Defense Waste Processing Facility (DWPF) Glycolate Mitigation: Scoping Test Results

C. A. Nash

T. B. Peters

May 2018

SRNL-STI-2018-00175, Revision 0

DISCLAIMER

Printed in the United States of America

Prepared for
U.S. Department of Energy

SRNL-STI-2018-00175
Revision 0

Keywords: *DWPF, Recycle Collection Tank, Condensate, Oxidation*

Retention: *Permanent*

Defense Waste Processing Facility (DWPF) Glycolate Mitigation: Scoping Test Results

C. A. Nash
T. B. Peters

May 2018

Prepared for the U.S. Department of Energy under contract number DE-AC09-08SR22470.

Savannah River National Laboratory™
OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

REVIEWS AND APPROVALS

AUTHORS:

C. A. Nash, Advanced Characterization and Processing Date

T. B. Peters, Advanced Characterization and Processing Date

TECHNICAL REVIEW:

M. S. Williams, Process Tech Programs
Reviewed per E7 2.60 Date

APPROVAL:

B. J. Wiedenman, Manager Date
Advanced Characterization and Processing

D. E. Dooley, Director Date
Chemical Processing Technologies

E. J. Freed, Manager Date
Defense Waste Processing Facility & Saltstone Facility Engineering

EXECUTIVE SUMMARY

A series of initial reactions were performed at SRNL with the goal of arriving at a general understanding of the conditions required to destroy glycolate. A simulant solution representing a composite of the Recycle Condensate Tank (RCT), the Slurry Mix Evaporator Condensate Tank (SMECT), and/or the Off-Gas Condensate Tank (OGCT) was prepared. Two oxidizers were used, hydrogen peroxide and sodium permanganate. Ten tests and a control reaction were performed. The temperature was not controlled, but remained in the range of 18-21 °C. The initial glycolate concentrations were nominally either 250 or 2000 ppm. The test volume was 500 mL and stirring was provided by a magnetic stirrer.

The results of the testing showed that both hydrogen peroxide and sodium permanganate provided good results in terms of glycolate destruction. Complete destruction of glycolate could occur in as little as two hours.

At this time, a preferred oxidation method cannot be chosen. Follow-on prototypic testing will be performed in conjunction with Savannah River Remediation (SRR) to define the mitigation strategy by: 1) completing the oxidant down-selection, 2) verifying the oxidant/glycolic reaction rates and process mass balance, and 3) development of the process protocol addition rate and minimum cycle time for normal and foam-over conditions.[i]

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ABBREVIATIONS

AD	Analytical Development
CPC	Chemical Process Cell
DWPF	Defense Waste Processing Facility
HGR	Hydrogen Generation Rate
IC-A	Ion chromatography - anions
OGCT	Off-Gas Condensate Tank
RCT	Recycle Condensate Tank
SMECT	Slurry Mix Evaporator Condensate Tank
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
TAR	Technical Assistance Request
TTQAP	Task Technical and Quality Assurance Plan
TTR	Task Technical Request

1.0 Introduction

Savannah River Remediation (SRR) is seeking to replace formic acid with glycolic acid in the Defense Waste Processing Facility (DWPF) as a chemical reductant. A small amount of glycolate added in DWPF will be sent to the Tank Farm via the DWPF recycle stream, which may contribute to the thermolytic hydrogen generation rate (HGR). Testing is currently in progress by Savannah River National Laboratory (SRNL) (as defined in X-TTR-S-00067 [ii]) to evaluate the significance of this impact to Tank Farm flammability. If the simulant and radioactive testing with representative glycolate concentrations demonstrates significant Tank Farm impacts, system engineering solutions may be considered to restrict the amount of glycolate sent to the Tank Farm. One possible solution is to destroy the glycolate in DWPF with a system compatible chemical additive, thereby mitigating glycolate introduction to the Tank Farm.[iii] This option is to briefly be explored with a permanganate additive or metallic ion catalyzed hydrogen peroxide as glycolate destructive agents in X-TAR-S-00007. [iv] This report completes the scope request/deliverable of the Technical Assistance Request (TAR). A Task Technical and Quality Assurance Plan (TTQAP) is not required for this scoping work. Future work (X-TTR-S-00068 [i]) is planned to examine beneficial co-destruction of antifoam, antifoam degradation products, and organic mercury.

2.0 Experimental Procedure

Glycolate destruction could be required in the RCT or the OGCT/SMECT. A foam-over in the CPC or entrainment in the melter could produce a concentration of 2000 mg/L of glycolate in the RCT. During normal processing (no CPC foam-over), the glycolate concentration is expected to be less than 250 mg/L. In order to streamline the scoping testing, a single nonradioactive solution was prepared for the RCT from equal volume of OGCT and SMECT simulants that were combined. The simulant recipe was derived from tabulated data from DWPF. The simulant was simple in composition and did not include oxalate or formate salts, nor did it include antifoam or other constituents. The nominal composition (no foam-over in the CPC, no entrainment in the melter) is given in Table 1.[v]

Table 1. Nominal Composition of the Composite Simulant

Analyte	Concentration (M)
sodium	0.045
Fe(III)	0.0036
Mn(II)	0.0016
nitrate	0.027 [1]
nitrite	0.032
glycolate	0.027 or 0.0034
pH	~4

---

[1] This does not account for a variable amount of nitric acid used in preparation of the OGCT/SMECT simulant.

Given the low pH of the final simulant, it is quite possible that the nitrite in solution is subject to some decomposition.

2.1 Destruction Reactions

All of the control and destruction reactions were performed in the same general manner. A glass reactor vessel, with an approximate 3L working volume was used. A magnetic stirrer and stir bar was used to agitate the 500 mL of simulant solution. Addition of the oxidants was performed using a syringe pump. All reactions were run for 24 hours, with the oxidant being added over a period of 2 or 8 hours. Only one oxidant was used in each test as both would react with each other.

Unless otherwise noted, the simulant solution was adjusted to pH 3 using 3M nitric acid before the start of the experiment. The temperature was not controlled, but remained in the range of 18-21 °C. The initial glycolate concentrations were nominally either 250 or 2000 ppm.

Hydrogen peroxide was used as a nominal 28 wt% solution (confirmed by density beforehand). The 2-3.9 M solution of sodium permanganate was prepared just before use. The complete oxidation of glycolic acid to carbon dioxide follows the theoretical pathways below.

$$C_2H_4O_3 + 3H_2O_2 \rightarrow 2CO_2 + 5H_2O$$
$$C_2H_4O_3 + 2NaMnO_4 \rightarrow 2CO_2 + H_2O + 2NaOH + 2MnO_2$$

It takes three moles of hydrogen peroxide or two moles of sodium permanganate to completely oxidize a mole of glycolic acid to carbon dioxide. The nitrite in the simulant is a competitor as it can also be oxidized to nitrate; this is not a desired reaction as it wastes oxidant.

Sampling was performed throughout testing. ~12 mL of sample were pulled at 0 (just before addition of oxidant), 1, 2, 4, 8, and 24 hours and analyzed for glycolate content and pH. The 24 hour sample was also analyzed for anion content (IC-Anions). To each pulled sample was added either ~0.2 g of sodium carbonate (time 0 samples) or sodium sulfite [2] (other samples) in order to quench the reaction. While the time 0 samples had no oxidant to quench, the added salts increase the pH which ensures no further reaction.

2.2 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60.[vi] For SRNL documents, the extent and type of review using the SRNL Technical Report Design Checklist is outlined in WSRC-IM-2002-00011, Rev. 2.[vii] Records for this work are contained in an electronic notebook.[viii] The electronic pH probe was calibrated with pH standards.

---

[2] Sodium sulfite was used in cases where residual oxidants needed to be quenched to prevent further reactions.

3.0 Results and Discussion

3.1 Results from the Control

A single control experiment (nominally 2000 ppm) was performed to determine if glycolate destruction would occur without the addition of any oxidant. In this case, samples were pulled only at 0, 24, and 96 hours.

Table 2. Results from the Control Reaction (mg/L)

Analyte	Time 0	Time 24	Time 96
glycolate	1660	1710	1640
nitrate	4530	5680	5760
nitrite	1220	46.2	<10
pH	3.02	2.42	2.45

The uncertainty is 10% except for pH which should be 0.2 pH units.

The gap between the nominal and the measured values could indicate a small reaction is happening before the addition of the oxidants. The simulant was prepared two days before use, so a destruction reaction, if occurring, is too slow to be credited. Future work will use a simulant that is initially prepared at higher pH to avoid any potential pre-start reactions.

The starting nitrate content, from all sources in simulant preparation and pH adjustment, should be 3345 mg/L. At time 0 there is already more than that, 4530 mg/L, and by 96 hours, there is 5760 mg/L. This can be explained by the decrease in nitrite and increase in nitrate. The low pH condition is oxidizing most, if not all, of the nitrite to nitrate.

$$NO_2^- + \frac{1}{2} O_2 \longrightarrow NO_3^-$$

This is corroborated by the observation that no red-brown gas (NO_x) was observed at any point. The starting simulant has 0.032 M, or 1470 mg/L of nitrite. If all of this is converted to nitrate, this would correspond to an increase of 1980 mg/L. In turn, this would give a final expected nitrate concentration of 5330 mg/L (this includes the added nitric acid), compared to the measured 5760 mg/L, which is within analytical uncertainty.

3.2 Glycolate Results from the First Ten Tests

Eleven tests were performed. The conditions for each test are listed in Table 3.

Table 3. Test Conditions

Test	Nominal Conditions				
	Oxidant	**pH**	**moles oxidant/moles glycolate**	**Duration Oxidant Addition (h)**	**Glycolate, mg/L**
1 (control)	none	3	none	NA	2000
2	H_2O_2	3	2 ×	8	2000
3	$NaMnO_4$	3	2 ×	8	2000
4	H_2O_2	3	3 ×	8	2000
5	$NaMnO_4$	3	3 ×	8	2000
6	$NaMnO_4$	5	2 ×	8	2000
7	H_2O_2	3	3 ×	2	2000
8	$NaMnO_4$	3	3 ×	2	2000
9	H_2O_2	3	2.5 ×	2	250
10	$NaMnO_4$	3	2.5 ×	2	250
11	$NaMnO_4$	11	2.5 ×	2	250

The first column under conditions is the oxidant used; either hydrogen peroxide or sodium permanganate. The second column is the pH that the solution was adjusted to before starting the addition of the oxidant. The third column is the amount of oxidant relative to the glycolate, in molar terms. For the fourth column, addition of the oxidants was made over the first 8 hours, except for those tests that used 2 hours for addition (tagged as “4 × rate” on Figures 1 and 2). The fifth column describes the nominal glycolate concentration. Reactions noted as “250 ppm glycolate” nominally had 250 ppm of glycolate instead of 2000 ppm.

Table 4 lists the glycolate results for all sample pulls, in mg/L. The time of each sample is nominally as listed. For those tests that showed complete destruction by 8 hours, the rate of glycolate destruction is reported in mM/minute.

Table 4. Glycolate Results from the Tests (mg/L)

Test	Time 0h	Time 1h	Time 2h	Time 4h	Time 8h	Time 24h	8 hour rate (mM/min)
1 (control)	1660	NM	NM	NM	NM	1710	NA
2	1700	1340	1100	916	405	68.6	NA
3	1680	1630	1540	1460	595	261	NA
4	1700	1630	1520	828	165	<10	NA
5	1660	1630	1390	440	<10	<10	0.023
6	1530	1500	1260	821	199	12.9	NA
7	1813	1200	1041	642	118	<50	NA
8	1794	463	119	<50	<50	<50	0.025
9	105	88.6	68.2	67.5	66.9	63.9	NA
10	87.5	20.7	<10	<10	<10	<10	0.00028
11	97.5	91.7	71.6	39.2	17.6	<10	NA

The analytical uncertainty is 10%. “NM” indicates the analyte was not measured. “NA” indicates the value is not calculated.

In about half the cases, the glycolate was completely destroyed, within the analytical detection limits. While the ion chromatography detection limit is normally <10 ppm, some samples showed poor response (generating a detection limit of <50 ppm) on the detector. This also applies to values in Table 5. AD is working to eliminate this problem. There are some initial indications that the accelerated oxidant addition rate works better for the permanganate, but this will require further confirmation.

As with the control test, there is a gap between the nominal glycolate concentration and the measured time 0 values. This could be due to an ongoing reaction before the oxidant is added, but this also requires further confirmation.

Tests 5, 8, and 10 were complete in 8 hours and are given a rate of glycolate destruction. The far lower rate for Test 10 is likely due to the much lower starting glycolate concentration in that test.

Figures 1 and 2 show the graphical representation of the glycolate over time for each test. The nominal 2000 mg/L tests are shown separately from the 250 mg/L tests for clarity.

Figure 1. Glycolate Concentrations Over Time for 2000 mg/L Tests (mg/L)

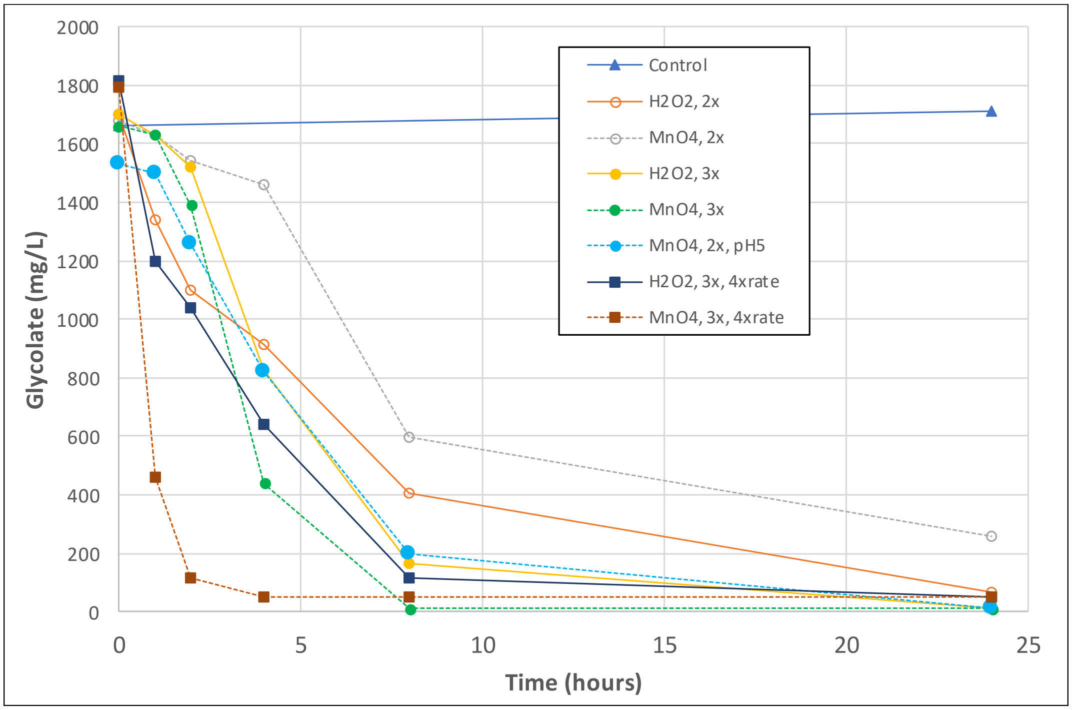
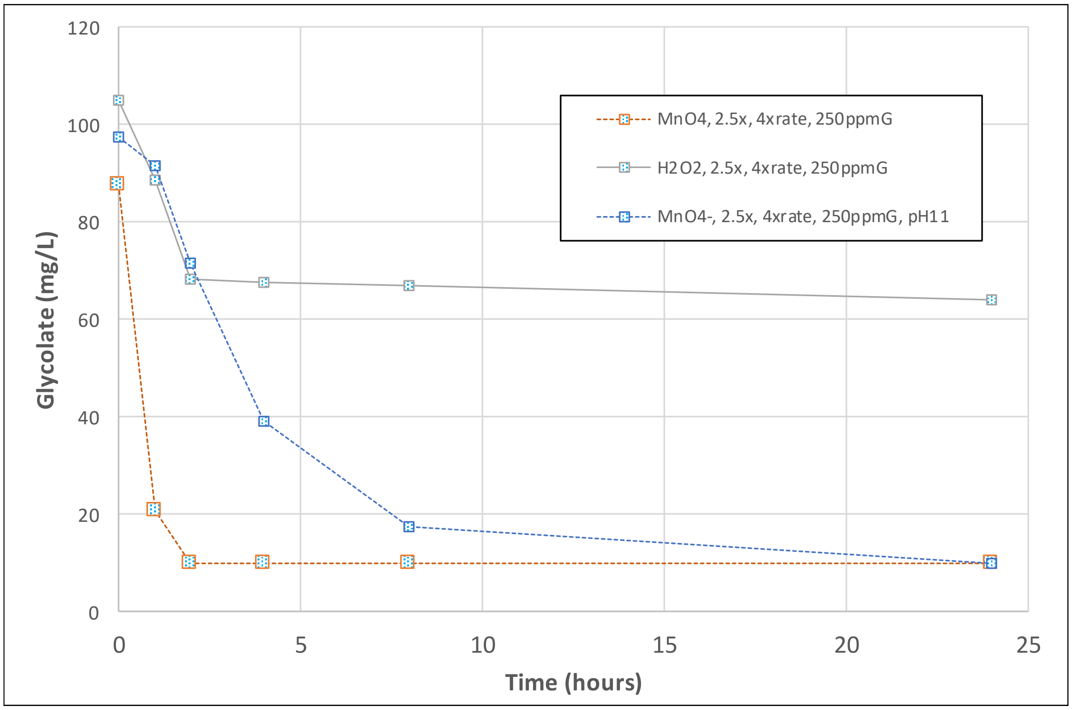


Figure 2. Glycolate Concentrations Over Time for 250 mg/L Tests (mg/L)



In addition to the glycolate analyses, the anion concentrations were measured for the 24-hour samples. Of the anions, only nitrate, nitrite, oxalate and formate were relevant. Oxalate and formate were considered to be possible decomposition products of the glycolate, although they might also be subject to oxidative destruction. Results of the 24 hours samples are shown in Table 5.

In all cases but two (control and Test 11), the nitrite was below detection. The nitrate levels were above the nominal nitrate that was added, and this increase almost exactly corresponds to the ~100% conversion of nitrite to nitrate. That is to say, the acidic and/or oxidizing environment completely converts the starting nitrite to nitrate.

Some of the reactions show oxalate and/or formate present at the end, although there is not a clear pattern at this time. Oxalate and formate must be generated by the oxidative degradation of the glycolate and then in turn are broken down, presumably all the way to carbon dioxide. Presumably further time and/or oxidant would destroy any residual oxalate and formate.

Table 5. 24-hour Sample Anion Results from the Tests (mg/L)

Test	nitrate	nitrite	formate	oxalate
1 (control)	5680	46.2	<10	<10
2 (H_2O_2)	4970	<10	272	87.5
3 (MnO_4^-)	5408	<10	789	<10
4 (H_2O_2)	5387	<10	<50	187
5 (MnO_4^-)	5853	<10	<50	<10
6 (MnO_4^-)	4450	<10	<50	941
7 (H_2O_2)	5510	<10	297	180
8 (MnO_4^-)	4840	<10	<50	49
9 (H_2O_2)	4970	<10	<50	<10
10 (MnO_4^-)	5040	<10	<50	<10
11 (MnO_4^-)	NM	1050	<10	89.2

The analytical uncertainty is 10%. “NM” indicates the analyte was not measured.

In addition to the glycolate and anion measurements, the pH of each test was measured at the time the other samples were removed. The measurement was performed by a portable pH probe that had been previously calibrated. The results are reported in Table 6.

Table 6. pH Results from the Tests (pH)

Test	Time 0	Time 1	Time 2	Time 4	Time 8	Time 24
1	3.02	NM	NM	NM	NM	2.42
2	3.04	2.78	2.74	2.66	2.70	2.90
3	3.05	3.28	3.8	3.72	5.00	7.22
4	3.09	2.7	2.61	2.63	2.78	2.92
5	3.00	3.72	3.38	4.92	7.68	8.38
6	5.17	5.65	7.28	10.21	8.80	8.87
7	3.05	2.10	2.11	2.14	2.18	2.22
8	3.04	6.11	7.35	7.43	7.53	7.76
9	2.95	2.71	2.43	2.31	2.25	2.22
10	3.00	2.56	2.67	2.75	2.78	2.83
11	11.3	10.3	10.4	10.1	9.88	10.8

The analytical uncertainty is 0.2 pH units.

The tests using hydrogen peroxide show a different pH response (slight decrease in pH) than those using permanganate (pH increase). This is more easily discerned in Figures 3 and 4.

Figure 3. pH Response in the Tests Using H_2O_2

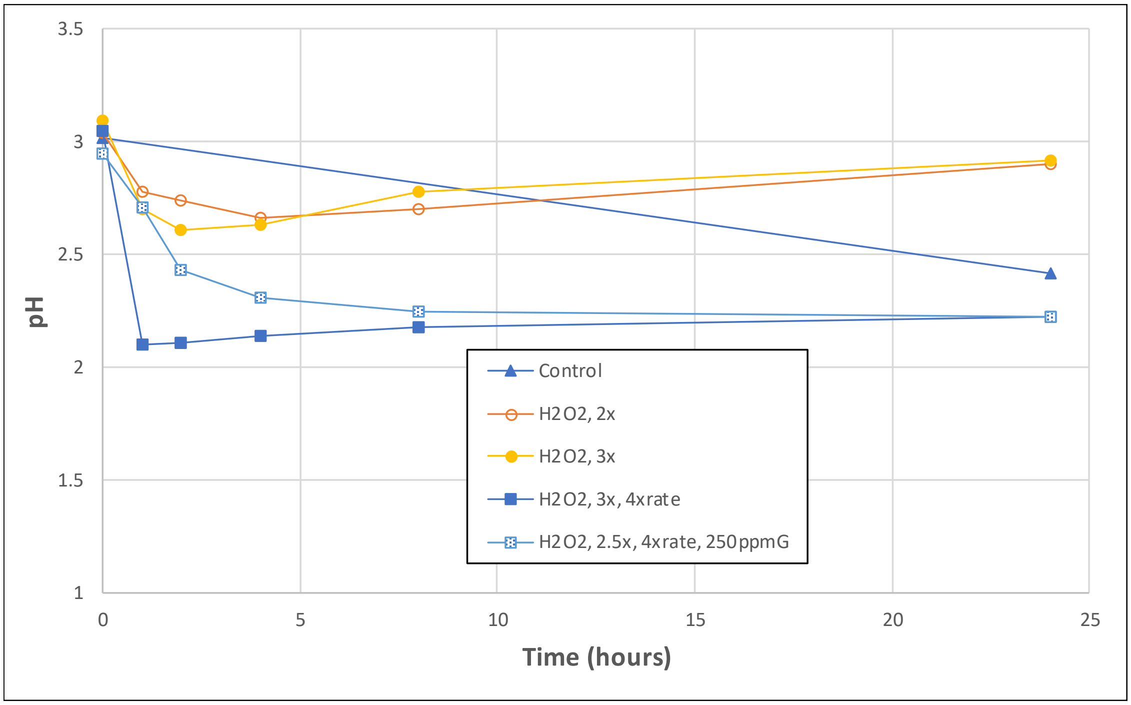
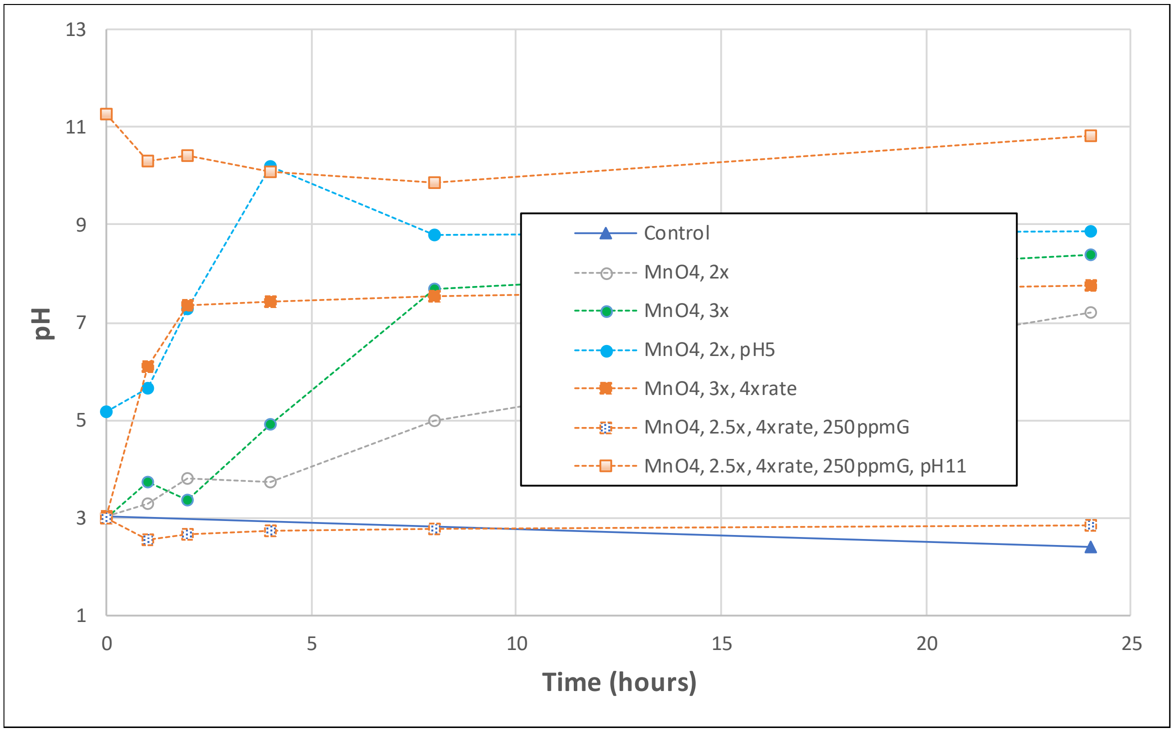


Figure 4. pH Response in the Tests Using Permanganate



Tests using H_2O_2 showed a moderate decline in pH, from the starting 3, roughly bracketing the pH effects from the control reaction that used no oxidant.

The permanganate tests have a stronger effect on the solution pH, drifting upwards in those cases where there is a significant amount of glycolate present. The low glycolate test more closely follows the control pH. More glycolate means a higher final pH, suggesting caustic materials are generated, likely from the MnO_2 (the byproduct of permanganate reduction) or derived compounds.

4.0 Conclusions

A series of initial reactions were performed at SRNL with the goal of arriving at a general understanding of the conditions required to destroy glycolate in a simulant solution representing a composite of the RCT, SMECT, and/or the OGCT. Two oxidizers were used, hydrogen peroxide and sodium permanganate. Ten tests and a control reaction were performed. The low initial pH of the simulant degrades the nitrite content before the test has formally begun. Future simulants will avoid nitrite loss by being created at a higher pH. There is some evidence that a starting low pH achieves a slight glycolate destruction before any oxidant addition, as evidenced by lower than nominal glycolate values at time 0.

Both oxidants were capable of achieving complete destruction in 24 hours, within the limits of analytical detection. Complete destruction was also noted in as little as 2 hours, in the case of a single permanganate test. The tests indicate that a 2 to 3-fold molar excess of oxidant to glycolate is adequate for complete or near-complete glycolate destruction within a reasonable time, although longer times may be required with lesser oxidant amounts.

At this time, a preferred oxidation method cannot be chosen. Follow-on prototypic testing will be performed in conjunction with SRR to define the mitigation strategy by: 1) completing the oxidant down-selection, 2) verifying the oxidant/glycolic reaction rates and process mass balance, and 3) development of the process protocol addition rate and minimum cycle time for normal and foam-over conditions.[i]

5.0 References

---

[i] G. Chen, M. C. Clark, "Evaluation of Chemical Additives for Glycolate Mitigation", X-TTR-S-00068, Rev. 0, 2018.

[ii] E. W. Holtzscheiter, "Simulant and Radioactive Testing – Impact of Glycolate on Tank Farm", X-TTR-S-00067, Rev. 1, 2017.

[iii] W. G. Ramsey, "Destruction/Mitigation of Glycolate in DWPF Recycle: Optioneering Meeting Results", SRNL-L3100-2017-00140, Rev.0, 2017.

[iv] G. Chen, E. W. Holtzscheiter, "Screen Study: Chemical Additives for Low Concentration Glycolate Decomposition in Defense Waste Processing Facility (DWPF) Recycle Stream to Tank Farm", X-TAR-S-00007, Rev. 0, 2017.

[v] W. G. Ramsey, "X-TAR-S-00007: Glycolate Mitigation – Run Plan", SRNL-L3100-2018-00002, Rev.1, 2018.

[vi] "Technical Reviews", Manual E7 , Procedure 2.60, Rev. 17, 2016.

[vii] "Savannah River National Laboratory Technical Report Design Check Guidelines", WSRC-IM-2002-00011, Rev. 2, 2004.

[viii] T. B. Peters, "Glycolate Destruction", ELN-A4571-00084-37.

Distribution:

timothy.brown@srnl.doe.gov
alex.cozzi@srnl.doe.gov
david.crowley@srnl.doe.gov
david.dooley@srnl.doe.gov
a.fellinger@srnl.doe.gov
samuel.fink@srnl.doe.gov
connie.herman@srnl.doe.gov
frank.pennebaker@srnl.doe.gov
william.ramsey@SRNL.DOE.gov
boyd.wiedenman@srnl.doe.gov
bill.wilmarth@srnl.doe.gov
charles.nash@srnl.doe.gov
Records Administration (EDWS)

jeffrey.crenshaw@srs.gov
roberto.gonzalez@srs.gov
patrick.jackson@srs.gov
patricia.suggs@srs.gov

phoebe.fogelman@srs.gov
vijay.jain@srs.gov
eric.freed@srs.gov
ryan.mcnew@srs.gov
grace.chen@srs.gov
bill.holtzscheiter@srs.gov
dan.lambert@srnl.doe.gov
chris.martino@srnl.doe.gov

thomas.colleran@srs.gov
mason.clark@srs.gov
Rachel.Smith@srs.gov
christie.sudduth@srs.gov
victoria.kmiec@srs.gov
stephanie.harrington@srs.gov
jeff.ray@srs.gov
george.matis@srs.gov
william.pepper@srs.gov
john.iaukea@srs.gov
richard.edwards@srs.gov
maria.rios-armstrong@srs.gov
Jocelin.Stevens@srs.gov
Kevin.Brotherton@srs.gov
john.occhipinti@srs.gov