



Destruction of Oxalate in HB-Line using Sodium Permanganate

R. A. Pierce and C. A. Nash

May 2014

SRNL-STI-2014-00213, Revision 0



DISCLAIMER

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U.S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied:

1. warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or
2. representation that such use or results of such use would not infringe privately owned rights; or
3. endorsement or recommendation of any specifically identified commercial product, process, or service.

Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.

Printed in the United States of America

**Prepared for
U.S. Department of Energy**

Keywords: *HB-Line, oxalate,
permanganate*

Retention: *Permanent*

Destruction of Oxalate in HB-Line using Sodium Permanganate

R. A. Pierce and C. A. Nash

May 2014

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



REVIEWS AND APPROVALS

AUTHORS:

R. A. Pierce, Separation & Actinide Science Programs	Date
--	------

C. A. Nash, Advanced Characterization and Processing Technology	Date
---	------

TECHNICAL REVIEW:

M. L. Crowder, Separation & Actinide Science Programs	Date
---	------

S. L. Garrison, H-Canyon Outside Fac & Tech Support	Date
---	------

APPROVAL:

T. B. Brown, Manager Separation & Actinide Science Programs	Date
--	------

S. L. Marra, Manager Environmental & Chemical Process Technology Research Programs	Date
---	------

J. E. Therrell, Manager HB-Line Engineering	Date
--	------

EXECUTIVE SUMMARY

During HB-Line Pu-239 operations, plutonium (Pu) is precipitated as Pu(IV) oxalate $[\text{Pu}(\text{C}_2\text{O}_4)_2]$ using oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$). Following the removal of precipitate by filtration, the $\text{H}_2\text{C}_2\text{O}_4$ must be removed from solution before the filtrate can be discharged to H-Canyon under one criticality-control strategy. HB-Line uses sodium permanganate (NaMnO_4) solution to oxidize $\text{H}_2\text{C}_2\text{O}_4$ to carbon dioxide (CO_2) and water. Excess NaMnO_4 , which reacts to form manganese dioxide (MnO_2) solids, is converted to soluble manganese via a reaction with sodium nitrite (NaNO_2). HB-Line Engineering requested the Savannah River National Laboratory (SRNL) to verify the quantities and addition rates of NaMnO_4 and NaNO_2 required to react excess oxalic acid and MnO_2 solids without over-pressurization of the reaction vessel.

According to the literature, the oxidation of $\text{H}_2\text{C}_2\text{O}_4$ by permanganate involves three concurrent chemical reactions. The net effect of the three reactions is that there is an observed incubation period at the outset of the process chemistry. However, as the reaction progresses, the reaction rate accelerates until the end point is reached. The end point is visibly identified by the formation of brown MnO_2 solids.

Four titration experiments at 1.0-6.0 M HNO_3 confirmed that the $\text{H}_2\text{C}_2\text{O}_4$ oxidation reaction proceeds by both the kinetics and stoichiometry reported in the literature. The data show that as NaMnO_4 is added the Na and Mn concentrations increased while the $\text{H}_2\text{C}_2\text{O}_4$ concentration decreased. However, once the $\text{H}_2\text{C}_2\text{O}_4$ was below detectable limits, the addition of NaMnO_4 caused the soluble Mn concentration to decrease (from the formation of MnO_2 solids) while the Na concentration continued to increase.

Process flowsheet testing confirmed that the reaction behavior and chemical ratios demonstrated during oxalate titration testing are applicable during conditions of continuous NaMnO_4 feeding. In seven experiments ranging from 1.4 M to 7.0 M HNO_3 , the system behavior was consistent with the reactions described in the literature.

Gas samples collected from four experiments showed less-than-detectable concentrations of H_2 gas. In each test, the gas contained air diluted with CO_2 released from the oxidation of $\text{H}_2\text{C}_2\text{O}_4$. Using baseline flowsheet feed rates for NaMnO_4 , the maximum gas generation rate per liter of reaction solution was consistently 750-800 mL/min, and was not a function of HNO_3 concentration. The quantity of gas collected was 94-95% of the theoretical value.

After the oxidation of $\text{H}_2\text{C}_2\text{O}_4$ is complete, the addition of excess NaMnO_4 yields MnO_2 solids. The filtrate must be free of solids prior to being discharged to H-Canyon. Therefore, the MnO_2 solids are dissolved through the addition of NaNO_2 solution. Experimentation confirmed that the quantity of NaNO_2 required to dissolve MnO_2 solids can be accurately calculated from the amount of excess NaMnO_4 added (present as MnO_2 solids). Experimental data show good agreement between theoretical and actual NaNO_2 addition quantities.

Periodically, the precipitator tanks will be cleaned of residual $\text{Pu}(\text{C}_2\text{O}_4)_2$ using 14 M HNO_3 . The oxalate associated with the $\text{Pu}(\text{C}_2\text{O}_4)_2$ solids will also be oxidized with NaMnO_4 . Using cerium as a surrogate for Pu, the reactions described in the literature govern the oxidation of oxalate at 1.4-7.0 M HNO_3 . At 10-14 M HNO_3 , reactions with cerium result in consumption of higher quantities of NaMnO_4 when compared to the tests at 1.4-7.0 M. Based on data in the literature, the potential exists for similar high-acid reactions when processing Pu. Therefore, precipitator clean-out solution should be diluted to 1.4-7 M HNO_3 prior to the addition of NaMnO_4 .

Quantities and flow rates of NaMnO_4 and NaNO_2 rates have been recommended for the baseline process flowsheet and the precipitator clean-out operation. A sampling strategy has also been proposed.

TABLE OF CONTENTS

LIST OF TABLES	vii
LIST OF FIGURES	vii
LIST OF ABBREVIATIONS	viii
1.0 Overview	1
1.1 Quality Assurance	1
2.0 Background	1
2.1 Chemistry	1
2.2 Process Flowsheet	2
2.3 Precipitator Tank Clean Out.....	3
3.0 Experimental Procedure.....	3
3.1 Stock Solution Preparation	3
3.2 Oxalate Titration	3
3.3 Process Flowsheet Testing	4
3.4 Precipitator Tank Clean-Out Solution	7
4.0 Results and Discussion	8
4.1 Oxalate Titration	8
4.2 Process Flowsheet Testing	10
4.2.1 Oxalate Destruction Solution Analyses	11
4.2.2 Oxalate Destruction Gas Generation	12
4.2.3 Sodium Nitrite Addition	15
4.3 Precipitator Tank Clean-Out Solution	17
5.0 Conclusions	20
5.1 Oxalate Titration	20
5.2 Process Flowsheet Testing	20
5.3 Precipitator Tank Clean-Out Solution	21
6.0 Recommendations.....	22
6.1 Baseline Process Flowsheet.....	22
6.2 Precipitator Clean-Out Operations	22
7.0 Operational Improvements.....	23
8.0 References.....	24
9.0 APPENDIX.....	25
9.1 Gas-Volume Collection Data from Process Flowsheet Tests.....	25

LIST OF TABLES

Table 3-1. Experimental Solutions for Oxalic Acid Titration.....	3
Table 3-2. Experimental Solutions for Process Flowsheet Testing	5
Table 3-3. Experimental Solutions for Precipitator Clean-Out Testing.....	7
Table 4-1. Times (M:SS) of Solution Color Observations for 1.0 M HNO ₃ Test.....	8
Table 4-2. Solution Analyses for Oxalate Titration Experiments	9
Table 4-3. Process Behavior Based on Solution Analyses	10
Table 4-4. Solution Concentrations for Process Flowsheet Tests	11
Table 4-5. NaMnO ₄ Added to Precipitate MnO ₂	11
Table 4-6. Total Gas Volumes from Process Flowsheet Testing	14
Table 4-7. Gas Analyses from Process Flowsheet Testing	15
Table 4-8. Initial and Maximum Temperatures during Process Flowsheet Testing	15
Table 4-9. Sodium Nitrite Addition Data and Calculations for Process Flowsheet Tests	16
Table 4-10. Solution Data during Sodium Nitrite Addition.....	16
Table 4-11. Sodium Nitrite Addition Data and Calculations for Precipitator Clean-Out Tests.....	19

LIST OF FIGURES

Figure 3-1. Process Flowsheet Test Equipment.....	4
Figure 3-2. Solutions after MnO ₂ Precipitation and Settling	6
Figure 3-3. Solutions after MnO ₂ Dissolution with NaNO ₂	6
Figure 4-1. Gas Generation Data for Process Flowsheet Tests.....	13
Figure 4-2. Gas Generation Rates for Process Flowsheet Tests	14
Figure 4-3. Ce(III) and Ce(IV) Oxalate in 1.4 M HNO ₃	17
Figure 4-4. Ce(III) and H ₂ C ₂ O ₄ in 10 M, 12 M, and 14 M HNO ₃	18
Figure 4-5. Ce(III) and H ₂ C ₂ O ₄ in 10 M, 12 M, and 14 M HNO ₃ after First NaMnO ₄ Aliquot	18
Figure 4-6. Ce(III) and H ₂ C ₂ O ₄ in 10 M, 12 M, and 14 M HNO ₃ after 21 NaMnO ₄ Aliquots	19
Figure 6-1. Comparison of MnO ₂ Solids (left) and Pu(IV) Oxalate Solids (right)	23

LIST OF ABBREVIATIONS

DI	deionized
GC	gas chromatography
ICPES	inductively coupled plasma emission spectroscopy
IC	ion chromatography
rpm	revolutions per minute
SRNL	Savannah River National Laboratory

1.0 Overview

During HB-Line Pu-239 operations, plutonium (Pu) is precipitated as plutonium(IV) oxalate $[\text{Pu}(\text{C}_2\text{O}_4)_2]$ using oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$). An excess amount of $\text{H}_2\text{C}_2\text{O}_4$ is used. Following the removal of precipitate by filtration, the filtrate is discharged to H-Canyon. The receipt tank for the filtrate in H-Canyon is not geometrically favorable. With $\text{H}_2\text{C}_2\text{O}_4$ present, the potential exists for the precipitation of $\text{Pu}(\text{C}_2\text{O}_4)_2$ in the H-Canyon receipt tank; this presents a criticality-control concern. One mitigating strategy entails oxidizing the excess $\text{H}_2\text{C}_2\text{O}_4$ with sodium permanganate (NaMnO_4) in HB-Line. A second reaction employed in the flowsheet is the reaction of sodium nitrite (NaNO_2) with excess NaMnO_4 to eliminate the presence of manganese dioxide (MnO_2) solids which form as a result of excess NaMnO_4 addition.

A previous HB-Line flowsheet for Pu-239 operations incorporated an $\text{H}_2\text{C}_2\text{O}_4$ destruction step using permanganate.^[1] However, the reference flowsheet accounted for the presence of hydrazine and ascorbic acid in solution with the excess $\text{H}_2\text{C}_2\text{O}_4$. The current HB-Line flowsheet omits hydrazine and ascorbic acid, and precipitates plutonium as Pu(IV) oxalate instead of Pu(III).^[2] It is expected that the flowsheet volumes and addition rates for NaMnO_4 can be adjusted to yield a more efficient process and result in waste minimization.

HB-Line Engineering requested the Savannah River National Laboratory (SRNL) to investigate the applicability of the previous oxalate destruction chemistry to the current flowsheet.^[3] The SRNL investigation should verify both the quantities and addition rates of NaMnO_4 and NaNO_2 required to completely react excess oxalic acid and MnO_2 solids without over-pressurization of the reaction vessel.

1.1 Quality Assurance

The task technical approach and quality assurance requirements are described in a Task Technical and Quality Assurance Plan.^[4] 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.

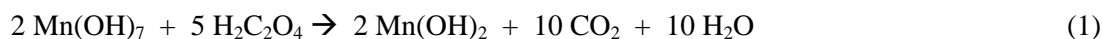
2.0 Background

The $\text{H}_2\text{C}_2\text{O}_4$ destruction reaction depends upon the reaction of permanganate ion $[\text{MnO}_4^-]$ with $\text{H}_2\text{C}_2\text{O}_4$. Previous studies at SRNL observed the oxidation of $\text{H}_2\text{C}_2\text{O}_4$ in a solution that also included the presence of hydrazine and ascorbic acid.^{[5][6]} The specific reaction of permanganate with $\text{H}_2\text{C}_2\text{O}_4$ was obscured by reactions of permanganate with the other components, particularly the ascorbic acid. The work by Gray^[6] became the basis for the HB-Line Pu-239 processing flowsheets.^{[1][2]}

In this study, two types of experiments were performed to evaluate the flowsheet – titrations and process flowsheet tests. Titrations involve the careful addition of one compound to another where the end point of the reaction is depicted by a physical change, such as color or the appearance of a precipitate. Process flowsheet tests approximated the process conditions and flow rates of the HB-Line process as a means of validating the flowsheet. Ten titrations and nine process flowsheet tests were completed.

2.1 Chemistry

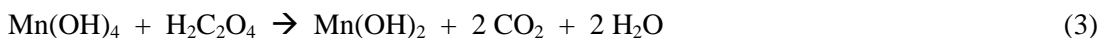
According to the literature, the oxidation of $\text{H}_2\text{C}_2\text{O}_4$ by permanganate $[\text{MnO}_4^- \text{ or } \text{Mn(VII)}]$ involves three concurrent chemical reactions.^[7] The first reaction is the reaction of Mn(VII) directly with $\text{H}_2\text{C}_2\text{O}_4$ to form the manganese (II) ion, carbon dioxide (CO_2), and water (H_2O). This first reaction is slow. Although Mn ions will take a different form in HNO_3 , the first reaction has been written according to the conventions of the literature article as Reaction 1.^[7]



The second reaction requires the presence of the Mn(II) ion [written as the Mn(OH)₂ species]. It involves the reaction of Mn(VII) with Mn(II) to yield manganese dioxide [shown as the Mn(OH)₄ species in the literature article for Reaction 2]. Reaction 2 is a very fast reaction.^[7]

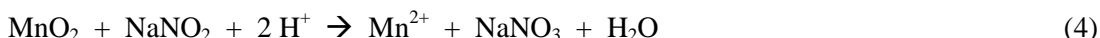


The third reaction is the oxidation of oxalic acid by MnO₂ [Mn(IV)]. The reaction, shown as Reaction 3, is also a fast reaction, but not as fast as Reaction 2.^[7]

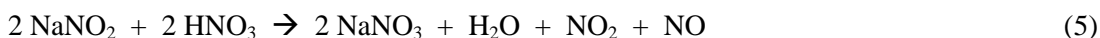


The combination of Reactions 2 and 3 yields Reaction 1; however, Reactions 2 and 3 occur at a much faster rate than Reaction 1. The net effect of the three reactions is that there is an observed incubation period at the outset of the process chemistry while Reaction 1 occurs and provides a source of Mn(II) for Reactions 2 and 3. It has been observed that the overall reaction rate increases as H₂C₂O₄ is oxidized due to the increasing Mn(II) concentration for Reaction 2. Last, Reaction 2 depicts that at the conclusion of the reaction, when all H₂C₂O₄ has been consumed, excess Mn(VII) will react rapidly with Mn(II) to form MnO₂ solids, which are brown. There will be no measurable excess Mn(VII) until all of the Mn(II) has been converted to MnO₂ via Reaction 2. Therefore, driving the reaction to a condition of measureable excess Mn(VII) is not necessary.

The reaction for dissolving MnO₂ with NaNO₂ is as follows.^[5]



A competing reaction for NaNO₂, particularly in high-acid conditions, decomposes NaNO₂ and is accompanied by the release of brown nitrogen dioxide (NO₂) gas. The NO gas generated by the reaction is converted to NO₂ by reaction with oxygen gas in the air.



2.2 Process Flowsheet

The proposed flowsheet for Pu recovery operations will yield a filtrate solution of 58.8 liters with 1.4 M nitric acid (HNO₃) and 0.1 M H₂C₂O₄. Based on the results from Gray^[6], the proposed flowsheet assumed that three moles of H₂C₂O₄ react with two moles of NaMnO₄ to yield two moles of MnO₂ plus CO₂ and water (H₂O); excess NaMnO₄ (10%) would also be added. Excess NaMnO₄ and MnO₂ are then reacted with NaNO₂ to produce the Mn(II) ion. The amount of NaNO₂ added is based on adding one mole of NaNO₂ per mole of MnO₂ and 2.5 moles of NaNO₂ per mole of unreacted NaMnO₄ plus 25% excess.

Based on these flowsheet assumptions, there will be 5.88 moles of H₂C₂O₄ in the filtrate solution. Based on previous assumptions,^[6] to that would be added 3.92 moles of NaMnO₄ to react the H₂C₂O₄ and 10% excess, or 0.39 moles of NaMnO₄ (total of 4.31 moles NaMnO₄). The reaction would yield 3.92 moles of MnO₂ and 0.39 moles of unreacted NaMnO₄. The MnO₂ would be reacted with 3.92 moles of NaNO₂ and the excess NaMnO₄ would be reacted with 0.98 moles of NaNO₂, or 4.90 moles of NaNO₂. Allowing for 25% excess (1.22 moles), the total NaNO₂ added would be 6.12 moles.

However, based on Reactions 1-3,^[7] the decomposition of 5.88 moles of H₂C₂O₄ requires 2.35 moles of NaMnO₄ plus 0.24 moles excess, or 2.59 moles total NaMnO₄ (compared to 4.31 moles above). The reaction of MnO₂ and NaMnO₄ to Mn(II) requires 2.59 moles of NaNO₂ plus 0.74 moles excess, or 3.33 moles total NaNO₂ (compared to 6.12 moles above).

2.3 Precipitator Tank Clean Out

Periodically, the precipitator tanks will have to be cleaned of residual $\text{Pu}(\text{C}_2\text{O}_4)_2$. The proposed solution for clean out is 14 M HNO_3 . Clean out of the precipitator will occur when the accountability system calculates the presence of 360 g of Pu in the precipitator tank, or sooner as needed. To protect against a maximum Pu concentration of 60 g/L, the volume of solution used for the precipitator tank clean out will be 12 liters, resulting in an expected Pu concentration of less than 30 g/L. The oxalate associated with these $\text{Pu}(\text{C}_2\text{O}_4)_2$ solids must be oxidized in a manner similar to what was described in Section 2.2. It is not known if Reactions 1-3 will apply to the oxidation of $\text{Pu}(\text{C}_2\text{O}_4)_2$ in 14 M HNO_3 . The precipitator tank clean out steps will be repeated until the tank has been adequately cleared of residual Pu precipitate.

3.0 Experimental Procedure

3.1 Stock Solution Preparation

Two stock solutions were prepared for the majority of the experiments. The first solution was 40 wt % $\text{NaMnO}_4\text{-H}_2\text{O}$ in deionized (DI) water (H_2O). I weighed 27.1823 g of $\text{NaMnO}_4\text{-H}_2\text{O}$ (Strem Chemicals, 98% min. purity) into a glass jar. To the jar was added 40.8020 g of DI H_2O and a TeflonTM-coated stir bar. The jar was covered and the contents stirred for more than 24 h. Five individual 5.00-mL aliquots of the jar were withdrawn and weighed. The average weight of the five samples was 6.6194 g (density of 1.324 g/mL). Based on the density, the calculated concentration of the NaMnO_4 solution was 3.31 M. The glass jar was stored in a stainless steel beaker to limit light into the glass jar.

The second stock solution was 5.65 M NaNO_2 . I added 19.4920 g of NaNO_2 (Fisher Scientific, 99.6% purity) to a 50-mL volumetric flask and filled the flask with DI H_2O to the line. A micro stir bar was added to the flask and the flask stirred until the contents dissolved. The stir bar was removed and the volume in the flask brought up to the 50-mL line using DI H_2O . The flask was capped and shaken to yield a uniform mixture.

3.2 Oxalate Titration

In the first phase of testing, four solutions of 0.15 M $\text{H}_2\text{C}_2\text{O}_4\text{-2H}_2\text{O}$ in HNO_3 were titrated with NaMnO_4 to compare behavior with that reported in the literature.^[7] Three HNO_3 concentrations were tested in parallel – 1.5 M, 4.0 M, and 6.0 M. Three experimental solutions were prepared in 100-mL volumetric flasks by combining the contents listed in Table 3-1. A fourth experiment was performed afterwards at 1.0 M HNO_3 . All solids were completely dissolved prior to titration.

Table 3-1. Experimental Solutions for Oxalic Acid Titration

HNO_3 (M)	$\text{H}_2\text{C}_2\text{O}_4\text{-2H}_2\text{O}$ (g)	15.7 M HNO_3 (mL)	DI H_2O (mL)
1.5	1.8928	9.6	To 100 mL
4.0	1.8923	25.5	To 100 mL
6.0	1.8920	38.2	To 100 mL
1.0	3.7856	12.7	To 200 mL

The three solutions were placed into individual 250-mL Erlenmeyer flasks along with a TeflonTM-coated stir bar. The 1.0 M solution was placed into a 1000-mL beaker. Each container was placed on a hot plate-stirrer and the stirrer speed set to 300 rpm (revolutions per minute). No heating was applied to the solution. Calculations determined that 1810 μL of 3.31 M NaMnO_4 stock solution would be required to completely convert the $\text{H}_2\text{C}_2\text{O}_4$ to CO_2 and H_2O according to Reactions 1-3 (3620 μL for 1.0 M test). Therefore, NaMnO_4 solution was added to each flask in 90.5 μL aliquots (181.0 μL for the 1.0 M test).

using a Rainin 1000 μL adjustable pipette. The setting of the pipette was verified every 15-20 aliquots by pipetting DI H_2O from a beaker on a balance and weighing the mass of water removed by the pipette. The pipette setting was stable throughout the experiments.

For each aliquot added, when the NaMnO_4 enters the solution, the solution turns either dark purple or dark brown. Typically, within three minutes of introducing an aliquot, the solution clears. When the solution clears, another aliquot of NaMnO_4 is added to the flask. After 10 aliquots, a sample was collected from each flask for analysis by ion chromatography (IC) for anions and inductively coupled plasma emission spectroscopy (ICPES) for cations. When the dark brown color persisted past three minutes, the end point of the reaction was reached, and a sample collected. An additional 10% excess NaMnO_4 was then added, the solution stirred for more than three minutes, and the solution sampled.

3.3 Process Flowsheet Testing

Process flowsheet testing entailed repeating the general approach discussed in Section 3.2. Differences included 1) the NaMnO_4 was metered in using a syringe pump, 2) the solution temperature was monitored, 3) the gas generation volume was measured, and 4) cerium (Ce) was used as a surrogate for Pu. The apparatus is shown in Figure 3-1.

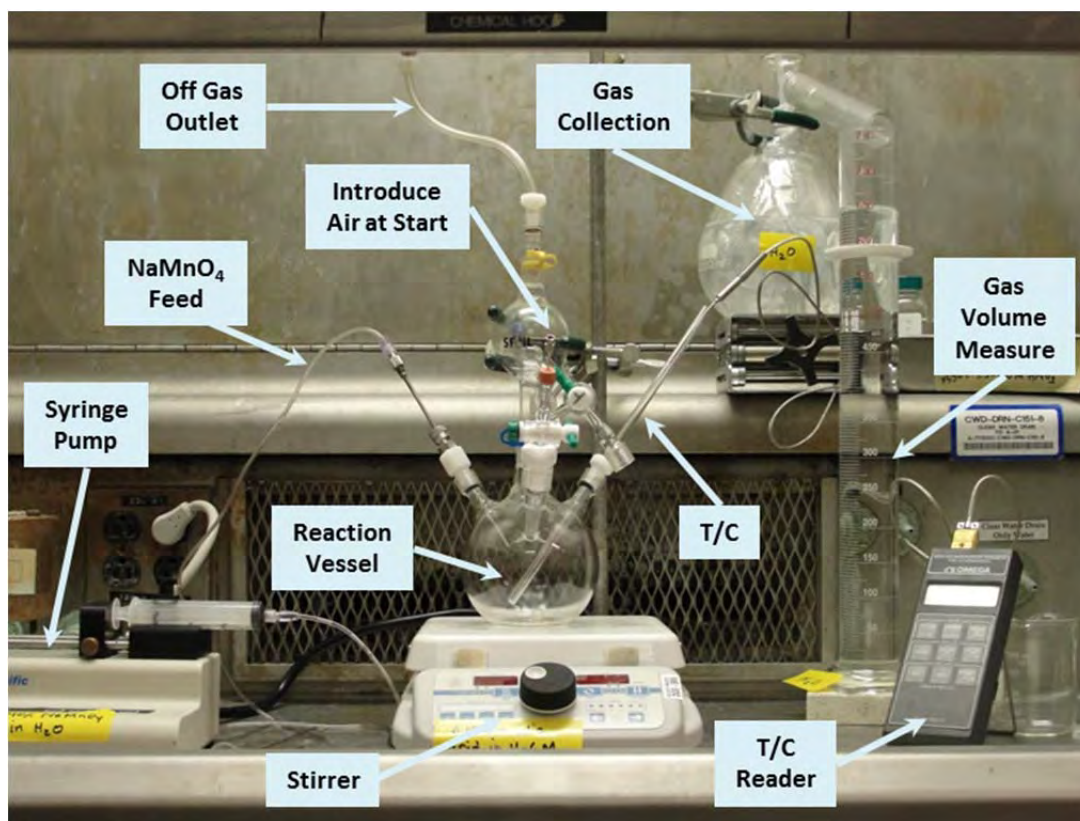


Figure 3-1. Process Flowsheet Test Equipment

Temperature was measured using a Type K thermocouple connected to an Omega Engineering Model HH22 thermocouple reader. Sodium permanganate solution was fed to the reaction vessel using a KD Scientific Model 780100 syringe pump. The syringe was fabricated from high density polyethylene. The NaMnO_4 feed line into the reaction vessel was 304 L stainless steel. The tubing between the syringe and

stainless steel feed line was made of clear Tygon™. Gas was collected in a Tedlar™ bag, and the gas volume was measured using water displacement to a graduated cylinder.

Eight experiments were conducted in the following manner. Each test solution was prepared separately by combining $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (0.15 M), cerous nitrate $[\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$, 15.7 M HNO_3 , and DI water to the 100-mL mark in a 100-mL volumetric flask according to the amounts listed in Table 3-2. Test P7 simulates process operations in which a tank heel from the previous oxalate-kill operation is mixed with the incoming filtrate solution. Similarly, Test P8 simulates process operations in which a tank heel from a previous precipitator clean-out operation is mixed with the incoming filtrate solution.

When all solids were dissolved, the contents of the flask were added to the reaction vessel (Figure 3-1). The stirrer speed was set to 300 rpm. Stock NaMnO_4 solution was drawn into the syringe through the entire feed line and the NaMnO_4 feed assembly was attached to the apparatus. For Test P5, the NaMnO_4 feed was prepared by dissolving 2.6380 g of $\text{NaMnO}_4 \cdot \text{H}_2\text{O}$ in water to a final volume of 10 mL. The system was sealed. Using a sealed gas syringe attached to a side port, air was introduced into the system until water overflowed from the gas collection flask into the gas volume measurement flask. The system was then sealed again.

Table 3-2. Experimental Solutions for Process Flowsheet Testing

Test #	Test Order	$\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (g)	$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (g)	15.7 M HNO_3 (mL)	Extra Solution	NaMnO_4 (M)	NaMnO_4 Rate (mL/h)
P1	1	1.8938	---	25.5	---	3.31	11.8
P2	2	1.8918	---	9.6	---	3.31	11.8
P3	3	1.8936	---	38.2	---	3.31	11.8
P4	4	1.8918	---	8.9	---	3.31	3.9
P5	8	1.8917	---	8.9	---	1.65	11.8
P6	5	1.9010	0.0174	8.9	---	3.31	11.8
P7	7	1.8923	---	8.9	9.1 mL from Test P4	3.31	11.8
P8	6	1.8927	---	8.9	9.1 mL of 14 M HNO_3	3.31	11.8
P9*	9	1.9990	4.1809	35.8	---	3.31	11.8
* Described in Section 3.4 (solution volume = 80 mL)							

Flow of NaMnO_4 solution was initiated by starting the syringe pump. When the first drop of NaMnO_4 was noted in the reaction vessel, the experiment timer was started and the total volume of feed noted on the pump display was recorded. Temperature and gas volume data were collected frequently (typically every 15 seconds). When the solution in the reaction vessel ceased reacting with the NaMnO_4 feed, the total feed on the pump display was recorded. Ten percent excess NaMnO_4 was added to the reaction vessel before NaMnO_4 feed was discontinued and the total volume of feed on the pump display recorded.

The syringe was emptied of NaMnO_4 stock solution into the original storage bottle, and the feed line was cleaned with DI H_2O and air until the line was clear. For Tests P1, P2, P3, P6, P7, and P8, end solution samples were collected for IC anion and ICPEs. For Tests P1, P2, and P3, gas samples were collected for analysis by gas chromatography (GC). The remaining test solution for each experiment was stored in a separate glass jar. At this stage of testing, each test solution contained MnO_2 solids which, if agitated, made the solution dark brown. Figure 3-2 shows the solutions from Tests P1 (4.0 M HNO_3), P2 (1.5 M HNO_3), and P3 (6.0 M HNO_3) after MnO_2 precipitated and settled.

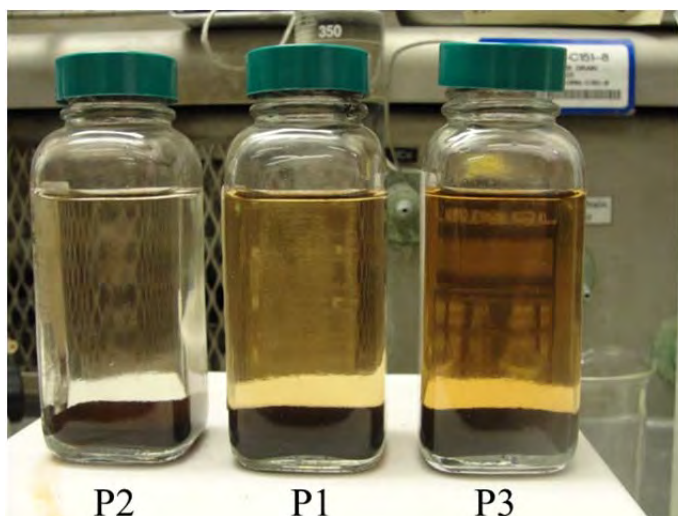


Figure 3-2. Solutions after MnO₂ Precipitation and Settling

The resulting test solutions were subsequently reacted with the 5.65 M NaNO₂ stock solution until the MnO₂ solids dissolved. For Tests P1, P2, and P3, the NaNO₂ solution was added using a pipette with intermittent sampling for IC anions and ICPES. With Test P1, 197.5 μ L of NaNO₂ was added, a sample collected, two 197.5- μ L aliquots of NaNO₂ were added, a sample collected, and 100 μ L of NaNO₂ added followed by sampling. For Test P2, two 80.5- μ L aliquots of NaNO₂ were added, a sample collected, four 80.5- μ L aliquots of NaNO₂ were added, a sample collected, and 100 μ L of NaNO₂ added followed by sampling. In Test P3, three 78.0- μ L aliquots of NaNO₂ were added, a sample collected, four 78.0- μ L aliquots of NaNO₂ were added, a sample collected, and 100 μ L of NaNO₂ added followed by sampling. In each of the above tests, the second sample corresponded to the complete dissolution of the MnO₂ solids. The test solutions following MnO₂ dissolution are depicted in Figure 3-3.

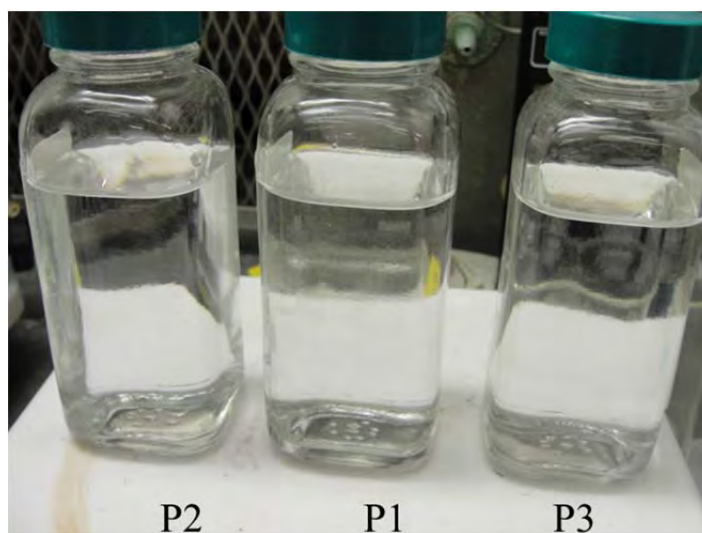


Figure 3-3. Solutions after MnO₂ Dissolution with NaNO₂

For Tests P4-P8, NaNO_2 solution was added using a burette. Sodium nitrite solution was added until the MnO_2 solids disappeared, a sample was collected for IC and ICPEs, 25% excess NaNO_2 was added, and a final sample collected. For Test P8, only an end sample was collected. For Test P5, no samples were obtained during NaNO_2 addition.

3.4 Precipitator Tank Clean-Out Solution

Experiments evaluating the behavior of the precipitator clean-out solution are variations of the titration tests described in Section 3.2 and the process flowsheet tests described in Section 3.3. The principle variation for precipitator clean-out tests is the presence of significant quantities of Ce, a surrogate for Pu, in the $\text{HNO}_3\text{-H}_2\text{C}_2\text{O}_4$ solution. Quantities of Ce simulate the molar equivalent of 57.1 g/L Pu for tests with Ce(III) and 42.8 g/L Pu for the test with Ce(IV). Cerium (III) was added as $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ (Alfa-Aesar, 99.5% purity); the source for Ce(IV) was ceric ammonium nitrate $[(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6]$ (J. T. Baker, 99.8% purity). Quantities of $\text{H}_2\text{C}_2\text{O}_4$ were based on the precipitating oxalate species plus 10% molar excess; the $\text{H}_2\text{C}_2\text{O}_4$ concentration was maintained for each test.

Six titration tests and one process flowsheet test were completed. The chemical make-up of each titration test, prepared, is shown in Table 3-3. In each test, a portion of the acid was used to dissolve the $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ and the remainder of the acid was used to dissolve the Ce salt. Once both components dissolved completely, the two acid solutions were combined. The volume was adjusted to 50 mL, and the solution stirred for 15-30 min to allow precipitation to occur. The $\text{H}_2\text{C}_2\text{O}_4$ was then reacted with 3.31 M NaMnO_4 , which was pipetted into the solution in 120 μL aliquots. As described in Section 3.2, the end point was determined by the persistence of a brown MnO_2 precipitate in the solution. When the end point was achieved, samples were obtained for analysis by IC anion and ICPEs.

Table 3-3. Experimental Solutions for Precipitator Clean-Out Testing

Test	$\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ (g)	$\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ (g)	$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ (g)	HNO_3 (M)
A	2.4844	5.1846	---	1.4
B	2.4837	---	4.9065	1.4
C	2.4868	5.1815	---	10.0
D	2.4870	5.1821	---	12.0
E	2.4860	5.1817	---	14.0
F	2.4874	5.1834	---	14.0 \rightarrow 7.0*
* Solution initially prepared as 50 mL of 14.0 M HNO_3 and then diluted with 50 mL DI H_2O to 7.0 M				

Tests C-F were subsequently reacted with 5.65 M NaNO_2 in 25 μL aliquots until the brown MnO_2 solids dissolved. No samples were collected after addition of NaNO_2 .

Test P9 was a process flowsheet test run in a manner similar to that described in Section 3.3 using solution concentrations similar to Test F. The test solution (40 mL) was prepared by combining 1.9990 g $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$, 4.1809 g $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$, 35.8 mL 15.7 M HNO_3 and DI H_2O to 40 mL. The solution was mixed for 15 min at 300 rpm. To this solution was added 40 mL of DI H_2O followed by an additional 30 min of stirring.

The oxalate in Test P9 was then reacted with 3.31 M NaMnO_4 fed by the syringe pump at 11.8 mL/h. The gas from the reaction was collected. The temperature and gas release volume were recorded in 15-60 second intervals. After the end point was reached, 10% excess NaMnO_4 was added. At this point of the

test, the solution contained sufficient MnO_2 solids to make the solution dark brown when agitated. The process solution with excess NaMnO_4 was subsequently reacted with 5.65 M NaNO_2 until the MnO_2 solids dissolved completely. Since no samples were collected, no excess NaNO_2 was added.

4.0 Results and Discussion

4.1 Oxalate Titration

Calculations based on Reactions 1-3 determined that 1810 μL should be required to completely oxidize the $\text{H}_2\text{C}_2\text{O}_4$ in solution. This quantity was arbitrarily divided by 20 to arrive at a targeted aliquot of 90.5 μL so that each aliquot could theoretically consume 5% of the $\text{H}_2\text{C}_2\text{O}_4$. In all three experiments, brown MnO_2 solids persisted in the solution (Figure 3-2) after addition of the 21st aliquot, indicating the oxalate had been completely consumed. Two aliquots of excess were added (for a total of 23) after the end point was achieved.

Visual observations of the oxalate titration experiments indicate that the reactions discussed in Section 2.1 represent the system behavior. For all three tests – 1.5 M, 4.0 M, and 6.0 M HNO_3 – the initial system behavior is described by Reaction 1. When the first aliquot of NaMnO_4 was added to each solution, the solution remained dark purple for one to two minutes before changing color; the higher acid concentrations cleared faster than the 1.5 M HNO_3 test. This response is consistent with the literature which states that Reaction 1, the direct reaction of NaMnO_4 with $\text{H}_2\text{C}_2\text{O}_4$, is a slow reaction.^[7]

Each subsequent aliquot of NaMnO_4 cleared faster than the previous addition. The reaction kinetics change because, according to Reactions 2 and 3, which are both fast reactions, the accumulation of Mn(II) in solution facilitates rapid oxidation of $\text{H}_2\text{C}_2\text{O}_4$ by MnO_2 . Consistent with Reactions 2 and 3, the purple color attributed to Mn(VII) changes to brown (MnO_2), and then the solution clears. By about the 15th (out of 21) aliquot, the disappearance of the purple and brown colors occurs in less than five seconds.

The behavior can be understood better from the data in Table 4-1. The data depict the approximate time at which the solution becomes a particular color. The data is arbitrary as the transition from purple to brown contains a mixture of both. A similar point can be made with regard to the brown-to-clear transition as there are periods where the solution color is yellow or beige. Regardless, the effect of the ingrowth of Mn(II) from Reaction 1 and the prominence of Reactions 2 and 3 in the latter stage of the experiment is unmistakable.

Table 4-1. Times (M:SS) of Solution Color Observations for 1.0 M HNO_3 Test

Aliquot	Purple	Brown	Clear
1	0:01	3:30	7:30
6	0:01	0:35	3:15
11	0:01	0:10	1:45
16	n/a	0:01	0:45
20	n/a	0:01	0:25
21	n/a	0:01	n/a

Samples were collected from each test solution after 0, 10, 15, 21, and 23 aliquots. All were analyzed by IC anion. Aliquots 10, 21, and 23 were analyzed by ICPEs. The data are reported in Table 4-2. The calculated initial oxalate ion concentration is ~13,200 mg/L (0.15 M).

Table 4-2. Solution Analyses for Oxalate Titration Experiments

HNO₃ (M)	Aliquot	C₂O₄²⁻ (mg/L)* [M]	NO₃⁻ (mg/L)* [M]	Mn (mg/L)[#] [M]	Na (mg/L)[#] [M]
1.0	0	12,500 [0.142]	62,300 [1.00]	---	---
	10	5930 [0.067]	61,600 [0.99]	1690 [0.0308]	794 [0.0346]
	15	2510 [0.029]	61,900 [1.00]	2510 [0.0457]	1150 [0.0500]
	21	<100 [0.001]	60,200 [0.97]	3540 [0.0644]	1650 [0.0718]
	23	<100 [0.001]	59,000 [0.95]	2990 [0.0544]	1760 [0.0766]
1.5	0	13,200 [0.150]	93,500 [1.51]	---	---
	10	5990 [0.068]	91,200 [1.47]	1630 [0.0297]	<1230 [<0.0535]
	15	2380 [0.027]	90,300 [1.46]	---	---
	21	<100 [0.001]	89,000 [1.44]	3170 [0.0577]	1540 [0.0670]
	23	<100 [0.001]	88,600 [1.43]	2660 [0.0484]	1640 [0.0714]
4.0	0	12,800 [0.145]	248,000 [4.00]	---	---
	10	5940 [0.068]	252,000 [4.06]	1620 [0.0295]	<1230 [<0.0535]
	15	2290 [0.026]	244,000 [3.94]	---	---
	21	<100 [0.001]	246,000 [3.97]	3160 [0.0575]	1520 [0.0661]
	23	<100 [0.001]	245,000 [3.95]	2660 [0.0484]	1670 [0.0727]
6.0	0	13,200 [0.150]	372,000 [6.00]	---	---
	10	5730 [0.065]	372,000 [6.00]	1620 [0.0295]	<1230 [<0.0535]
	15	2240 [0.025]	365,000 [5.89]	---	---
	21	<100 [0.001]	365,000 [5.89]	3110 [0.0566]	1490 [0.0648]
	23	<100 [0.001]	363,000 [5.85]	2550 [0.0464]	1650 [0.0718]
* Measured by IC Anion (method uncertainty = 10%)					
[#] Measured by ICPEs (method uncertainty = 10%)					

The data enable several conclusions. Analysis of the starting (Aliquot 0) oxalate and nitrate concentrations confirms that the solutions were prepared correctly. Similarly, for the analysis of Mn, calculations indicate that ten aliquots of 3.31 M NaMnO₄ into 100 mL of solution should yield a Mn concentration of 1631 mg/L (see Table 4-3). The analyses of Na are 105-109% of what is expected based on a NaMnO₄ concentration of 3.31 M, but are within the analytical method uncertainty of 10%.

Table 4-3 compares measured versus calculated values for C₂O₄²⁻ and Mn concentrations. A comparison of the measured versus calculated values for Mn shows that at 10 aliquots, as discussed above, the measured and calculated values are the same. After 21 aliquots, the measured Mn is slightly lower than the calculated value, presumably due to MnO₂ precipitation, although the difference is within the analytical method uncertainty. However, after 23 aliquots, the measured Mn decreased and is much lower than the amount added, which is clear evidence that soluble Mn(VII) is being converted to insoluble Mn(IV) according to Reaction 2.

Table 4-3. Process Behavior Based on Solution Analyses

HNO ₃ (M)	Aliquot	C ₂ O ₄ ²⁻ (M)*	Mn (M)	Calc Mn Added (M)	Δ C ₂ O ₄ ²⁻ (M)	Δ C ₂ O ₄ ²⁻ based on Mn Added (M)
1.0	0	0.142	---	---	---	---
	10	0.067	0.0308	0.0297	-0.0747	-0.0742
	21	<0.001	0.0644	0.0617	-0.141	-0.154
	23	<0.001	0.0544	0.0675	---	---
1.5	0	0.150	---	---	---	---
	10	0.068	0.0297	0.0297	-0.0819	-0.0742
	21	<0.001	0.0577	0.0617	-0.149	-0.154
	23	<0.001	0.0484	0.0675	---	---
4.0	0	0.145	---	---	---	---
	10	0.068	0.0295	0.0297	-0.0780	-0.0742
	21	<0.001	0.0575	0.0617	-0.144	-0.154
	23	<0.001	0.0484	0.0675	---	---
6.0	0	0.150	---	---	---	---
	10	0.065	0.0295	0.0297	-0.0849	-0.0742
	21	<0.001	0.0566	0.0617	-0.149	-0.154
	23	<0.001	0.0464	0.0675	---	---
* Based on mass of H ₂ C ₂ O ₄ ·2H ₂ O, the concentrations at Aliquot 0 are 0.150 M						

The change in measured C₂O₄²⁻ versus calculated C₂O₄²⁻ suggests that the change in oxalate concentration after 10 aliquots was 105-114% of the expected amount based on Reactions 1-3 and the amount of Mn added; it was 91-97% of the theoretical amount after 21 aliquots. A difference of 14% is outside of the individual method uncertainties of 10%. However, visual observations for all three test solutions indicated that they reached their end points within one aliquot (5%) of excess NaMnO₄. The difference between the measured and calculated concentrations after 10 aliquots might be due to oxalate forming intermediate compounds not measured by IC anion which, nonetheless, consume Mn(VII) and Mn(IV) as part of Reactions 1 and 3. The literature proposes several pathways for the oxidation of oxalate by permanganate.^[7]

4.2 Process Flowsheet Testing

Process flowsheet testing, in which NaMnO₄ solution is pumped continuously into a solution of HNO₃-H₂C₂O₄, had several objectives. Among these objectives were 1) correlate the observations from titration testing (Section 4.1) with continuous processing, 2) confirm complete oxidation of C₂O₄²⁻ in solution, 3) measure gas generation volumes as a function of time, 4) analyze the off gas for hydrogen (H₂) gas, and 5) establish a protocol for process implementation in HB-Line. Process flowsheet testing also included experiments to determine the quantity of NaNO₂ required for digestion of residual MnO₂ solids at the conclusion of the C₂O₄²⁻ conversion reaction.

The overall reaction behavior for the process flowsheet tests mirrored those of the titration experiments. The reaction behavior reflected in the data of Table 4-1 described the solution characteristics during continuous NaMnO₄ addition. At first, the solution is only purple (except for Test P7). It gradually shifts to a mixture of purple and brown. After about half of the NaMnO₄ has been added, the purple associated with new NaMnO₄ additions disappears almost instantly. Eventually, the solution ceases to be brown and fluctuates between yellow-beige (when NaMnO₄ drops recently entered the reaction vessel) and clear.

When the $\text{H}_2\text{C}_2\text{O}_4$ reaction end point is reached, the solution quickly turns brown due to the presence of MnO_2 , which readily settle (Figure 3-2) in the absence of agitation.

4.2.1 Oxalate Destruction Solution Analyses

Data analyses in Section 4.1 demonstrated that $\text{C}_2\text{O}_4^{2-}$ is not present in solution when MnO_2 solids form and persist. Because the process flowsheet tests were concerned with measurement of gas volumes, the system was not opened up for sampling at the perceived end point of the $\text{C}_2\text{O}_4^{2-}$ reaction. Samples were obtained from Tests P1, P2, P3, P6, P7, and P8 after 10% excess NaMnO_4 was added. The analyses are listed in Table 4-4. The analyses demonstrate that $\text{C}_2\text{O}_4^{2-}$ is reacted to below the method detection limit. The nitrate concentrations are consistent with the solution preparation. The final Mn and Na concentrations are comparable to those reported in Table 4-2 after 23 aliquots.

Table 4-4. Solution Concentrations for Process Flowsheet Tests

Test #	$\text{H}_2\text{C}_2\text{O}_4$ (M)	HNO_3 (M)	$\text{C}_2\text{O}_4^{2-}$ (mg/L)	NO_3^- (mg/L)	NO_2^- (mg/L)	NaMnO_4 (mmol)	Mn (mg/L)	Na (mg/L)
P1	0.150	4.0	<100	264,000	<100	7.18	2370	1730
P2	0.150	1.5	<100	94,000	<100	7.12	2370	1660
P3	0.150	6.0	<100	358,000	<100	7.35	2470	1690
P6	0.151	1.4	<100	85,500	<100	7.32	2030	1630
P7	0.150	1.4	<100	88,500	<100	7.02	2370	1770
P8	0.150	2.4	<100	147,000	<100	10.3	1790	1550

With each test, the pump display volumes were noted when the first drop of NaMnO_4 was introduced into the reaction and when precipitation of MnO_2 occurred and persisted. Consequently, the total mass of NaMnO_4 required to completely oxidize $\text{C}_2\text{O}_4^{2-}$ can be calculated. The data are presented in Table 4-5. Of particular interest is the last column of the table. The data for Tests P1, P2, P3, P4, P5, and P7 are consistently at a $\text{H}_2\text{C}_2\text{O}_4$ - NaMnO_4 mole ratio of 2.26-2.37; even Test P6, which had a slight irregularity, is of a similar mole ratio. The amount of NaMnO_4 added exceeded the theoretical minimum required since the ratios are slightly less than the stoichiometric value of 2.5. This indicates that the system is slightly past the end point when MnO_2 forms and persists.

Table 4-5. NaMnO_4 Added to Precipitate MnO_2

Test Order	Test #	$\text{H}_2\text{C}_2\text{O}_4$ (M)	HNO_3 (M)	NaMnO_4 (M)	NaMnO_4 to Ppt. (mL)	Mol $\text{H}_2\text{C}_2\text{O}_4$: Mol NaMnO_4
1	P1	0.150	4.0	3.31	1.95	2.33
2	P2	0.150	1.5	3.31	1.93	2.35
3	P3	0.150	6.0	3.31	2.01	2.26
4	P4	0.150	1.4	3.31	1.91	2.37
5	P6	0.151	1.4	3.31	1.98	2.30
6	P8	0.150	2.4	3.31	2.06*	2.20
7	P7	0.150	1.4	3.31	1.92	2.36
8	P5	0.150	1.4	1.65	5.79	1.57
9	P9	0.159	7.0	3.31	2.85	1.68
* Several bubbles in NaMnO_4 feed line during first two minutes of feeding						

The mole ratios for Tests P5 and P9 (Table 4-5) are notably lower. It is believed that there was partial plugging of the discharge side of the NaMnO_4 feed line which distorted the actual volume of NaMnO_4 fed. The impact of the feed line was particularly noted during Test P9 when there was a period where the flow was temporarily interrupted and noticeably slower thereafter. This behavior is readily correlated with the off gas data presented below. In retrospect, based on the data in Table 4-5 and the off gas data discussed below, Test P5 was impacted by a similar issue. The line clean-out activity with water and air between Tests P5 and P9 was not sufficient.

4.2.2 Oxalate Destruction Gas Generation

The complete list of gas generation data is provided in Appendix 9.1. The data are plotted in Figure 4-1. The data are plotted as a function of equivalent NaMnO_4 addition rates. What this means is that for Test P4, in which the NaMnO_4 feed rate was one-third that of the baseline rate, the pump times in Appendix 9.1 are divided by three to allow a direct comparison with the baseline feed rate. Similarly, for Test P5, in which the NaMnO_4 feed concentration was one-half that of the baseline rate, the pump times in Appendix 9.1 are divided by two to allow a direct comparison with the baseline feed concentration.

Several conclusions can be drawn from Figure 4-1. First, Tests P2, P3, P6, P7, and P8 have comparable gas-generation profiles. Test P1 probably would have been similar to those five tests except that a couple of drops from the feed tube got into the reaction vessel during assembly. Consequently, although the gas generation for Test P1 (4.0 M HNO_3) appears to begin sooner than Tests P2 (1.5 M) and P3 (6.0 M), this is likely an artifact of the operator technique during the first process flowsheet experiment.

A comparison of Tests P2 and P7 shows little difference in the gas-generation profiles. Test P2 was a baseline experiment at 1.5 M HNO_3 . Test P7 contained a 9.1 mL “heel” from Test P4. The premise was that the heel from Test P4 would contain both Mn(II) and residual NaNO_2 . As a result, the presence of the heel would cause Reaction 2 and 3 to occur sooner in Test P7 than in Test P2, and that the difference would be evident in a comparison of the gas-generation profiles. During Test P7, the NaMnO_4 added to the reaction vessel turned from purple to brown almost immediately (compared to 2-3 min for Test P2). Also, the gas-generation profile for Test P7 begins to rise about a minute before Test P2. However, the overall gas-generation profiles of the two tests were not significantly different.

It is worth noting within this discussion of the effect of Mn(II) on gas generation that Test P4 exhibited the fastest initial gas generation rates (until gas bag issues at ~7 min). Test P4 was conducted at a NaMnO_4 feed rate of one-third the baseline rate. Consequently, there was a three-fold amount of time for the reactions to completely convert oxalate to CO_2 .

In the earlier discussion associated with Table 4-5, it was noted that Tests P5 and P9 required significantly higher volumes of NaMnO_4 feed to react all of the $\text{H}_2\text{C}_2\text{O}_4$ and produce MnO_2 solids. The gas-generation data in Figure 4-1 provide additional evidence of a partial line blockage. The data for Test P5 (which was completed just prior to P9) exhibit an initial gas release consistent with the other experiments. However, at about four minutes pump time, the gas generation rate exhibits a reduced generation rate that produces a gas-release profile markedly different from the previous seven experiments. Test P9 exhibits a prolonged delay in gas generation; this delay in gas generation was accompanied by visible evidence of NaMnO_4 flow inconsistencies.

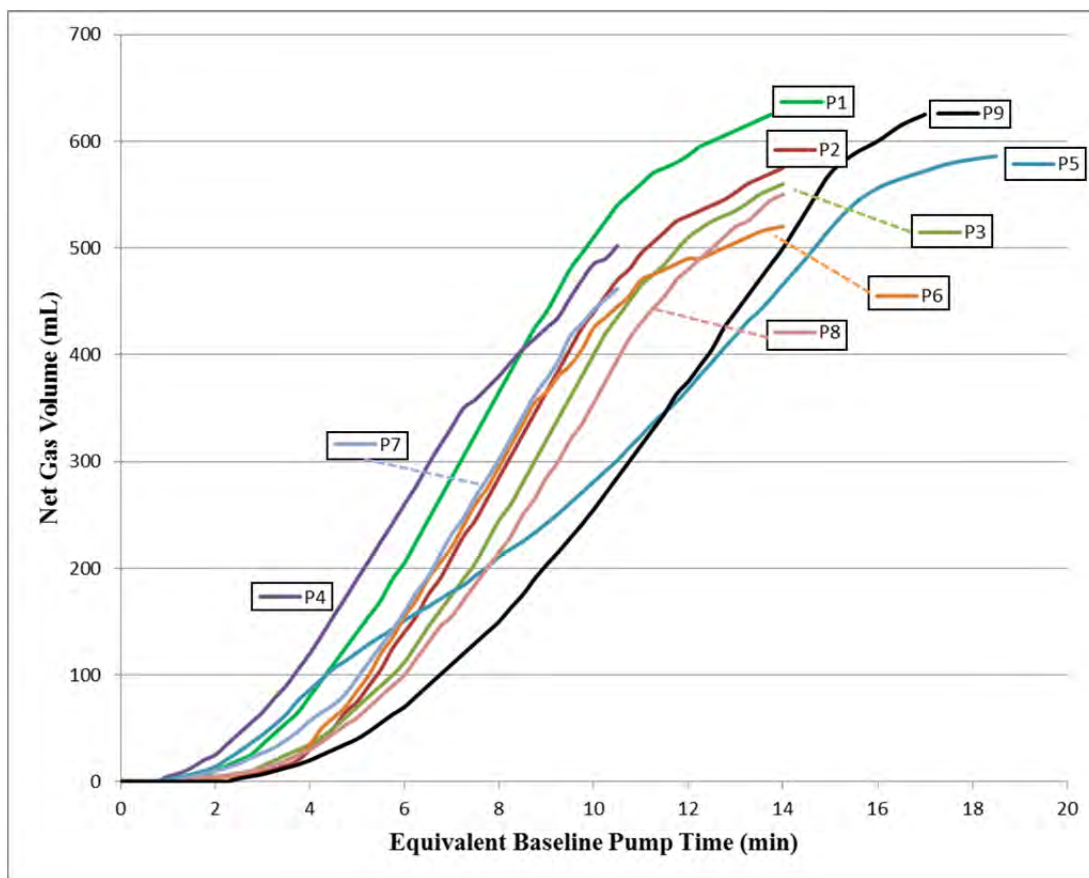


Figure 4-1. Gas Generation Data for Process Flowsheet Tests

The slopes of the gas-generation profiles for the first seven experiments are comparable. The data for gas generation rates across 60-second intervals (equivalent baseline pump time) is graphed in Figure 4-2. The maximum gas generation rate for each of the first six experiments at the baseline NaMnO_4 feed rate was 78-80 mL/min per 100 mL of solution. The maximum generation rates occurred at 7-11 min. The highest gas generation rate for a 15-second interval, which occurred only once in Test P7, was 23 mL (92 mL/min). All other 15-second readings were 20 mL or lower. The experiments conducted by Hill (which contained oxalic acid, hydrazine, and ascorbic acid) reported typical maximum gas generation rates of 170-250 mL/min, with the maximum generation rate occurring at 4-7 min.^[5]

Figure 4-2 again highlights the earlier onset of gas generation associated with Test P4, which had a reduced maximum rate of 73 mL/min due to the NaMnO_4 feed rate being one-third that of the baseline rate. Figure 4-2 also depicts more clearly the NaMnO_4 feed irregularities associated with Tests P5 and P9. For those tests in which gas generation was discontinued prematurely because of issues with the gas-collection bag (Tests P4 and P7), the gas generation rates not recorded were lower than the peak rates shown in Figure 4-2.

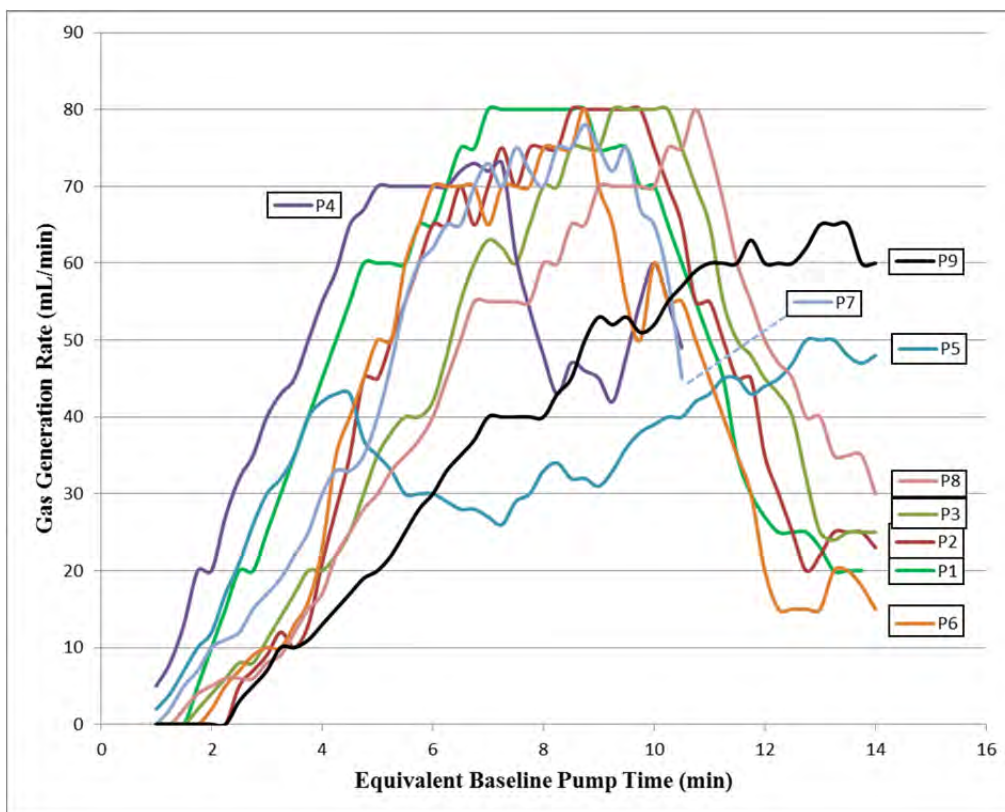


Figure 4-2. Gas Generation Rates for Process Flowsheet Tests

The total volume of gas collected for each test is listed in Table 4-6 along with the expected volume from calculations based on Reactions 1-3. In four of the experiments, gas entrained in the folds of the gas sample bag distorted the total measured gas volume. As the bag expands, gas in the folds of the bag releases out of the liquid reservoir; this causes a net volume decrease in the gas collection vessel. The cause was not clearly understood at first, and the first replacement bag did not correct the issue. For the five experiments without issue, the measured quantity of gas was 93-95% of the expected volume. Test P1 may have exceeded 95% had gas collection not been discontinued prematurely. Previous studies by Hill observed similar variability between measured and expected gas volumes.^[5]

Table 4-6. Total Gas Volumes from Process Flowsheet Testing

Test	P1	P2	P3	P4	P5	P6	P7	P8	P9
Total (mL)	625 [†]	640	635	502 [#]	591*	570*	630	462 [#]	675
Calc (mL)	672	672	672	672	672	676	672	672	710
% of Theory	93	95	94	74	88	84	94	69	95
[†] Gas collection discontinued prematurely [#] Issue with gas-collection bag; data collection discontinued during experiment * Issue with gas-collection bag; data collection continued to end of experiment									

Samples from the gas collection bag were obtained for Tests P1, P2, P3, and P5 and analyzed by GC. Of particular interest was the presence of H₂ and CO₂. Based on Reactions 1 and 3, there should be an in-

growth of CO₂ and no H₂. The GC data are provided in Table 4-7. The method uncertainty for H₂, nitrogen (N₂), and oxygen (O₂) is 10%; uncertainty for CO₂ is 20-25%.

Table 4-7. Gas Analyses from Process Flowsheet Testing

Test #	HNO ₃ (M)	H ₂ (vol %)	N ₂ (vol %)	O ₂ (vol %)	CO ₂ (vol %)	Total (vol %)	N ₂ :O ₂
P1	4.0	<0.1	56	14	29	99	4.0
P2	1.5	<0.1	46	13	25	84	3.5
P3	6.0	<0.1	55	14	25	94	3.9
P5	1.4	<0.1	25	6.8	68	99.8	3.7

As expected, there was no detectable H₂ and air was displaced by CO₂. The N₂:O₂ ratios for Tests P1, P3, and P5 are consistent with the N₂:O₂ ratio for air (3.95). The N₂:O₂ ratio and low total for Test P2 suggests that the reported N₂ concentration may be low.

Temperature was measured throughout each of the process flowsheet tests. In each case, the temperature gradually increased throughout the test until the H₂C₂O₄ oxidation end point was achieved. The initial and maximum temperatures for each test are presented in Table 4-8. It was noted that the onset of temperature increase typically preceded gas generation by about 30-45 seconds. The temperature change for P4 is lower because the experiment used a feed rate of one-third the baseline; Test P5 encountered inconsistencies and disruptions in the NaMnO₄ feed rate due to feed line restrictions.

Table 4-8. Initial and Maximum Temperatures during Process Flowsheet Testing

Test	P1	P2	P3	P4	P5*	P6	P7	P8	P9
Initial T (°C)	20.4	20.1	20.5	21.3	21.4	21.7	21.8	23.2	25.7
Maximum T (°C)	28.1	27.6	28.8	27.0	26.6	29.2	28.7	29.8	32.5
ΔT (°C)	7.7	7.5	8.3	5.7	5.2	7.5	6.9	6.6	6.8
* Issue with consistency of NaMnO ₄ feed rate									

4.2.3 Sodium Nitrite Addition

At the conclusion of each process flowsheet test, the excess Mn (present as MnO₂) was converted to soluble Mn(II) using 5.65 M NaNO₂ solution. Every mole of excess NaMnO₄ creates 2.5 moles of MnO₂ according to Reaction 2. Dissolution of one mole of MnO₂ to soluble Mn(II) requires one mole of NaNO₂. Based on the amount of initial H₂C₂O₄·2H₂O and the total NaMnO₄ added to the reaction vessel, the required volume of 5.65 M NaNO₂ for dissolving excess MnO₂ can also be calculated. The calculated quantities and actual volume of NaNO₂ added are provided in Table 4-9.

The data show good agreement between the “NaNO₂ Required” and “NaNO₂ Added to Clear” columns, except for Test P5 and P9 which likely experienced NaMnO₄ feed issues. It is worth noting that “NaNO₂ Added” is frequently lower than the “NaNO₂ Required”. The difference may be attributable to the removal of analytical samples. Test P1 having a higher “NaNO₂ Added” quantity is likely the result of that test using large incremental additions of NaNO₂ (197.5 μL) instead of titration from a burette. It is not known why Test P7 does not follow the trend observed in Tests P2, P3, P4, P6, and P8. Minimal amounts of NO₂ gas (by Reaction 5) were noted during NaNO₂ addition at 1.4-7.0 M HNO₃.

Table 4-9. Sodium Nitrite Addition Data and Calculations for Process Flowsheet Tests

Test #	C ₂ O ₄ ²⁻ (mmol)	Required NaMnO ₄ (mmol)	Added NaMnO ₄ (mmol)	NaNO ₂ Required (mmol)	NaNO ₂ Required (μL)	NaNO ₂ Added to Clear (μL)	Note
P1	15.02	6.01	7.18	2.93	519	592.5	Not clear at 395 μL
P2	15.01	6.00	7.12	2.79	493	483	Not clear at 402.5 μL
P3	15.02	6.01	7.35	3.35	593	546	Not clear at 468 μL
P4	15.01	6.00	6.98	2.45	434	400	---
P5	15.01	6.00	10.28	10.69	1893	1480	NaMnO ₄ flow issue
P6	15.08	6.03	7.32	3.21	568	520	---
P7	15.01	6.00	7.02	2.53	448	550	Contains Test P4 heel
P8	15.01	6.01	7.51	3.77	667	610	---
P9	15.86	6.34	10.43	10.21	1807	2720	NaMnO ₄ flow issue

During some of the NaNO₂ addition experiments, samples were collected for analysis by IC anion and ICPS. For Tests P1, P2, and P3, samples were obtained at partial MnO₂ dissolution, complete MnO₂ dissolution, and addition of excess NaNO₂. During Tests P4, P6, and P7, samples were collected at the point of complete MnO₂ dissolution and after the addition of 25% excess NaNO₂. For Test P8, the only sample collected was after the addition of 25% excess NaNO₂. The data are listed in Table 4-10.

Table 4-10. Solution Data during Sodium Nitrite Addition

Test	Condition	C ₂ O ₄ ²⁻ (mg/L)	NO ₃ ⁻ (mg/L)	NO ₂ ⁻ (mg/L)*	Mn (mg/L)	Na (mg/L)
P1	Partial MnO ₂ Diss.	<100	248,000	<100	2880	1940
	Full MnO ₂ Diss.	<100	251,000	<100	3780	2490
	Excess NaNO ₂	<100	256,000	<100	3770	2620
P2	Partial MnO ₂ Diss.	<100	95,900	<100	2800	1830
	Full MnO ₂ Diss.	<100	95,800	<100	3690	2260
	Excess NaNO ₂	<100	95,000	<100	3690	2400
P3	Partial MnO ₂ Diss.	<100	362,000	<100	3050	1950
	Full MnO ₂ Diss.	<100	366,000	<100	3710	2360
	Excess NaNO ₂	<100	358,000	<100	3700	2490
P4	Full MnO ₂ Diss.	<100	87,300	<100	3450	2110
	25% Excess NaNO ₂	<100	87,500	<100	3450	2240
P6	Full MnO ₂ Diss.	<100	87,700	<100	3580	2320
	25% Excess NaNO ₂	<100	87,600	<100	3580	2500
P7	Full MnO ₂ Diss.	<100	88,400	<100	3630	2350
	25% Excess NaNO ₂	<100	89,600	<100	3670	2570
P8	25% Excess NaNO ₂	<100	150,000	<100	3490	2540
* NO ₂ ⁻ is always below the method detection limit, even though added in excess, because it decomposes in the presence of HNO ₃						

The data demonstrate the fundamentals of the MnO₂ dissolution step. For each test, the Na concentration increases as NaNO₂ is added. Also, the Mn concentrations for Tests P1, P2, and P3 increase from “Partial MnO₂ Dissolution” to “Full MnO₂ Dissolution” as MnO₂ solid is reacted with NaNO₂ to form soluble Mn(II). However, after full MnO₂ dissolution, additional NaNO₂ does not produce an increase in Mn

concentration, as seen in the “Excess NaNO_2 ” sample. These results confirm that MnO_2 dissolution is complete.

4.3 Precipitator Tank Clean-Out Solution

Periodic clean-out of the precipitator will create a condition in which plutonium ions, oxalate ions, and potentially plutonium oxalate solids are present. The maximum allowable concentration of Pu is 60 g/L (or 0.25 M), and the corresponding oxalate concentration is 0.50 M. The baseline flowsheet employs 14 M HNO_3 for the clean-out process because of the solubility of $\text{Pu}(\text{C}_2\text{O}_4)_2$ in strong acid. Testing was completed using Ce as a simulant for Pu, even though the suitability of Ce is limited. In HNO_3 , Pu has three common valence states – Pu(III), Pu(IV), and Pu(VI). The electrochemical potential between Pu(III) and Pu(IV) is -0.92 V, between Pu(IV) and Pu(VI) is -1.10 V, and between Pu(III) and Pu(VI) is -1.04 V.^[8] Cerium has two common valence states in HNO_3 – Ce(III) and Ce(IV) – with an electrochemical potential of -1.72 V between Ce(III) and Ce(IV).^[9] When the electrochemical potential of a chemical species is more negative than another chemical species in contact with it, the potential exists for the more-negative species to be reduced and the less-negative species to be oxidized. As the difference between the electrochemical potentials of the two species increases, the reaction becomes more favorable.

Prior to evaluating the baseline flowsheet, a determination had to be made regarding the appropriate initial valence state for Ce in testing – Ce(III) as $\text{Ce}(\text{NO}_3)_3$ or Ce(IV) as $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$. Into 1.4 M HNO_3 , Ce(IV) was prepared at 0.179 M Ce and oxalate was 0.394 M ($0.179 \times 2 + 10\%$ excess). Cerium(III) was similarly prepared in 1.4 M HNO_3 with an equivalent concentration of oxalate (0.394 M) and Ce(III) at a concentration (0.238 M) to yield an excess oxalate concentration of 10%. At 1.4 M HNO_3 , both solutions produced visible quantities of cerium-oxalate precipitate (Figure 4-3). Cerium(IV) in HNO_3 solution is yellow. It should be noted that when Ce(IV) solution was combined with $\text{H}_2\text{C}_2\text{O}_4$ solution (Section 3.4) there was a release of colorless gas, suggesting some reaction between Ce(IV) and $\text{H}_2\text{C}_2\text{O}_4$. The use of Ce(IV) for the oxidation of organics has been evaluated for the destruction of organic-based wastes.^[8] Oxidation of NH_4^+ by Ce(IV) is not likely because such a reaction would have 1) released brown NO_2 gas (the gas was colorless) and 2) required an increased quantity of NaMnO_4 for the reaction [the Ce(IV) test required less NaMnO_4 than the Ce(III) test].

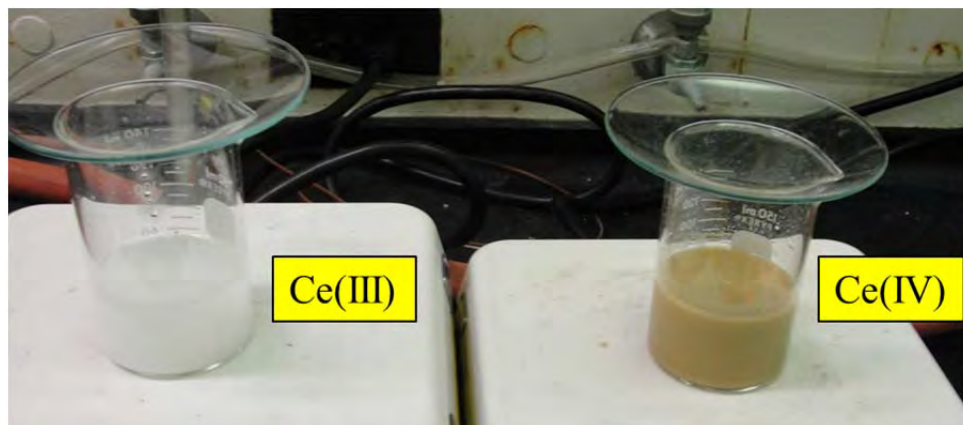


Figure 4-3. Ce(III) and Ce(IV) Oxalate in 1.4 M HNO_3

Similar to the titration experiments discussed in Section 4.1, both solutions were titrated by pipetting 3.31 M NaMnO_4 into them. The volume of each aliquot was 120 μL , which is theoretically sufficient to react all of the $\text{H}_2\text{C}_2\text{O}_4$ with 20 aliquots. Similar to earlier titration experiments, the Ce(III) test required 21 aliquots for MnO_2 solids to form and persist; the beaker with Ce(IV) required only 16 aliquots, thus

providing further evidence of reaction between Ce(IV) and $\text{H}_2\text{C}_2\text{O}_4$. After 15 aliquots, the solution from the Ce(IV) test was clear and colorless like that of the Ce(III) test. Consequently, Ce(III) was selected as the preferred Ce valence state because, similar to Pu(III) and Pu(IV), it does not react to oxidize $\text{H}_2\text{C}_2\text{O}_4$. Based on the electrochemical potential of Pu(VI) being similar to that of Pu(III) and Pu(IV),^[9] it is expected that Pu(VI) will not react to oxidize $\text{H}_2\text{C}_2\text{O}_4$.

Three parallel experiments were conducted in 10 M, 12 M, and 14 M HNO_3 (Tests C, D, and E of Table 3-3). The Ce and $\text{H}_2\text{C}_2\text{O}_4$ concentrations were similar to the Ce(III) test above – 0.238 M Ce and 0.394 M $\text{H}_2\text{C}_2\text{O}_4$. When each of the three test solutions was fully prepared, the amount of solids in the 10 M solution was barely visible and there were no solids in either the 12 M or 14 M solutions. The 14 M test solution had a slight yellow tint (Figure 4-4).

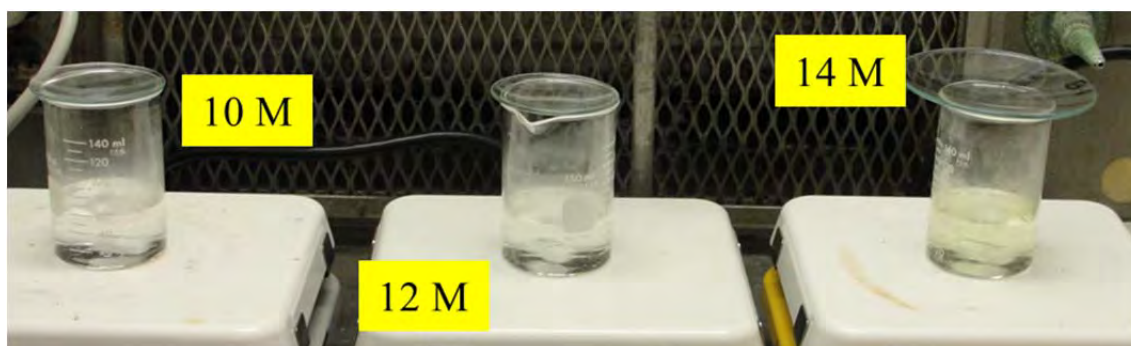


Figure 4-4. Ce(III) and $\text{H}_2\text{C}_2\text{O}_4$ in 10 M, 12 M, and 14 M HNO_3

The three solutions were titrated by adding 120 μL aliquots of 3.31 M NaMnO_4 to each beaker. Based on previous testing, the expected end point was 21 aliquots. However, with the first addition of NaMnO_4 , there appeared to be an interaction between the Ce and permanganate, especially in 14 M HNO_3 (Figure 4-5). The electrochemical potential for MnO_4^- to Mn^{2+} is 1.507 V.^[10] Although, by itself, MnO_4^- cannot convert Ce(III) to Ce(IV) [1.72 V], the conversion may be possible in a strong oxidizing acid. Apart from change in coloration, the reaction of NaMnO_4 with $\text{H}_2\text{C}_2\text{O}_4$ occurred in a manner reported above.

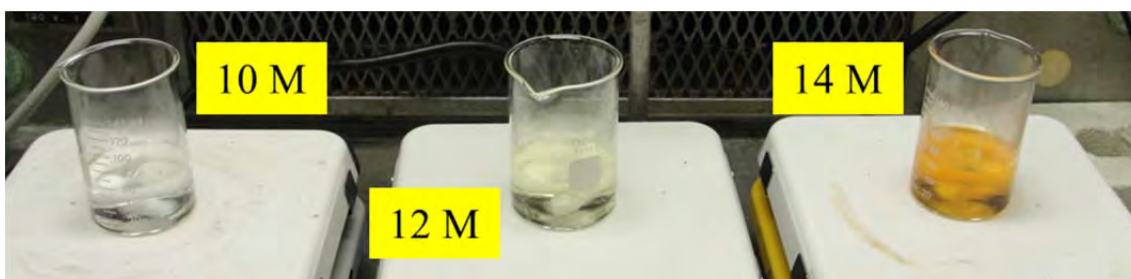


Figure 4-5. Ce(III) and $\text{H}_2\text{C}_2\text{O}_4$ in 10 M, 12 M, and 14 M HNO_3 after First NaMnO_4 Aliquot

The titration data indicate some interaction between NaMnO_4 and Ce(III) to consume NaMnO_4 [presumably resulting in the formation of yellow Ce(IV)]. Instead of requiring 21 aliquots to reach the end point, the 10 M, 12 M, and 14 M solutions required 23, 25, and 28 aliquots, respectively. The interaction can be seen after 21 aliquots (Figure 4-6), just prior to the formation of MnO_2 in the 10 M solution.

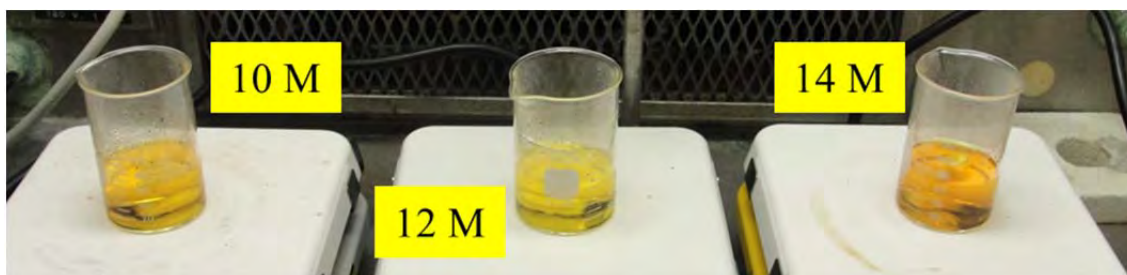


Figure 4-6. Ce(III) and H₂C₂O₄ in 10 M, 12 M, and 14 M HNO₃ after 21 NaMnO₄ Aliquots

The 14 M HNO₃ experiment was repeated with one variation. The solution was diluted with an equal volume of DI H₂O to 7 M HNO₃ (Test F of Table 3-3). When titrated with 3.31 M NaMnO₄, the solution required 21 of the 120-μL aliquots for MnO₂ solids to appear and persist, the same as the experiments described in Section 4.1. The reduced acid concentration either prevented the formation of Ce(IV) or enabled any Ce(IV) that may have formed to react with H₂C₂O₄. Similar to the 1.4 M HNO₃ experiments, the solution was clear and colorless prior to the NaMnO₄ aliquot that surpassed the end point.

Addition of NaMnO₄ to Tests C-F was discontinued when MnO₂ solids formed and persisted. These four solutions (with solids) were titrated with 5.65 M NaNO₂ until all MnO₂ solids disappeared. The NaNO₂ was fed with a pipette in 25-μL aliquots. Visible NO₂ gas (due to NaNO₂ reaction with HNO₃) was observed in Tests C-E, with increased visibility as temperature increased, as described by Reaction 5. However, the amount of NO₂ generation did not indicate significant conversion of NaNO₂ to NO₂.

Tests C-F required 450, 575, 625, and 275 μL of 5.65 M NaNO₂, respectively, to visibly dissolve the MnO₂ solids. Calculations compare the amount of NaNO₂ added with the expected amount required based on the excess NaMnO₄ added relative to the initial quantity of H₂C₂O₄ (Table 4-11).

Table 4-11. Sodium Nitrite Addition Data and Calculations for Precipitator Clean-Out Tests

Test #	HNO ₃ (M)	C ₂ O ₄ (mmol)	Required NaMnO ₄ (mmol)	Added NaMnO ₄ (mmol)	NaNO ₂ Required (mmol)	NaNO ₂ Required (μL)	NaNO ₂ Added to Clear (μL)
C	10.0	19.73	7.89	9.14	3.11	551	450
D	12.0	19.73	7.89	9.93	5.10	902	575
E	14.0	19.72	7.89	11.12	8.08	1431	625
F	7.0	19.73	7.89	8.34	1.12	199	275

Unlike the data of Table 4-9, where the calculated and actual quantities of NaNO₂ corresponded, the amount of NaNO₂ added to the tests of Table 4-11 at 10-14 M HNO₃ were notably lower than the calculated amount. Furthermore, the difference between the actual and calculated amounts increased with increasing HNO₃ concentration. This means that some of the excess NaMnO₄ added did not have to be dissolved with NaNO₂, and that fraction increased with increasing acidity. These data provide further evidence that some of the NaMnO₄ reacted with Ce(III) to form Ce(IV) and soluble Mn(II) (Figure 4-5) and that the Ce(IV) was stable in the presence of H₂C₂O₄. At 7 M HNO₃, the calculated and actual quantities of NaNO₂ corresponded, although a somewhat larger NaNO₂ excess was needed than in tests at lower HNO₃ concentrations.

5.0 Conclusions

5.1 Oxalate Titration

The oxidation of $\text{H}_2\text{C}_2\text{O}_4$ in 1.0-7.0 M HNO_3 with NaMnO_4 is consistent with Reactions 1-3, as reported in the literature.^[7] The initial reaction of NaMnO_4 directly with $\text{H}_2\text{C}_2\text{O}_4$ to produce CO_2 , H_2O , and Mn(II) is slow. The in-growth of Mn(II) enables NaMnO_4 to quickly form MnO_2 , which reacts rapidly with $\text{H}_2\text{C}_2\text{O}_4$. The rate of $\text{H}_2\text{C}_2\text{O}_4$ oxidation increases as the concentration of soluble Mn(II) increases. The quantity of NaMnO_4 required to react all of the $\text{H}_2\text{C}_2\text{O}_4$ can be calculated from the stoichiometry of Reaction 1, which is two moles of NaMnO_4 per five moles of $\text{H}_2\text{C}_2\text{O}_4$. It is assumed in these calculations that the concentration of Pu in the filtrate solution is minimal. As discussed in Section 5.3, Pu in solution may be converted to a higher valence state and consume NaMnO_4 , with increasing likelihood at higher HNO_3 concentration.

When all of the $\text{H}_2\text{C}_2\text{O}_4$ has been converted to CO_2 , excess NaMnO_4 reacts rapidly with Mn(II) to form brown MnO_2 solids according to Reaction 2. The presence of MnO_2 solids (not excess permanganate) indicates that the end point of the $\text{H}_2\text{C}_2\text{O}_4$ oxidation reaction has been achieved. The accumulation of MnO_2 solids upon addition of NaMnO_4 will continue until all Mn(II) is consumed. Only after all Mn(II) has been reacted with NaMnO_4 to form MnO_2 solids will there be detectable MnO_4^- in solution.

The data show that as Mn is added as NaMnO_4 that the Na and Mn concentrations increase while the $\text{C}_2\text{O}_4^{2-}$ concentration decreases. However, once the $\text{C}_2\text{O}_4^{2-}$ is below detectable limits, the addition of NaMnO_4 caused the Na concentration to continue to increase while the soluble Mn concentration decreased (from the formation of MnO_2 solids).

5.2 Process Flowsheet Testing

Process flowsheet testing confirmed that the reaction behavior and chemical ratios demonstrated during oxalate titration testing are applicable during conditions of continuous NaMnO_4 feeding. In seven experiments ranging from 1.4 M to 6.0 M HNO_3 , the system behavior was consistent with Reactions 1-3. Initial consumption of NaMnO_4 was slow due to Reaction 1. Once Mn(II) accumulated in solution, the overall reaction rate accelerated via Reactions 2 and 3. Throughout testing, MnO_2 solids did not persist in the reaction vessel until all $\text{H}_2\text{C}_2\text{O}_4$ was oxidized to CO_2 .

Gas samples collected from four experiments showed less-than-detectable concentrations of H_2 gas. In each test, the gas contained air diluted with CO_2 released from the oxidation of $\text{H}_2\text{C}_2\text{O}_4$. Using HB-Line baseline flowsheet feed rates for NaMnO_4 (5.46 L/h of 3.83 M NaMnO_4), the maximum gas generation rate per liter of reaction solution was consistently 750-800 mL/min; this generation rate is less than half the rate of the previous flowsheet.^[5] A single 15-second rate of 230 mL per liter of solution was observed, or 920 mL/min. For experiments without issues during gas collection, the quantity of gas collected was 94-95% of the theoretical value. The gas generation rate was not a function of HNO_3 concentration.

The presence of MnO_2 solids, which form because of the addition of excess NaMnO_4 in the oxidation of $\text{H}_2\text{C}_2\text{O}_4$, is undesirable. Therefore, these solids are dissolved through the addition of NaNO_2 solution. Experimentation confirmed that the quantity of NaNO_2 required to dissolve MnO_2 solids can be accurately calculated from the amount of excess NaMnO_4 added (present as MnO_2 solids). Experimental data show good agreement between theoretical and actual NaNO_2 addition quantities. This applies only to solutions with minimal concentrations of Pu in solution. As discussed in Section 5.3, Pu in solution may be converted to a higher valence state and consume NaMnO_4 , thereby reducing the amount of NaNO_2 required when compared to the calculated value.

5.3 Precipitator Tank Clean-Out Solution

The addition of Ce as a surrogate for Pu does not alter the fundamental $\text{H}_2\text{C}_2\text{O}_4$ oxidation chemistry described in Section 2.1. However, the presence of Ce does require additional NaMnO_4 in 10-14 M HNO_3 due to oxidation of $\text{C}_2\text{O}_4^{2-}$ and Ce(III) to Ce(IV) by $\text{MnO}_4^-/\text{MnO}_2$. Cerium(IV) was not stable in 1.4-7.0 M HNO_3 . Therefore, the presence of Ce(III) at 1.4-7.0 M did not result in an increase in the amount of NaMnO_4 required above that needed to oxidize $\text{C}_2\text{O}_4^{2-}$. At 1.4 M HNO_3 , Ce(IV) reacted with $\text{C}_2\text{O}_4^{2-}$ to reduce the volume of NaMnO_4 required to consume the $\text{C}_2\text{O}_4^{2-}$. In the case of Ce, the appropriate approach for handling a precipitator clean-out operation would be to clean out with 14 M HNO_3 and then dilute the acid to 1.4-7 M prior to oxidizing the $\text{C}_2\text{O}_4^{2-}$ with NaMnO_4 .

Although the behavior of Ce offers an indication of how the presence of Pu will affect the process during the precipitator clean-out operation, there should be significant differences. The difference is attributed to the electrochemical potential of Ce(III)-Ce(IV) compared to that of Pu(III)-Pu(IV)-Pu(VI) and Mn(II)-Mn(IV)-Mn(VII). The electrochemical potential of the Mn(II)-Mn(VII) couple is 1.51 V and the potential for the Mn(II)-Mn(IV) couple is 1.22 V.^[10] It would appear that the electrochemical potential of the Ce(III)-Ce(IV) couple is sufficiently high (1.72 V) to preclude Mn(IV) or Mn(VII) from reacting with Ce(III) to form Ce(IV). Such was the case in 1.4-7.0 M HNO_3 , but in a strong oxidizing acid (10-14 M HNO_3), the NaMnO_4 reacted with Ce(III) to form Ce(IV).

The Pu(III)-Pu(VI) couple (1.04 V) and Pu(IV)-Pu(VI) couple (1.10 V) have significantly lower electrochemical potential than the Ce(III)-Ce(IV) couple.^[9] Furthermore, the potentials for the Pu(III)-Pu(VI) and Pu(IV)-Pu(VI) couples are lower than the Mn(II)-Mn(IV) and Mn(II)-Mn(VII) couples. Consequently, it is expected that Mn(IV) and Mn(VII) will react with Pu(III) and Pu(IV) to form Pu(VI), and consume excess NaMnO_4 to accomplish this oxidation of Pu. Once oxidized, it is expected that the Pu(VI) will not react with $\text{C}_2\text{O}_4^{2-}$ the way Ce(IV) did in 1.4 M HNO_3 . The basis for this conclusion is that the electrochemical potential for the Pu(III)-Pu(IV) couple (which is 0.92 V) is similar to that of the Pu(III)-Pu(VI) and Pu(IV)-Pu(VI) couples. Since Pu(IV) does not have sufficient potential to oxidize $\text{C}_2\text{O}_4^{2-}$, it is probable that Pu(VI) will not oxidize $\text{C}_2\text{O}_4^{2-}$.

The literature indicates that both Mn(VII) and Mn(IV) react with Pu(IV) in HNO_3 to produce Pu(VI).^[9] The reaction of Mn(VII) with Pu(IV) in 1 M HNO_3 is listed with a $t_{1/2}$ of 50 min. The reaction of Mn(IV) with Pu(IV) in 5 M HNO_3 is identified as “slow”. This suggests that the reaction to convert Pu(IV) to Pu(VI) is considerably slower than the $\text{C}_2\text{O}_4^{2-}$ oxidation reaction, especially in the presence of soluble Mn(II), according to Reaction 2. The data in the literature also suggest that the reaction of $\text{C}_2\text{O}_4^{2-}$ will occur continuously with the addition of NaMnO_4 , and that when all $\text{C}_2\text{O}_4^{2-}$ has been consumed, excess NaMnO_4 will be converted rapidly to MnO_2 solids. The MnO_2 reaction with Pu(IV) is “slow”. Consequently, the end point of the $\text{C}_2\text{O}_4^{2-}$ oxidation reaction should be identifiable by the presence of MnO_2 solids.

Just as the reactions with Ce indicate a benefit from reducing the HNO_3 concentration from 14M to 7M prior to oxidizing the $\text{C}_2\text{O}_4^{2-}$, a similar benefit is expected where Pu is present instead of Ce. Therefore, the $\text{Pu}(\text{C}_2\text{O}_4)_2$ clean-out operation should be performed in 14 M HNO_3 , and the resulting solution diluted to 1.4-7 M HNO_3 prior to addition of NaMnO_4 to oxidize $\text{C}_2\text{O}_4^{2-}$.

It should be noted that the magnitude of the impact of Pu will be proportional to its concentration. Consequently, in a series of precipitator clean-out operations with decreasing concentrations of $\text{Pu}(\text{C}_2\text{O}_4)_2$, the first cycle will likely be the only cycle requiring a significant volume of NaMnO_4 . Subsequent cycles are expected to have relatively low Pu and $\text{C}_2\text{O}_4^{2-}$ concentrations.

6.0 Recommendations

6.1 Baseline Process Flowsheet

SRNL verified that the nominal baseline NaMnO_4 addition rate of 5.46 L/h of 3.83 M NaMnO_4 is valid for this aspect of the flowsheet, or 0.35 mol $\text{NaMnO}_4/\text{min}$. This NaMnO_4 addition rate, because of the different contents of the filtrate tank, will yield a maximum gas-generation rate of one-third to one-half as much as the previous flowsheet which included the oxidation of hydrazine and ascorbic acid. If a more-dilute solution of NaMnO_4 is used, a corresponding increase in flow rate is acceptable.

Per liter of filtrate solution, assuming a flowsheet of 0.1 M excess $\text{H}_2\text{C}_2\text{O}_4$, 0.044 mol of NaMnO_4 should be added to convert the $\text{H}_2\text{C}_2\text{O}_4$ to CO_2 and H_2O (or 11.5 mL of 3.83 M NaMnO_4 per liter of filtrate). This will provide 10% molar (theoretical) excess of NaMnO_4 . The amount of residual Pu in the filtrate solution does not significantly affect the quantity of NaMnO_4 that should be added. The excess NaMnO_4 will react with any Mn(II) in solution to form MnO_2 solids – the permanganate is reduced to MnO_2 while the Mn(II) is oxidized to MnO_2 . The addition of 0.044 mol of NaMnO_4 per liter of filtrate solution may be scaled linearly to any oxalate concentrations less than 0.2 M. The amount of NaMnO_4 addition can be calculated as 0.44 mol of NaMnO_4 per 1.0 mol of oxalate; this results in a 10% molar excess of NaMnO_4 . Sample at least three minutes after NaMnO_4 addition is complete. If brown solids are present, analyze the solution by IC anion to verify that $\text{C}_2\text{O}_4^{2-}$ is less than detectable.

Following the addition of NaMnO_4 , the excess, which will be present as MnO_2 solids, is dissolved by the addition of NaNO_2 solution. The nominal baseline NaNO_2 addition rate of 7.2 L/h of 5.65 M NaNO_2 is valid for this aspect of the flowsheet. Per liter of solution, to react the 0.004 mol of excess NaMnO_4 [present as 0.01 mol of MnO_2 from its reaction with 0.006 mol Mn(II)], at least 0.0125 mol NaNO_2 should be added to convert MnO_2 to soluble Mn(II) [or 2.2 mL of 5.65 M NaNO_2]. This will provide 25% molar excess of NaNO_2 . The excess NaNO_2 can potentially react with HNO_3 per Reaction 5 to produce NO_2 and NO gases. Although very little NO_x generation was observed, based on the total quantity of NaNO_2 , the excess will produce a maximum of 0.2 moles of NO_x per mole of NaNO_2 added.

6.2 Precipitator Clean-Out Operations

During precipitator clean-out operations, it is expected that Pu and $\text{C}_2\text{O}_4^{2-}$ will be soluble, although the presence of $\text{Pu}(\text{C}_2\text{O}_4)_2$ solids does not change the method or amounts. The quantities of NaMnO_4 and NaNO_2 recommended are based on 100 g of Pu present as 173.6 g of dissolved $\text{Pu}(\text{C}_2\text{O}_4)_2$. It is assumed that NaMnO_4 will be consumed principally by the oxidation of $\text{C}_2\text{O}_4^{2-}$ and only minor amounts by the conversion of Pu(IV) to Pu(VI). The addition of 25% excess is recommended to compensate for the Pu(IV)-Pu(VI) couple.

The precipitator clean-out should continue to be performed using 14 M HNO_3 . As discussed above, when the clean-out operation is complete, the resulting solution should be diluted with H_2O to 1.4-7 M HNO_3 to potentially suppress the Pu(IV) oxidation reaction. Per 100 g of Pu expected in the precipitator or measured in the filtrate tank, add at least 0.42 mol of NaMnO_4 (or 110 mL of 3.83 M NaMnO_4) at the baseline flow rate of 0.35 mol $\text{NaMnO}_4/\text{min}$. Sample after three minutes for brown MnO_2 solids. If brown solids are present, analyze the solution by IC anion to verify that $\text{C}_2\text{O}_4^{2-}$ is less than detectable.

If there is uncertainty regarding whether the solids present in a sample are MnO_2 or Pu-oxalate, the uncertainty can be removed by combining the sample with a solution that contains a large excess of NaNO_2 in 1-7 M HNO_3 and stirring the combined solution for 3-5 minutes. If the solids are MnO_2 , they will dissolve. If the solids are Pu oxalate, they will remain. A comparison of MnO_2 solids and Pu(IV) oxalate solids is shown in Figure 6-1.

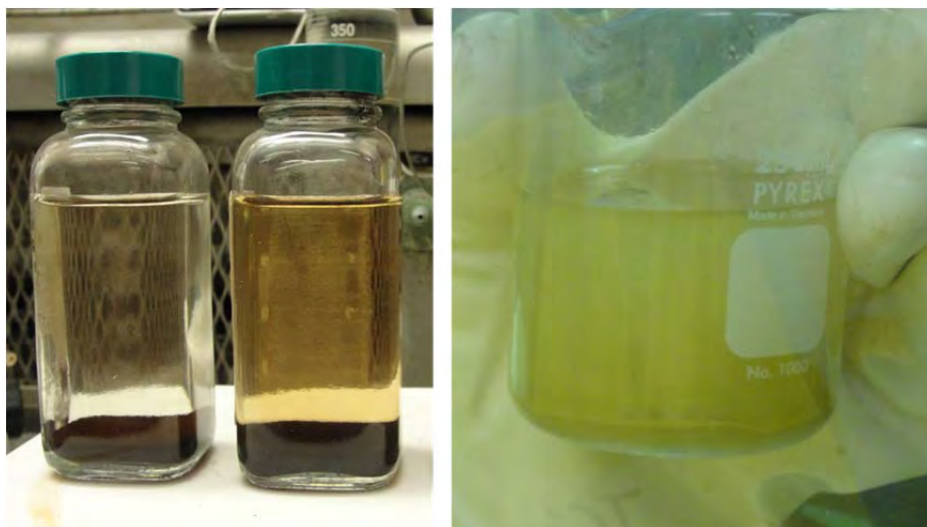


Figure 6-1. Comparison of MnO_2 Solids (left) and Pu(IV) Oxalate Solids (right)

Assuming that the residual solids in the sample were MnO_2 , the resulting solution in the HB-Line process vessel, with a nominal excess NaMnO_4 of 0.084 mol per 100 g Pu, is reacted with NaNO_2 to dissolve any residual MnO_2 solids. Dissolution of the MnO_2 solids will require 0.21 mol NaNO_2 (or 37 mL of 5.65 M NaNO_2) per 100 g Pu. Allowing for at least 33% excess, it is recommended that at least 0.28 mol NaNO_2 (or 50 mL of 5.65 M NaNO_2) be added per 100 g Pu to completely dissolve the MnO_2 solids.

For the precipitator clean-out operation, it is recommended that minimum quantities of NaMnO_4 and NaNO_2 added correspond to an assumed quantity of 50 g Pu as $\text{Pu}(\text{C}_2\text{O}_4)_2$. If analyses indicate that 50 or fewer grams of Pu remain in the precipitator, assume the presence of 50 g. The flowsheet would entail adding at least 0.21 mol of NaMnO_4 (or 55 mL of 3.83 M NaMnO_4) for $\text{C}_2\text{O}_4^{2-}$ oxidation and at least 0.14 mol NaNO_2 (or 50 mL of 5.65 M NaNO_2) for MnO_2 dissolution. These quantities are sufficiently small that it may be appropriate to add them through a charge funnel rather than with short pump cycles (i.e., 36 s for NaMnO_4 addition and 25 s for NaNO_2 addition).

7.0 Operational Improvements

All testing has demonstrated that the end point can be determined through visual inspection of the filtrate solution. When brown MnO_2 solids form and persist in solution, analyses have consistently shown that the $\text{C}_2\text{O}_4^{2-}$ concentration is less than 100 mg/L. During ramp-up operations, it is advised that HB-Line establish a basis for visual inspection by correlating visual inspections with IC anion analyses. This could be accomplished by interrupting the feeding of NaMnO_4 at approximately 75% of the recommended amount (chosen arbitrarily), collecting a sample, noting its visual characteristics for brown solids, completing the recommended feed amount and, if brown solids are present, withdrawing another sample. Analyze both samples by IC anion to demonstrate that the presence of brown solids corresponds to the absence of $\text{H}_2\text{C}_2\text{O}_4$. If validated, for full-scale operations use visual observations to determine the reaction end point with occasional spot checks.

During ramp-up operations, it is also advisable for NaNO_2 additions that HB-Line establish a basis for visual inspection by correlating them with ICPES analyses. This could be accomplished by interrupting the feeding of NaNO_2 at approximately 90% of the recommended amount, collecting a sample, and noting its visual characteristics for brown solids. If the sample still contains solids, add 10% of the recommended amount and sample again. Repeat this cycle until the solution contains no visible MnO_2 .

solids. When the sample is free of visible solids, retain the sample for analysis and complete NaNO_2 addition by adding 25% of the recommended volume of NaNO_2 solution. Collect a second sample and analyze both samples by ICPEs. Both samples should analyze at the same Mn concentration but different Na concentrations. This will demonstrate that a solution visibly free of brown solids does not contain residual MnO_2 . Once validated, full-scale operations would be able to use visual observations to determine that the NaNO_2 addition end point has been achieved. Because there are no Pu-bearing solids in the samples, continued sampling and analyses beyond this process validation step could be omitted.

8.0 References

1. R. H. Smith and P. H. Werling, "HB-Line Pu-239 Flow Sheet (U)", NMS-EHB-2000-00045 R2, October 2001.
2. S. L. Garrison, "HB-Line Flowsheet for Production of Plutonium Oxide in Phase II", "SRNS-F3100-2012-0011 R1, February 2013.
3. S. B. Beck, "Insure Previous Pu Campaign Permanganate Reaction Kinetics Are Valid for Current HB-Line Waste Minimization Strategy", Technical Task Request NMMD-HTS-2014-3292, February 2014.
4. C. A. Nash, R. A. Pierce, and M. L. Crowder, "Task Technical and Quality Assurance Plan for HB Line Permanganate-Oxalate Reaction Kinetics", SRNL-RP-2014-00230, March 2014.
5. B. C. Hill and M. G. Bronikowski, "Gas Generation during Sodium Permanganate Addition to HB-Line Phase II Filtrate Tank (U)", WSRC-TR-2002-00350, August 2002.
6. J. H. Gray, "The Formation and Dissolution of Plutonium Oxalate Solids in HB-Line Phase II Filtrate Streams", WSRC-TR-2001-00317, July 2001.
7. R. S. McBride, "The Standardization of Potassium Permanganate Solution by Sodium Oxalate", Bulletin of the Bureau of Standards, Vol. 8, 611-642, 1913.
8. N. Nelson, "Mediated Electrochemical Oxidation of Mixed Wastes", Hazardous and Radioactive Waste Treatment Technologies Handbook, Section 5.2.3, CRC Press, 2001.
9. O. J. Wick (ed), Plutonium Handbook, A Guide to the Technology, Volumes 1 and 2, Section 13-1, American Nuclear Society, 1980.
10. CRC Handbook of Chemistry and Physics, 94th Edition, Internet Version, 5-80, 2014.

9.0 APPENDIX

9.1 Gas-Volume Collection Data from Process Flowsheet Tests

	P1	P2	P3	P6	P7	P8	P9		P4	P4		P5	P5
Pump	Cylinder	Cylinder	Cylinder	Cylinder	Cylinder	Cylinder	Cylinder		Pump	Cylinder		Pump	Cylinder
Time	Volume	Volume	Volume	Volume	Volume	Volume	Volume		Time	Volume		Time	Volume
(min)	(mL)	(mL)	(mL)	(mL)	(mL)	(mL)	(mL)		(mm:ss)	(mL)		(mm:ss)	(mL)
0.00	25	25	40	30	33	25	25		0.00	45		0.00	34
0.25	25	25	40	30	33	25	25		0.75	45		0.50	34
0.50	25	25	40	30	33	25	25		1.50	45		1.00	34
0.75	25	25	40	30	33	25	25		2.25	45		1.50	34
1.00	25	25	40	30	33	25	25		3.00	50		2.00	36
1.25	25	25	40	30	35	25	25		3.75	53		2.50	38
1.50	25	25	40	30	38	27	25		4.50	58		3.00	41
1.75	30	25	42	30	40	29	25		5.25	65		3.50	44
2.00	35	25	44	32	43	30	25		6.00	70		4.00	48
2.25	40	25	46	35	46	31	25		6.75	80		4.50	55
2.50	45	30	48	37	50	33	28		7.50	90		5.00	62
2.75	50	32	50	39	55	35	30		8.25	100		5.50	70
3.00	60	34	55	42	60	38	32		9.00	110		6.00	78
3.25	70	37	60	45	65	40	35		9.75	123		6.50	87
3.50	80	40	65	50	72	45	38		10.50	135		7.00	97
3.75	90	45	70	55	80	50	41		11.25	150		7.50	110
4.00	105	55	75	65	90	55	45		12.00	165		8.00	120
4.25	120	65	82	80	98	62	50		12.75	182		8.50	130
4.50	135	75	90	90	105	70	55		13.50	200		9.00	140
4.75	150	90	100	100	115	78	60		14.25	217		9.50	147
5.00	165	100	110	115	130	85	65		15.00	235		10.00	155
5.25	180	115	120	130	145	95	72		15.75	252		10.50	163
5.50	195	130	130	150	160	105	80		16.50	270		11.00	170
5.75	215	150	140	165	175	115	88		17.25	287		11.50	177
6.00	230	165	152	185	192	125	95		18.00	305		12.00	185
6.25	250	180	168	200	210	140	105		18.75	322		12.50	192
6.50	270	200	185	220	225	155	115		19.50	342		13.00	198
6.75	290	215	200	235	245	170	125		20.25	360		13.50	205
7.00	310	235	215	250	265	180	135		21.00	377		14.00	212
7.25	330	255	230	270	280	195	145		21.75	395		14.50	218
7.50	350	270	245	290	300	210	155		22.50	403		15.00	227
7.75	370	290	265	305	317	225	165		23.25	414		15.50	235
8.00	390	310	285	325	335	240	175		24.00	425		16.00	245
8.25	410	330	300	345	355	255	188		24.75	438		16.50	252
8.50	430	350	320	365	375	275	200		25.50	450		17.00	259
8.75	450	370	340	385	395	290	215		26.25	460		17.50	267
9.00	465	390	360	395	410	310	228		27.00	470		18.00	276
9.25	485	410	380	410	427	325	240		27.75	480		18.50	285
9.50	505	430	400	420	450	345	253		28.50	498		19.00	295
9.75	520	450	420	435	462	360	266		29.25	515		19.50	305
10.00	535	465	440	455	475	380	280		30.00	530		20.00	315
10.25	550	480	460	465	485	400	295		30.75	535		20.50	325
10.50	565	495	475	475	495	420	310		31.50	547		21.00	335
10.75	575	505	490	485		440	325					21.50	347
11.00	585	520	505	500		455	340					22.00	358
11.25	595	530	515	505		468	355					22.50	370
11.50	600	540	525	510		480	370					23.00	380
11.75	605	550	538	515		495	388					23.50	390
12.00	612	555	550	520		505	400					24.00	402
12.25	620	560	558	520		515	415					24.50	415
12.50	625	565	565	525		525	430					25.00	427
12.75	630	570	570	530		535	450					25.50	440
13.00	635	577	575	535		545	465					26.00	452
13.25	640	585	582	540		550	480					26.50	465
13.50	645	590	590	545		560	495					27.00	475
13.75	650	595	595	550		570	510					27.50	487
14.00		600	600	548		575	525					28.00	500
15.00		613	618	560		590	595					28.50	512
16.00		625	630	570		603	625					29.00	525
17.00		638	640	575		615	650					29.50	540
18.00		642	647	580		620	665					30.00	552
19.00		646	652	585		628	675					30.50	565
20.00		650	658	590		635	682					31.00	575
21.00							688					32.00	590
22.00							691					33.00	599
END		665	675	600		655	700					34.00	606
												35.00	613
												36.00	617
												END	625

Distribution:

S. L. Marra, 773-A
T. B. Brown, 773-A
D. H. McGuire, 999-W
S. D. Fink, 773-A
C. C. Herman, 773-A
E. N. Hoffman, 999-W
F. M. Pennebaker, 773-42A
W. R. Wilmarth, 773-A
R. A. Pierce, 773-A
T. C. Shehee, 773-A
C. A. Nash, 773-A
M. L. Crowder, 773-A
P. R. Jackson, 703-46A

Records Administration (EDWS)

S. L. Garrison, 704-2H
P. B. Andrews, 704-2H
K. P. Burrows, 704-2H
S. L. Hudlow, 221-H
A. E. Kelly, 221-H
J. L. Bodkin, 221-H
K. J. Usher, 704-2H
J. B. Schaade, 704-2H
M. J. Lewczyk, 221-H
K. J. Gallahue, 221-H
J. E. Therrell, 704-2H
J. M. Jordan, 704-2H
K. D. Scaggs, 704-2H
T. E. Worth, 221-H
A. T. Masterson, 704-2H
A. B. Hickman, 704-2H
C. E. Johnson, 704-2H
J. Mancilla, 704-2H
M. T. Pelc, 704-2H
J. L. Varble, 704-2H
R. M. Mobley, 704-2H