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Modeling of Glycolate Destruction in the Recycle Collection Tank

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EXECUTIVE SUMMARY

This report presents process modeling supporting the Defense Waste Processing Facility (DWPF) plan to implement the Nitric-Glycolic (NG) acid flowsheet. The new flowsheet replaces the formic acid reductant with glycolic acid.

A chemical kinetic model with permanganate loss term had been developed and its rate mechanics are here applied for detailed glycolate destruction predictions. The model specifically addresses various process strategies for destroying residual glycolate that carries over to the DWPF Recycle Collection Tank (RCT). The model describes the kinetics of glycolate destruction via chemical oxidation with sodium permanganate when RCT liquid is pre-adjusted with caustic and nitrite before permanganate addition. The Post-Strike process strategy has been found to be most effective for the nominal goal of reducing glycolate concentration to below 1 mg/L in four hours. The Post-Strike strategy charges the RCT with a batch of condensate to be treated. Caustic adjustment can be done in the tank heel or after feed is charged to the RCT. Permanganate is then added to complete the glycolate mitigation. Less effective alternatives use different feed or permanganate addition sequences to the RCT, such as pre-charging the RCT with sodium permanganate. The pre-charge strategy of adding permanganate first is referred to as Pre-Strike. Double-Strike, instant Post-Strike, and reduced permanganate strike volume strategies are also considered.

Previous testing has demonstrated the efficacy of a sodium permanganate strike to destroy glycolate in the DWPF RCT prior to transfer to Tank 22. The mechanistic chemical kinetic model used in this report includes a glycolate/permanganate reaction along with a permanganate loss term. It is conservative with respect to experimental data that has been reported in the past.

This work indicates the following:

- Both the Post-Strike and Pre-Strike strategies can reduce glycolate concentration in the RCT to less than 1 mg/L in 4 hours, starting from up to 250 mg/L using a full 135 gallon strike from the permanganate delivery tank.
- The Post-Strike strategy will process 25 mg/L glycolate in 4 hours using less than 60 gallons of sodium permanganate reactant solution. This includes a 50% increase in added solution over the nominal calculation.
- The reaction between permanganate and nitrite at high pH was estimated from a literature model and was found to be bounded by the loss term in the current kinetic model.
- The Post-Strike strategy works better than the Pre-Strike and Double-Strike strategies. It also would not see permanganate loss from permanganate reacting in the RCT with nitrite or heel sludge before feeding commences.
- This work estimates leftover permanganate that would represent soluble manganese that might have downstream impacts.
- Efficiency of reagent permanganate use is estimated and found to be highest when glycolate concentration is high. While the model does not take credit for an apparent improved stoichiometry of use at high reactant concentrations, it predicts permanganate usage efficiencies exceeding 95% for glycolate exceeding 375 mg/L.
- Literature on alkaline manganese chemistry indicates that soluble manganese should be partly present as permanganate downstream of the RCT. Such permanganate would provide mechanisms for further residual glycolate destruction. The literature also provides reaction pathways to insoluble manganese.

Following the permanganate strike in the RCT, residual manganese and <1 mg/L glycolate will enter the Concentration, Storage and Transfer Facilities (CSTF) as a constituent in the recycle stream via Tank 22.

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LIST OF ABBREVIATIONS

CSTF	Concentration, Storage and Transfer Facilities
DWPF	Defense Waste Processing Facility
mmol	millimole
NG	Nitric-Glycolic (Flowsheet)
OGCT	Offgas Condensate Tank
P/G	Permanganate to glycolate initial molar ratio
ppm	parts per million by mass
RCT	Recycle Collection Tank
RK-2	Second-order Runge-Kutta method
SME	Slurry Mix Evaporator
SMECT	Slurry Mix Evaporator Condensate Tank
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request

1.0 Introduction

The Savannah River Site's DWPF is being upgraded with the introduction of the NG flowsheet. Glycolic acid has been shown to be a superior alternative to formic acid for sludge processing. The new flowsheet improves or maintains necessary parameters such as 1) reduction of mercury, 2) adjustment of feed rheology, 3) pH stability, and 4) adjustment of melter oxidation/reduction potential. Further, the use of glycolic acid virtually eliminates the potential for catalytic hydrogen generation in DWPF processing.[1]

DWPF process condensates are collected and returned to the Savannah River Site (SRS) CSTF. The RCT collects off-gas condensate during chemical processing, vitrification, and other unit operations performed in DWPF and is the singular return vessel delivering recycle effluent back to CSTF. Each batch of recycle will have a small amount of glycolate from chemical processing and melter off-gas condensates. To avoid potential flammability issues due to thermolysis of glycolate in the CSTF, Savannah River National Laboratory (SRNL) provided to Savannah River Remediation (SRR) at their request a Task Technical and Quality Assurance Plan (TTQAP) to quantify and mitigate glycolate returns via DWPF's recycle stream.[2] The request included testing of a process to oxidize glycolate and other organic species that are responsible for hydrogen generation from thermolysis.

Following that work SRR provided a Task Technical Request (TTR) that requested process modeling.[3] In 2021 a TTQAP was issued to cover the modeling work.[4] Modeling draws data from laboratory scale studies using chemical simulants and radioactive waste samples. Chemical kinetic modeling was performed to evaluate the feasibility of using sodium permanganate to destroy glycolate in the RCT. The results from the laboratory studies were summarized in a series of reports.[5-9] Reference 9 is a report of lab scale processing of actual DWPF Slurry Mix Evaporate Condensate Tank (SMECT) and Offgas Condensate Tank (OGCT) samples in the SRNL Shielded Cells.

Tests at caustic conditions demonstrated sodium permanganate was effective in converting glycolate to oxalate, and permanganate (Mn^{7+}) is reduced to manganate (Mn^{6+}) with no significant formation of carbon dioxide or carbonate. Equation (1) was found to best describe the observed reaction of glycolate with permanganate under nominal (60 to 145 mg/L in RCT) glycolate entrainment conditions.[7]

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

Determination of the mechanistic chemical reaction confirmed the oxidant stoichiometry is effectively defined by the molar ratio of permanganate to glycolate (P/G). The report describes the application of a kinetic model to conservatively predict glycolate destruction with sodium permanganate solution at the process scale. The goal of mechanistic reaction modeling using initial permanganate and glycolate concentrations is to reduce glycolate concentrations to a desired value in the RCT in practical time.

In Equation (1) both permanganate and manganate are water-soluble species. These are observed in the chemical reaction in the lab, but manganese dioxide solids also formed. In terms of the plant process, 135 gallons of 20 wt% sodium permanganate solution added to an RCT batch would ultimately produce 72.4 kg of manganese dioxide. Nominally 7000 gallons of feed to the RCT would generate this amount of fine solids in the RCT and downstream.

Following the permanganate strike in the RCT, residual glycolate will enter the CSTF as a constituent in the recycle stream via Tank 22. Given that glycolate has been observed to produce hydrogen gas in CSTF waste,[10] it is important to understand the maximum concentration achievable in the CSTF. Residual glycolate will see some concentration during tank farm evaporator operations. Glycolate is expected to reach its highest concentrations in the 2H evaporator.

Data used to model glycolate destruction using sodium permanganate in the RCT were sourced from previous studies on glycolate destruction using simulants[7,8] and radioactive waste samples.[9] All the tests had similar characteristics such as:

- Test batches were pre-adjusted with NaOH and were alkaline with most containing a small amount of Slurry Mix Evaporator (SME) product sludge or a SME simulant,
- Chemical processing at room temperature, typically around 20 °C,
- 20 – 65 minute addition time for the permanganate strike,
- Monitoring of glycolate concentration for 3 hours or more. Glycolate in later samples was often found to be below the analytical reporting limit (at the time) of 10 mg/L,
- Samples being sulfite quenched immediately when taken, and
- Essential data from each test included initial glycolate concentration, initial P/G ratio, and glycolate concentration as a function of time.

This current report applies the model and statistics to high carryover experimental data not previously considered. High carryover events of approximately 5000 mg/L glycolate into the RCT had been simulated in seven laboratory experimental datasets.[7,8] The data newly considered was found to indicate that the kinetic model described herein provides increased conservatism over cases where initial glycolate in the RCT is in the range of nominal conditions (60 – 145 mg/L in lab experiments). The 4:1 P/G stoichiometric ratio appears to be about 2:1 when chemical concentrations are in the very high range (initial value 5000 mg/L) from these large carryovers. The usage efficiency of reagent permanganate is thus about double the efficiency seen at nominal glycolate concentrations, such as 125 mg/L. Reaction efficiency is further discussed in Section 3.7 below.

1.1 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2. The current work proceeds from a TTR[3] issued by SRR and a TTQAP[4] in response to that TTR.

These calculations were performed by using Mathematica 12.0.0.[11] Mathematica has not been evaluated for a software classification for use at SRS, so a subset of calculations was technically reviewed via design verification by alternate calculations (per technical review requirements in E7, 2.60) to ensure accuracy. The alternate calculations used a second order Runge-Kutta method in a spreadsheet. Technical review of this report further confirmed that Mathematica accurately integrates the model. Commercial software JMP Pro Version 11.2.1 was used for statistical work.[12] JMP software is classified as Level D.[13] The outputs included from both software packages were independently verified using an alternate software package as part of the design verification meeting the requirements for safety significant work.

2.0 Methods and Modeling Approach

2.1 Kinetic Modeling of Glycolate Destruction

The goal of modeling the experimental data for glycolate oxidation is to predict residual glycolate concentration as a function of initial glycolate and permanganate concentrations. This is to provide a conservative estimate of glycolate removal along with amount of unused permanganate (soluble manganese). Residual glycolate would increase thermolytic hydrogen production in the SRS Tank Farm. Soluble manganese from the glycolate destruction process would be expected to produce manganese dioxide as a post process precipitate downstream.

Zamecnik et al.[7] examined kinetic models for the permanganate oxidation of glycolate. One model applied to their data set was first order in each of glycolate and permanganate. This approach is reasonable since both species are relatively dilute in the RCT batch to be processed. The species would react when one molecule of permanganate finds a molecule of glycolate in solution. The basic model expression was:

$$d[G]/dt = -K * [G] * [P] \tag{2}$$

where,

[G] is glycolate concentration in mmol L^{-1},
[P] is permanganate concentration in mmol L^{-1},
t is time in minutes, and
K is a kinetic rate constant in L^2 $mmol^{-1}$ min^{-1}.

Concentrations would be in mmol/L though the reference used mmol/kg.[7] The mmol/kg is multiplied by density in kg/L as needed in the current work. Zamecnik provided an analytical solution where G(t) can be obtained explicitly. Such solution contains the initial mole ratio of permanganate to glycolate, P/G. That solution can be inverted to obtain t as an explicit function of G. The Zamecnik work[7] found that their "Reagent" and dilute Sludge Receipt and Adjustment Tank (SRAT) product tests supported a stoichiometric ratio of P/G of 4:1. Use of permanganate for the oxidation reaction appeared more efficient if sludge was present in the feed batch.

To account for the presence of reactions with other species, the current work uses a model with an additional loss term for permanganate.[14] The model with a loss term involving a rate term K_x provides two equations which are shown below. Units of the loss term K_x is inverse minutes. Equation (3) has the "4" in its first term to account for stoichiometry of permanganate to glycolate as discussed in Zamecnik et al.[7] Oxidizing one mole of glycolate consumes four moles of permanganate ion in that stoichiometry.

$$d[P]/dt = -K_1 * 4 * [G] * [P] - K_x * [P] + a * P_a \tag{3}$$

$$d[G]/dt = -K_1 * [G] * [P] + a * G_a \tag{4}$$

The terms involving "a" on the right side of the equations are included to account for additions of feed or permanganate reagent during processing. The constant "a" would be feed rate, liters/minute. P_a and G_a would be the concentration in millimolar of permanganate or glycolate, respectively, in the incoming flow. In the modeling work one of the two P_a , G_a feed concentration terms would be zero while the other is a positive constant for initial processing. After an addition is complete, the constant "a" is set to zero and the volume of the batch stops increasing. The integration in time would continue at constant volume for a typical processing period of 6 to 8 hours total.

The equations together do not have an analytical equation that can be written out; numerical methods are required to obtain results. The P/G ratio is not present in the solution and the initial value problem requires initial permanganate and glycolate concentrations P_0 and G_0 respectively. The current work thus relies upon numerical initial value solutions from Mathematica. The work is verified using spreadsheets that implement a second-order Runge-Kutta method as described in Carnahan et al.[15] Past work (reference 14) with this model used an analytical simplification of Equations (3) and (4) to remove one variable, but that strategy is not available to the current work. The current work requires that volume and permanganate addition vary with time. No analytical strategy is available for this more complex implementation, so numerical integration of equations (3) and (4) is required. The model mechanism and kinetic coefficients are the same as in reference 14. The model has not changed for the current work. It is still based on the previous SMECT real waste testing.[9]

The model with permanganate loss term, Equations (3) and (4), was found to fit real waste data better than the second order model expressed in Equation (2) without permanganate loss. This model with loss term is referred to as the "current model" in this report. The goal is to have a model that is mechanistic and conservative late in the reaction so that it does not underestimate residual glycolate.

A key goal of modeling the glycolate oxidation kinetics is to produce a mechanistic model that predicts glycolate concentration on the high side of what is realized with time. This is referred to as conservative here because it is desired to reduce glycolate concentration below measurable values to reduce thermolytic hydrogen downstream. The model from the Zamecnik report[7] and the current model are both mechanistic, being based on chemical rate laws. The approach for conservative estimation of residual glycolate used the following steps:[14]

1. Use JMP® software and a regression fit that could be handled by JMP® to evaluate uncertainties of modeling.
2. Fit the model of Equations (3) and (4) with the SMECT real waste data only to obtain a K_1 and K_x. The SMECT run was found to be conservative (bounding the body of data on the upper side) when compared with the body of simulant and real waste data. The body of simulant and radioactive waste sample data is thereby represented by a regression fit that is only used for JMP application.
3. The SMECT model with loss term is shown to be conservative with respect to the body of data and regression fit that was used.
4. The SMECT model is then used to make conservative predictions of residual glycolate in liquid product to be sent to the Tank Farm.

Additional information on data processing and statistical development are in Appendix B of the previous model report.[14] The theoretical model was shown to be a conservative predictor of G compared to the body of 95 data points (from 26 simulant tests and 2 real waste tests). Several of the tests only have measured data early on because glycolate dropped below the reporting limit of 10 mg/L. SRNL is currently at work to improve (reduce) analytical detection and reporting limits for glycolate in typical high sodium solutions.

The past statistics are to be applied to the work in this report, because the new statistical workup, Appendix C, found that high glycolate processing is more efficient and is thus not as conservative for low glycolate calculations.[14] The past work found that the model bounds low glycolate results 95% of the time with 88% confidence (single point) and 84% of the time (multiple point). The focus of the calculations here is low glycolate, targeting <1 mg/L at the end of a batch process.

2.2 Inputs and Assumptions

2.2.1 Inputs

Inputs were provided by the customer (see Appendix A) and by past SRNL reports on the implementation of the NG flowsheet.

- The RCT can work with up to 9000 gallons.[7]
- The RCT heel is 1400 gallons.[7]
- The sodium permanganate solution to be used is 20 wt%, which is 1630 millimoles per liter.
- The sodium permanganate delivery system to the RCT will provide 135 gallons of solution in nominally 30 minutes. Modeling examines variations on the delivery rate. See inputs, Appendix A.
- The customer requests examination of condensate feed containing 25, 125, 500, and 2000 mg/L glycolate. In addition, this work considered 250 mg/L glycolate because it is found to be an important nominal concentration where a batch meets processing goals in 4 hours.[2]

- The permanganate to glycolic reaction mole stoichiometry is 4:1 per model development from experimental work at initial glycolate concentrations below approximately 150 mg/L.[14] Experiments starting at approximately 5000 mg/L glycolate show a more favorable stoichiometry of 2:1. While this work uses the low-glycolate 4:1 ratio, it includes discussion of high efficiency use of permanganate (Section 3.7).
- Nitrite can react with permanganate at high pH values, as was found in experimental work from literature. See Section 3.9 below.
- The range of model applicability is based on the body of experimental data used for fitting and comparisons. Temperature range is thus from 17 to 25 °C, room temperature as specified for experimentation.
- Caustic conditions are those provided by a normal caustic adjustment for the glycolate destruction process. These caustic conditions are as found in past experimental work, references 5 to 9 (pH 13 or above). Nitrite is approximately 0.2 M.

2.2.2 Assumptions

- The 1400 gallon heel contains no glycolate. The previous process batch glycolate concentration is to be less than 1 mg/L, a small number relative to new feed. Calculations have shown that the glycolate concentration drops below the 1 mg/L target in normal processing so that any trace glycolate is not significant relative to new RCT feed.
- The nominal condensate volume of 7000 gallons is used in this work. This plus the heel sums to 8400 gallons leaving room for several 135 gallon permanganate strikes if needed. Further calculations assume that the RCT total volume is no more than 8935 gallons.
- The Double-Strike strategy delivers a second addition of permanganate in 2 hours. Calculations have shown that the initial permanganate-glycolic reaction has completed for the most part in that time.
- The plant RCT processing temperature is assumed to still be room temperature and under caustic conditions, similar to experimental work supporting the model. Note that process reaction rates are expected and are assumed to be faster if temperature was higher, such as if cesium content were higher. Faster reactions should add conservatism as more glycolate destruction would be expected in a window of processing time, such as 4 hours, compared to the room temperature case.

3.0 Results and Discussion

3.1 Model Comparisons with High-Glycolate Experiments

High glycolate carryover datasets not previously considered are here compared with the kinetic model for completeness. The mechanistic model has not changed for this work, but its calculations were compared to the new dataset. Statistical work with the model included comparisons with four high carryover (~5000 mg/L glycolate) experiments from reference 7 and three from reference 8. Run 10 of reference 8 was excluded from consideration because all glycolate results for that run after time zero were below detection. Table 1 below provides the input conditions for the seven experiments.

Initial glycolate values in the table are values adjusted from mg/kg mass ratios in the reports using solution density. The adjustment factor is a multiplier of 1.02 kg/L which is the solution density given in Table 14 of reference 7.

Table 1. High Glycolate Experiments for Comparison with Modeling

Reference	Run Designator	Initial P/G Ratio	Initial Glycolate mg/L	Glycolate mg/L at 90 Minutes	Glycolate mg/L at 180 Minutes
Ref. 8	9	2.2	5200	104	<100***
	8	2.6	5200	260	208
	8b	2 x (1.3)	5200	832*	<100***
	Run Designator	**Initial P/G Ratio**	**Initial Glycolate mg/L**	**Glycolate % and mg/L at 3 hours****	**Glycolate mg/L at 6 hours*****
Ref. 7	18a	1.53	4539	81% (877)	820
	20a	1.60	4539	85% (695)	646
	19a	2.03	4539	99% (80)	43
	17	2.31	4539	99% (66)	39

*Just before the second strike of permanganate solution.
**Percentage is of destruction. For example, 877 mg/L is 4539 mg/L reduced by 81%.
***Glycolate detection limit has improved with time as analysis refinement continued – see paragraph below.

Values were converted to millimole/liter units for the sake of comparison to model results in the statistical work. This is done by dividing the concentration, mg/L, by the molecular weight of glycolate, which is 75 grams per mole.

The glycolate detection limit for sample solutions has continuously improved over time. Reference 8 results show a glycolate detection limit of 10 to 100 mg/L, while the later work of reference 7 shows a limit of 10 mg/kg, 10x improved. Reference 8 also contains discussion of some adjustments to the ion chromatography analysis method to reduce the detection limit. Such adjustments include varied sample dilution and use of a guard column. While method development continues and also now considers nuclear magnetic resonance techniques, the glycolate destruction target has also been reduced. It is now 1 mg/L.

3.2 Definition of Processing Strategy Cases for Modeling

This work defined process strategies for modeling. The Pre-Strike strategy places a charge of 135 gallons (1.63 M with this volume = 832889 millimoles) of sodium permanganate in the heel of the RCT, then 7000 gallons of new feed is added, nominally at 100 gpm. There is zero initial glycolate in the heel. The chemical reaction commences on feeding and continues after feeding stops 70 minutes later. In the Post-Strike strategy, the RCT is charged with 7000 gallons of feed along with the 1400 gallon heel, and the 8400 gallon batch is processed with the same permanganate addition, this time made in 30 minutes. The reaction again continues after reagent addition stops. In the Double-Strike strategy, half of the permanganate is added in post-strike fashion (15 minutes, half of 135 gallons). After a two hour waiting period, the other half of the 135 gallon strike is added, again in 15 minutes. In addition to evaluating the Double-Strike method, this calculation provides insight into what half a strike will do to destroy glycolate.

Cases 16 – 18 examine the effect of an extra-large feed batch, 7400 gallons of fresh feed vs. the nominal 7000 gallons. Heel, feed, and permanganate sum to 8935 gallons in that case – within 100 gallons of the tank volume limit. Instant Post-Strike cases 19 – 23 bound plant cases where permanganate is delivered at higher rates than anticipated and where feed volume is at a maximum (7400 gallons). Case 24 is a "half-life" case to demonstrate the kinetic model loss term, which provides a first order permanganate loss rate covering side reactions outside of permanganate destruction. Sections 3.5 and 3.9 below discuss such losses, and a permanganate reaction with nitrite is identified as an example of a known loss.

Cases 25 – 29 examine Pre-Strike strategy performance at the lower bound on feed rate, 85 gpm per Appendix A. That strategy is impacted negatively by slow feeding.

Cases 30 – 31 examine limited permanganate feeding at the nominal 100 gpm rate for the Post-Strike strategy. The limit is set so that the 1 mg/L glycolate target is reached in 4 hours of processing in the RCT. These cases are important in determining the ability to reduce the amount of manganese added to the system while completing an RCT batch.

Cases for the work are listed in the following table.

Table 2. Description of Calculated Cases

Case Number	Strategy	RCT Heel, (feed volume), gallons	Feed (F) or Permanganate (P)** flow rate, gpm	Feed glycolate concentration, mg/L
1 - 5	Pre-Strike	1535 (7000)	100 (F)	25, 125, 250, 500, 2000
6 - 10	Post-Strike	1400 (7000)	4.5 (P)	25, 125, 250, 500, 2000
11 - 15	Double-Strike	1400 (7000)	4.5 (P)	25, 125, 250, 500, 2000
16 - 18	Post-Strike	1400 (7400)	4.5 (P)	25, 125, 250
19 - 23	Instant Strike	(8935)	All instant at start	25, 125, 250, 500, 2000
24	Half -life run			
25 - 29	Pre-Strike	1535 (7000)	85 (F)	25, 125, 250, 500, 2000
30 - 31	Post-Strike	1400 (7000)	4.5 (P), Meet goal*	25, 125

* The goal here is to reduce glycolate to less than 1 mg/L at 4 hours while using the minimum charge of permanganate (permanganate flow is cut off as soon as possible).
** Added permanganate (aqueous) solution is always 20 wt%.

3.3 Checking Mathematica Performance with a Runge-Kutta Spreadsheet

Independent checks of Mathematica results with those of a spreadsheet using a second-order Runge-Kutta method (RK-2) were performed for a few cases. This was done to make sure that the method of numerical solution of the model was correct. Plant cases 1 and 7 as described in Section 3.2. Table 3 shows that the numerical results are very close, indicating that the independent check of Mathematica validates its implementation. The right hand column shows ratios of glycolate results/permanganate results.

Table 3. Comparing Mathematica with Spreadsheet Results

CASE	Time, minutes from start	RK-2 Glycolate, millimoles	RK-2 Permanganate, millimoles	Mathematica Glycolate, millimoles	Mathematica Permanganate, millimoles	Ratio of RK-2 to Mathematica Result
1	30	838.9	755264	838.8	755363	1.0001/0.9999
	90	550.2	620337	559.7	620664	0.9830/0.9995
	150	25.35	523804	27.0	524053	0.9390/0.9995
	360	0.01	293334	0.01	293469	1.000/0.9995
7	30	16821	693599	16820	693609	1.000/0.9999
	90	716.5	530778	716.1	530788	1.0006/0.9999
	120	185.8	486582	185.7	486593	0.9984/1.0000
	360	0.1	250477	0.098	250482	1.0001/1.0000

3.4 Mathematica Modeling Results for the Process Strategy Cases

Table 4 shows results from the first 10 cases using 135 gallons of 20 wt% sodium permanganate (832,889 millimoles) in each case. In Table 4 it is clear that the Post-Strike processing strategy performance always exceeds that of the Pre-Strike method. Post-Strike glycolate concentrations are always lower than corresponding Pre-Strike results. Table 4 shows that both methods meet the goal of less than 1 mg/L glycolate in four hours for feed glycolate concentrations of up to 250 mg/L. This is ample coverage for normal processing when no carryover event is detected.

Table 4. Pre-Strike and Post-Strike Results

Case Number and starting mg/L Glycolate	Hours after Start of Processing, and mg/L Glycolate at time given				Unused Permanganate at 6 hours, kg as Mn
Pre-Strike	2 hours	3 hours	4 hours	6 hours	
1, 25 mg/L	0.27	0.02	0.00	0.00	16.1
2, 125 mg/L	2.43	0.26	0.04	0.00	12.8
3, 250 mg/L	9.87	2.12	0.59	0.08	8.6
4, 500 mg/L	63.6	41.2	32.2	24.8	0.86
5, 2000 mg/L	1181	1181	1181	1181	0.0
Post-Strike	2 hours	3 hours	4 hours	6 hours	
6, 25 mg/L	0.03	0.00	0.00	0.00	16.9
7, 125 mg/L	0.43	0.04	0.01	0.00	13.8
8, 250 mg/L	2.78	0.51	0.12	0.01	9.8
9, 500 mg/L	37.4	22.8	16.2	10.5	1.7
10, 2000 mg/L	1163	1163	1163	1163	0.0

The “Unused Permanganate” in the right column of Table 4 is the model result for remaining permanganate (converted to kg as elemental Mn) at 6 hours. The reactions to use and lose permanganate continue beyond 6 hours, but this time can be used for comparisons of cases. The model predicts disappearance of permanganate though does not say whether it produces soluble manganate or insoluble manganese dioxide. Both products have consistently been seen in experimental works. Additional work was done in Section 3.8 below to examine reducing the use of permanganate from a full to a partial charge from the permanganate delivery tank. Appendix B provides some examples of glycolate concentration with time for these two strategies.

Unused permanganate in solution has highly visible color. Reference 7 includes photographs of laboratory liquid samples after permanganate processing of simulant solutions. They have a strong blue appearance and spectroscopic data there had indicated that the color was a mixture of purple permanganate (Mn^{7+}) and green manganate (Mn^{6+}) species. Reference 7 photographs provide qualitative information on decay of these forms of soluble manganese to manganese dioxide over time. The visual information shows that the decay took months. It is expected that conditions like temperature, radiation, free hydroxide, presence of manganese dioxide, and nitrite concentration would affect the decay rate. Section 3.9 of this report gives further information on the reaction rate for permanganate and nitrite in caustic solutions.

Table 5 below shows calculated results for a Double-Strike strategy where equal amounts of permanganate (each being half of a 135 gallon delivery) are added at the beginning of processing and then two hour later. Results are slightly worse than the performance of the Pre-Strike strategy. No advantage is seen in implementing this more complex Double-Strike strategy.

Cases 16 to 18 examine the Post-Strike strategy if a 7400 gallon feed batch is charged to the RCT. Comparison of results with Table 4 show a slight increase in glycolate as expected, though no significant impact on ability to meet processing goals.

Table 5. Double-Strike and Post-Strike at Increased Feed Volume

Case Number and starting mg/L Glycolate	Hours after Start of Processing, and mg/L Glycolate at time given			
Double-Strike	2.5 hours	4 hours	6 hours	8 hours
11, 25 mg/L	0.26	0.00	0.00	0.00
12, 125 mg/L	4.06	0.08	0.00	0.00
13, 250 mg/L	24.49	1.22	0.07	0.01
14, 500 mg/L	144.7	33.9	15.5	10.2
15, 2000 mg/L	1239	1163	1163	1163
Post-Strike, feed 7400 gallons	2 hours	3 hours	4 hours	6 hours
16, 25 mg/L	0.04	0.00	0.00	0.00
17 125 mg/L	0.59	0.06	0.01	0.00
18, 250 mg/L	3.75	0.79	0.22	0.03

Table 6 presents an ideal case where a Post-Strike strategy is able to add the 135 gallons of permanganate instantly. Comparison of these five cases with the corresponding cases 6 through 10, where the permanganate strike takes 30 minutes, shows that the process works best when permanganate addition is as fast as possible.

Table 6. Ideal Instant (Post) Strike Results

Case Number and starting mg/L Glycolate	Hours after Start of Processing, and mg/L Glycolate at time given				Unused Permanganate at 6 hours, kg as Mn
Instant Post-Strike	2 hours	3 hours	4 hours	6 hours	
19, 25 mg/L	<0.02	0.00	0.00	0.00	16.2
20, 125 mg/L	0.28	0.03	0.01	0.00	13.2
21, 250 mg/L	1.99	0.42	0.11	<0.02	9.33
22, 500 mg/L	32.5	21.1	15.7	10.7	1.55
23, 2000 mg/L	1111.	1111.	1111.	1111.	0.00

3.5 Loss of Permanganate in the RCT

The kinetic model predicts that permanganate declines in concentration, including when no glycolate is present. The kinetic model takes on a first-order reaction form when only the loss term is active. Table 7 shows the model prediction assuming the amount of permanganate in a 135 gallon addition. The model thus gives a 251 minute half-life. It is believed that reaction with nitrite is part of the loss in reality. Leftover permanganate in the RCT heel cannot be credited for usefulness in glycolate processing of the next batch.

Table 7. Permanganate Decline with Time

Time, hours	Millimoles Permanganate		Time, hours	Millimoles Permanganate
0	832889		4	429448
1	705778		5	363908
2	598066		6	308370
3	506792			

3.6 Unreacted Permanganate

Process outputs will include a solids bearing slurry where almost all of the solids are manganese dioxide from the spent permanganate. Formation of such solids was observed in laboratory tests. However, the processing does not use all of the permanganate in normal operations because the nominal permanganate addition provides extra reagent required to reduce the glycolate concentration to below 1 mg/L in 4 hours. Assessing the downstream impacts of solids and added manganese is a recommendation.

This section provides model predictions of the amount of unreacted permanganate which would continue to be soluble in the process. The manganate has reaction pathways back to permanganate and will convert to manganese dioxide over time. This is further discussed in Section 3.9.5. The kinetics are not known but may continue for weeks or months given photographic observations of color in solutions.[7] Soluble manganese would pass through a filtration operation if filtration was added to the flowsheet – an example being recycle diversion. It is more likely that soluble manganese would lead to post precipitation of manganese dioxide downstream, probably in a tank like Tank 22. Manganese dioxide from the RCT would also settle in the same tank. Small amounts of manganese dioxide may also appear in an evaporator due to the higher temperature there breaking down soluble manganese.

Table 8 shows the unreacted permanganate at 6 hours for the Pre-Strike cases at a lower bound on feed rate. Feed rate is nominally 100 gpm, but a slower rate uses permanganate less efficiently. The effect would be seen by comparing the five cases in Table 8 to Cases 1 – 5 of Table 4.

Table 8. Pre-Strike Strategy at Lower Bound Feed Rate

Case Number and starting mg/L Glycolate	Hours after Start of Processing, and mg/L Glycolate at time given				Unused Permanganate at 6 hours, kg as Mn
Pre-Strike, 85 gpm	2 hours	3 hours	4 hours	6 hours	
25, 25 mg/L	0.48	0.03	0.003	0	16.1
26, 125 mg/L	3.88	0.42	0.07	0.004	12.7
27, 250 mg/L	13.76	2.98	0.85	0.12	8.45
28, 500 mg/L	72.51	46.28	36.24	28.46	0.78
29, 2000 mg/L	1183	1183	1183	1183	0.0

3.7 Efficiency in the use of the Permanganate Reagent

Model Equation (4) in Section 2.1 describes the disappearance of the added permanganate reagent by reaction with glycolate and also by a loss reaction. The right-hand terms can thus provide an instantaneous efficiency of permanganate use. This is:

$$\text{Percent Efficiency} = 100\,\% * (\mathbf{K_1 * 4 * [G] * [P]}) / (\mathbf{K_1 * 4 * [G] * [P] + K_x * [P]}) \qquad (5)$$

Permanganate concentration [P] thus cancels out in this expression so that instantaneous efficiency is only a function of glycolate concentration **[G].** This further shows that efficiency is near 100% at high glycolate concentration as shown in Table 9. Since the model is integrated over time, and since reactions consume both permanganate and glycolate, efficiency starts high and declines as glycolate concentration declines. This is true for all strategies considered in this report. Instantaneous efficiency is a lower bound on overall process efficiency because earlier efficiencies were always higher. Table 9 shows only 5% efficiency at the target concentration of 1 mg/L glycolate, but the quantities of chemicals are very low in that range. At high concentrations of glycolate 4 moles of permanganate destroy 1 mole of glycolate.

Table 9. Efficiency of Use of the Permanganate Reagent

Millimolar Glycolate	Glycolate mg/L	Instantaneous Efficiency %
10	750	97.6
6.6667	500	96.5
5	375	95.4
3.3333	250	93.3
1.6667	125	87.4
1	75	80.6
0.3333	25	58.0
0.1	8	29.3
0.05	4	17.2
0.013	1	5.1

The most significant conclusion from this perspective on efficiency is that a processing strategy works best when glycolate concentration is as high as possible. There is a strong contrast between Pre-Strike and Post-Strike strategies in this regard. In the Pre-Strike strategy, glycolate concentration starts at zero and rises slowly as glycolate-bearing feed is added to the total amount of permanganate reagent already charged to the RCT. This keeps the glycolate concentration relatively low and this is inefficient. The Post-Strike strategy, in contrast, starts with the glycolate concentration as high as possible in the RCT, and it remains relatively high because the permanganate reagent is metered in at the initial phase of processing. The permanganate reagent thus sees the highest glycolate concentration possible, and this favors good efficiency in the use of that reagent.

3.8 Minimizing use of the Permanganate Reagent

It is possible that the operations can deliver a dose of reagent permanganate that is less than 135 gallons. For the case of 25 mg/l glycolate and 125 mg/L, the P/G ratio is 94 and 19 respectively for 135 gallon permanganate additions. These are high values that would waste some permanganate – 135 gallons is much more than needed to reduce glycolate to less than 1 mg/L in the process. The Post-Strike strategy was thus considered in calculating minimum permanganate needed to reach the 1 mg/L glycolate concentration goal in 4 hours. In Case 30 a 25 mg/L feed batch of 7000 gallons was first added to a 1400 gallon heel. It was found that the goal was met if the 4.5 gpm permanganate delivery lasted only 8 minutes (36 gallons, 27% of a full permanganate addition). If the batch was instead 7000 gallons of liquid containing 125 mg/L glycolate, Case 31, the initial permanganate addition would have to be 17 minutes (77 gallons, 57% of a full addition). The capability to deliver a measured short portion of permanganate solution versus the full 135 gallons would result in significant savings in terms of reduced manganese for the waste system. Both of these results are still below 135 gallons if a 50% conservative margin on permanganate addition is imposed. For example, 77 gallons plus 50% is 116 gallons, allowing processing with one charge to the permanganate delivery tank.

Table 10. Post-Strike Strategy minimizing Permanganate Use

Case Number and starting mg/L Glycolate	Hours after Start of Processing, and mg/L Glycolate at time given				Unused Permanganate at 6 hours, kg as Mn
Post-Strike, min Permanganate	2 hours	3 hours	4 hours	6 hours	
30, 25	3.46	1.77	1.01	0.424	3.72
31, 125	5.63	1.99	0.84	0.22	5.78

3.9 Reaction of Permanganate and Nitrite

Obuchi et al. published experimental work that is relevant to the permanganate process where nitrite and permanganate co-exist in alkaline solution.[16] Obuchi provided a chemical kinetic expression, Equation (6), and also provided quantitative information on the rate constants.

The proposed Obuchi reaction and kinetic equation leads to the following form that includes initial values of chemical concentrations.

$$\frac{d[NO_2^-]}{dt} = \frac{-K_1*[NO_2^-]*[MnO_4^-]}{\sqrt{[NO_2^-(0)]}} \quad \textbf{(6)}$$

for the reaction:

$$NO_2^- + 2\ MnO_4^- + 2OH^- \Rightarrow NO_3^- + 2\ MnO_4^{--} + H_2O \quad \textbf{(7)}$$

This is an initial value calculation where $[NO_2^-(0)] = [NO_2^-]$ at time zero.

Two moles of permanganate are thus consumed for each mole of nitrite oxidized to nitrate. The time zero value of nitrite is a constant that is determined as an input for each case under consideration. This is in contrast to the variable nitrite concentration in brackets in the equation.

3.9.1 Effect of Temperature

Obuchi et al. provided an Arrhenius plot for their work (Figure 7 in the paper).[16] They found that the activation energy of the reaction is 9.5 kcal/g-mole. Use of this value to estimate relative reaction rates is provided in Table 11 below. It is seen that since most of Obuchi's data is taken at 60 °C, the reaction rate would be about (7.09/1.71) or 4.2 times slower at 30 °C.

Table 11. Relative Nitrite/Permanganate Reaction Rate at Temperature

Temperature, °C	Relative Rate		Temperature, °C	Relative Rate
20	1.00		50	4.55
25	1.31		60	7.09
30	1.71		70	10.8
40	2.83		80	16.0

3.9.2 Effect of Free Hydroxide

Obuchi performed a scan of free hydroxide to find its effect on reaction rate.[16] Table 12 below provides the results in terms of a relative rate, and where the chemical reaction rate is normalized to 0.2 M free hydroxide. This is done because the caustic adjustment for the RCT provides free hydroxide just below about 0.2 M free hydroxide. The progression of values in the table are not linear. The highest free hydroxide shown slows the reaction. There seems to be a plateau of reduced kinetic effect from 1 to 0.01 M free hydroxide. The reaction rate picks up significantly below 0.01 M free hydroxide (pH 12).

Table 12. Relative Effect of Free Hydroxide on Nitrite/Permanganate Kinetics

Free OH, M	Relative Rate		Free OH, M	Relative Rate
2	0.43		0.01	1.14
1	0.82		0.001	5.64
0.2	1.00		0.0001	9.00

3.9.3 Integrated Kinetic Model

The proposed Obuchi reaction and kinetic equation leads to the following form, Equation (8), that includes initial values of chemical concentrations.

$$\frac{d[NO_2^-]}{dt} = \frac{-K_1 * [NO_2^-] * [MnO_4^-(0)] + 2 * ([NO_2^-] - [NO_2^-(0)])}{\sqrt{[NO_2^-(0)]}} \qquad (8)$$

Note that $[NO_2^-]$ is the variable in this equation. Nitrite and permanganate values denoted with **(0)** are initial values. The equation is integrated to provide:

$$\left(-\frac{1}{a}\right) * \ln\left[\frac{a}{[NO_2^-]} + 2\right] = \frac{-K_1 * t}{\sqrt{[NO_2^-(0)]}} \qquad (9)$$

where a is $([MnO_4^-(0)] + 2 * ([NO_2^-])$.

This is an initial value calculation where $[NO_2^-(0)] = [NO_2^-]$ at time zero. In the example that follows, initial nitrite exceeds initial permanganate concentration by a factor of 20, so the small relative decline of nitrite with time makes this calculation close to a first order reaction consuming permanganate with time.

3.9.4 Example of Nitrite Permanganate Kinetics in Solution

From past experimental laboratory work at SRNL it is reasonable to assume a case where free hydroxide is 0.2 M, temperature is 30 °C, nitrite ion is 0.2 M, and permanganate is 0.01 M. A fresh batch of 135 gallons of 20 wt% sodium permanganate and 7000 gallons of feed would have 0.03 M permanganate. The 0.01 M value used here assumes consumption of some of the 0.03 M starting concentration.

Figure 1 shows that under these conditions permanganate concentration has a half-life of about 1020 minutes (17 hours). Its concentration is much lower than typical nitrite concentrations, so nitrite loss will be a minor impact. Given the stoichiometry of Equation (7), 0.01 M permanganate would oxidize 0.02 M of nitrite to nitrate. Permanganate loss by this reaction is bounded by the loss term in the kinetic model.

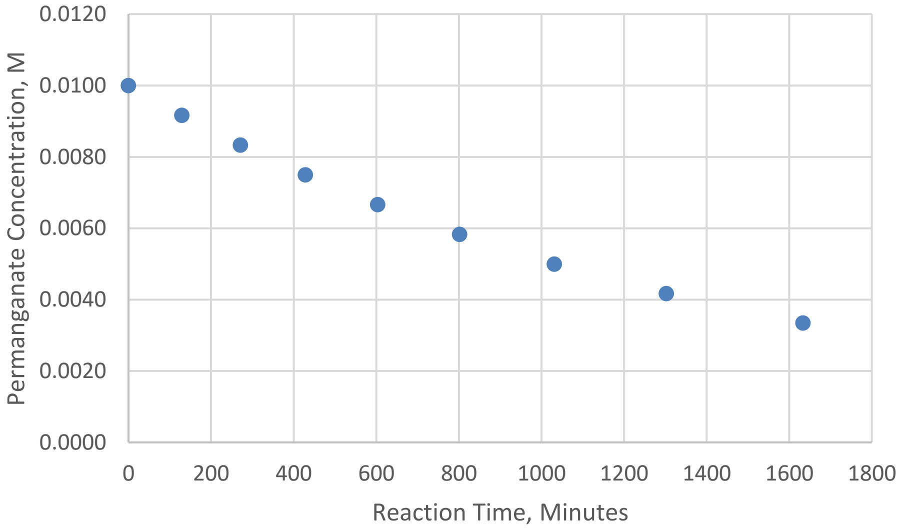


Figure 1. Example Case - Reaction of Permanganate with 0.02 M Nitrite in Solution

The overall impact of this calculation is that the glycolate processing strategy should add permanganate to the RCT only when the new feed and its glycolate are already present for reaction. Adding permanganate to a heel with nitrite and no glycolate will reduce active permanganate because of the nitrite side reaction. Adding the nitrite adjustment at the end of glycolate processing would also reduce permanganate loss by its reaction with nitrite. The conversion of permanganate to manganate is not desired because the oxidation rate between manganate and glycolate has not been determined. Manganate kinetics to oxidize glycolate are likely slower than those of permanganate.

3.9.5 Information on Soluble Manganese Reactions

Scientific literature provides some insight into the fate of soluble manganese that is left from the glycolate destruction process. Ruby found that there is an equilibrium between permanganate (Mn^{7+}) and manganate (Mn^{6+}) in aqueous alkaline solutions that he studied at 45 °C.[17] He reported the reaction as Equation (10) below. This shows a reaction pathway to form manganese dioxide. A key result of Ruby's work is that in all conditions observed, permanganate and manganate species came to co-exist when the solutions were allowed to age and reach an equilibrium. Ruby's experiments started with either Mn^{7+} or with Mn^{6+} but both oxidation states were observed after some time. No kinetic information was given, though experiments were given from one week to four months before equilibrium measurements were made.

$$\mathbf{3MnO_4^{2-} + 2H_2O = MnO_2\ (solid) + 2MnO_4^- + 4OH^-} \qquad \mathbf{(10)}$$

Ruby's equilibrium expression leads to the conclusion that manganate is present in an alkaline permanganate solution and that increased free hydroxide drives the equilibrium towards an increased amount of manganate. Ruby also reports a reaction when permanganate contacts manganese dioxide solids and some soluble manganate is found in the alkaline solution as part of reaching equilibrium.

Azevedo da Rocha et al. describe chemical steps to recover manganese as manganate from spent dry cells.[18] The chemical steps they describe address the interconversion of permanganate (Mn^{7+}) and manganate (Mn^{6+}) in aqueous alkaline solutions, finding that manganate is only stable above pH 13. They further point out that manganese dioxide in an alkaline environment with oxygen gas will oxidize to manganate. No kinetic data are given. However, process steps for dry cell reclamation are on the order of a few hours given that the goal of that work is to process dry cells rapidly and economically.

Since these works support the continual co-existence of permanganate (Mn^{7+}) and manganate (Mn^{6+}) in alkaline solutions, permanganate will always be present to react with glycolate and nitrite, in effect consuming manganate. It is not known if alkaline manganate destroys glycolate directly. Soluble manganese will continue to degrade trace glycolate downstream of the RCT.

The eventual fate of all the manganese from glycolate destruction is as manganese dioxide solids. Further reduction of glycolate levels is expected when manganate (and thus permanganate) is present. Such glycolate would convert to oxalate. There will also be some oxidation of nitrite, but the manganese concentration is much lower than that of nitrite in the waste, thus not leading to significant impacts.

4.0 Conclusions

A kinetic model with an additional loss term for permanganate is provided to conservatively predict glycolate content in the RCT and reaction durations required to reduce initial glycolate concentrations to a desired value in the RCT. This work indicates the following:

- The Pre- and Post-Strike strategies with a full 135 gallon addition volume of permanganate can reduce glycolate to less than 1 ppm in four hours. These strategies can accomplish this for glycolate in the RCT at initial glycolate concentrations fed to the RCT of up to 250 mg/L.
- The Post-Strike strategy is the best process performer of the strategies examined. Reduced usage of permanganate can be realized when feed glycolate is known to be below a given concentration.
- Less than 135 gallon strikes of 20 wt% permanganate solution will be successful in reducing glycolate to less than 1 mg/L in the RCT in 4 hours. If the glycolate carryover started at a concentration of 25 mg/L, only 36 gallons of permanganate is needed to meet the goal in that time. If the initial glycolate was 125 mg/L, 77 gallons of permanganate would be needed. Reductions below 135 gallons are still realized if a 50% conservatism is added to these permanganate volumes.
- The model predicts efficiency of permanganate use is higher when glycolate is high, such as several hundred ppm or more. In addition to that, experimental work had reported that reaction stoichiometry becomes more favorable when substantial carryovers (1000's mg/L glycolate) occur.
- Nitrite does react with permanganate, and the rate is estimated using a study found in the literature. The rate is not fast enough to impact processing in the 4-hour range. It would impact a Pre-Strike strategy if permanganate is allowed to sit for an indefinite period with nitrite present before glycolate-bearing feed is introduced. It would be best to add nitrite as late as possible in the process.
- Cases exceeding 250 mg/L glycolate in feed (significant foamover/carryover) would require at least a second strike to complete the processing to below 1 mg/L.
- Permanganate and manganate in alkaline solution interconvert, causing manganate to be a continual source of permanganate. The kinetic rate of interconversion is not known.

5.0 Recommendations, Path Forward or Future Work

- It is recommended to take advantage of the less-than-135 gallon 20 wt% permanganate additions calculated in this work. Significant savings in added manganese are realized, even with an added conservatism of more-than-calculated volumes.
- Assessment of downstream impacts of added manganese and solids is recommended.
- Quantifying permanganate stability in solution when nitrite is present could verify the Obuchi work with our specific solution chemistry. While not a concern for the process, mixing high concentrations of nitrite and permanganate, with time delay before processing, would not be advised.
- Both glycolate and nitrite reduce permanganate leading to some manganate (Mn^{6+}), a soluble form. Stability and alkaline reactions of manganate under conditions found in tank farm chemistry may be beneficial.

6.0 References

1. D.P. Lambert, M.S. Williams, C.H. Brandenburg, M.C. Luther, J.D. Newell, and W.H. Woodham, "Sludge Batch 9 Simulant Runs Using the Nitric-Glycolic Acid Flowsheet," Savannah River National Laboratory, **SRNL-STI-2016-00319, Rev. 0**, 2016.
2. D.P. Lambert, "Task Technical and Quality Assurance Plan for Evaluation of Chemical Additives for Glycolate Mitigation," Savannah River National Laboratory, Aiken, SC, **SRNL-RP-2018-00358, Rev. 0**, 2018.
3. E.W. Holtzscheiter, "Models for the Destruction of Glycolate in the RCT," Savannah River Remediation, LLC, Aiken, SC, **X-TTR-S-00083, Rev. 1**, 2021.

4. C. A. Nash, “Task Technical and Quality Assurance Plan for Glycolate Destruction Modeling in the Recycle Collection Tank (RCT)”, **SRNL-RP-2021-00279, Rev. 0**, 2021.
5. T.B. Peters and C.A. Nash, "Defense Waste Processing Facility (DWPF) Glycolate Mitigation: Scoping Test Results," Savannah River National Laboratory, Aiken, SC, **SRNL-L3100-2018-00043, Rev. 0**, 2018.
6. D.P. Lambert, A.M. Howe, M.S. Williams, C.L. Trivelpiece, and R.G. William, "Evaluation of Chemical Additives for Glycolate Destruction in the Recycle Collection Tank," Savannah River National Laboratory, Aiken, SC, **SRNL-STI-2018-00585, Rev. 1**, 2019.
7. J.R. Zamecnik, D.P. Lambert, W.T. Riley, and W.G. Ramsey, "Permanganate Oxidation of Defense Waste Processing Facility (DWPF) Recycle Collection Tank (RCT) Simulants – Protocol Runs for Nominal and Chemical Process Cell (CPC) Foamover Conditions," Savannah River National Laboratory, Aiken, SC, **SRNL-STI-2019-00292, Rev. 0**, 2019.
8. M.J. Siegfried, W.G. Ramsey, and M.S. Williams, "Permanganate Oxidation of Defense Waste Processing Facility (DWPF) Recycle Collection Tank (RCT) Simulants Larger Scale Protocol Runs - Chemical Process Cell (CPC) Nominal and Foamover Conditions," Savannah River National Laboratory, **SRNL-STI-2019-00588, Rev. 0**, 2019.
9. C.A. Nash and M.J. Siegfried, "Permanganate Oxidation of Actual Defense Waste Processing Facility (DWPF) Slurry Mix Evaporator Concensate Tank (SMECT) and Offgas Condensate Tank (OGCT) Samples to Remediate Glycolate," Savannah River National Laboratory, **SRNL-STI-2020-00012, Rev 0**, 2020.
10. W.H. Woodham and C.J. Martino, "Evaluation of Thermolytic Production of Hydrogen from Glycolate and Common Tank Farm Organics in Simulated Waste," Savannah River National Laboratory, Aiken, SC, **SRNL-STI-2019-00605, Rev. 1**, 2020.
11. Mathematica 12.0.0 Kernel for Microsoft Windows (64-bit) Copyright 1988-2019 Wolfram Research, Inc.
12. JMP® Statistical Discovery Software, Professional Version 11.2.1, 64-bit, SAS Institute, Inc.,Cary, NC.
13. T.B. Edwards, "JMP Pro Version 11.2.1," **B-SWCD-W-00023, Rev. 0**, 2014.
14. M. J. Siegfried, S. P. Harris, C. A. Nash, W. H. Woodham, and T. L. White, “Modeling the Destruction of Glycolate in the Defense Waste Processing Facility (DWPF) Recycle Stream and Concentration Factors for Glycolate in the 2H Evaporator”, Savannah River National Laboratory, Aiken, SC, **SRNL-STI-2020-00247, Rev. 0**, 2020.
15. B. Carnahan, H.A. Luther, and J.O. Wilkes, “Applied Numerical Methods”, Section 6.5, J. Wiley & Sons, New York, 1969.
16. A. Obuchi, A. Okuwaki, and T. Okabe, “The Rate of Oxidation Reaction of Nitrite in an Alkaline Permanganate Solution”, Nippon Kagaku Kaishi, Vol. 8, pp. 1425-1429 (1974).
17. C.E. Ruby, “The Equilibrium Conditions of the Reaction Between Manganate, Permanganate, and Manganese Dioxide”, Journal of the American Chemical Society, Vol. 43, pp. 294-301 (1921).
18. R. Azevedo da Rocha, C.L. Quintanilha, T.V. Lanxin, J.C. Afonso, C.A. Vianna, V. Gante, and J.L. Mantovano, “Production of potassium manganate and barium manganate from spent zinc-MnO2 dry cells via fusion with potassium hydroxide”, Journal of Power Sources, Vol. 268, pp. 831-840, (2014).

Appendix A. SRR Input emails

Input email from Dennis Clark, Saltstone/DWPF Mechanical Systems Engineering (SRR)

Charles Nash

From: Dennis Clark
Sent: Monday, March 15, 2021 9:22 AM
To: William Dean; Maria Rios-Armstrong; Bill Holtzscheiter; Charles Nash
Subject: RE: Dump rate
Information on the Sodium Permanganate Feed Tank.
The tank is rated at 185 gallons.
There is a 1" dia. overflow pipe approx. 10 inches +/-, below the top of the tank.
The High-High tank fill limit is set at 160 gallons.
The Low level limit is set at 25 gallons.
The transfer pump is interlocked to shut down or prevented to start when at the tank's is at its Low level.
160 gallons – 25 gallons = 135 gallons that the pump can actually transfer out.
The Sodium Permanganate Feed Tank Transfer Pump is rated at 5 gallons per minute.
135 / 5 = 27 minutes it will take for the transfer pump out its contents.
Dennis J. Clark
Saltstone/DWPF Mechanical Systems Engineer
Building 704-24S,
Office: 803-208-6918
Cell: 803-646-0915

Input email from Aubrey Silker, Process and Regulatory Engineering, (SRR):

Charles Nash

From: Aubrey Silker
Sent: Thursday, May 06, 2021 11:48 AM
To: Charles Nash
Cc: Terri Fellinger; Bill Holtzscheiter
Subject: RE: Permanganate
Attachments: RCT Inflow vs Outflow.xlsx
Hi Charles!
I've done some sleuthing in PI to get a better feel for the RCT inflow and outflow rates (see attached spreadsheet). I
looked into two processing periods—August 2013 and February/March 2021. I chose August 2013 as it was the month
when DWPF poured a record number of canisters and it would be representative of a high processing period. February
and March of this year would be times of slower processing.
It looks like SMECT material is added to the RCT at a flowrate of 85-90 gpm, whereas OGCT material is added at a
flowrate of 140-145 gpm. This was true regardless of the processing period. There was good agreement between the
change in the RCT liquid level and change in SMECT/OGCT liquid levels (see below for an example). Transfers from the
SMECT took approximately an hour and transfers from the OGCT took about 30 minutes. I think 85 gpm would be a fair

lower bound for transfers into the RCT.

2

The RCT outflow rate was approximately 110-120 gpm. However, to transfer a batch out of the RCT, 2-3 transfers are
made over the course of a couple of hours. How quickly these transfers occurred varied by the processing period. In
August 2013, this transfer period was generally no more than ~2.5 hours (see below). The resultant "overall" flowrate is
40-60 gpm. Recently the transfer period has been longer, up to 12 hours. Based on this information, using a transfer
period of 2.5-3 hours would be reasonable.

3

The last item I looked into was sodium hydroxide and sodium nitrite additions to the RCT. 75 gal of sodium hydroxide and
215 gal of sodium nitrite are added at the start of each RCT batch (see below—not all additions are circled). These took
15-30 minutes regardless of the processing period.

Thank you for your patience. I hope this helps further refine your calculations/the time study.

Hope you have a great weekend!

4

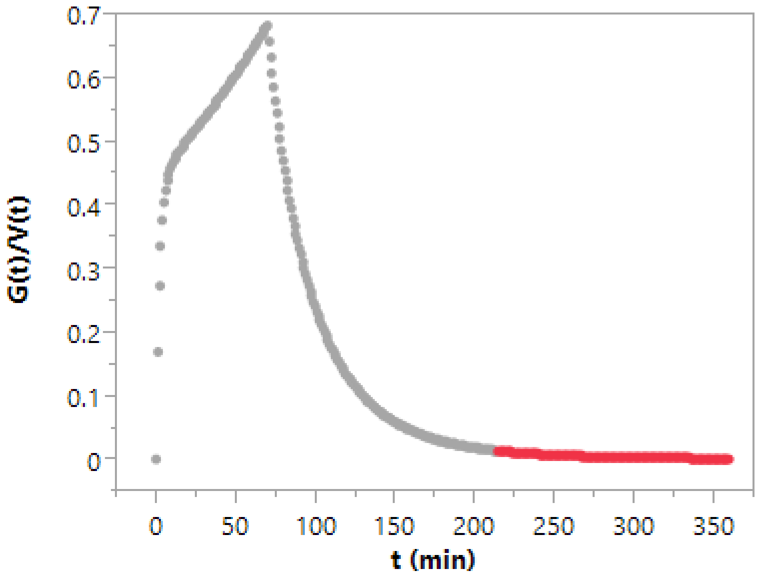
Best,

Aubrey Silker
766-H 2040
O: (803) 208-0235
C: (407) 221-7389

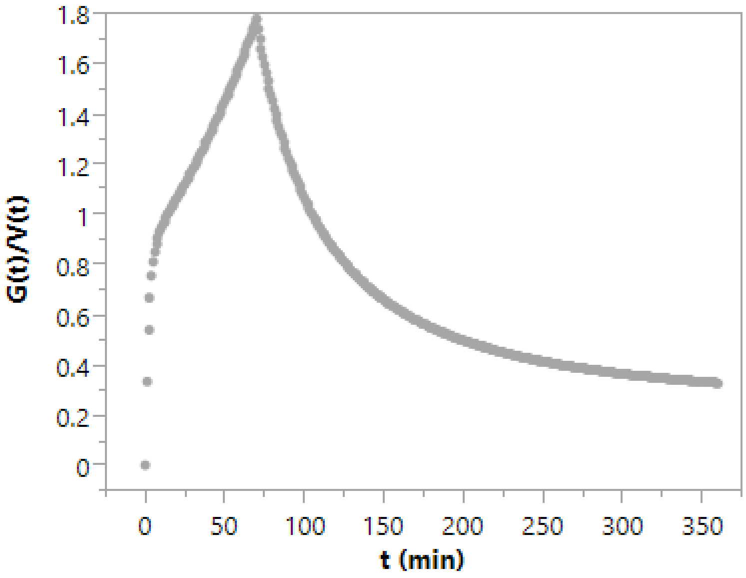
Appendix B. Figures from Several Cases

This appendix provides visual results from selected model runs. Charts from case 3 and 4 below show how glycolate concentration increases during the feeding phase of the pre-strike strategy while the glycolate/permanganate reaction proceeds. The y-axis units are millimoles per liter. The reaction continues after feeding is complete, and Case 3 reaches the 1 mg/L goal as shown by the red portion of the curve on the plot. Case 4 at higher glycolate content does not reach the goal.

Case 3 Glycolate Concentration with time, feed glycolate 250 mg/L.

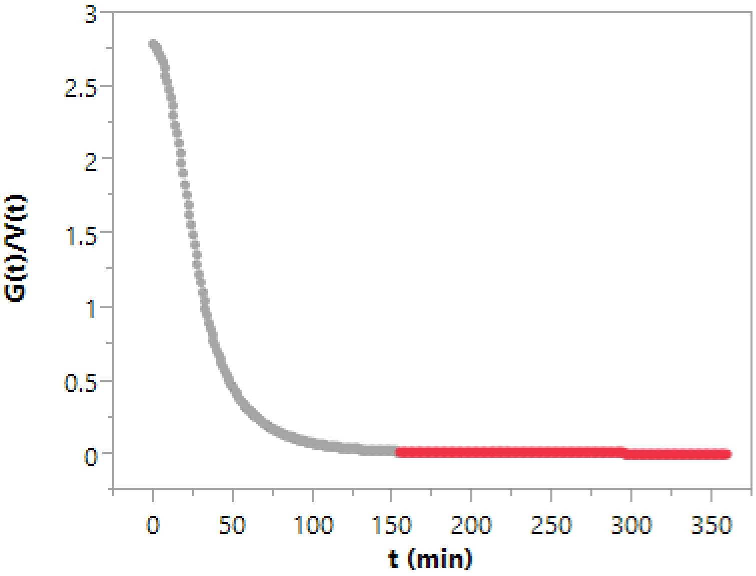


Case 4 Glycolate Concentration with time, feed glycolate 500 mg/L.

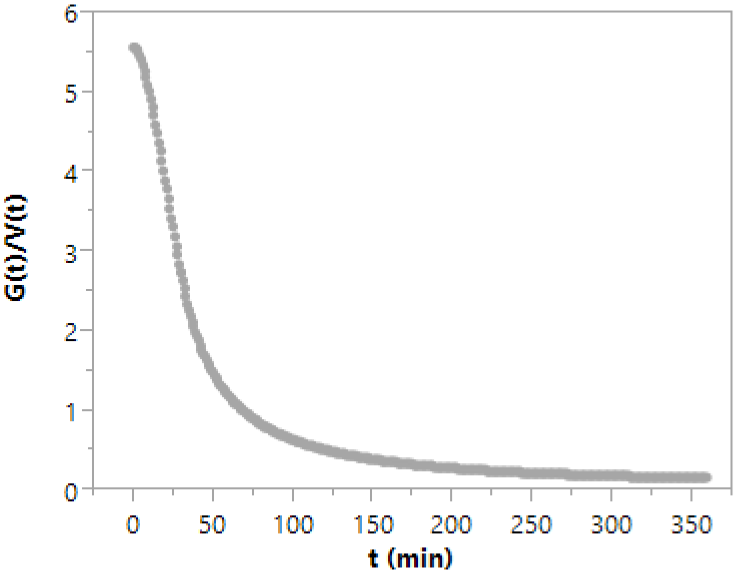


The two plots below show glycolate concentration (y-axis units millimoles per liter) for the Post-Strike strategy at 250 and 500 mg/L initial glycolate. The strategy is more efficient that the pre-strike strategy because glycolate and permanganate are both high at the beginning of processing. The strategy meets the 0.0133 millimole/liter (1 mg/L) goal for glycolate in less than 4 hours at 250 mg/L.

Case 8 Glycolate Concentration with time, feed glycolate 250 mg/L.

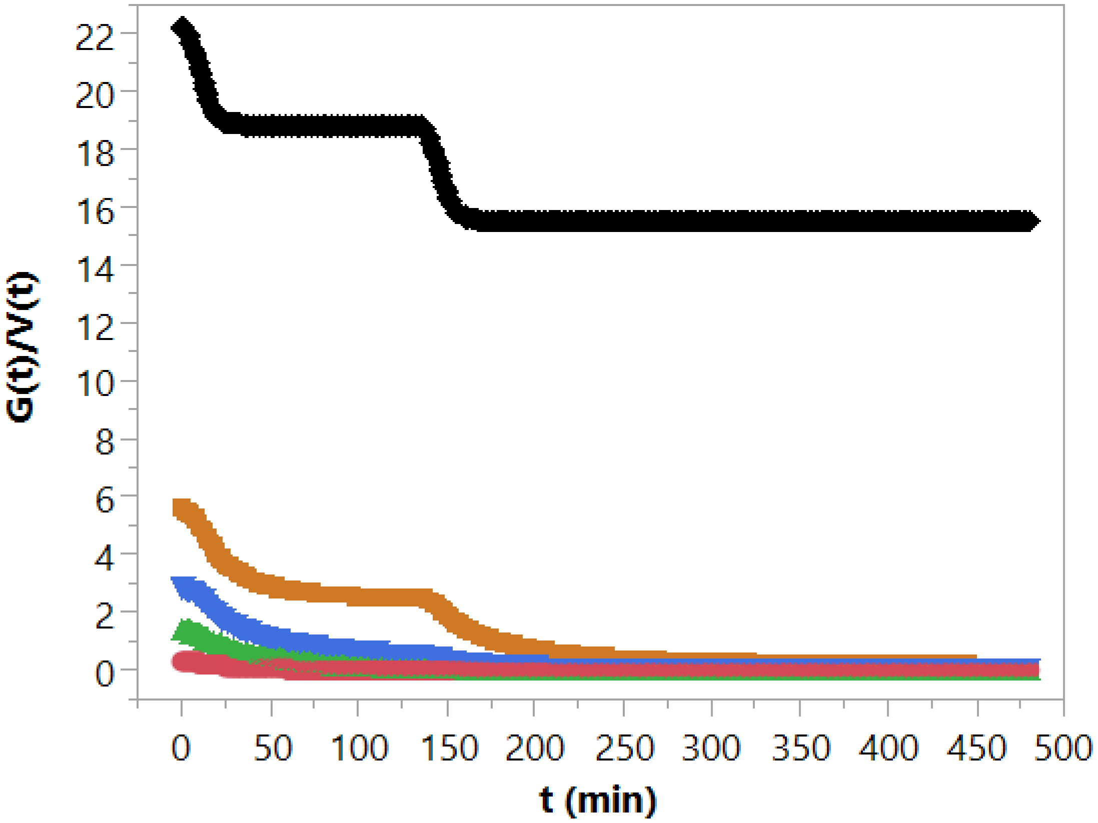


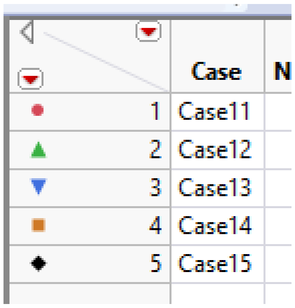
Case 9 Glycolate Concentration with time, feed glycolate 500 mg/L.



The plot below shows glycolate concentration (millimole/liter) with time for the five Double-Strike strategy calculations, with cases 11 to 15 being respectively 25, 125, 250, 500, and 2000 mg/L initial glycolate. The process tends to be efficient and completes relatively rapidly on the first strike because glycolate concentration is high. The second strike commences after the glycolate concentration has mostly stabilized.

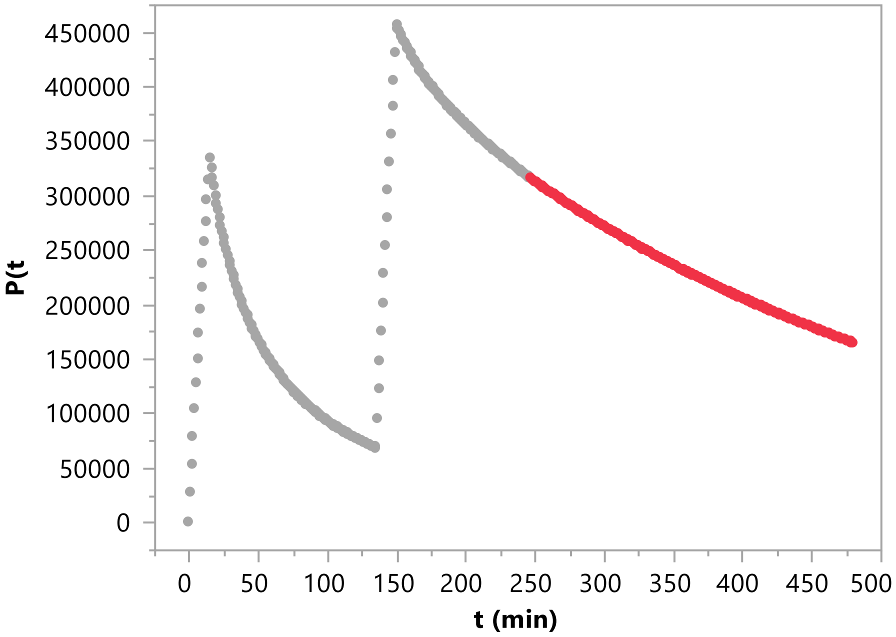
The plot for case 13 (250 mg/L glycolate), next page, shows the permanganate in the process (millimoles) during the Double-Strike process.





		Case	N
●	1	Case11	
▲	2	Case12	
▼	3	Case13	
■	4	Case14	
◆	5	Case15	

Case 13 Permanganate Concentration with time, feed glycolate 250 mg/L.



Appendix C. Statistical Treatment for the Kinetic Model

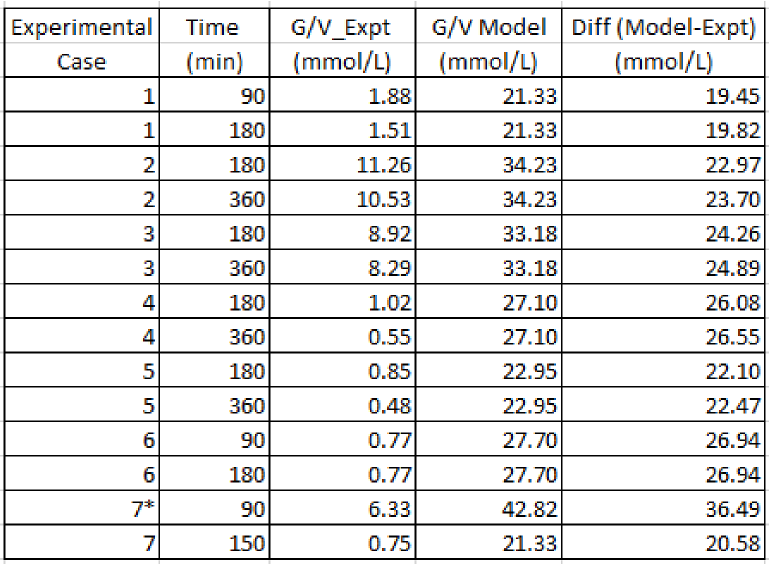
The following statistical analysis applies the kinetic model to seven "carryover" experimental runs where initial glycolate was 4539 and 5200 mg/L per Section 3.1 in the body of the report. These high glycolate runs performed much faster and more efficiently than the previous statistical analysis with the model at lower initial glycolate.

Experimental Data vs Model Predictions

Statistical analysis of experimental data has shown that the model predictions provide conservative bounds for the quantity of glycolate in the tank (mmol/L) as a function of time (minutes). The ratio of glycolate (mmol) to tank volume (L) is defined as G/V. The initial volume for seven experimental cases was either 1.6 or 1.8 liters with glycolate between 21.3 mmol/L to 66.7 mmol/L. As glycolate was added to the tank, the G/V ratio (G/V Expt) was determined for each experimental run, for set time, as displayed in Figure A-1. Predictions for each experimental run were based on the Mathematica solutions for the model (G/V Model) predictor equations. The difference between the model results and experimental results was calculated as (G/V Model minus G/V Expt) and displayed as Diff (Model-Expt) in Figure A-1.

The difference data was analyzed using the JMP(1) statistical software. While conducting the analysis an outlier on the high side was identified (Case 7, 90 min). The outlier (36.49 mmol/L) was deleted from the data set before proceeding. As such, the resulting statistical analysis is conservative because interest focuses of determining a lower bound for the difference.

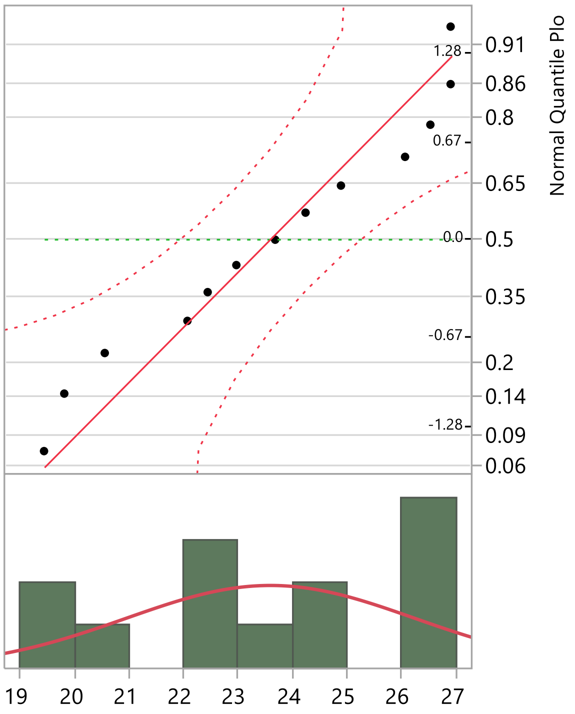
The mean for the difference is 23.60 mmol/L and the standard deviation is 2.643 mmol/L. It was determined that a normal distribution provided an adequate fit to the data (Shapiro-Will Test; Prob<W=0.35). A normal lower tolerance bound is 13.93 mmol/L for at least 99% of the distribution with 95% confidence. The bound was calculated by JMP and verified as mean-K (standard deviation) where the K is a unitless tabulated value. For the case of N=13 data points, the K value is 3.659 (2), 23.60-(3.659)(2.643)=13.93 mmol/L. As such, the model prediction is expected to provide an upper bound for the G/V ratio for at least 99% of the time with 95% confidence. Earlier work based on a theoretical model for low initial glycolate (0.85 to 2.439 mmol) has been documented in SRNL-STI-2020, Rev. 0. The theoretical model was shown to conservatively bound at least 84.2% of the data distribution (complete calculation through time) with 95% confidence. The theoretical model, evaluated using the numerical integration function NIntegrate in Mathematica Ver. 12.0.0, fits the SMECT data with rate constants K_1 = 0.00286 1/min/mmol and K_x = 0.00276 1/min. The theoretical model for low glycolate was determined to be conservative and is reasonably expected to predict a higher G (mmol) on average than would be seen in a batch reaction.



Experimental Case	Time (min)	G/V_Expt (mmol/L)	G/V Model (mmol/L)	Diff (Model-Expt) (mmol/L)
1	90	1.88	21.33	19.45
1	180	1.51	21.33	19.82
2	180	11.26	34.23	22.97
2	360	10.53	34.23	23.70
3	180	8.92	33.18	24.26
3	360	8.29	33.18	24.89
4	180	1.02	27.10	26.08
4	360	0.55	27.10	26.55
5	180	0.85	22.95	22.10
5	360	0.48	22.95	22.47
6	90	0.77	27.70	26.94
6	180	0.77	27.70	26.94
7*	90	6.33	42.82	36.49
7	150	0.75	21.33	20.58

Figure A-1: Experimental and Model Results
Outlier Deleted (*)

Diff (Model-Experimental) (mmol/L)



Quantiles

100.0%	maximum	26.935

75.0%	quartile	26.3149
50.0%	median	23.7034
25.0%	quartile	21.338
0.0%	minimum	19.447

Summary Statistics

Mean	23.595462
Std Dev	2.6426191
Std Err Mean	0.7329307
Upper 95% Mean	25.19238
Lower 95% Mean	21.998543
N	13

Fitted Normal

Parameter Estimates

Type	Parameter	Estimate	Lower 95%	Upper 95%
Location	μ	23.595462	21.998543	25.19238
Dispersion	σ	2.6426191	1.8949851	4.3622642

Goodness-of-Fit Test

Shapiro-Wilk W Test

W	Prob<W
0.931193	0.3533

Note: Ho = The data is from the Normal distribution. Small p-values reject Ho.

One-sided Tolerance Interval

Proportion	Lower TI	Upper TI	1-Alpha
0.990	13.9256	.	0.950

(1) JMP Pro Ver 11.2.1, SAS Institute, Cary, N.C.

(2) Oden, R.E. and Qwen, D.B. (1980), *Tables for Normal Tolerance Limits, Sampling Plans, and Screening*, Marcel Dekker, Inc., NY

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