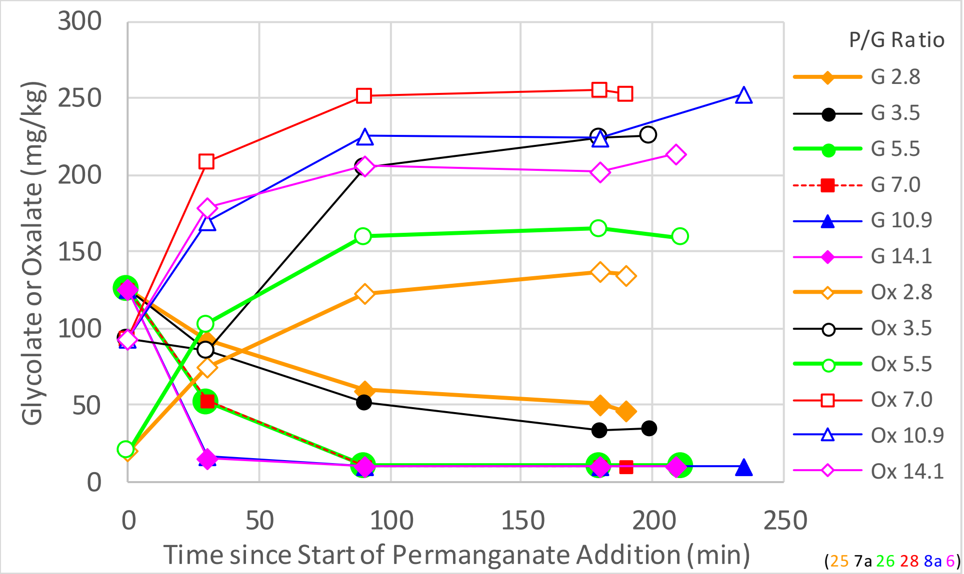


Figure 6. Example Glycolate and Oxalate Concentrations versus Time

There is no evidence of any effect of the nitrite to nitrate (N/N) ratio or the presence of SRAT product sludge components on the oxidation for the 125 mg/kg glycolate tests. The glycolate concentrations for several different P/G ratios are shown in Figure 7 to compare the effect of the nitrite to nitrate ratio. Lines of the same color represent similar P/G ratios but different N/N. The results show that there is no apparent effect of N/N on the rate of glycolate oxidation.

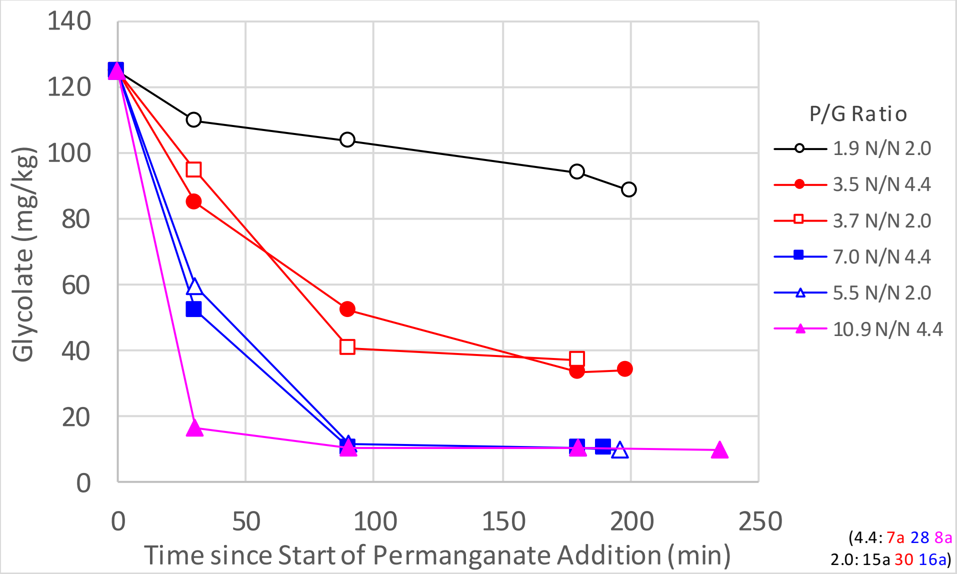


Figure 7. Glycolate Concentration Comparison versus Nitrite to Nitrate Ratio

No significant effect of the presence of the sludge solids from the SRAT product was found in the tests at low sludge content where the sludge contributed the glycolic acid at 125 mg/kg. Figure 8 shows that at similar P/G ratio, there is insignificant differences between the data for the Reagent and SRAT Product simulants. In this figure, colors represent similar P/G, solid symbols filled with colors are SRAT product runs (SP), and open symbols are Reagent runs (R).

The data for the addition of 200 mg/kg of Hg as mercuric nitrate in Figure 9 shows that there was no effect of added mercury. The runs with added Hg are shown by open symbols (Hg) and runs with similar P/G are shown by colors.

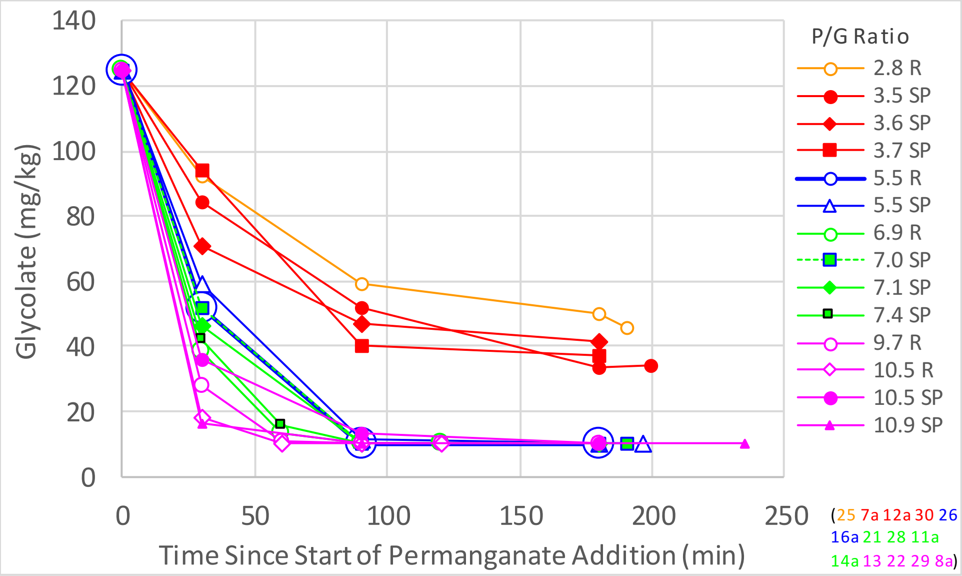


Figure 8. Glycolate Concentration Comparison versus Reagent and SRAT Product Simulants

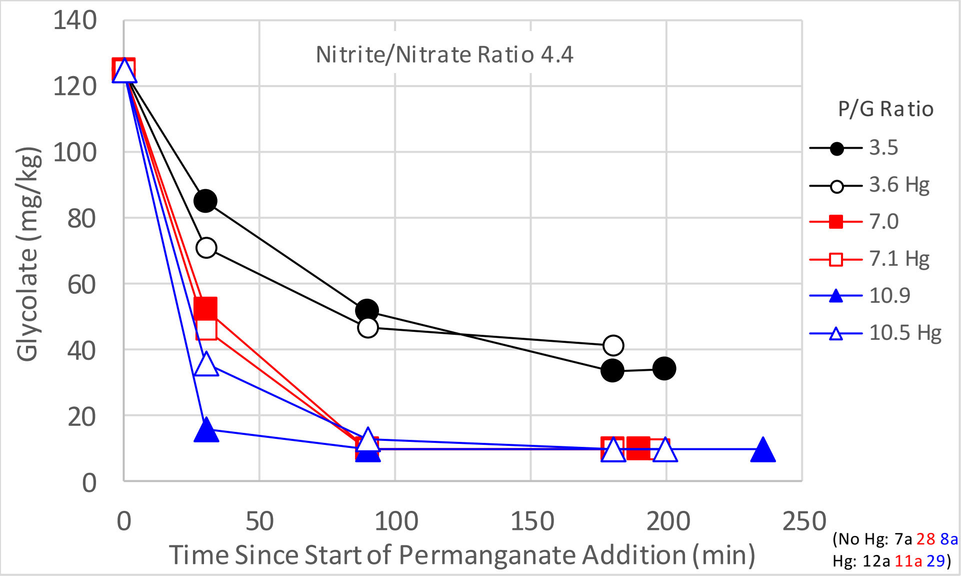


Figure 9. Effect of Added Mercuric Nitrate on Glycolate Oxidation

The glycolate and oxalate concentration results for the foamover runs are shown graphically in Figures 10–11. The oxalate concentrations increase by approximately the same molar amount as the glycolate decreases except for P/G 1.5 where the oxalate values are biased low. The carbon balances are within 5% except for P/G 1.5 which is 16% low. Figure 11 shows the concentration of glycolate between 100 and 400 minutes for the P/G 2.0 and 2.3 runs. These results are almost identical at the end. For both runs, the <10 mg/kg glycolate target was not met. For all four tests, the concentration of glycolate at 90 minutes has decreased to within 97% of its final value at 360 minutes, so (in Figure 10), the additional time beyond 90 minutes has little effect. The glycolate concentration essentially flattens out rather than continuing to decrease smoothly. This behavior is indicative of depleting permanganate and is discussed further in the Reaction Kinetics section (4.4).

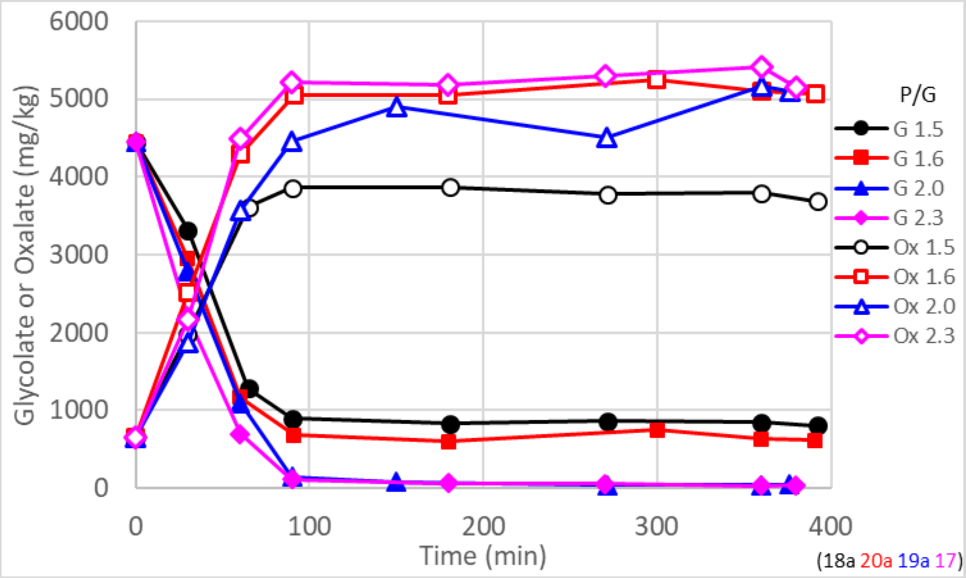


Figure 10. Glycolate and Oxalate for Foamover Runs

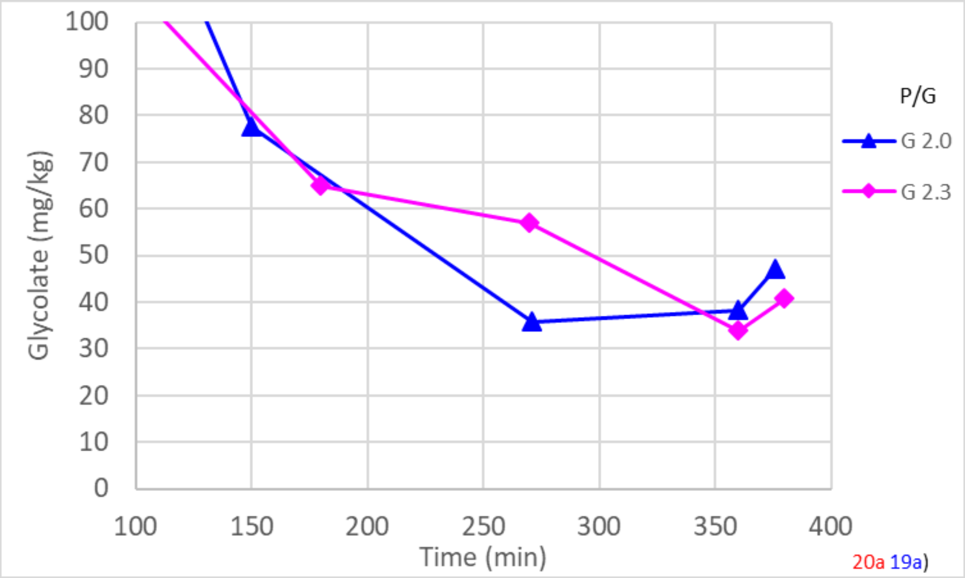


Figure 11. Glycolate and Oxalate for Foamover Runs at Longer Time

Figure 12 shows the higher P/G foamover runs glycolate concentrations compared to two of the runs done with 125 mg/kg initial glycolate (one Reagent and one SRAT Product run). The elapsed time scales for the foamover data have been adjusted by subtracting 90 minutes from the time so that at adjusted time zero for the foamover runs, the glycolate concentrations are similar to the time zero values in the 125 mg/kg runs (1.67 mmol/kg). This comparison shows that at the end of these two foamover runs, the concentration of glycolate versus time is similar to that seen in the 125 mg/kg tests. This amount of excess permanganate would be sufficient, assuming MnO_2 stoichiometry (Equation 3), to continue oxidizing glycolate, so it is apparent that the remaining manganese species is probably not permanganate and is more likely manganate, which would not reduce the glycolate.

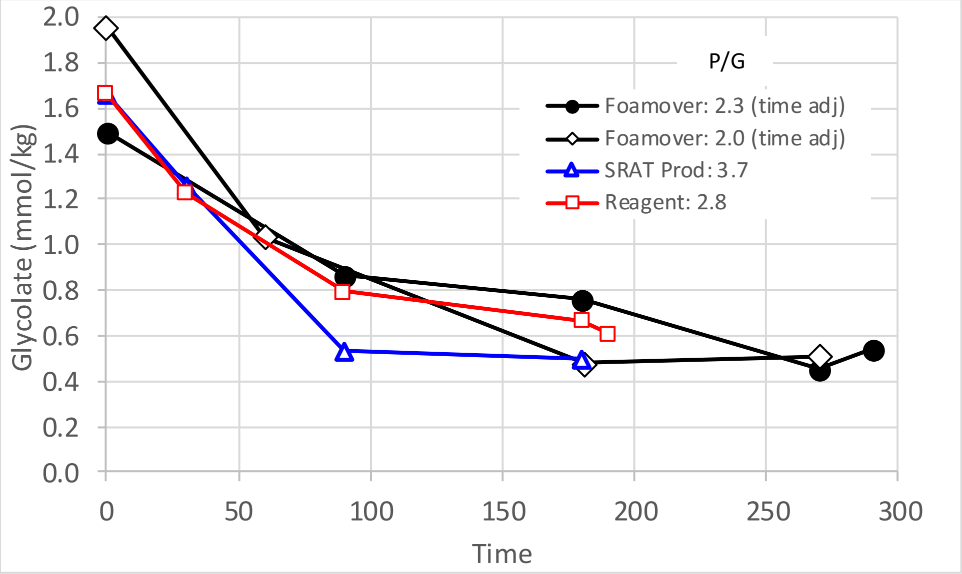


Figure 12. Comparison of Foamover and 125 mg/kg Glycolate Test Glycolate Concentrations

The glycolate concentrations at six hours are shown versus the P/G ratio in Figure 13. The flattening of the relationship at higher than P/G=2 shows that it would be hard to predict how much higher P/G ratio would be needed to reach 10 mg/kg glycolate. A linear extrapolation from the final two measurements suggests a P/G value of about 3.7.

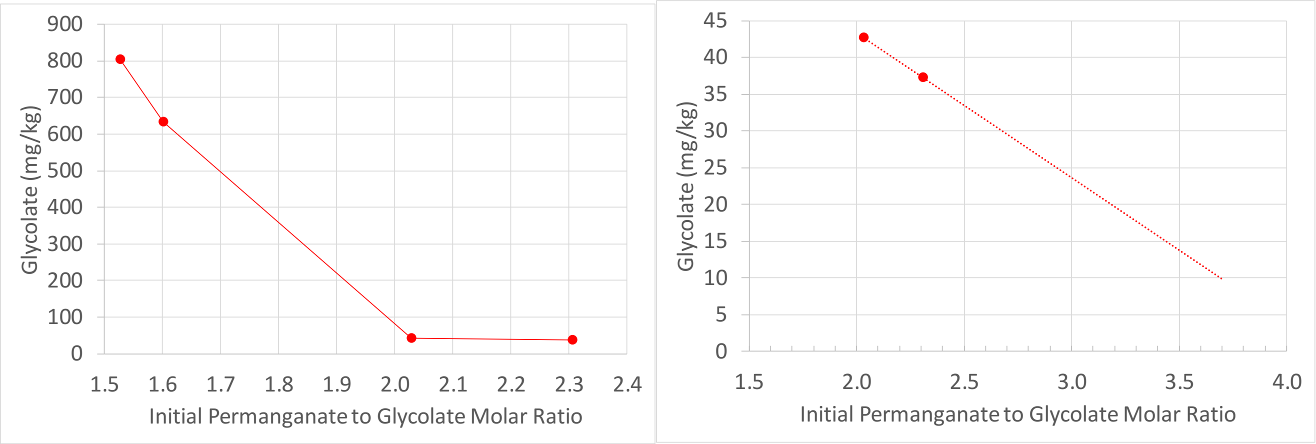


Figure 13. Glycolate at 6 Hours versus P/G

The additional amount of permanganate added initially from P/G 2.0 to 2.3 does not have much effect on the final (6 hour) glycolate concentration. Rather than increase the initial amount of permanganate to P/G of 3 or higher, a possible way to reduce the glycolate concentration further would be to perform a second strike of a small amount of fresh permanganate after the oxidation rate has decreased to near zero (3 hours).

4.3 Qualitative Residual Manganese Species Results

The residual manganese species in solution were compared by color and intensity qualitatively by side-by-side comparison. Approximately 1 mL of product solutions were placed in test tubes and the colors were compared. Identical LED flashlights were used to illuminate each test tube. Effort was made to light each set of samples similarly and to take the photos from the same angles and distance. Comparison of the product solutions from some runs is shown in Figure 14. Products with similar conditions are grouped in rows. The age of samples increases from top to bottom. The columns are organized by approximate P/G ratio.

Row 1 shows three products at N/N 4.4 with 200 mg/kg added mercuric ion. Row 2 shows similar conditions but without added mercury. Both sets show that the there is less intense blue color when less permanganate was used. Some solutions were more green than blue – compare the results at P/G 10.5 and 10.9. The manganate ion Mn^{6+} has a characteristic blue-green color that matches row 2 10.9 best. The difference in intensity between rows 1 and 2 is most likely due to the row 2 being older. The solution color and oxidation state of the manganese will be discussed in more detail in the scaling study.

Row 3 compared to row 1 is similar, showing that the N/N ratio does not have a noticeable effect. Row 4 shows additional decreases in intensity compared to the previous rows. Row 5 shows more effect of time decreasing the intensity. Samples that have sat for 100 or more days are all totally clear with no visible blue tint, and there is a fine black precipitate of (presumably) MnO_2 on the bottle walls. Permanganate and manganate are known to decompose in the presence of light, so decomposition on the surfaces of the bottles is not surprising.

P/G:	~14	~11	~5.5-7	~3.5	~2
1 **SRAT Product** **Nitrite/Nitrate** **Ratio 4.4** **Added Hg**		**10.5** (29, 14 days) 	**7.1** (11a, 15 days) 	**3.6** (12a, 15 days) 	
2 **SRAT** **Product** **Nitrite/Nitrate** **Ratio 4.4** **No Added Hg**	**14.2** (6, 16 days) 	**10.9** (8a, 19 days) 	**7.0** (28, 20 days) 	**3.5** (7a, 20 days) 	
3 **SRAT Product** **Nitrite/Nitrate** **Ratio 2.0** **No Added Hg**			**5.5** (16a, 13 days) 	**3.7** (30, 13 days) 	**1.9** (15a, 14 days) 
4 **Reagent** **Nitrite/Nitrate** **Ratio 4.4** **No Added Hg**	**14.0** (27, 29 days) 		**5.5** (26, 29 days) 	**2.8** (25, 30 days) 	
5 **Reagent** **Nitrite/Nitrate** **Ratio 4.4** **No Added Hg**			**6.9** (21, 70 days) 		

Figure 14. Comparison of Product Solution Colors

4.4 Reaction Kinetics: Proposed Rate Equations for Glycolate Oxidation

The reactions as conducted are of a semi-batch nature. Semi-batch means that one component is all present at the start of the reaction (simulant containing glycolate) and one component is added as a flow (permanganate addition). The solution to the semi-batch reaction kinetics equations requires numerical equation solving, whereas if both reactive species are present at the start, explicit solutions can be determined. As an approximation, it was assumed that all the permanganate was present at the start of the reactions. Assuming what is a higher concentration will result in rate constants that are smaller than the actual values since rate = rate constant * concentration. For the runs where there was a great excess of permanganate, this effect is less because the permanganate concentration does not change appreciably. Although these approximations do not result in the correct rate constants, the rate constants determined were found to correlate the data well.

4.4.1 *First Order in Glycolate Only*

The first order rate of disappearance of glycolate can be described by:

$$\frac{d\xi}{dt} = k_1 C_G = k_1 (C_{Go} - \xi) \tag{5}$$

where C_G = concentration of glycolate (mmol/kg)
C_{Go} = initial concentration of glycolate (mmol/kg)
ξ = extent of reaction (mmol/kg)
k_1 = first order rate constant (min^{-1})

Integration with $\xi=0$ at $t=0$ gives:

$$\ln\left(\frac{C_{Go} - \xi}{C_{Go}}\right) = -kt \tag{6}$$

Or in terms of fraction conversion $f_G = \xi/C_{Go}$:

$$\ln\left(1 - f_G\right) = -kt \tag{7}$$

A plot of $\ln(1-f_G)$ versus $-kt$ will be linear if the reaction is first order in glycolate only.

4.4.2 *First Order in Both Glycolate and Permanganate (Second Order Overall)*

The following analysis is based on Illustration 3.2 in Reference [25].

If the reaction is first order in both glycolate and permanganate, and

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

then the following equation applies if glycolate is the limiting reactant:

$$\frac{d\xi_G}{dt} = k_2 C_G C_P = k_2 (C_{Go} - \xi_G)(C_{Po} - 4\xi_G) \tag{8}$$

where C_G = concentration of glycolate (mmol/kg)
C_{Go} = initial concentration of glycolate (mmol/kg)
C_P = concentration of permanganate (mmol/kg)
C_{Po} = initial concentration of permanganate (mmol/kg)
ξ_G = extent of reaction in terms of glycolate (mmol/kg)
k_2 = second order rate constant (kg^2 mmol^{-1} min^{-1})

Integration with $\xi_G=0$ at $t=0$ gives:

$$\frac{1}{C_{Po} - 4C_{Go}} \ln\left[\frac{\left(C_{Po} - 4\xi_G\right)}{\left(C_{Go} - \xi_G\right)} \frac{C_{Go}}{C_{Po}}\right] = k_2 t \tag{9}$$

Or in terms of fraction conversion of glycolate $f_G = \xi_G/C_{Go}$:

$$\frac{1}{C_{Po}-4C_{Go}}\ln\left[\frac{\left(\frac{C_{Po}}{C_{Go}}-4f_G\right)}{\left(1-f_G\right)}\frac{C_{Go}}{C_{Po}}\right]=k_2t \tag{10}$$

A plot of the left side of equation (10) versus time will give the second order rate constant.

If permanganate is the limiting reactant and f_P as the fraction conversion of permanganate, then equation (10) becomes:

$$\frac{1}{C_{Po}-4C_{Go}}\ln\left[\frac{\left(1-f_P\right)}{\left(\frac{C_{Go}}{C_{Po}}-\frac{f_P}{4}\right)}\frac{C_{Go}}{C_{Po}}\right]=k_2t \tag{11}$$

If the reaction uses 4/3 permanganate per reaction (3), then all of the values ‘4’ in equations (8) through (11) are changed to ‘4/3’.

4.4.3 *Rate Constants for Oxidation of Glycolate*

The first and second order rate constants for each test were determined using these equations. The resulting rate constants are tabulated in Table 17 in order of increasing initial P/G ratio for both 125 mg/kg runs and the foamover runs. The final calculated P/G ratios are also shown. The first order rate constants are plotted versus the P/G ratio in Figure 15 (the foamover tests are not included in this analysis). The reasonable correlation shows that the rate constants are dependent on the P/G ratio, and so the reaction is likely to depend on the permanganate concentration. A first order dependence on permanganate was then also assumed for an overall second order model.

Table 17. Kinetics of Oxidation Reactions

Run	Simulant Type	Nitrite to Nitrate Ratio in Heel	Initial Permanganate to Glycolate Molar Ratio	Final Permanganate to Glycolate Molar Ratio	Glycolate Destruction (≥%) @ 3 h	Glycolate Concentration (mg/kg) @ 3 h (6 h)	Apparent First Order Rate Constant (min^{-1})	Second Order Rate Constant (kg mmol-1 min-1)
	Starting pH >12, 125 mg/kg Glycolate, NaOH Added Before Permanganate, $NaNO_2$ After							
15a	SRAT Prod	2.0	1.88	0.69	25%	88	0.00174	0.00102
25	Reagent	4.4	2.80	0.69	60%	50	0.00557	0.00330
7a	SRAT Prod	4.4	3.49	2.06	72%	33	0.00792	0.00329
12a	SRAT Prod	4.4	3.55	2.59	67%	41	0.0104	0.00366
30	SRAT Prod	2.0	3.69	1.58	70%	37	0.0123	0.00398
26	Reagent	4.4	5.50	22.2	92%	<10	0.0282	0.00619
16a	SRAT Prod	2.0	5.49	22.1	92%	<10	0.0265	0.00573
21	Reagent	4.4	6.89	29.0	92%	<10	0.0378	0.00517
28	SRAT Prod	4.4	7.04	41.1	92%	<10	0.0281	0.00388
11a	SRAT Prod	4.4	7.06	41.3	92%	<10	0.0285	0.00392
14a	Reagent	2.0	7.38	44.8	92%	<10	0.0304	0.00384
13	Reagent	2.0	9.72	72.8	92%	<10	0.0422	0.00356
22	Reagent	4.4	10.5	83.6	92%	<10	0.0466	0.00357
29	SRAT Prod	4.4	10.5	83.1	92%	<10	0.0267	0.00202
8a	SRAT Prod	4.4	10.9	87.7	92%	<10	0.0683	0.00492
4	Reagent	4.4	13.8	124	92%	<10	0.0672	0.00358
3	Reagent	4.4	13.8	123	92%	<10	0.0431	0.00232
10a	Reagent	4.4	13.9	124	92%	<10	0.0842	0.00457
27	Reagent	4.4	14.0	126	92%	<10	0.0805	0.00426
6	SRAT Prod	4.4	14.1	127	92%	<10	0.0711	0.00372
9	Reagent	4.4	15.1	138	92%	<10	0.0632	0.00303
5	Reagent	4.4	20.9	207	92%	<10	0.0842	0.00284
							Mean	**0.00375**
							Std. Deviation	**0.00117**
	Starting pH >12, ~4450 mg/kg Glycolate, NaOH Added Before Permanganate, $NaNO_2$ After							
18a	Foamover	4.4	1.53	2.41	81%	860 (804)	0.0177	0.000366
20a	Foamover	2.0	1.60	3.27	85%	681 (633)	0.0206	0.000420
19a	Foamover	4.4	2.03	66.9	99.0%	78 (38-47)	0.0322	0.000510
17	Foamover	4.4	2.31	108	99.1%	65 (34-41)	0.0368	0.000466
							Mean	**0.000518**

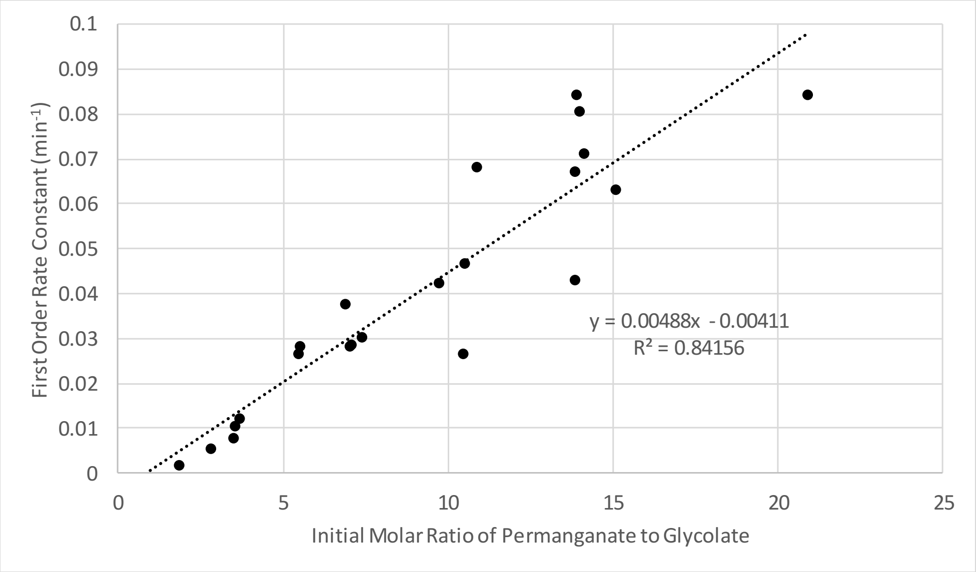


Figure 15. Correlation of First Order Rate Constants with P/G Ratio

The data were fit to the second order model where it was assumed that the amount of permanganate versus time was the initial amount minus four times the amount of glycolate reacted. These rate constants, in the last column of Table 17, are for the most part approximately all the same value; the variation in values appears to be random. The average second order rate constant is 0.00375. These rate constants (the foamover tests are not included in this analysis) are plotted in Figure 16, showing that the mean is the best approximation since there is almost no slope.

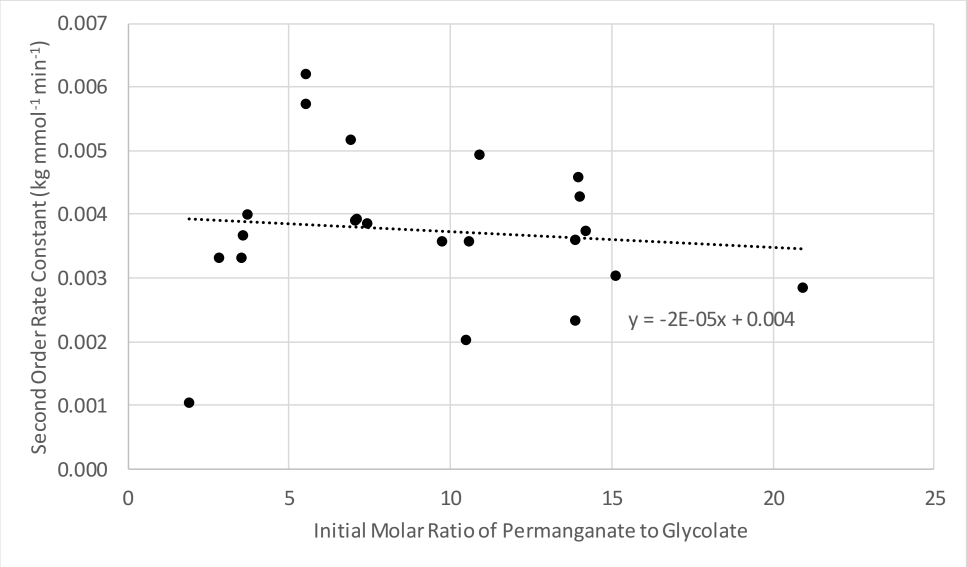
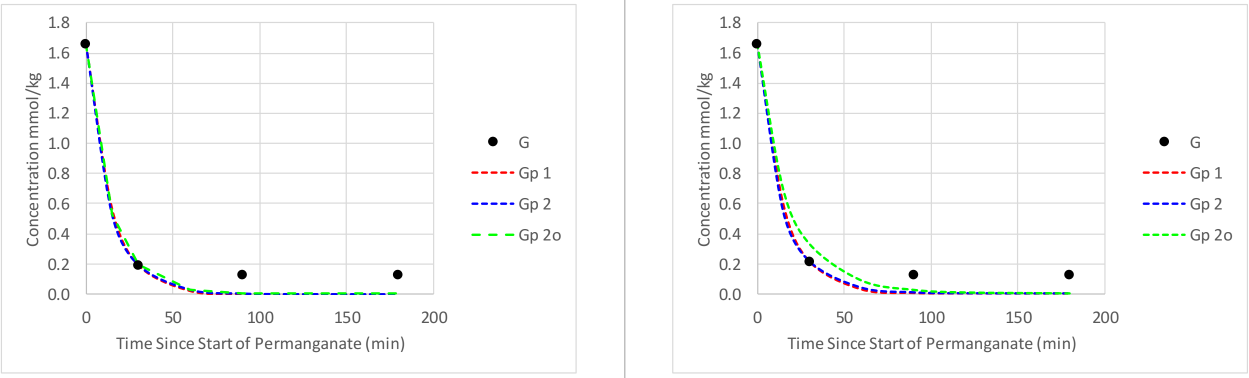
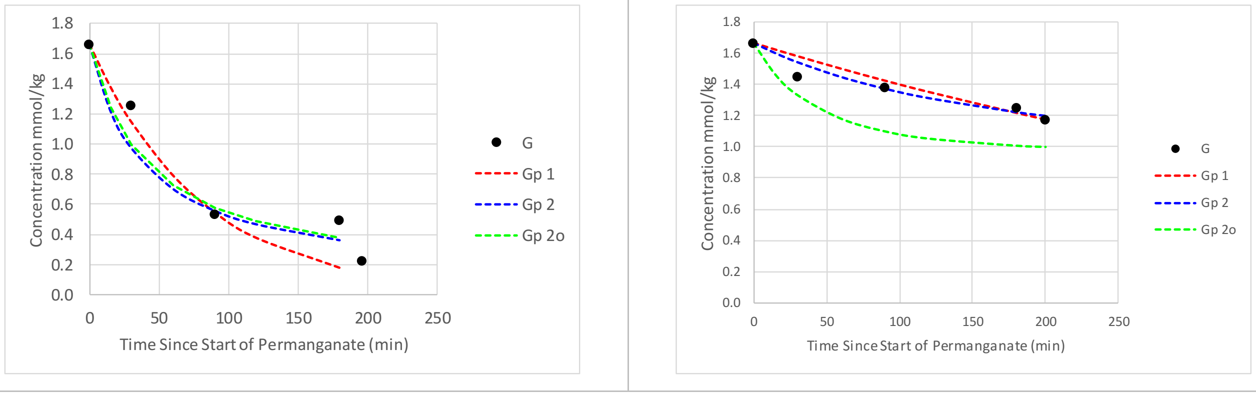


Figure 16. Second Order Rate Constants versus P/G Ratio

Several data sets are shown with the first and second order fits and the overall second order fit with the average rate constant value in Figure 17. All the data set fits are summarized in Appendix A. The overall second order model tends to overpredict the oxidation of glycolate at low P/G because the model assumes all of permanganate is present at the start. When there is less than the stoichiometric amount of permanganate (<4), the second order models correctly predict that the oxidation will stop when there is no more permanganate; the first order models all predict that glycolate should go to zero.


Run 6. P/G=14.2 Run 8a. P/G=10.86


Run 30. P/G=3.69 Run 15a. P/G=1.88

(black dots are glycolate concentration; red lines are first order fits; blue lines are second order fits for individual data set; green lines are second order fits using the average rate constant)

Figure 17. Example Fits of 125 mg/kg Glycolate Rate Data

The first order rate constants for the foamover runs were very well correlated with P/G, but the second order rate constants were not constant, indicating that the second order model is not correct. The correlation of the first order rate constants with P/G is shown in Figure 18. The second order rate constants are shown in Figure 19; there is less correlation than the first order rate constants. It seems likely that one or more of the following could be possible explanations for this behavior:

1. The reaction is not first order in permanganate, but rather some non-integer or higher order.
2. The reaction mechanism changes during the oxidation such that different rate equations apply at different times, or that several may apply at the same time in varying proportions.
3. There is an additional reaction or reactions that have not been considered.

The possibility of additional reactions may explain why the oxidation in the presence of sludge is closer to requiring P/G of 4/3 rather than 4. This possibility is discussed further in section 4.4.4.

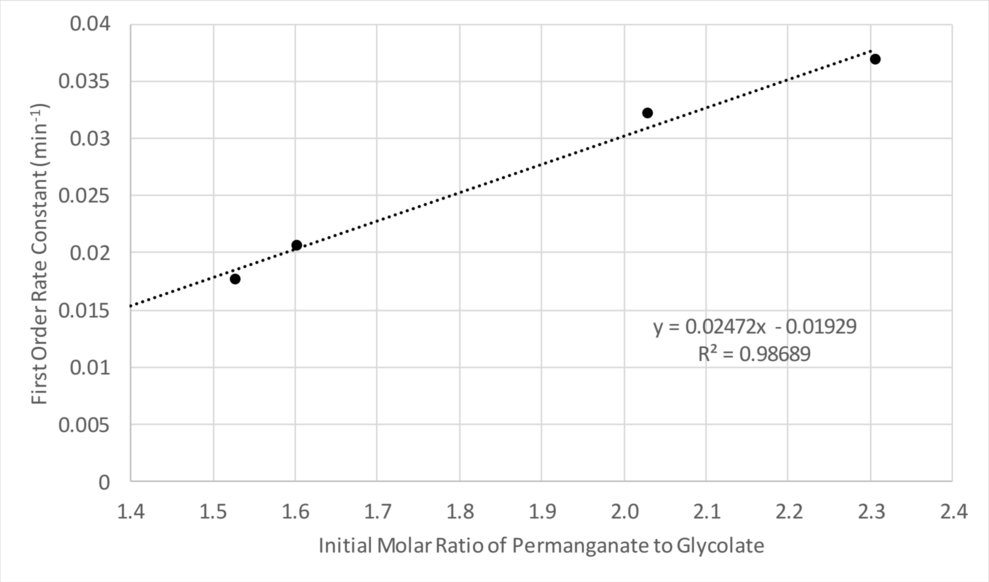


Figure 18. First Order Rate Constants for Foamover Runs versus P/G

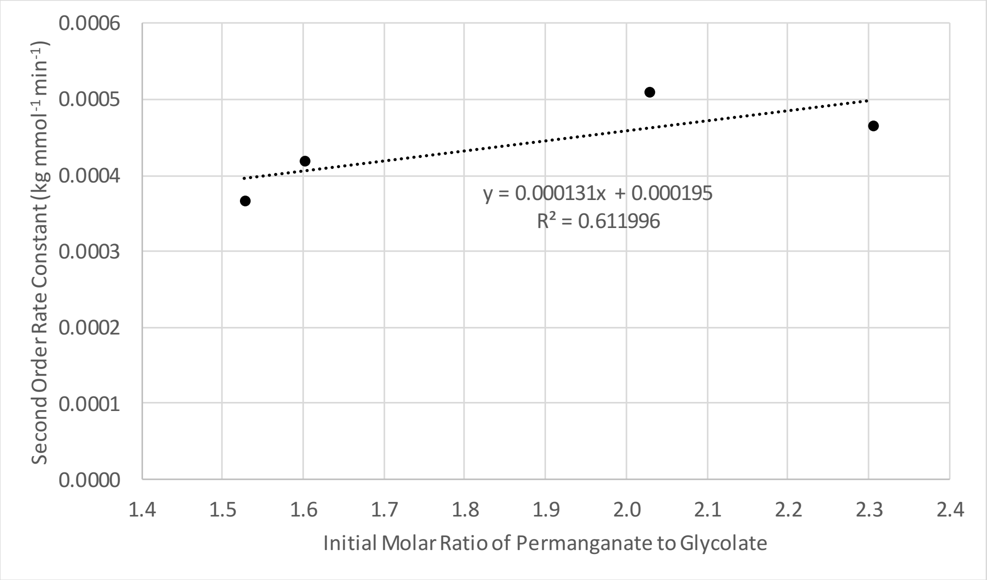
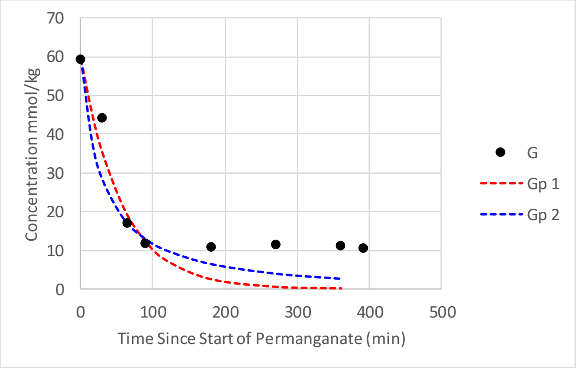


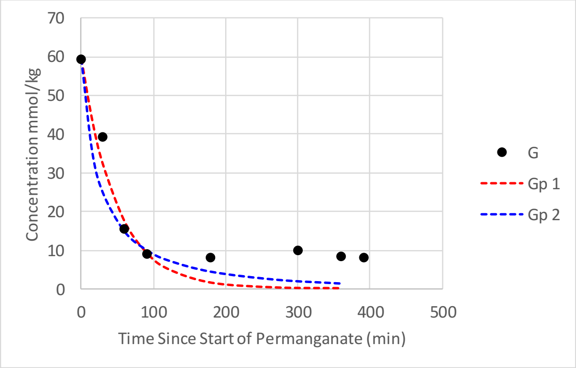
Figure 19. Second Order Rate Constants for Foamover Runs versus P/G

The concentrations versus time for the foamover runs are summarized in Figure 20. The lower (<4mM/kg) glycolate concentrations of the P/G 2.0 and 2.3 runs are shown at the bottom. All the graphs show that the first and second order models overpredict the destruction of glycolate because the destruction stops before all of the glycolate and apparent permanganate are destroyed. Note that the final P/G ratios for runs 18a and 20a are very close to the initial values, while 19a and 17 have significantly higher values since there is much less glycolate remaining.

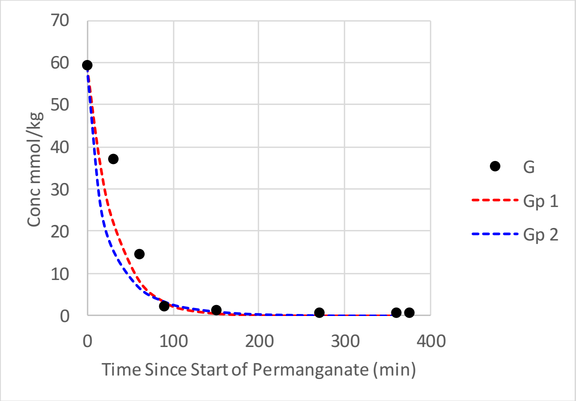
Run 18a. P/G=1.53 initial, 2.41 final



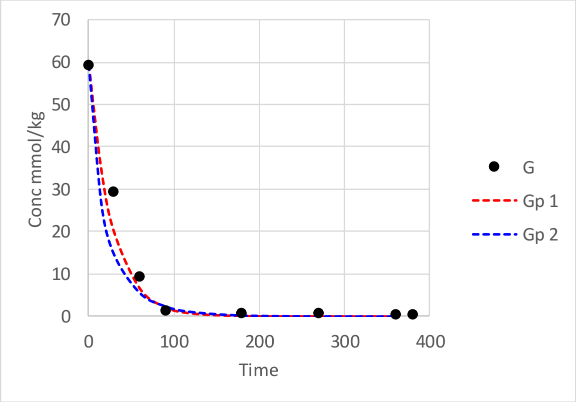
Run 20a. P/G=1.60 initial, 3.27 final



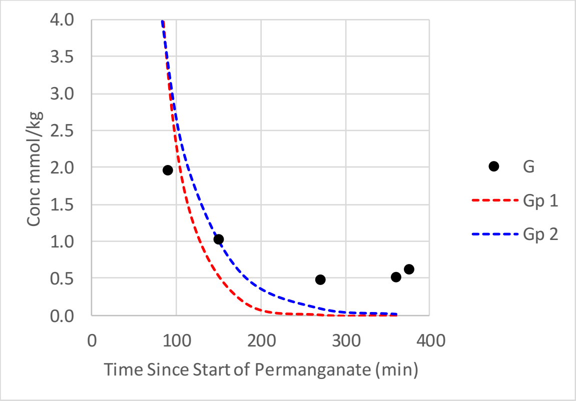
Run 19a. P/G=2.03 initial, 66.9 final



Run 17. P/G=2.31 initial, 108 final



Run 19a.



Run 17.

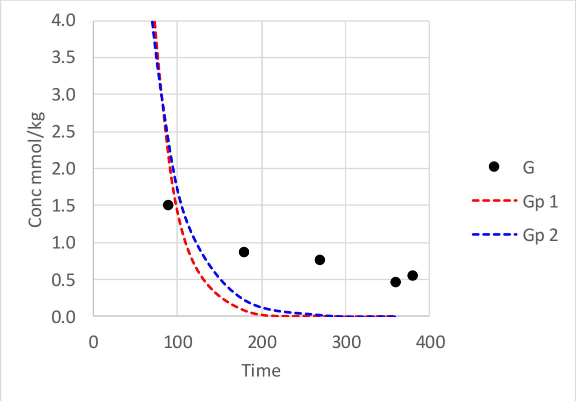


Figure 20. Foamover Runs Data Fits

4.4.4 *Possible Reactions in the Presence of Sludge*

A plausible, but unproven, reaction scheme for the oxidation of glycolate to oxalate with the permanganate becoming more reduced than manganate is described below for the foamover cases. The final Mn product is MnO_2, thus giving an overall stoichiometric coefficient on permanganate of 4/3 rather than the value of 4 observed in the Reagent and dilute SRAT product tests. In this scheme below, the relatively high amount of Mn^{2+} present from the SRAT product is used to generate the powerful oxidant[20, 26] Mn^{3+} from the manganate or directly from permanganate.

First oxidize glycolate to oxalate and generate manganate:

$$C_2H_3O_3^- + 4\,MnO_4^- + 5\,OH^- = C_2O_4^{2-} + 4\,MnO_4^{2-} + 4\,H_2O \qquad \xi_1$$

Using the manganous Mn^{2+} ion present from the SRAT product sludge, oxidize manganate to generate Mn^{3+}, which is a known strong oxidant for organics.

$$MnO_4^{2-} + 3\,Mn^{2+} + 4\,H_2O = 4\,Mn^{3+} + 8\,OH^- \qquad \xi_3$$

or, more likely in caustic solution, where the manganese hydroxide is likely insoluble:

$$MnO_4^{2-} + 3\,Mn^{2+} + 4\,OH^- + 4\,H_2O = 4\,Mn(OH)_3\,(s) \qquad \xi_3'$$

The Mn^{3+} could also be formed directly from permanganate and Mn^{2+}:

$$MnO_4^- + 4\,Mn^{2+} + 4\,H_2O = 5\,Mn^{3+} + 8\,OH^- \qquad \xi_6$$

or

$$MnO_4^- + 4\,Mn^{2+} + 7\,OH^- + 4\,H_2O = 5\,Mn(OH)_3\,(s) \qquad \xi_6'$$

The Mn^{3+} generated could then also oxidize glycolate to oxalate:

$$C_2H_3O_3^- + 4\,Mn^{3+} + 5\,OH^- = C_2O_4^{2-} + 4\,Mn^{2+} + 4\,H_2O \qquad \xi_2$$

The Mn^{2+} generated by ξ_2 would then react further by ξ_3 (or by ξ_6) to generate more Mn^{3+}.

Reactions ξ_2 and ξ_6 are similar to the reaction for production of MnO_2 from permanganate and Mn^{2+}. The formation of the more stable MnO_2 would end the reaction sequence:

$$2\,MnO_4^- + 3\,Mn^{2+} + 4\,OH^- = 5\,MnO_2 + 2\,H_2O \qquad \xi_4$$

$$MnO_4^{2-} + Mn^{2+} = 4\,MnO_2 \qquad \xi_5$$

Other reduced metals, such as Fe^{2+}, could also be involved in the formation of Mn^{3+}, with the oxidation of the Fe^{2+} to Fe^{3+}. The REDOX pairs Ni^{2+}, Ni^{3+} and Cu^+, Cu^{2+} could also possibly be involved.

Combining equations ξ_1-ξ_5, it can be shown that for Run 17, glycolate can be completely oxidized to oxalate while permanganate forms a final product mixture containing manganate and MnO_2. Here it has been assumed that due to their reactivity, neither Mn^{2+} or Mn^{3+} will exist at the end of the reaction.

It should be noted that the ratio of initial Mn^{2+} to permanganate in the dilute SRAT product tests was similar to the foamover tests, but no such reactions were observed. However, the concentration of Mn^{2+} was about 35 times higher in the foamover tests. Since reaction rates are concentration dependent, this concentration difference could account for higher reactivity of Mn^{2+} in the foamover case. The Mn^{2+} in the more concentrated foamover runs is likely to be complexed by glycolate (e.g., $Mn(C_2H_3O_3)^+$, $Mn(C_2H_3O_3)_2$, $Mn(C_2H_3O_3)_3^-$) which could make it less reactive than Mn^{2+} alone. The combination of the manganese REDOX reactions with the glycolate oxidation, which is also a REDOX reaction, could stabilize some of the intermediate manganese species such as the Mn^{3+}.

Although not proving that Mn^{2+} is what allows permanganate to become more reduced than manganate, this reaction scheme shows that it may be reasonable for such reactions to occur.

4.4.5 *Oxidation of Antifoam Analog PEG*

The antifoam straight chain analog PEG was reacted with permanganate using the stoichiometric equation in Table 11. The 100% stoichiometric amount, or 112/3 mol per mol of PEG, was used. The PEG was added at 3000 mg/kg in a pH 13 RCT simulant with N/N 4.4 and with no other organics. The permanganate was added over 20 minutes and the samples were taken to six hours duration. The samples were analyzed for anions, TIC, and TOC. Offgases were monitored during the run and none were detected.

The initial TOC calculated from the PEG added was 1490 mg/kg. The measured TOC was 1630 mg/kg. All the samples taken during the run had TOC values of 1890-1910 mg/kg. It is unclear why the values would be higher than the initial value. No TIC was detected. Formate was detected at 20 mg/kg in all samples, and oxalate was found to increase from 10 mg/kg at 30 minutes to 90 mg/kg at 360 minutes. Oxalate is a likely oxidation product from PEG since the chain section is O-CH_2-CH_2-O and oxalate is OOC-COO. The final oxalate would be about 1.5% of the initial PEG.

Overall, it appears that the PEG is very stable towards oxidation by permanganate.

5.0 Conclusions

The following conclusions are drawn from this work.

General Conclusions:

1) At pH greater than 12, nitrite is not oxidized to nitrate by permanganate.

Therefore, nitrite can probably be added to the RCT prior to permanganate.

2) At pH greater than 12, glycolate is oxidized to oxalate with no significant formation of CO_2 or carbonate.
3) Formate and oxalate do not appear to be oxidized.
4) Formate does not appear to be generated from glycolate.
5) The nitrite to nitrate ratio does not affect the oxidation of glycolate. As a result, the oxidant stoichiometry should be based on the permanganate to glycolate molar ratio.
6) Added mercuric ion at 200 mg/kg does not affect the oxidation of glycolate.
7) Sulfite quenched samples are not stable over long times, so samples should be analyzed as soon as possible after being taken.

Conclusions per the simulated 14.5 gallon carryover experiments follow:

8) At low initial glycolate (125 mg/kg), the minimum theoretical initial permanganate to glycolate (P/G) molar ratio (based on reaction 4) to reduce glycolate below 10 mg/kg is 4.0.
    a) An excess of about 4-6X is required to achieve complete oxidation to below 10 mg/kg (detection limit).
    b) For the duration of the experiment, the permanganate (Mn^{7+}) is reduced to manganate (Mn^{6+}) and not to MnO_2 (Mn^{4+}).

9) At low glycolate (125 mg/kg), the presence of SRAT product sludge does not affect the oxidation of glycolate.
10) The data for the low 125 mg/kg glycolate tests was fit well by a second order kinetic model that is first order in the glycolate and permanganate concentrations. In this testing, oxidation time was less than three hours for reducing the glycolate below 10 mg/kg.
11) The antifoam straight-chain analog PEG was not significantly oxidized by permanganate at pH 12-13.

Conclusions per the simulated 500 gallon carryover experiments follow:

12) The permanganate required per mole of glycolate is less than for low glycolate (14.5 gallon carryover).
    a) The presence of sludge components at these levels does affect the course of the oxidation reaction.
    b) Permanganate must be at least partially reduced to MnO_2 rather than to only manganate, so relatively less is required.
13) Greater than 99% of the glycolate in the foamover tests was destroyed with a permanganate to glycolate molar ratio of 2.0.
    a) The target <10 mg/kg glycolate was not reached with P/G 2.3; glycolate was ~40 mg/kg. A second strike might be needed to reduce the glycolate concentration below 10 mg/kg.
14) The individual foamover runs data were fit well by a model first order in glycolate, and the rate constants correlated well with the P/G ratio, but a similar second order model did not describe the data well.
    a) The reactions with the additional sludge are more complicated than with much less sludge present.
    b) The effect of the sludge may be caused by the presence of reduced metal ions such as Mn^{2+} and Fe^{2+} that could generate the strong oxidant Mn^{3+}.

6.0 Recommendations

Recommendations for follow-on SRNL work on glycolate oxidation by permanganate are summarized below.

1) Scaled testing at 125 mg/kg glycolate should concentrate in and around the permanganate to glycolate (P/G) initial molar ratio region of 4.0-5.2.
2) Further testing of 500 gal foamover conditions should examine P/G ratios greater than 2.3.
    a) P/G at about 2.0 should be tested with a late addition (after oxidation slows significantly) of additional permanganate as a possible way to minimize the total permanganate needed.
3) Tests should be performed with nitrite added with caustic before permanganate to demonstrate that added nitrite will not be oxidized.
4) Samples taken for nitrite and nitrate as 1000X dilutions should have NaOH added to raise the pH to 12-13 to minimize reaction of the permanganate that could occur at the lower diluted pH.

Recommendation for DWPF operation:

At low glycolate (125 mg/kg), about 5 moles of permanganate should be added per mole of glycolate to oxidize it to less than 10 mg/kg.

7.0 References

1. (a) Pickenheim, B. R.; Stone, M. E.; Newell, J. D. *Glycolic - Formic Acid Flowsheet Development*; SRNL-STI-2010-00523, Revision 0; Savannah River National Laboratory, Aiken, SC, 2010; (b) Lambert, D. P.; Koopman, D. C. *Glycolic-Formic Acid Flowsheet Sludge Matrix Study*; SRNL-STI-2011-00275, Revision 0; Savannah River National Laboratory, Aiken, SC, 2011; (c) Lambert, D. P.; Pickenheim, B. R.; Stone, M. E.; Newell, J. D.; Best, D. R. *Glycolic-Formic Acid Flowsheet Final Report for Downselection Decision*; SRNL-STI-2010-00523, Revision 1; Savannah River National Laboratory, Aiken, SC, 2011; (d) Lambert, D. P.; Zamecnik, J. R.; Best, D. R. *FY13 Glycolic-Nitric Acid Flowsheet Demonstrations of the DWPF Chemical Process Cell with Simulants*; SRNL-STI-2013-00343, Revision 0; Savannah River National Laboratory, Aiken, SC, 2014; (e) Lambert, D. P.; Zamecnik, J. R.; Newell, J. D.; Martino, C. J. *Impact of Scaling on the Nitric-Glycolic Acid Flowsheet*; SRNL-STI-2014-00306, Revision 0; Savannah River National Laboratory, Aiken, SC, 2016; (f) Lambert, D. P. *Recommendations for Sludge Batch 9 Qualification Processing Under the Nitric-Glycolic Acid Flowsheet in the Shielded Cells*; SRNL-L3100-2016-00077, Rev. 1; Savannah River National Laboratory, Aiken, SC, 2016.
2. Martino, C. J.; Pareizs, J. M.; Newell, J. D. *Thermolytic Hydrogen Generation Testing of Tank 22 Material*; SRNL-STI-2018-00385, Revision 0; Savannah River National Laboratory, Aiken, SC, 2018.
3. Ramsey, W. G. *Destruction / Mitigation of Glycolate in DWPF Recycle: Optioneering Meeting Results*; SRNL-L3100-2017-00140, Revision 0; Savannah River National Laboratory, Aiken, SC, 2017.
4. Chen, G.; Clark, M., Evaluation of Chemical Additives for Glycolate Mitigation. Savannah River Remediation, LLC, Aiken, SC: 2018.
5. Lambert, D. P., Task Technical and Quality Assurance Plan for Evaluation of Chemical Additives for Glycolate Mitigation. Savannah River National Laboratory, Aiken, SC: 2018.
6. Chen, G.; Holtzscheiter, E. W., Screening Study: Chemical Additives for Low Concentration Glycolate Decomposition in Defense Waste Processing Facility (DWPF) Recycle Stream to Tank Farm. Savannah River Remediation, LLC, Aiken, SC: 2017.
7. Peters, T. B.; Nash, C. A., Glycolate Mitigation Run Plan without Off-Gas Testing. Savannah River National Laboratory, Aiken, SC: 2018.
8. Peters, T. B.; Nash, C. A., Defense Waste Processing Facility (DWPF) Glycolate Mitigation: Scoping Test Results. Savannah River National Laboratory, Aiken, SC: 2018.
9. Lambert, D. P.; Williams, M. S.; Edwards, T. B., Run Plan #1: Determining Optimum Processing Conditions for Oxidation of Organic Species in a Typical Recycle Collection Tank Simulant. Savannah River National Laboratory, Aiken, SC: 2018.
10. Lambert, D. P.; Howe, A.; Williams, M. S.; Trivelpiece, C.; Ramsey, W. G., Evaluation of Chemical Additives for Glycolate Destruction in the Recycle Collection Tank. Savannah River National Laboratory: 2019.
11. *Conduct of Engineering Technical Reviews, Manual E7, Procedure 2.60, Revision 17*; Savannah River Site: Aiken, SC, 2016.
12. *Savannah River National Laboratory Technical Report Design Check Guidelines*; WSRC-IM-2002-00011, Revision 2; Savannah River National Laboratory, Aiken, SC, 2004.
13. Zamecnik, J. R., Run Plan for Permanganate Oxidation of Defense Waste Processing Facility (DWPF) Recycle Collection Tank (RCT) Simulants Protocol Runs - Nominal and Chemical Process Cell (CPC) Foamover Conditions. 2018.
14. Zamecnik, J. R., Emails Regarding DWPF RCT Tank. Savannah River National Laboratory: 2018.

15. (a) Broomfield, R. *SW4-15.76-2.8, Rev. 16, Nitric Acid Addition to SMECT*; USQ-WD-2016-00140; Savannah River Remediation LLC, Aiken, SC, 2016; (b) Cardona-Quiles, O. *SW4-15.76-2.8, Rev. 17, Nitric Acid Addition to SMECT*; USQ-WD-2016-00586; Savannah River Remediation LLC, Aiken, SC, 2016.
16. Bradley Pickenheim, B.; Bibler, N. E.; Lambert, D. P.; Hay, M. S., Glycolic Acid Physical Properties and Impurities Assessment. Savannah River National Laboratory: 2017.
17. Lambert, D. P.; Williams, M. S.; Brandenberg, C. H.; Luther, M. C.; Newell, J. D.; Woodham, W. H., Sludge Batch 9 Simulant Runs Using the Nitric-Glycolic Acid Flowsheet. Savannah River National Laboratory, Aiken, SC: 2016.
18. Riddick, E. F. *Purge Requirements for the Recycle Collection Tank*; X-CLC-S-00315, Revision 1; Savannah River Remediation, LLC, Aiken, SC, 2014.
19. *E&CPT Research Programs Section Manual: Calibration and Verification of Orion Star/Star Plus and A210/A220 Series pH Meters*; Manual: L29, Procedure: ITS-0221, Revision: 0; Savannah River National Laboratory, Aiken, SC, 2018.
20. Gao, Y.; Jiang, J.; Zhou, Y.; Pang, S. Y.; Ma, J.; Jiang, C. C.; Wang, Z.; Wang, P. X.; Wang, L. H.; Li, J., Unrecognized role of bisulfite as Mn(III) stabilizing agent in activating permanganate (Mn(VII)) for enhanced degradation of organic contaminants. *Chem. Eng. J.* **2017,** *327*, 418-422.
21. Sun, B.; Rao, D. D.; Dong, H. Y.; Guan, X. H., Comparing the suitability of sodium hyposulfite, hydroxylamine hydrochloride and sodium sulfite as the quenching agents for permanganate oxidation. *RSC Adv.* **2016,** *6* (16), 13335-13342.
22. (a) Petrissans, S. A.; Zoulalian, A., Influence of the pH on the Interactions between nitrite and sulfite ions. Kinetic of the Reaction at pH 4 and 5. *Ind. Eng. Chem. Res.* **2001,** *40* (26), 6068-6072; (b) Oblath, S. B.; Markowitz, S. S.; Novakov, T.; Chang, S. G., KINETICS OF THE INITIAL REACTION OF NITRITE ION IN BISULFITE SOLUTIONS. *J. Phys. Chem.* **1982,** *86* (25), 4853-4857; (c) Oblath, S. B.; Markowitz, S. S.; Novakov, T.; Chang, S. G., KINETICS OF THE FORMATION OF HYDROXYLAMINE DISULFONATE BY REACTION OF NITRITE WITH SULFITES. *J. Phys. Chem.* **1981,** *85* (8), 1017-1021; (d) Oblath, S. B.; Markowitz, S. S.; Novakov, T.; Chang, S. G., REACTION OF NITRITE ION WITH HYDROXYLAMINE-N-SULFONATE IN AQUEOUS-SOLUTION. *Inorg. Chem.* **1983,** *22* (4), 579-583; (e) Rollefson, G. K.; Oldershaw, C. F., THE REDUCTION OF NITRITES TO HYDROXYLAMINE BY SULFITES. *J. Am. Chem. Soc.* **1932,** *54* (3), 977-979.
23. (a) Gauger, A. M.; Hallen, R. T., Individual Reactions of Permanganate and Various Reductants. Pacific Northwest National Laboratory: 2012; (b) Walton, J.; Labine, P.; Reidies, A. In *The Chemistry of Permanganate in Degradative Oxidations*, Chemical Oxidation: Technologies for the Nineties, Vanderbilt University, Nashville, TN, Eckenfelter, W. W.; Bowers, A. R.; Roth, J. A., Eds. Vanderbilt University, Nashville, TN, 1991; pp 205-221.
24. Dash, S.; Patel, S.; Mishra, B. K., Oxidation by permanganate: synthetic and mechanistic aspects. *Tetrahedron* **2009,** *65* (4), 707-739.
25. Charles G. HIll, J., *An Introduction to Chemical Engineering Kinetics & Reactor Design*. John Wiley & Sons: 1977.
26. Hu, E.; Zhang, Y.; Wu, S. Y.; Wu, J.; Liang, L. Y.; He, F., Role of dissolved Mn(III) in transformation of organic contaminants: Non-oxidative versus oxidative mechanisms. *Water Res.* **2017,** *111*, 234-243.

8.0 Appendixes

Appendix A – Sample Analyses A-2
Appendix B – Determination of Rate Constants B-1
Appendix C – Statistical Analysis of RCT Concentrations C-1
Appendix D -- Calculated Permanganate to Glycolate Molar Ratio for Downselect Tests D-1

Appendix A: Sample Analyses

Blank cells: analysis not requested												suspect values from sulfite quench							
			From 10X Dilution			From 100X Dilution			From 1000X Dilution										
	PSAL Sample #	PSAL Request #	Glycolate mg/kg	Formate mg/kg	Oxalate mg/kg	Glycolate mg/kg	Formate mg/kg	Oxalate mg/kg	Glycolate mg/kg	Formate mg/kg	Oxalate mg/kg	Nitrite	Nitrate	Total Solids wt%	Supernate Solids wt%	Insoluble Solids wt%	Slurry Density kg/L	Total OH M	pH
PROT-1-PCOND-Q	8615	1188	112.3	29.3	18.6							1430	2960						
PROT-1-POG-Q	8617	1188	116.0	34.7	18.8							1534	3622						
PROT-1-030-Q	8618	1188	77.5	52.1	35.4							211	3615						
PROT-1-060-Q	8620	1188	62.3	35.7	55.8							206	3889						
PROT-1-090-Q	8622	1188	52.6	48.2	73.2							292	3866						
PROT-1-120-Q	8624	1188	45.4	41.0	68.8							283	3942						
PROT-1-180-Q	8626	1188, 1203	19.5	25.2	85.9							188	4156						
PROT-1-PNO2-Q	8628	1188, 1203	<10	<10	112.8							1345	6114						
PROT-1-PNO2-P	8629	1188												3.38%		0.36%	1.0207		
PROT-2-PCOND-Q	8630	1189	111.9	50.5	15.3							1161	3562						
PROT-2-POG-Q	8632	1189	111.7	41.8	14.9							1015	3595						
PROT-2-030-Q	8633	1189	55.6	35.5	24.8							127	4288						
PROT-2-060-Q	8635	1189	37.0	30.9	45.2							131	4078						
PROT-2-090-Q	8637	1189	27.4	30.1	58.9							138	4371						
PROT-2-120-Q	8639	1189	19.8	27.6	88.3							147	4404						
PROT-2-180-Q	8641	1189, 1203	<10	22.0	102.6							189	4220						
PROT-2-PNO2-Q	8643	1189, 1203	<11	<11	129.9							1471	9384						
PROT-2-PNO2-P	8644	1189												3.70%		0.52%	1.0218		
PROT-2-D21-Q	8660	1202																	
PROT-25-030-QD10	8902	1229	92.1	30.0	74.3														
PROT-25-090-QD10	8903	1229	59.6	28.0	122.5														
PROT-25-180-QD10	8904	1229	50.1	30.0	136.6														
PROT-25-180-D1K	8905	1229										2286	4868						
PROT-25-PNO2-QD10	8906	1229	45.7	35.0	134.5														
PROT-25-PNO2-D1K	8907	1229										11361	4303						
PROT-25-PNO2-MISC	8908	1229												3.12%			1.0217	0.2062	
PROT-21-030-Q	8742	1209	38.6	<10	108.6							330	3976						
PROT-21-060-Q	8743	1209	13.2	<10	144.2							323	3921						
PROT-21-090-Q	8744	1209	<10	<10	153.2							311	3825						
PROT-21-120-Q	8745	1209	<10	<10	154.3							322	4059						
PROT-21-180-Q	8746	1207	14.2	22.2	153.7														
PROT-21-180-DIL	8747	1208										1020	3772						
PROT-21-PNO2-Q	8748	1207	<10	<10	148.2														
PROT-21-PNO2-DIL	8749	1208										9178	3225						
PROT-21-PNO2-P	8750	1209												2.98%	3.15%		1.0216		
PROT-23-030-Q	8760	1209	119.3	<10	18.7							399	3814						
PROT-23-060-Q	8761	1209	65.7	<10	66.5							348	3913						
PROT-23-090-Q	8762	1209	40.2	<10	85.9							371	3772						
PROT-23-180-Q	8764	1207	6.4	20.0	146.6														
PROT-23-180-DIL	8765	1208										937	3818						
PROT-23-PNO2-Q	8766	1207	2.9	1.5	144.7														
PROT-23-PNO2-DIL	8767	1208										9266	3649						
PROT-23-PNO2-P	8768	1209												2.96%	3.10%		1.0215		
PROT-26-030-QD10	8926	1236	51.7	24.6	102.2														
			50.9	38.1	91.6														
PROT-26-090-QD10	8927	1236	<10	19.0	159.6														
PROT-26-180-QD10	8928	1236	<10	19.9	164.9														
PROT-26-180-D1K	8929	1237										2089	4017						

Blank cells: analysis not requested												suspect values from sulfite quench							
				From 10X Dilution			From 100X Dilution			From 1000X Dilution									
	PSAL Sample #	PSAL Request #	Glycolate mg/kg	Formate mg/kg	Oxalate mg/kg	Glycolate mg/kg	Formate mg/kg	Oxalate mg/kg	Glycolate mg/kg	Formate mg/kg	Oxalate mg/kg	Nitrite	Nitrate	Total Solids wt%	Supernate Solids wt%	Insoluble Solids wt%	Slurry Density kg/L	Total OH M	pH
PROT-26-180-D1K	8929	1238										2019	3938						
PROT-26-180-D1K	8929	1238										2139	5207						
PROT-26-PNO2-QD10	8930	1236	<10	21.6	158.7														
PROT-26-PNO2-D1K	8931	1237										10544	3651						
PROT-26-PNO2-D1K	8931	1238										10146	3810						
PROT-26-PNO2-D1K	8931	1238										10246	3919						
PROT-26-PNO2-MISC	8932	1238												3.16%			1.0220		
PROT-22-030-Q	8751	1209	18.0	<10	134.1							309	4000						
PROT-22-060-Q	8752	1209	<10	<10	157.2							328	4156						
PROT-22-090-Q	8753	1209	<10	<10	151.9							363	3912						
PROT-22-120-Q	8754	1209	<10	<10	157.5							322	3865						
PROT-22-180-Q	8755	1207	12.7	19.9	158.2														
PROT-22-180-DIL	8756	1208										377	4655						
PROT-22-PNO2-Q	8757	1207	1.3	2.4	149.8														
PROT-22-PNO2-DIL	8758	1208										8755	3972						
PROT-22-PNO2-P	8759	1209												3.04%	3.06%		1.0216		
PROT-24																			
PROT-3-030-Q	8645	1190	29.6	<10	89.4							212	4067						
PROT-3-060-Q	8646	1190	<10	<10	115.2							194	4061						
PROT-3-090-Q	8647	1190	<10	<10	115.4							194	3937						
PROT-3-120-Q	8648	1190	<10	<10	110.5							187	3940						
PROT-3-180-Q	8649	1190, 1203	<10	22.5	188.1							301	3128						
PROT-3-PNO2-Q	8650	1190	<10	<10	182.0							1643	8008						
PROT-3-PNO2-P	8651	1190												3.22%		0.23%	1.0191		
PROT-27-030-QD10	8933	1241	<10	22.0	165.9														
PROT-27-090-QD10	8934	1241	<10	33.5	169.9														
PROT-27-180-QD10	8935	1241	<10	27.5	174.7														
PROT-27-180-D1K	8936	1242										1972	3875						
PROT-27-PNO2-QD10	8937	1241	15.4	28.8	156.7														
PROT-27-PNO2-D1K	8938	1242										10363	3731						
PROT-27-PNO2-MISC	8939	1243												3.31%			1.0232		
PROT-4-030-Q	8652	1193	16.7	53.6	108.2							146	3662						
PROT-4-060-Q	8653	1193	<10	37.5	129.8							174	3723						
PROT-4-090-Q	8654	1193	<10	41.3	113.1							160	3646						
PROT-4-120-Q	8655	1193	<10	46.3	115.8							150	3847						
PROT-4-180-Q	8656	1193, 1203	13.4	20.9	166.7							278	3097						
PROT-4-PNO2-Q	8657	1193, 1203	<10	<10	188.2							979	7636						
PROT-4-PNO2-P	8658	1193												3.15%		0.26%	1.0197		
PROT-4-D20-Q	8662	1202																	
PROT-5-030-Q	8706	1197	<10	36.9	106.4							157	3847						
PROT-5-060-Q	8707	1197	<10	37.2	120.2							152	4114						
PROT-5-090-Q	8708	1197	<10	40.2	116.4							143	4109						
PROT-5-120-Q	8709	1197	<10	38.7	112.8							146	4096						
PROT-5-180-Q	8710	1197	<10	40.8	118.5							145	4216						
PROT-5-PNO2-Q	8711	1197, 1203	<10	<10	180.1							692	8612						
PROT-5-PNO2-P	8712	1197												3.50%		0.20%	1.0201		
PROT-5-D1-Q	8663	1202	<10	<10	196.5							626	5343						

Blank cells: analysis not requested												suspect values from sulfite quench							
			From 10X Dilution			From 100X Dilution			From 1000X Dilution										
	PSAL Sample #	PSAL Request #	Glycolate mg/kg	Formate mg/kg	Oxalate mg/kg	Glycolate mg/kg	Formate mg/kg	Oxalate mg/kg	Glycolate mg/kg	Formate mg/kg	Oxalate mg/kg	Nitrite	Nitrate	Total Solids wt%	Supernate Solids wt%	Insoluble Solids wt%	Slurry Density kg/L	Total OH M	pH
PROT-10a-030-Q	8720	1200	<10	26.9	157.4							193	3856						
PROT-10a-060-Q	8721	1200	<10	25.8	166.4							178	4093						
PROT-10a-090-Q	8722	1200	<10	37.7	169.4							279	3962						
PROT-10a-120-Q	8723	1200	<10	24.6	164.8							155	4293						
PROT-10a-180-Q	8724	1200	<10	28.3	168.0							185	3968						
PROT-10a-PNO2-Q	8725	1200	<10	19.8	165.2							1802	10926						
PROT-10a-PNO2-P	8726	1200												3.24%		0.80%	1.0197		
PROT-9-030-Q	8713	1198	18.8	<10	123.3							1601	3946						
PROT-9-060-Q	8714	1198	11.4	<10	142.8							1529	4269						
PROT-9-090-Q	8715	1198	<10	<10	141.7							1346	3922						
PROT-9-120-Q	8716	1198	<10	<10	145.3							1283	3999						
PROT-9-180-Q	8717	1198	<10	<10	133.9							1377	3986						
PROT-9-PNO2-Q	8718	1198, 1203	<10	<10	142.0							577	8200						
PROT-9-PNO2-P	8719	1198												3.48%		0.21%	1.0209		
PROT-14a-030-Q	8734	1204	41.9	<10	100.5							177	3194						
PROT-14a-060-Q	8735	1204	15.6	<10	167.4							180	3603						
PROT-14a-090-Q	8736	1204	<10	<10	153.7							200	3472						
PROT-14a-120-Q	8737	1204	<10	<10	171.4							190	3467						
PROT-14a-180-Q	8738	1204	<10	<10	155.3							180	3397						
PROT-14a-PNO2-Q	8739	1204	<10	<10	173.2							597	4831						
PROT-14a-PNO2-P	8740	1204												2.65%		0.80%	1.0134		
PROT-13-030-Q	8727	1201	27.9	<10	126.0							137	3447						
PROT-13-060-Q	8728	1201	11.1	<10	143.5							139	3300						
PROT-13-090-Q	8729	1201	<10	<10	152.8							161	3196						
PROT-13-120-Q	8730	1201	<10	<10	156.0							154	3398						
PROT-13-180-Q	8731	1201	<10	<10	160.5							156	3435						
PROT-13-PNO2-Q	8732	1201	<10	<10	154.3							47	4953						
PROT-13-PNO2-P	8733	1201												2.60%		0.33%	1.0138		
PROT-7a-030-QD10	8953	1247	84.7	23.7	85.6														
PROT-7a-090-QD10	8954	1247	52.0	23.5	125														
PROT-7a-180-QD10	8955	1247	33.4	18.8	139														
PROT-7a-180-D1K	8956	1248										1873	2846						
PROT-7a-PNO2-DQ10	8957	1247	34.1	22.5	140														
PROT-7a-PNO2-D1K	8958	1248										10561	3237						
PROT-7a-PNO2-MISC	8959	1249												3.00%			1.0206	0.2011	
PROT-28-030-QD10	8975	1251	52.0	24.4	126														
PROT-28-090-QD10	8976	1251	<10	23.5	172														
PROT-28-180-QD10	8977	1251	<10	19.0	180														
PROT-28-180-D1K	8978	1252										1163	1753						
PROT-28-PNO2-DQ10	8979	1251	<10	20.7	174														
PROT-28-PNO2-D1K	8980	1252										9990	2692						
PROT-28-PNO2-MISC	8981	1253												3.11%			1.0212		
PROT-8a-030-QD10	9073	1257	16.1	40.6	153														
PROT-8a-090-QD10	9074	1257	<10	37.9	190														
PROT-8a-180-QD10	9075	1257	<10	31.4	189														
PROT-8a-180-D1K	9077	1258										1973	2821						
PROT-8a-PNO2-QD10	9076	1257	<10	37.4	205														

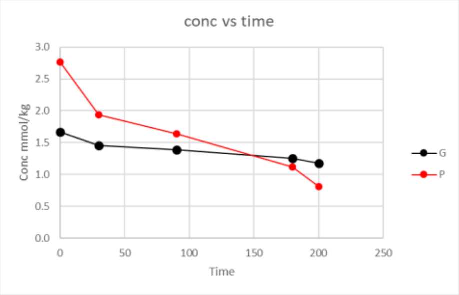
Blank cells: analysis not requested												suspect values from sulfite quench							
			From 10X Dilution			From 100X Dilution			From 1000X Dilution										
	PSAL Sample #	PSAL Request #	Glycolate mg/kg	Formate mg/kg	Oxalate mg/kg	Glycolate mg/kg	Formate mg/kg	Oxalate mg/kg	Glycolate mg/kg	Formate mg/kg	Oxalate mg/kg	Nitrite	Nitrate	Total Solids wt%	Supernate Solids wt%	Insoluble Solids wt%	Slurry Density kg/L	Total OH M	pH
PROT-8a-PNO2-D1K	9078	1258										10015	2623						
PROT-8a-PNO2-MISC	9079	1259												3.20%			1.0218		
PROT-6-030-QD10	9085	1261	14.8	34.6	152														
PROT-6-090-QD10	9086	1261	<10	31.3	180														
PROT-6-180-QD10	9087	1261	<10	27.8	176														
PROT-6-180-D1K	9089	1262										5935	3091						
PROT-6-PNO2-QD10	9088	1261	<10	21.0	183														
PROT-6-PNO2-D1K	9090	1262										10198	2901						
PROT-6-PNO2-MISC	9091	1263												3.25%			1.0223		
PROT-12a-030-QD10	9111	1267	71.1	28.1	82														
PROT-12a-090-QD10	9112	1267	46.8	21.5	123														
PROT-12a-180-QD10	9113	1267	41.3	18.5	140														
PROT-12a-180-D1K	9115	1268										1215	1903						
PROT-12a-PNO2-QD10	9114	1267	24.7	19.6	141														
PROT-12a-PNO2-D1K	9116	1268										10533	2668						
PROT-12a-PNO2-MISC	9117	1269												3.21%			1.0208	0.2029	
PROT-11a-030-QD10	9104	1264	46.5	26.7	115														
PROT-11a-090-QD10	9105	1264	<10	26.3	168														
PROT-11a-180-QD10	9106	1264	<10	23.7	176														
PROT-11a-180-D1K	9108	1265										2099	3185						
PROT-11a-PNO2-QD10	9107	1264	<10	31.6	177														
PROT-11a-PNO2-D1K	9109	1265										9645	2489						
PROT-11a-PNO2-MISC	9110	1266												3.20%			1.0213		
PROT-29-030-QD10	9118	1270	36.0	<10	138														
PROT-29-090-QD10	9119	1270	13.1	<10	181														
PROT-29-180-QD10	9120	1270	<10	<10	176														
PROT-29-180-D1K	9122	1271										1857	3058						
PROT-29-PNO2-QD10	9121	1270	<10	<10	180														
PROT-29-PNO2-D1K	9123	1271										10235	2824						
PROT-15a-030-QD10	9125	1273	109.3	8.5	40.2														
PROT-15a-090-QD10	9126	1273	103.9	7.9	65.4														
PROT-15a-180-QD10	9127	1273	94.1	8.4	88.6														
PROT-15a-180-D1K	9129	1274										865	2958						
PROT-15a-PNO2-QD10	9128	1273	88.3	11.3	79.1														
PROT-15a-PNO2-D1K	9130	1274										9738	2877						
PROT-15a-PNO2-MISC	9131	1275												2.74%			1.0194	0.2069	
PROT-30-030-QD10	9132	1276	94.4	27.0	91.1														
PROT-30-090-QD10	9133	1276	40.3	24.8	170.9														
PROT-30-180-QD10	9134	1276	37.3	17.5	168.7														
PROT-30-180-D1K	9136	1277										832	3012						
PROT-30-PNO2-QD10	9135	1276	17.0	20.0	178.9														
PROT-30-PNO2-D1K	9137	1277										9708	2889						
PROT-30-PNO2-MISC	9138	1278												2.77%			1.0197	0.2092	
PROT-16a-030-QD10	9139	1279	59.4	11.4	109														
PROT-16a-090-QD10	9140	1279	11.3	16.8	174														
PROT-16a-180-QD10	9141	1279	<10	11.4	176														

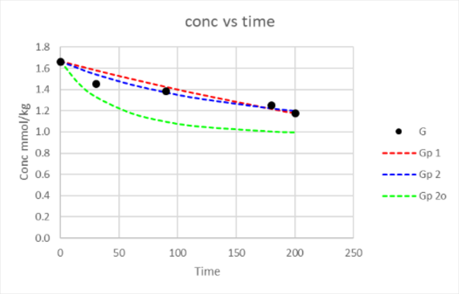
Blank cells: analysis not requested												suspect values from sulfite quench							
				From 10X Dilution			From 100X Dilution			From 1000X Dilution									
	PSAL Sample #	PSAL Request #	Glycolate mg/kg	Formate mg/kg	Oxalate mg/kg	Glycolate mg/kg	Formate mg/kg	Oxalate mg/kg	Glycolate mg/kg	Formate mg/kg	Oxalate mg/kg	Nitrite	Nitrate	Total Solids wt%	Supernate Solids wt%	Insoluble Solids wt%	Slurry Density kg/L	Total OH M	pH
PROT-16a-180-D1K	9143	1280										911	3069						
PROT-16a-PNO2-QD10	9142	1279	<10	21.0	176														
PROT-16a-PNO2-D1K	9144	1280										9424	2949						
PROT-16a-PNO2-MISC	9145	1281												2.82%			1.0198		
			Analysis from best dilution shown.																
PROT-18a-SIM	9147	1287					503	801	4785			1807	4744	2.99%	2.24%	0.76%	1.0151	0.1462	12.45
PROT-18a-030-QD10	9148	1284																	
PROT-18a-030-QD100	9149	1284				3316		1984											
PROT-18a-060-QD10	9150	1284																	
PROT-18a-060-QD100	9151	1284				1282		3616											
PROT-18a-090-QD10	9152	1284		<10															
PROT-18a-090-QD100	9153	1284				897		3863											
PROT-18a-180-QD10	9154	1284																	
PROT-18a-180-QD100	9155	1284				829		3868											
PROT-18a-270-QD10	9156	1284																	
PROT-18a-270-QD100	9157	1284				860		3781											
PROT-18a-360-QD10	9158	1284		<10															
PROT-18a-360-QD100	9159	1284				847		3794											
PROT-18a-PNO2-QD10	9160	1284																	
PROT-18a-PNO2-QD100	9161	1284				804		3691											
PROT-18a-360-D1K	9162	1285										1915	3843						
PROT-18a-PNO2-D1K	9163	1285										13753	3422						
PROT-18a-PNO2-MISC	9164	1286												3.42%	4.08%	-0.69%	1.0412	0.1449	
PROT-20a-SIM	9218	1296		92.1		3675		582				460	5534	3.11%	2.16%	0.98%		0.1550	
PROT-20a-030-QD100	9219	1297				2949													
PROT-20a-030-QD1000	9220	1297									2514								
PROT-20a-060-QD100	9221	1297				1164													
PROT-20a-060-QD1000	9222	1297									4297								
PROT-20a-090-QD100	9223	1297				681													
PROT-20a-090-QD1000	9224	1297									5060								
PROT-20a-180-QD100	9225	1297				603													
PROT-20a-180-QD1000	9226	1297									5049								
PROT-20a-270-QD100	9227	1297				747													
PROT-20a-270-QD1000	9228	1297									5243								
PROT-20a-360-QD10	9229	1297		69.9															
PROT-20a-360-QD100	9230	1297				633													
PROT-20a-360-QD1000	9231	1297									5095								
PROT-20a-PNO2-QD10	9232	1297		76.0															
PROT-20a-PNO2-QD100	9233	1297				617													
PROT-20a-PNO2-QD1000	9234	1297									5069								
PROT-20a-360-D1K	9235	1298										865	4016						
PROT-20a-PNO2-D1K	9236	1298										6841	4087						
PROT-20a-PNO2-MISC	9237	1299												5.07%	3.18%	1.95%	1.0342	0.1520	
PROT-19a-030-QD100	9165	1288				2780	11.0	1880											
PROT-19a-030-QD1000	9166	1288							2963		1464								
PROT-19a-060-QD100	9167	1288				1092	14.8	3552											
PROT-19a-060-QD1000	9168	1288							1351		3564								
PROT-19a-090-QD100	9169	1288				147	50.0												
PROT-19a-090-QD1000	9170	1288									4456								

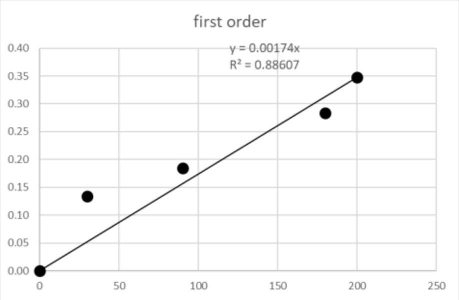
Blank cells: analysis not requested												suspect values from sulfite quench							
			From 10X Dilution			From 100X Dilution			From 1000X Dilution										
	PSAL Sample #	PSAL Request #	Glycolate mg/kg	Formate mg/kg	Oxalate mg/kg	Glycolate mg/kg	Formate mg/kg	Oxalate mg/kg	Glycolate mg/kg	Formate mg/kg	Oxalate mg/kg	Nitrite	Nitrate	Total Solids wt%	Supernate Solids wt%	Insoluble Solids wt%	Slurry Density kg/L	Total OH M	pH
PROT-19a-180-QD100	9171	1288				77.6	18.1												
PROT-19a-180-QD1000	9172	1288									4907								
PROT-19a-270-QD100	9173	1288				35.8	17.9												
PROT-19a-270-QD1000	9174	1288									4515								
PROT-19a-360-QD10	9175	1288	38.3	9.9															
PROT-19a-360-QD100	9176	1288					12.9												
PROT-19a-360-QD1000	9210	1288									5175								
PROT-19a-PNO2-QD10	9177	1288	47.2	4.4															
PROT-19a-PNO2-QD100	9178	1288																	
PROT-19a-PNO2-QD1000	9211	1288									5102								
PROT-19a-360-D1K	9179	1289										1725	3811						
PROT-19a-PNO2-D1K	9180	1289										13484	3602						
PROT-19a-PNO2-MISC	9181	1290												6.44%		2.44%	1.0436	0.1585	
PROT-17-030-QD100	9182	1291				2208		2175											
PROT-17-030-QD1000	9183	1291							2129		2054								
PROT-17-060-QD100	9184	1291				696													
PROT-17-060-QD1000	9185	1291									4485								
PROT-17-090-QD100	9186	1291				112													
PROT-17-090-QD1000	9187	1291									5214								
PROT-17-180-QD100	9188	1291				65													
PROT-17-180-QD1000	9189	1291									5181								
PROT-17-270-QD100	9190	1291				57													
PROT-17-270-QD1000	9191	1291									5294								
PROT-17-360-QD10	9192	1291	33.9																
PROT-17-360-QD100	9193	1291																	
PROT-17-360-QD1000	9212	1291									5410								
PROT-17-PNO2-QD10	9194	1291	40.7																
PROT-17-PNO2-QD100	9195	1291																	
PROT-17-PNO2-QD1000	9213	1291									5156								
PROT-17-360-D1K	9196	1292										1589	4096						
PROT-17-PNO2-D1K	9197	1292										12983	3777						
PROT-17-PNO2-MISC	9198	1293												6.59%	4.26%	2.44%	1.0446	0.1637	
PROT-31-SIM	9240	1301										1687	2874	2.24%	2.36%	0.00%	1.0125		12.95
PROT-31-030-QD10	9241	1302	<10	21.4	<10														
PROT-31-060-QD10	9242	1302	<10	18.3	<10														
PROT-31-090-QD10	9243	1302	<10	18.5	15.4														
PROT-31-180-QD10	9244	1302	<10	21.7	34.5														
PROT-31-270-QD10	9245	1302	<10	19.2	59.4														
PROT-31-360-QD10	9246	1302	<10	19.0	88.6														
PROT-31-360-D1K	9247	1303										2003	2991						
PROT-31-PNO2-D1K	9248	1303										11154	2767						
PROT-31-PNO2-MISC	9249	1304												3.73%	3.35%	0.39%	1.0237	0.2226	
	AD LW-	Proj #	Density	TIC mg/L	TOC mg/L	TIC mg/kg	TOC mg/kg												
			kg/L		Target:	0	1629												
PROT-31-SIM-A	13428	190320	1.01	0	1510		1495												
PROT-31-030-QD10-A	13401	190320	1.01	0	1951		1932												
PROT-31-060-QD10-A	13402	190320	1.01	0	1922		1903												
PROT-31-090-QD10-A	13403	190320	1.01	0	1910		1891												
PROT-31-180-QD10-A	13404	190320	1.01	0	1922		1903												
PROT-31-270-QD10-A	13405	190320	1.01	0	1930		1911												
PROT-31-360-QD10-A	13406	190320	1.01	0	1922		1903												

Appendix B: Determination of Rate Constants

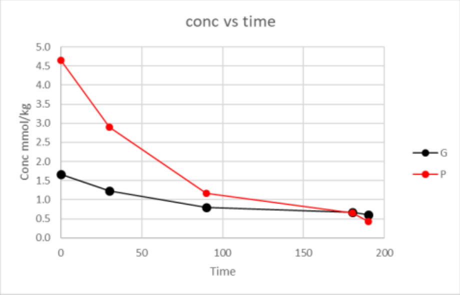
Run 15a

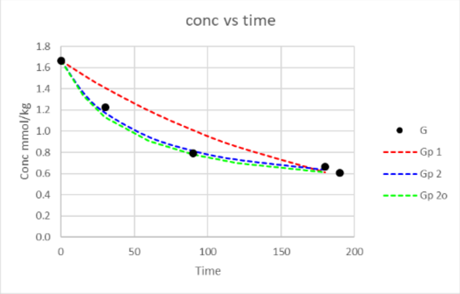


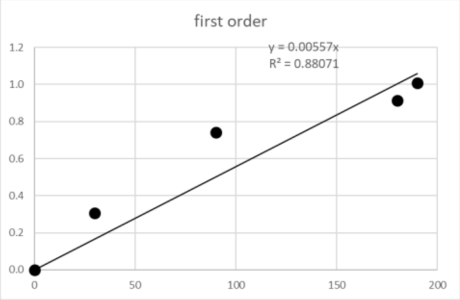




Run 25







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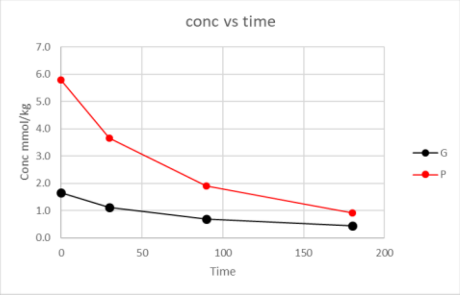

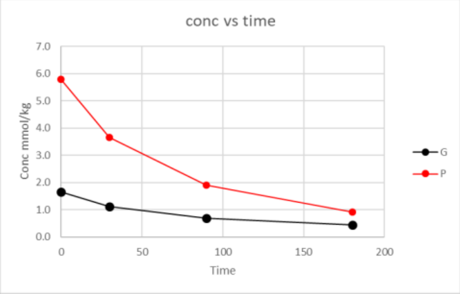

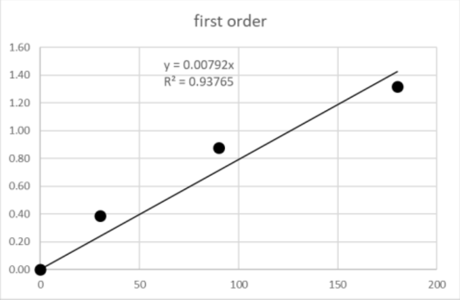

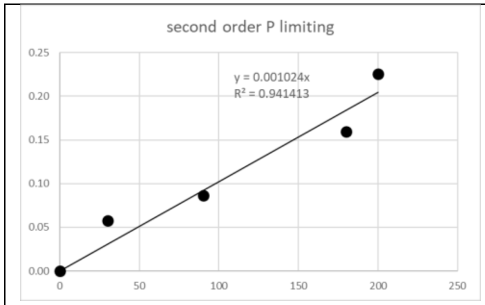

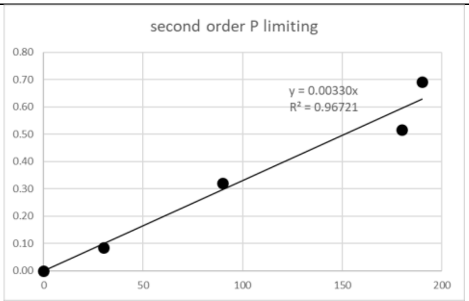

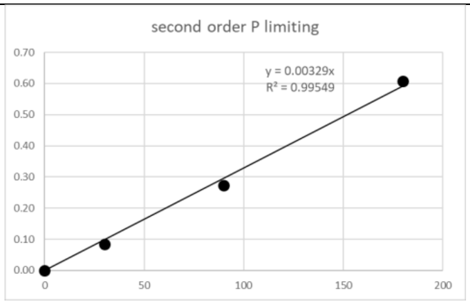

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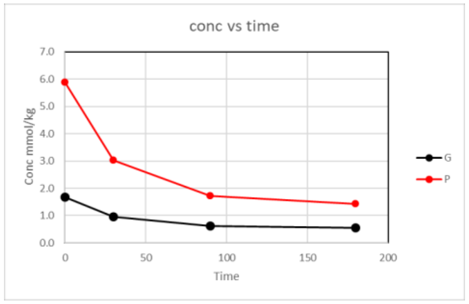

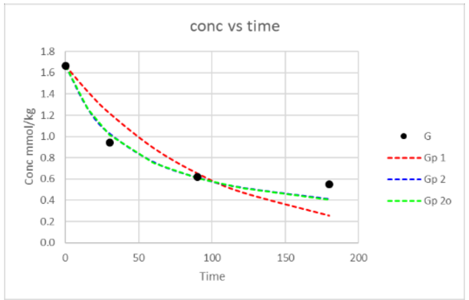

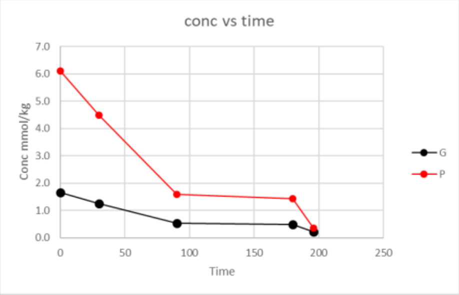

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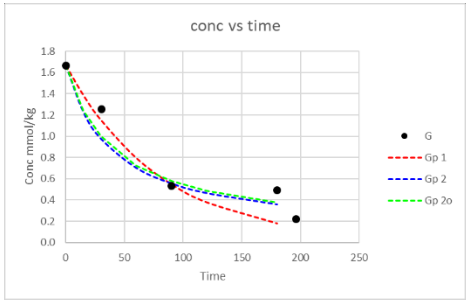
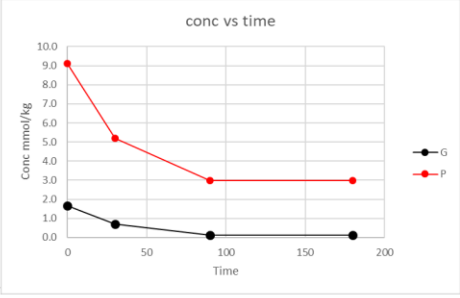
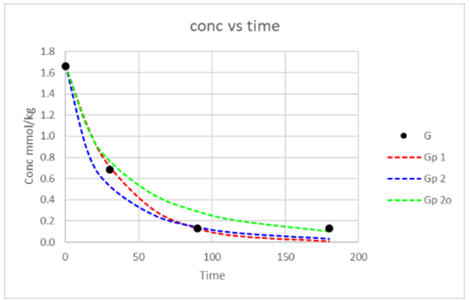
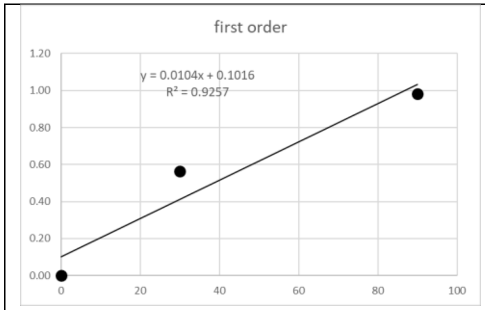
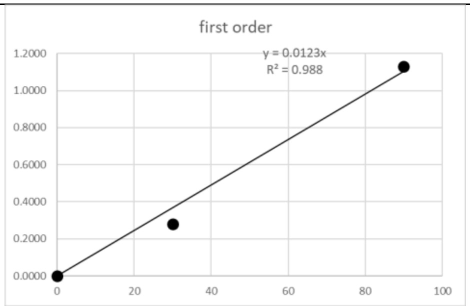


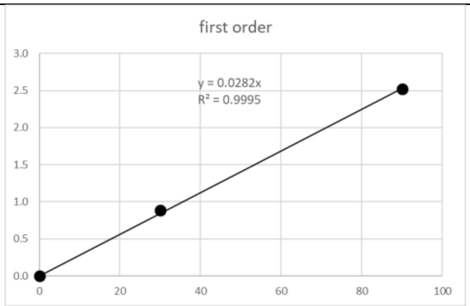


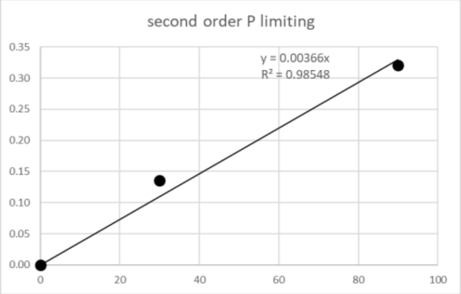
Run 26

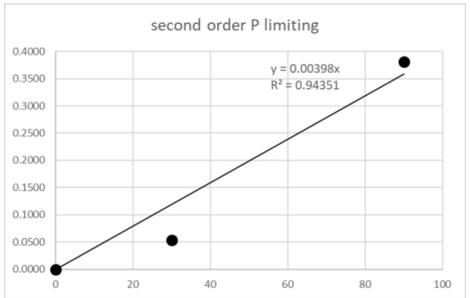


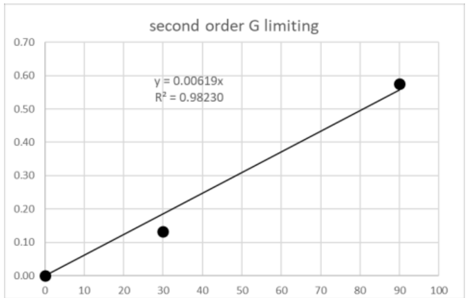




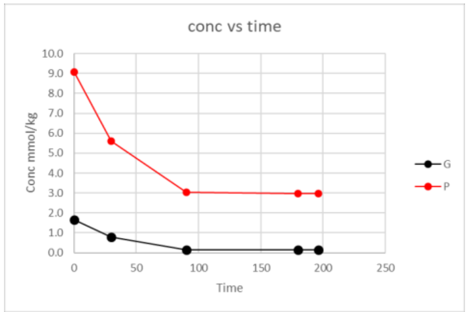


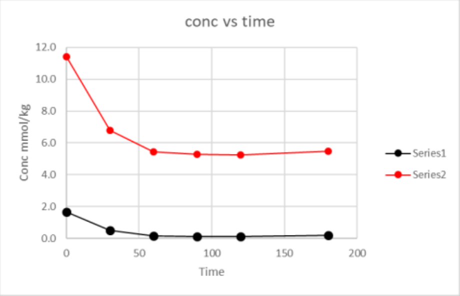




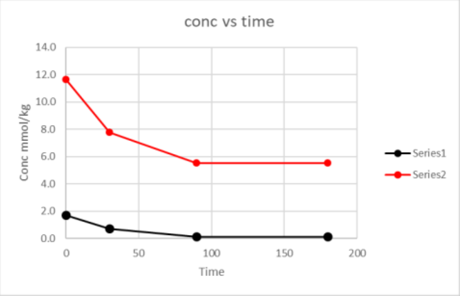


Run 16a

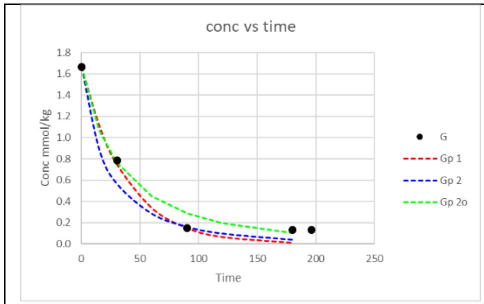


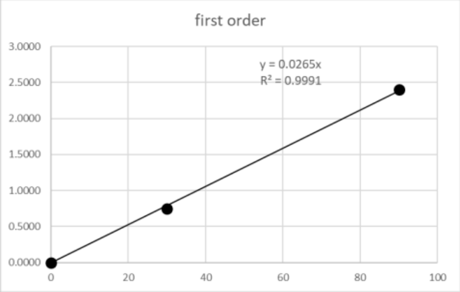


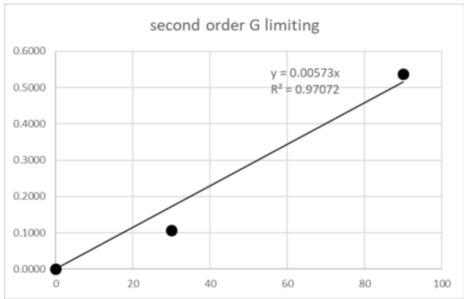
Run 21

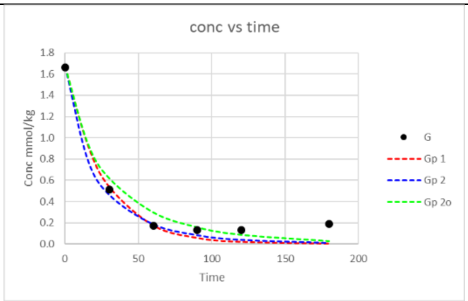


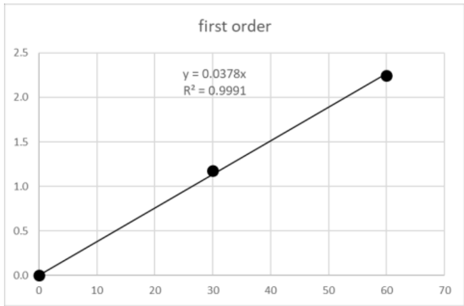
Run 28


conc vs time
Conc mmol/kg
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
50
100
150
200
250
Time
G
Gp 1
Gp 2
Gp 2o


first order
y = 0.0265x
R² = 0.9991
3.0000
2.5000
2.0000
1.5000
1.0000
0.5000
0.0000
0
20
40
60
80
100


second order G limiting
y = 0.00573x
R² = 0.97072
0.6000
0.5000
0.4000
0.3000
0.2000
0.1000
0.0000
0
20
40
60
80
100


conc vs time
Conc mmol/kg
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
50
100
150
200
Time
G
Gp 1
Gp 2
Gp 2o


first order
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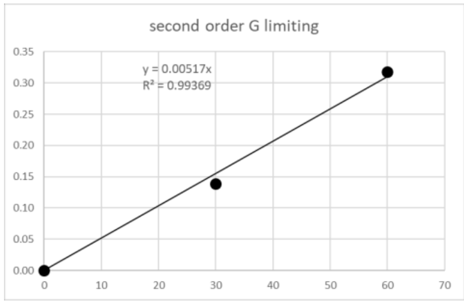
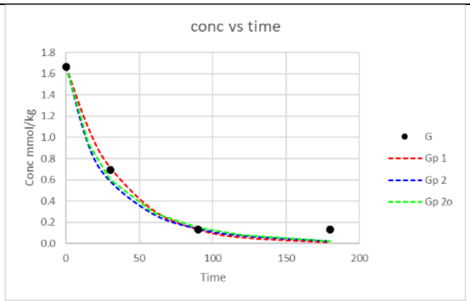
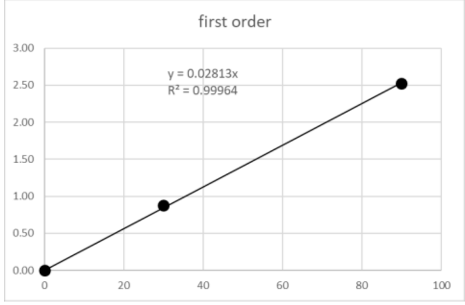
R² = 0.9991
2.5
2.0
1.5
1.0
0.5
0.0
0
10
20
30
40
50
60
70


second order G limiting
y = 0.00517x
R² = 0.99369
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0
10
20
30
40
50
60
70


conc vs time
Conc mmol/kg
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
50
100
150
200
Time
G
Gp 1
Gp 2
Gp 2o


first order
y = 0.02813x
R² = 0.99964
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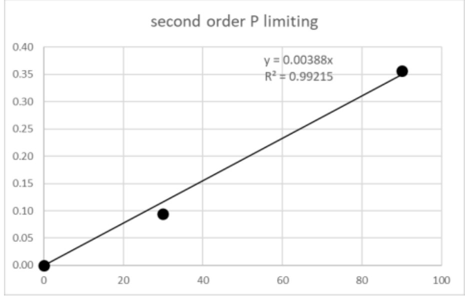
2.50
2.00
1.50
1.00
0.50
0.00
0
20
40
60
80
100


second order P limiting
y = 0.00388x
R² = 0.99215
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0
20
40
60
80
100

Appendix C: Statistical Analysis of RCT Historical Data

Historical data for the composition of the RCT was provided in a spreadsheet from Roger Mahannah of SRR/DWPF.

The data was analyzed statistically to determine typical nitrite and nitrate concentrations and nitrite to nitrate ratios. The nitrite to nitrate ratio (N/N) must be ≥ 1.66 for corrosion control in Tank 22. The dark circled values (below line) in Figure A- 1 were removed because nitrite is less than nitrate and so do not represent actual compositions that could have been sent to the tank farm.

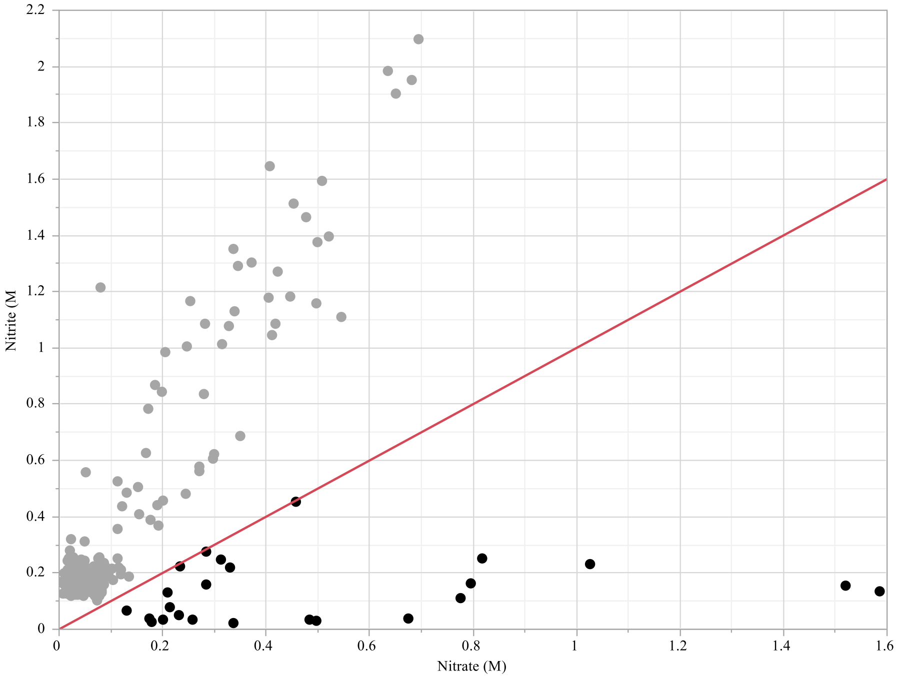
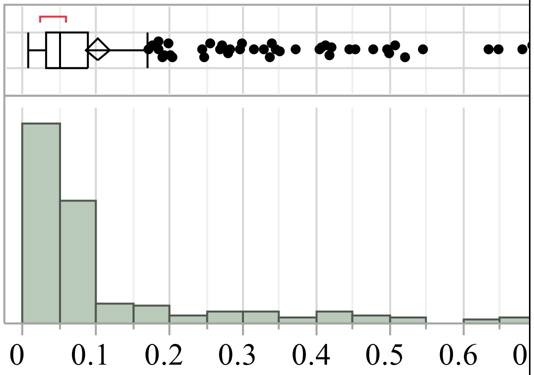


Figure A- 1. Screening of Nitrite Less than Nitrate

The distributions of the remaining points are shown in Figure A- 2. The median nitrate is around 3200 mg/L, while the mean of 6340 mg/L is skewed by a number of uncharacteristically large values. The nitrite median is about 8800 mg/L, while the mean is also skewed at 16,000 mg/L. For the purposes of this work, the median values are more representative of typical operation.

Nitrate (M)



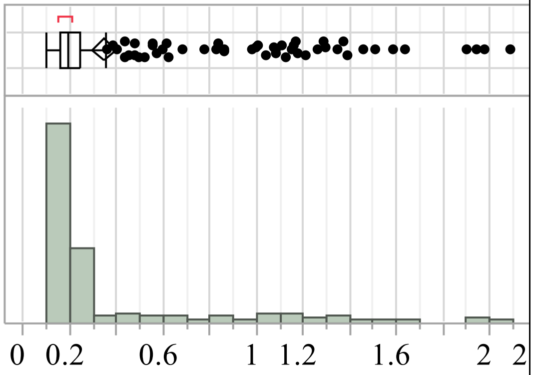
Quantiles

			Mg/L
100.0%	maximum	0.69485	
99.5%		0.6918	
97.5%		0.51876	
90.0%		0.29985	18600
75.0%	quartile	0.0875	5425
50.0%	median	0.05152	3194
25.0%	quartile	0.032	
10.0%		0.02138	
2.5%		0.01441	
0.5%		0.00805	
0.0%	minimum	0.008	

Summary Statistics

			Mg/L
Mean		0.1023497	6343
Std Dev		0.1340132	
Std Err Mean		0.0084588	
Upper Mean	95%	0.1190094	
Lower Mean	95%	0.0856901	
N		251	

Nitrite (M)



Quantiles

			Mg/L
100.0%	maximum	2.0953	
99.5%		2.0657	
97.5%		1.56604	
90.0%		1.03591	47652
75.0%	quartile	0.24041	11058
50.0%	median	0.19124	8797
25.0%	quartile	0.15937	
10.0%		0.13331	
2.5%		0.11932	
0.5%		0.10565	
0.0%	minimum	0.10167	

Summary Statistics

			Mg/L
Mean		0.3455783	15897
Std Dev		0.3902099	
Std Err Mean		0.0246298	
Upper Mean	95%	0.3940867	
Lower Mean	95%	0.2970698	
N		251	

Figure A- 2. Distributions of Nitrite and Nitrate Data

Figure A- 3 shows the nitrite to nitrate ratio plotted versus the nitrate concentration. The points with nitrate concentrations greater than 0.1 M (6200 mg/L) were then eliminated as untypically high. However, the nitrite to nitrate ratios were mostly greater than 1.66 and not too high (<5); the median was 2.92 and the mean 2.94. The points below 0.1 M nitrate were then further examined.

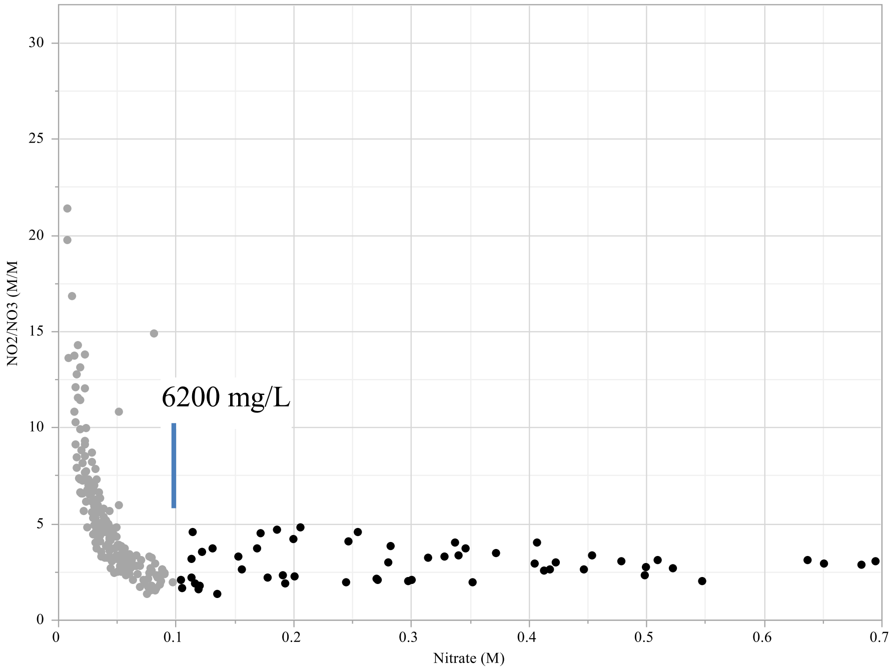


Figure A- 3. Plot of Nitrite to Nitrate Ratio for Screened Points

The data at nitrate less than 0.1 M was then further screened to eliminate low nitrate values where the nitrite to nitrate ratio was unusually high. Only values with nitrate greater than 0.025 M were kept. The mean nitrate value for the remaining points (dark circles) was 0.0499 M, or 3091 mg/L.

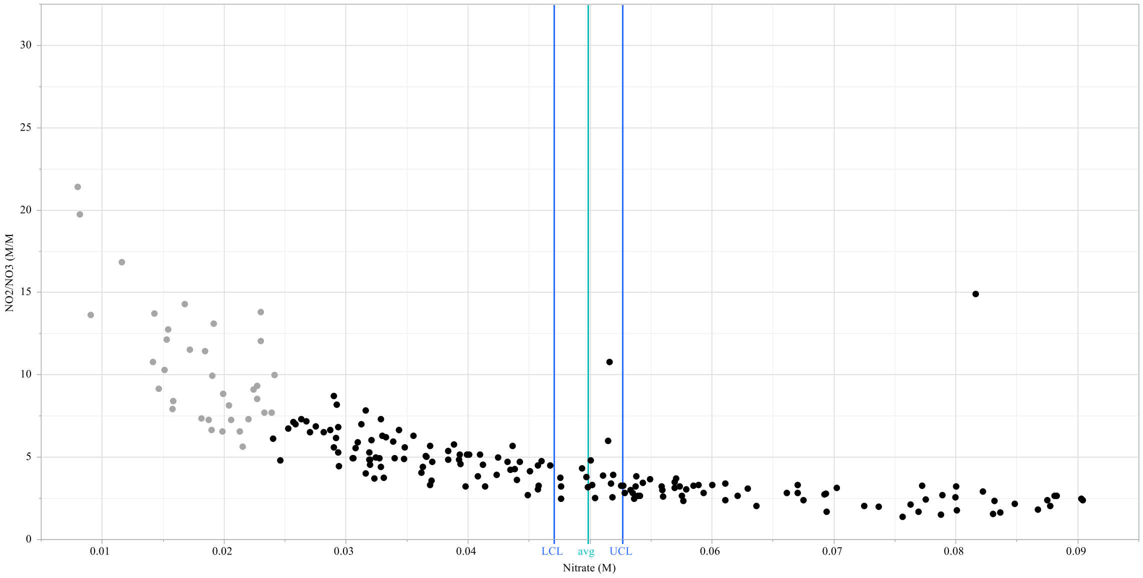


Figure A- 4. Nitrite to Nitrate Ratios with Nitrate Less Than 0.1 M

Statistical analysis of these remaining points (Figure A- 5) shows the median nitrite to nitrate ratio is 3.72 and the mean is 4.17. An upper 95% confidence on the mean is 4.46.

Based on this analysis, the typical value for the nitrite to nitrate ratio was defined as 4.4. With this value, the typical nitrite concentration is then 4.4 x 0.0499 M = 0.220 M, or 10,100 mg/L. The nitrite concentration *after* corrosion control nitrite addition was then targeted to be about 10,000 mg/L.

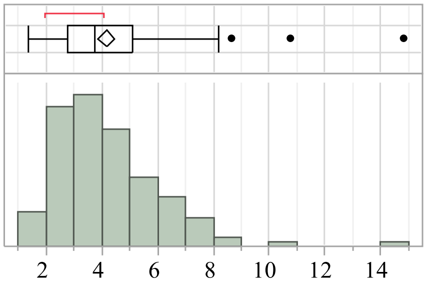
NO2/NO3 (M/M)	**Quantiles**			**Summary Statistics**	
	100.0%	maximum	14.87	Mean	4.1691195
	99.5%		14.87	Std Dev	1.8710193
	97.5%		8.19	Std Err Mean	0.1483815
	90.0%		6.62	Upper 95% Mean	4.4621866
	75.0%	quartile	5.12		
	50.0%	median	3.72	Lower 95% Mean	3.8760524
	25.0%	quartile	2.79		
	10.0%		2.33	N	159
	2.5%		1.64		
	0.5%		1.34		
	0.0%	minimum	1.34		

Figure A- 5. Statistical Analysis of Nitrite to Nitrate Ratio with Nitrate Between 0.025 and 0.1 M

Appendix D: Calculated Permanganate to Glycolate Molar Ratio for Downselect Tests

The table below summarizes the results of testing with sodium permanganate for the downselect runs. These runs used a very different simulant containing ten organic species so the P/G ratio is much higher than typical as enough oxidant was added to destroy each organic to CO_2.

Initial Glycolate mg/kg	Temperature °C	Permanganate Addition Time, min	Initial Permanganate to Glycolate Molar Ratio	Glycolate Destruction (≥%) @ 3 h
Starting pH ~3				
250	15	10	25.0	38%
125	50	120	30.8	92%
250	15	15	31.9	92%
125	50	10	56.3	90%
Starting pH ~8				
188	33	65	25.3	85%
188	33	65	33.1	92%
Starting pH >12				
250	50	10	16.5	88%
250	50	120	24.4	92%
125	15	120	39.5	68%
125	15	10	61.9	81%