WSRC-TR-2002-00350

Key Words: HB-Line
Oxalate
Gas Generation

# Gas Generation during Sodium Permanganate Addition to HB-Line Phase II Filtrate Tank(U)

B. C. Hill
M. G. Bronikowski

August 29, 2002

**Westinghouse Savannah River Company**
**Savannah River Site**
**Aiken, SC 29808**

Savannah River Technology Center
SRTC
We Put Science to Work

**PREPARED FOR THE U. S. DEPARTMENT OF ENERGY UNDER CONTRACT NO. DE-AC09-96SR18500**

**This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.**

## DISCLAIMER

**This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.**

**This report has been reproduced directly from the best available copy.**

**Available for sale to the public, in paper, from: U.S. Department of Commerce, National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161,**
**phone: (800) 553-6847,**
**fax: (703) 605-6900**
**email:** orders@ntis.fedworld.gov
**online ordering:** http://www.ntis.gov/help/index.asp

**Available electronically at** http://www.osti.gov/bridge
**Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from: U.S. Department of Energy, Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831-0062,**
**phone: (865)576-8401,**
**fax: (865)576-5728**
**email:** reports@adonis.osti.gov

WSRC-TR-2002-00350

# Gas Generation during Sodium Permanganate Addition to HB-Line Phase II Filtrate Tank(U)

B. C. Hill
M. G. Bronikowski

Author: ______________________________ Date: __________
Benjamin Hill, SMT/ATS

Author: ______________________________ Date: __________
Michael Bronikowski, SMT/ATS

Technical Reviewer:______________________________ Date: __________
Neal Askew, SMT/ATS

Manager: ______________________________ Date: __________
Alice Murray, SMT/ATS

Authorized Derivative Classifier: ______________________________

## ABSTRACT

HB-Line Phase II process requires the addition of sodium permanganate followed by a sodium nitrite addition to prevent the precipitation of plutonium solids in a non-geometrically safe vessel. Previous experimental work has shown this method effective. Current concerns are related to the gas generated by the reaction. Potential difficulties include tank over-pressurization and tank overflow due to foaming or eructation. It is also necessary to verify that the quantity of permanganate specified by the facility is sufficient to reach the desired endpoint in a single addition.

Several experiments were performed in which sodium permanganate and sodium nitrite were added to simulated, non-radioactive filtrate solutions at constant feed rates. The volume of gas generated by the reaction was monitored. Experiments were also performed using a “reverse addition” method. In this method the permanganate was added to the reaction vessel first, then the simulated filtrate solution was added to the vessel at a constant rate.

It was found that the gas generation rate is not a linear function of the permanganate feed rate. The gas generation rate peaked early during the permanganate addition for all of the standard addition experimental runs. The peak gas generation rate was found to be strongly dependent on the permanganate feed rate. No significant foaming or bubbling occurred at the feed rates tested.

Many technical issues make the “reverse addition” method an undesirable option. Problems associated with this method include excessive solids generation, increased $NO_x$ generation, and excessive gas generation.

Experimental results indicate the amounts of permanganate supplied as input by the facility are not sufficient to reach the desired endpoint.

# TABLE OF CONTENTS

## LIST OF FIGURES

## LIST OF TABLES

## INTRODUCTION

The HB-Line Phase II process involves the concentration and purification of plutonium solutions. The first stage of this process includes anion exchange followed by the precipitation of plutonium oxalate. Solids formed during precipitation are collected using filtration. The filtrate solution is to be recycled to recover plutonium that was not captured in the filtration process. The recycled filtrate solution will be sent to a non-geometrically favorable vessel where formation of solids must be avoided for criticality safety reasons. To prevent the precipitation of plutonium solids any oxalate ions or oxalate precursor, such as ascorbic acid, in the solution must be destroyed. Oxalate destruction can be accomplished by the addition of sodium permanganate to the filtrate tank. Sodium permanganate also oxidizes hydrazine and ascorbic acid, which are also present in the filtrate solution. The oxidation of oxalate, hydrazine, and ascorbic acid by the permanganate ion can be represented by the following equations:[1,2]

Partial reduction of permanganate: $\Delta H_r$ (kcal/mol Mn $O_4^-$)

$$2MnO_4^- + 3C_2O_4^{2-} + 8H^+ \rightarrow 2MnO_2 + 6CO_2 + 4H_2O$$

-118 (1)

$$20MnO_4^- + 3C_6H_8O_6 + 20H^+ \rightarrow 20MnO_2 + 18CO_2 + 22H_2O$$

-113 (2)

$$10MnO_4^- + 6N_2H_5^+ + 4H^+ \rightarrow 10MnO_2 + 3N_2O + 3N_2 + 17H_2O$$

-104 (3)

Complete reduction of permanganate:

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

-174 (4)

$$4MnO_4^- + C_6H_8O_6 + 12H^+ \rightarrow 4Mn^{2+} + 6CO_2 + 10H_2O$$

-166 (5)

$$2MnO_4^- + 2N_2H_5^+ + 4H^+ \rightarrow 2Mn^{2+} + N_2O + N_2 + 7H_2O$$

-151 (6)

As shown by the above equations, the addition of sodium permanganate generates large quantities of gas, so the feed rate of the sodium permanganate must be limited to avoid exceeding the venting capacity of the filtrate tank. An alternate “reverse addition” method is also being considered in which the sodium permanganate would be added to the filtrate collection tank prior to filtration. It should be noted that the venting capacity of the tank is greatly reduced during filtration.

Excess manganese oxide ($MnO_2$) solids formation may also be produced by partial reduction of permanganate via the Guyard Reaction (7):

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \rightarrow 5MnO_2 + 4H^+$$

-35 (7)

The Guyard reaction is catalyzed by the presence of $MnO_2$ solids, thus it is best to keep $MnO_2$ solids to a minimum during oxalate destruction. Note that if permanganate is only partially reduced, then manganese dioxides solids will be formed (Equation 1, 2, and 3) and the Guyard reaction will compete with the other partial oxidation reactions.

Any manganese oxide solids that are formed will be dissolved by the addition of sodium nitrite. The equation for the reaction of manganese oxide and nitrite is:

$$MnO_2 + NO_2^- + 2H^+ \rightarrow Mn^{2+} + NO_3^- + H_2O$$

-21 (8)

Competing with the reduction of $MnO_2$ is the loss of nitrite in acidic solution. High acid or nitrite concentration will increase this loss.

$$2NO_2^- + 2H^+ \rightarrow H_2O + NO + NO_2 \qquad 11 \qquad (9)$$

Two cases are of particular interest for facility operations. These cases are summarized in Table 1.

Table 1. Filtrate treatment scenarios.

| Case | Tank volume before additions, liters | Sodium permanganate added, liters | Sodium nitrite added, liters |
|---|---|---|---|
| 1 | 53 | 4.8 | 4 |
| 2 | 70 | 8.5 | 7 |

The addition of sodium permanganate followed by sodium nitrite has been shown effective in the removal of solids from the filtrate solution.[1] The focus of this series of experiments is to examine the potential for tank overpressurization due to excessive gas generation and the potential for tank overflow due to foaming or eructation. Experiments will also determine if the quantities of permanganate and nitrite specified in Table 1 are sufficient to provide complete oxidation of all of the species of interest and complete removal of any solids present.

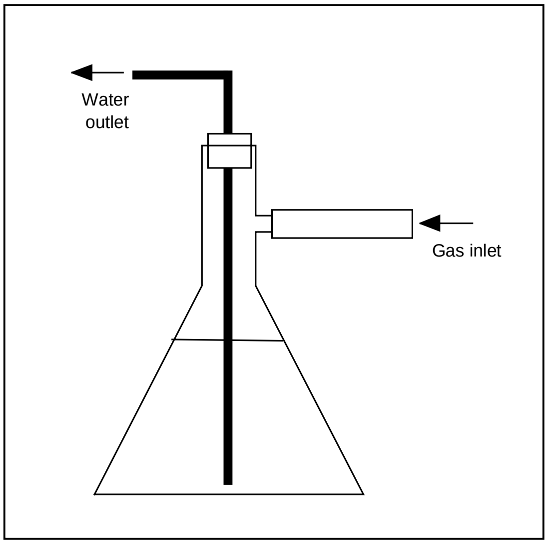
# DISCUSSION

## Apparatus

The reaction was carried out in a sealed glass vessel (5 inch diameter and 3 inch height) with several ports on the top. Three of the ports were used and the rest were sealed during experimental runs. One port was used as inlet to add solutions gradually using a pump. The second port was used to measure the temperature of the solution. The third port served as the gas outlet. Off-gas temperature was measured at the gas outlet of the reaction vessel.

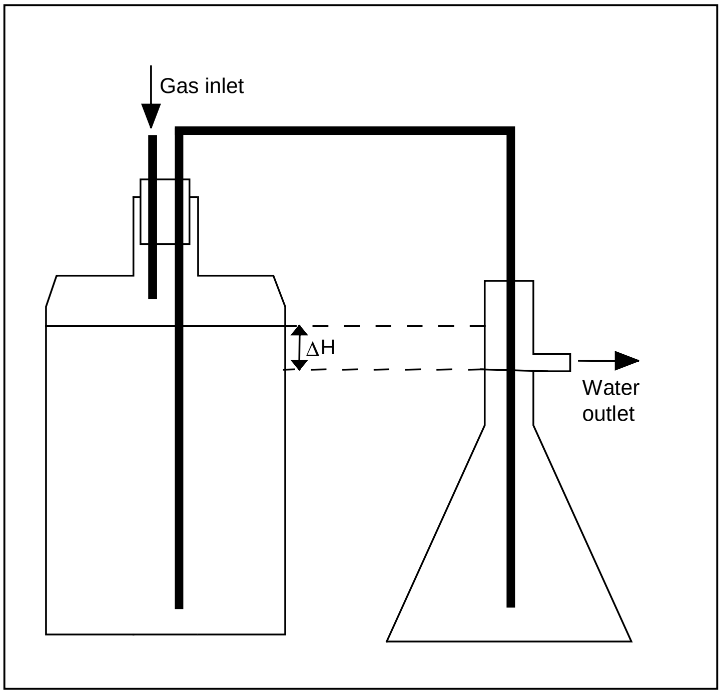
Two different gas collection setups were used. For the earlier experimental runs (Run # 1-8), gas was collected in a 2-liter filter flask (see Figure 1). The filter flask was filled almost full of water. As gas entered through the filter flask arm and it forced an approximately equal volume of water out of the flask through a piece of glass tubing that ran through the stopper and almost to the bottom of the flask. The water that was forced out of the flask was collected in graduated cylinders.

Figure 1. Simplified schematic of original gas collection apparatus.



For the later runs (Run #'s 9-12 and the reverse addition runs), the gas collection apparatus was modified (see Figure 2). The gas generated by the reaction was discharged into the headspace of an 8-liter jug, which was mostly filled with water. The 8-liter jug had both an air inlet and a water outlet. The tubing for the water outlet was well below the water level so that no gas would be discharged from the jug. This setup allowed a volume of water to be displaced from the jug that was equal to the volume of gas generated by the reaction. The water from the 8-liter jug was discharged at a constant head using a 2-liter filter flask as an overflow. Water was discharged into the flask from the jug and overflowed through the arm of the filter flask. The tubing between the jug and the flask was filled with water before each experimental run. The overflow was collected in graduated cylinders. The use of a constant head overflow minimized the head difference between the jug and the discharge. Other advantages of the modified apparatus were that it could collect a greater volume of gas and that it prevented back flow of the water during low gas flow rates.

Figure 2. Simplified schematic of modified gas collection apparatus.



## Experimental Methods

A simulated filtrate solution was prepared in the laboratory. The simulated filtrate solution contained 0.15 M oxalic acid, 0.056 M ascorbic acid, 3.95 M Nitric Acid, and 0.030 M hydrazine. A 3.8 M (40 wt. %) sodium permanganate solution was used for the permanganate addition. A 5.4 M sodium nitrite solution was used to destroy the manganese oxide solids.

### Standard Addition

The simulated filtrate solution was placed in the reaction vessel. Stirring of the filtrate solution was provided by a magnetic stir plate. Sodium permanganate was added to the filtrate solution at a constant rate with a peristaltic pump. Once a purple/pink color was noted in the solution, the permanganate addition was continued for 2-3 minutes to achieve an excess of permanganate. The sodium permanganate was weighed before and after the addition to determine the total amount of sodium permanganate used. Once the sodium permanganate addition was complete, the inlet tubing was rinsed thoroughly with de-ionized water. Sodium nitrite was then pumped into the simulated filtrate solution at a constant rate. Sodium nitrite addition continued until any solids created by the permanganate addition disappeared. During both the sodium permanganate and the sodium nitrite additions, the total amount of water displaced by gas generation was recorded at one-minute intervals. The temperature of the solution and temperature of the off-gas were also recorded at one-minute intervals.

Table 2 contains the experimental parameters for all of the standard addition runs. In Run #5, 0.897 grams of cerium oxalate were added to 100 ml of the simulated filtrate solution to act as a surrogate for plutonium oxalate solids. In Run #6, the solution was heated to approximately 30°C prior to permanganate addition. All other runs began with the solution at ambient temperature (approximately 20°C). Run #1 and #4 results are not reported due to problems with the gas collection apparatus and permanganate solution delivery.

Table 2. Experimental parameters.

| Run # | Initial solution temperature, °C | Volume of simulated filtrate solution, ml | Flow rate of sodium permanganate, ml/min | Total permanganate added, ml | Flow rate of sodium nitrite, ml/min | Total sodium nitrite added, ml |
|---|---|---|---|---|---|---|
| 2 | 19.5 | 100 | 0.43 | 13.0 | 0.99 | 12.9 |
| 3 | 20.2 | 100 | 0.90 | 12.6 | 1.16 | 11.6 |
| 5 | 20.5 | 100 | 0.42 | 15.4 | 0.55 | 16.9 |
| 6 | 32.2 | 100 | 0.50 | 13.9 | 0.60 | 14.3 |
| 7 | 19.9 | 100 | 0.25 | 13.8 | 0.58 | 12.8 |
| 8 | 20.1 | 300 | 1.44 | 41.9 | 1.71 | 35.9 |
| 9 | 20.0 | 100 | 0.90 | 18.1 | 0.93 | 23.3 |
| 10 | 20.1 | 100 | 0.71 | 14.2 | 0.66 | 17.7 |
| 11 | 19.8 | 200 | 1.43 | 28.5 | 1.52 | 25.9 |
| 12 | 20.3 | 200 | 1.53 | 30.5 | 1.59 | 33.2 |

Two duplicate runs were performed using the standard addition method (Run #11 and Run #12). Both of these runs used 200 ml of simulated filtrate solution and a permanganate addition rate of approximately 1.50 ml/min (0.75 ml/min per 100 ml of filtrate). This flow rate was chosen to be close to expected facility operating conditions. Permanganate was added at this rate for 20 minutes for a total sodium permanganate solution volume of ~30 ml (15 ml per 100 ml of filtrate).

### Reverse Addition

Two experimental runs were performed using a “reverse addition” method. In both runs, 15 ml of 40 wt% sodium permanganate solution was added to the reaction vessel prior to the addition of 100 ml of simulated filtrate solution pumped in at a constant rate. In reverse Run #1 and Run #2, the simulated filtrate solution was added over a 30-minute period and a 46-minute period, respectively. After addition of the filtrate solution was completed, sodium nitrite was added at a constant rate to destroy the any solids created by the permanganate addition. For both of the “reverse addition” runs gas temperature, solution temperature, and gas generation were monitored as described in the standard addition section.

## Results

### Standard Addition

All of the standard addition runs exhibited very similar appearance changes during the sodium permanganate and sodium nitrite addition. The simulated filtrate solution started out a clear to pale yellow color. The color of the filtrate solution depended on when it was prepared. Fresh solution was clear, while solution that had been prepared a few days earlier was a pale yellow color. This pale yellow color was most likely caused by the presence of ascorbic acid degradation products. Any yellow coloring present in the filtrate solution reacted, immediately, within the first drop or two of permanganate solution.

As sodium permanganate solution dripped into the filtrate, the added permanganate drops proceeded through a series of rapid color changes. The solution changed quickly through purple, cherry-red, brown, yellow, and clear. The different colors can be attributed to intermediates formed during the reaction between permanganate and oxalate. The $[Mn(C_2O_4)_3]^{3-}$ complex is red while the $[Mn(C_2O_4)_2(H_20)_2]^-$ complex is yellow.[2] Early in the addition, there was no evidence of manganese oxide solids. All of the permanganate added was completely reduced to the colorless $Mn^{2+}$ ion.

Two to five minutes into the addition, dark brown solids began to form. The brown manganese dioxide solids indicated that the permanganate ion was only partially reduced (see Reaction 1, 2, and 3). More solids formed as the addition continued and the solution quickly became opaque. Later in the addition, a ring of solids would develop on the edge of the reaction vessel just above the liquid level. Some bubbling was noted during the permanganate addition. Most of the bubbling occurred early in the addition, but no significant foaming was noted during any of the runs. A thin layer of foam was present during some runs, but the layer was always less than ¼ inch thick.

Early in the sodium nitrite solution addition, a light brown gas ($NO_x$) would begin to accumulate in the headspace of the reaction vessel. No brown gas was noted in the gas collection vessel. The appearance of the solution changed very little during the sodium nitrite addition. Approximately midway through the nitrite addition, the ring of manganese oxide solids on the side of the reaction vessel would begin to disappear. Later in the addition, the solution would become noticeably clearer as the solids were destroyed. Suddenly the solution would clear up. During some of the runs, manganese dioxide solids were deposited on the bottom of the vessel. These solids took slightly longer to destroy and tended to accumulate below the permanganate inlet.

All of the standard addition runs exhibited a peak in the gas generation rate after a short induction period. Table 3 contains the peak gas generation rate for each run and the time at which the peak occurred. Figure 3 is a plot of peak gas generation rate versus the permanganate addition rate. Data points from various runs are labeled. The peak gas generation rate was found to be strongly dependent upon the permanganate addition rate. Even though there were experimental parameters other than permanganate flow rate (ex. higher initial temperature on run #6, addition of cerium oxalate in Run #5, three filtrate volumes used, and various stirring rates) the data still roughly follow a straight line.

Table 3. Peak gas generation rates.

| Run # | Time to peak / total addition time, min | Maximum gas generation rate, ml/min per 100 ml of filtrate |
|---|---|---|
| 2 | 7 / 30 | 180 |
| 3 | 3 / 14 | 315 |
| 5 | 6 / 37 | 145 |
| 6 | 4 / 28 | 172 |
| 7 | 7 / 56 | 90 |
| 8 | 5 / 29 | 183 |
| 9 | 2-3 / 20 | 250 |
| 10 | 3 / 20 | 230 |
| 11 | 3-4 / 20 | 245 |
| 12 | 3-4 / 20 | 235 |

Table 4 contains the total amount of gas generated and the average gas temperature for each run. The moles of gas generated and the moles of gas expected are also included in Table 4. The total moles of gas generated were calculated using the average gas temperature.

Run #5 generated a greater volume of gas (per 100 ml of filtrate) than any of the other standard addition runs. The additional gas was due to oxidation of the increased oxalate ions present from the solid cerium oxalate added to this run. No significant increase in the peak gas generation rate (see Figure 3) was seen with the additional oxalate suggesting that the off gas peak is due to the oxidation of non-complexed oxalate ions. Complexed plutonium oxalate solids have been shown to react more slowly previously.[4]

Figure 3. Permanganate addition rate vs. peak gas generation rate.

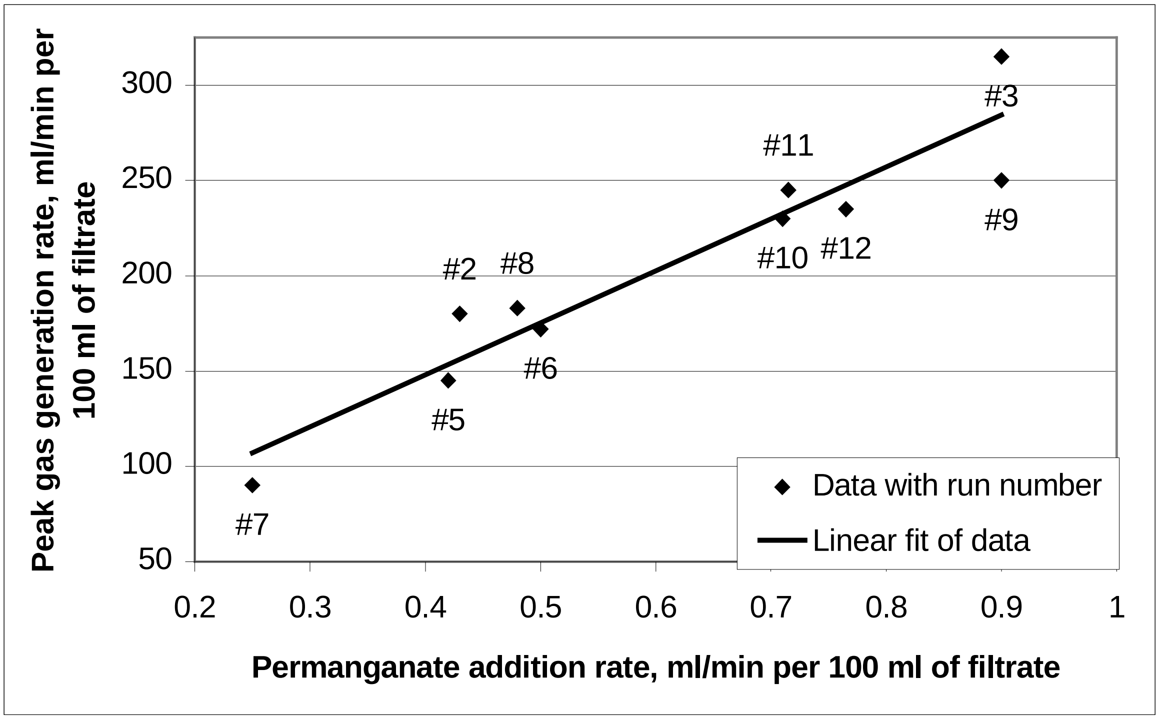


Table 4. Total gas generation, average gas temperature, and moles of gas expected.

| Run # | Total gas generation, liter per 100 ml of filtrate | Average gas temperature, C | Moles of gas generated per 100 ml of filtrate, moles | Moles of gas expected per 100 ml of filtrate, moles |
|---|---|---|---|---|
| 2 | 1.592 | 19.5 | 0.0663 | 0.0666 |
| 3 | 1.480 | 19.6 | 0.0616 | 0.0666 |
| 5 | 1.679 | 20.5 | 0.0697 | 0.0700 |
| 6 | 1.572 | 20.7 | 0.0652 | 0.0666 |
| 7 | 1.320 | 20.0 | 0.0549 | 0.0666 |
| 8 | 1.437 | 20.1 | 0.0597 | 0.0666 |
| 9 | 1.344 | 20.2 | 0.0558 | 0.0666 |
| 10 | 1.344 | 19.9 | 0.0559 | 0.0666 |
| 11 | 1.533 | 19.7 | 0.0638 | 0.0666 |
| 12 | 1.435 | 20.1 | 0.0596 | 0.0666 |

The off gas peak may be attributed to the oxidation of non-complexed oxalate ion via reaction 4. Reactions 1, 2, and 3 are ruled out because the off gas peak occurs prior to manganese oxide solids formation. Although hydrazine reacts immediately not enough is present to produce the amount of gas given off in the peak. The temperature profile for the reaction shows that much of the rise in solution temperature occurs prior to manganese oxide formation and corresponds to the off gas peak. Heats of reaction per mole of permanganate, calculated using the values of reference 3 and the amount of gas given off, also suggest reaction 4 produces the gas peak as it gives off more heat and gas per mole of permanganate than reaction 5. Finally, ascorbic acid produces oxalate as an intermediate,[5] and subsequently has been shown to react more slowly and less vigorously than oxalate when being oxidized by sodium permanganate.[6]

The maximum solution temperatures attained and change in temperatures for the solution are shown in Table 5. As noted above the fastest increase in temperature coincides with the off gas peak.

Table 5. Maximum solution temperature.

| Run # | Solution change in temperature ΔT °C | Maximum solution temperature, °C |
|---|---|---|
| 2 | 19.1 | 38.6 |
| 3 | 24.3 | 44.5 |
| 5 | 18.7 | 39.2 |
| 6 | 14.9 | 47.1 |
| 7 | 13.2 | 33.1 |
| 8 | 30.4 | 50.5 |
| 9 | 14.5 | 34.5 |
| 10 | 17.6 | 37.7 |
| 11 | 25.9 | 45.7 |
| 12 | 27.7 | 48.0 |

Two duplicate runs (#11 and #12) were performed where the scaled permanganate flow rate was set close to the expected permanganate feed rate in the facility. The permanganate addition rates for the two runs were 0.71 and 0.76 ml/min per 100 ml of filtrate with peak off-gassing rates of 245 and 235 ml/min per 100 ml of filtrate, respectively. Figure 4 shows the off-gassing rate over time for both runs. The shape of the curves is typical for the standard runs.

Figure 4. Gas generation rate vs. time for duplicate runs.

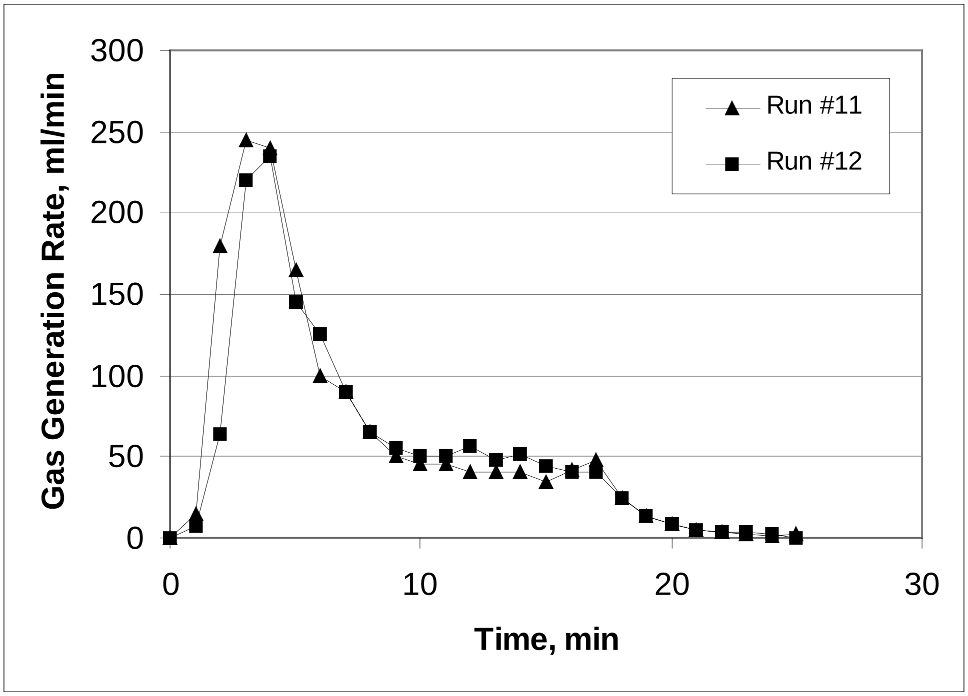
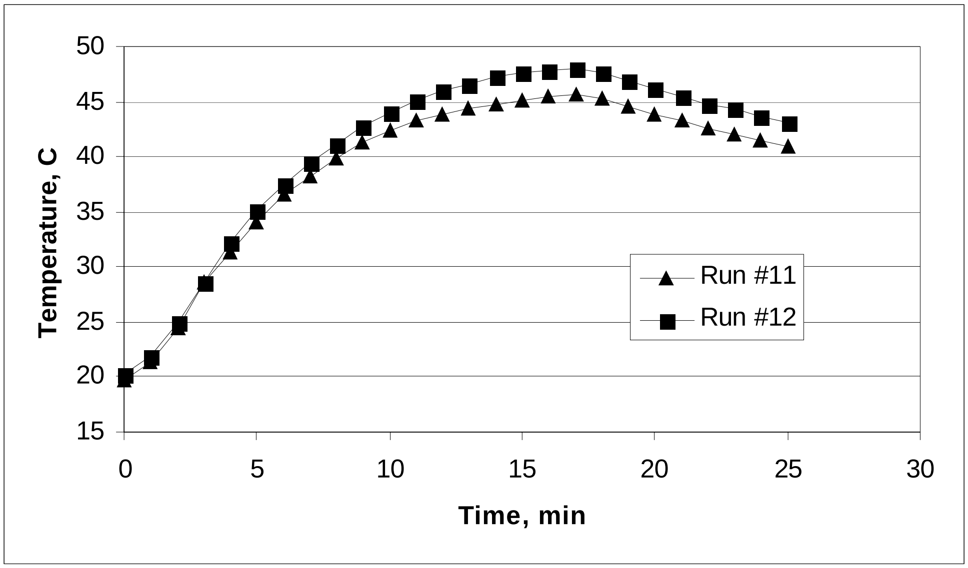


Figure 5. Solution temperature vs. time for duplicate runs.



No solids were observed on the bottom of the reaction vessel. Figure 5 contains a plot of the solution temperature versus time for Run #11 and #12. Figures 4 and 5 demonstrate the repeatability of the data. Run #11 had a slightly lower permanganate addition rate and a slightly lower initial temperature than Run #12. This could be the reason for the slightly lower reaction temperature during Run #11.

For cases in which permanganate is the limiting reagent, the maximum gas generation rate is dependent on the permanganate addition rate only. The ratio of maximum gas generation rate to permanganate addition rate can be calculated using the data from Table 2 and Table 3. The average ratio of gas generation rate to permanganate addition rate is 3.26 cfm/(mol of $MnO_4^-$/min) with a standard deviation of 0.37 cfm/(mol of $MnO_4^-$/min). This ratio can be multiplied by a permanganate addition rate (mol/min) to estimate the maximum gas generation rate (cfm at 25 C and 1 atm). The ratio can also be used to determine the maximum allowable permanganate feed rate for a given tank venting capacity. For example, assuming a tank venting capacity of 4 cfm, a maximum allowable permanganate feed rate of 1.23 mol/min can be calculated.

## Reverse Addition

The rate of gas generation for the two reverse additions was relatively constant over time (see Figure 6); however, it should be noted that rate of addition of the simulated filtrate solution was constant. It is not expected that the rate of addition would be this well controlled during the actual filtration process. The maximum rate of gas generation for Reverse Run #1 and Reverse Run #2 was 64 ml/min and 68 ml/min, respectively. These values correspond to a gas generation rate of approximately 1.2 cfm in the field, which may exceed the tank’s reduced gas discharge capacity during filtration.

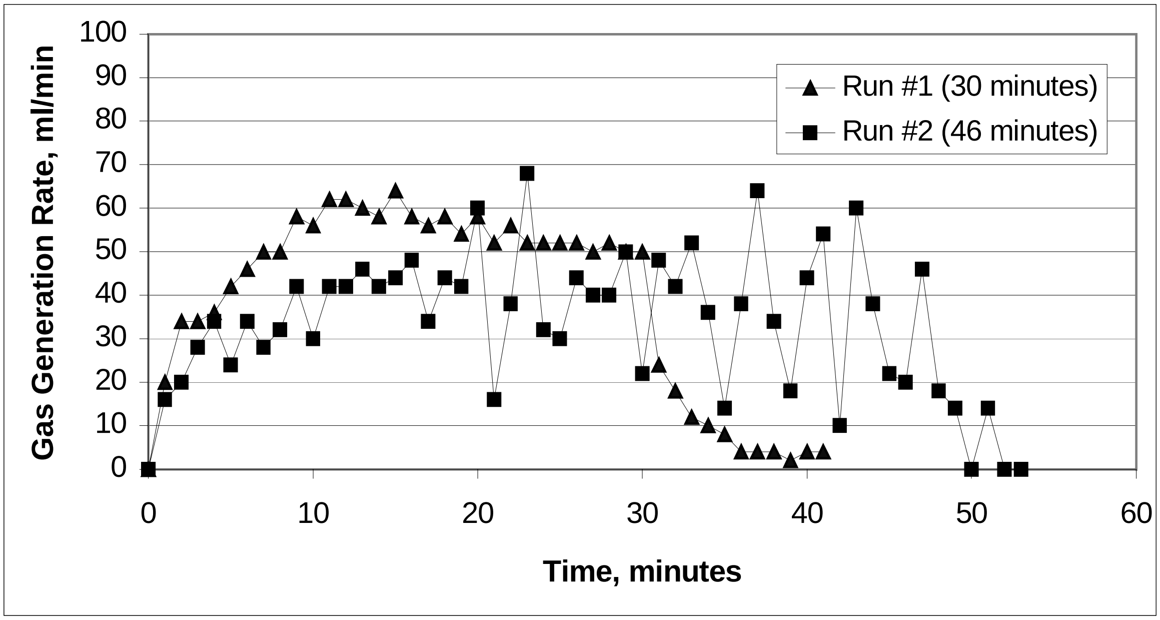
Several differences existed between the standard and the reverse addition. Manganese oxide solids formed during the standard addition tended to be small particles that would remain suspended in solution with agitation. More manganese oxide solids formed during the reverse addition. The solids had a greater tendency to form clumps and to adhere to the bottom of the vessel. Clumped solids can potentially interfere with sample collection in the facility, since they may have a tendency to form in the center of the tank away from the agitators and near the sampling port. Another problem associated with the larger, solid clumps is that they take longer to destroy than small solid particles suspended in solution. The larger clumps have a much smaller surface area available for the nitrite to attack. Because of this slow reaction time, excess nitrite can build up in solution causing the formation of $NO_x$ gas via reaction 9. Some $NO_x$ gas was noted in the reaction vessel during the experimental runs using the standard addition method, but a much greater quantity of $NO_x$ was observed during the reverse additions. The additional $NO_x$ increased amount of gas produced in reverse reaction 2. The gas present in the reaction vessel during the two reverse additions was a much darker brown color than the gas present during any of the standard additions. Brown gas was also observed in the gas collection vessel during both of the reverse additions. This phenomenon was never observed during any of the standard addition runs.

Table 6. Gas temperature and total gas generation for reverse additions.

| Run # | Total gas generation, liter per 100 ml of filtrate | Average gas temperature, C | Moles of gas generated | Moles of gas expected* |
|---|---|---|---|---|
| Reverse 1 | 1.518 | 19.4 | 0.0632 | 0.0666 |
| Reverse 2 | 1.698 | 20.2 | 0.0705 | 0.0666 |

*Does not include $NO_x$

Figure 6. Gas generation rate vs. time for reverse additions.



The excessive manganese oxide solids formation during the reverse addition may be partially due to the Guyard Reaction (reaction 7). During a standard addition, the concentration of $MnO_4^-$ and $Mn^{2+}$ will be low since a small volume of permanganate is being added to a large volume of filtrate solution and the permanganate quickly reacts with oxalate. During the initial stages of the reverse addition, the concentrations of $MnO_4^-$ and $Mn^{2+}$ will be high, which will promote the Guyard reaction and the formation of excess solids. Additionally, the Guyard reaction is catalyzed by the presence of the $MnO_2$ solids formed. The reaction also produces $H^+$ which would increase the production of $NO_x$ gases via reaction 9.

## Required Reactants

### Permanganate

Reference 1 recommends 22 ml of 3 molar sodium permanganate per 100 ml of filtrate solution to achieve a 10% excess of permanganate. This is equivalent to 17.4 ml of 3.8 molar (40 weight percent) sodium permanganate per 100 ml of filtrate solution. The experimental design used to determine this value was based on very conservative assumptions, including the assumption that no oxalic acid was removed with the filtered plutonium solids. As expected, this value is far greater than the amount of permanganate that was required to reach the endpoint plus 10% excess in all of the experimental runs. The amount of 3.8 M sodium permanganate required to reach the endpoint for each of the runs is contained in Table 7. The average permanganate that was required to reach the endpoint is 12.5 ml per 100 ml of filtrate with a standard deviation of 0.75 ml per 100 ml of filtrate. (Note run #5 is not included in the average due to the added cerium oxalate in this run.) The variance associated with this value is primarily due to the fact that observations were taken at one minute intervals and that it was difficult to detect color changes in the solution due to the dark brown suspended solids.

Table 7. Sodium permanganate required to reach the endpoint in experimental runs.

| Run # | $NaMnO_4$ required to reach endpoint, ml per 100 ml of filtrate | $NaMnO_4$ required to reach endpoint + 10% excess, ml per 100 ml of filtrate |
|---|---|---|
| 2 | 13.0 | 14.3 |
| 3 | 11.6 | 12.8 |
| 5 | 14.1 | 15.5 |
| 6 | 12.9 | 14.2 |
| 7 | 13.3 | 14.6 |
| 8 | 13.0 | 14.3 |
| 9 | 11.7 | 12.9 |
| 10 | 11.3 | 12.4 |
| 11 | 12.8 | 14.1 |
| 12 | 13.0 | 14.3 |

The stoichiometric amount of permanganate is between 8.2 and 13.6 ml per 100 ml of solution depending upon the reaction pathway. The reaction pathway of equations 4, 5, and 6 give the lower estimate and the alternate pathway of equations 1, 2, and 3 give the higher estimate. From the data reported here the reaction pathway is best represented by equations 6, followed by 4, and then when producing manganese oxide, equation 2. The stoichiometric amount of permanganate needed for the 6,4,2 reaction pathway is 12.0 ml per 100 ml of filtrate solution. Additional permanganate would be needed to reach the endpoint if oxalate solids were contained in the filtrate, unless the end solution is heated.[7] As an example, Run #5 required additional permanganate to oxidize the cerium oxalate that was added to the filtrate. With the 10% excess permanganate 13.2 ml of 40% wt sodium permanganate is needed per 100 ml.

For Case 1 and Case 2 of Table 1, the amount of 3.8 M permanganate specified by the flowsheet is 9.1 ml and 12.1 ml per 100 ml of filtrate, respectively. These values are very low compared to the amounts required in experimental runs. If the composition of the filtrate in the facility is similar to that of the simulated filtrate solution, then the permanganate volumes specified in Table 1 will not be sufficient to provide complete oxidation of the species of interest.

### Nitrite

From Equation 7, one mole of nitrite ion is required per mole manganese dioxide. Assuming that all of the permanganate added is transformed to manganese dioxide, one mole of sodium nitrite is required for each mole of sodium permanganate added to the filtrate. Table 8 contains the moles of sodium nitrite and sodium permanganate added during each test and the molar ratio of sodium nitrite to sodium permanganate. The experimental nitrite to permanganate ratios range from 1.21 to 2.17. These ratios indicate that in most tests a large excess of sodium nitrite was added. The large excess is most likely due to the nitrite addition method and loss of nitrite by reaction 9. Nitrite addition was continued until all of the solids disappeared. In many cases a few large clumps of solids remained after the majority of the solids had been destroyed. It is likely in many cases that sufficient nitrite was already present in the filtrate to dissolve these clumps.

Table 8. Total moles of permanganate and moles of nitrite added.

| Run # | Moles of $NaNO_2$ added | Moles of $NaMnO_4$ added | Molar ratio of $NaNO_2$ to $NaMnO_4$ |
|---|---|---|---|
| 2 | 0.0698 | 0.0498 | 1.40 |
| 3 | 0.0627 | 0.0484 | 1.30 |
| 5 | 0.0912 | 0.0590 | 1.55 |
| 6 | 0.0774 | 0.0532 | 1.45 |
| 7 | 0.0689 | 0.0529 | 1.30 |
| 8 | 0.0646 | 0.0535 | 1.21 |
| 9 | 0.1259 | 0.0692 | 1.82 |
| 10 | 0.0956 | 0.0543 | 1.76 |
| 11 | 0.0699 | 0.0546 | 1.28 |
| 12 | 0.0729 | 0.0585 | 1.25 |
| Reverse 1* | 0.1237 | 0.0570 | 2.17 |
| Reverse 2 | 0.0694 | 0.0574 | 1.21 |

* Reverse 1 was run to excess at a very fast addition rate (3.28 ml/min).

For Case 1 and Case 2 of Table 1, the amount of 5.4 M nitrite specified by the flowsheet is ~82% of the 3.8M permanganate volume used in both cases. These values are low compared to the amounts required in experimental runs by about ~11%. Experimentally, the average molar ratio of sodium nitrite to sodium permanganate is 1.33 ± 0.11 if runs 9, 10, and Reverse 1 of Table 8 are not included. These runs had the larger clumps of manganese oxide solids and/or an obvious excess of nitrite was added. Using the experimental average, 1 ml of 40% wt sodium permanganate would require 0.93 ml of sodium nitrite to react with all the manganese oxide solids. If the composition of the filtrate in the facility is similar to that of the simulated filtrate solution, then the nitrite volumes specified in Table 1 may not be sufficient to provide complete solids removal.

## CONCLUSIONS

Gas generation rates are not constant during the permanganate addition. Gas generation rates peak early in the sodium permanganate addition after a short induction period. The off gas peak can be explained by the oxidation of free oxalate by permanganate which is fully reduced to $Mn^{2+}$ and is strongly related to the permanganate addition rate. Foaming does not appear to be a significant problem at the permanganate feed rates that were tested, but permanganate feed rates must be carefully controlled to avoid over-pressurization of the reaction vessel.

If permanganate is the limiting reagent, the maximum gas generation rate is dependent on the permanganate addition rate only. The average ratio of the maximum gas generation rate to the permanganate addition rate is 3.26 cfm/(mol of $MnO_4^-$/min) with a standard deviation of 0.37 cfm/(mol of $MnO_4^-$/min). This ratio can be multiplied by a permanganate addition rate (mol/min) to estimate the maximum gas generation rate (cfm at 25 C and 1 atm).

Values specified by the facility (see Table 1) may not provide sufficient sodium permanganate for the complete oxidation of oxalate, ascorbic acid, and hydrazine. The amount of 40 wt% sodium permanganate at a 10% excess was determined be 13.2 ml per 100 ml filtrate solution. This value was calculated using a reaction pathway in which hydrazine and free oxalate were oxidized prior to $MnO_2$ solid formation. Ascorbic acid was then oxidized next with production of manganese oxide solids. The stoichiometry of the reaction pathway is given by equations 6, 4, and 2.

The required volume of sodium nitrite specified by the facility (see Table 1) was found to be 11% low. Experimentally, it was determined that on average 0.93 ml of 5.4M $NaNO_2$ are needed for every ml of 40 wt% sodium permanganate used.

The use of the reverse addition method is not recommended. The reverse method produces more manganese oxide solids via the Guyard reaction thus more nitrite is needed to dissolve them. The experimental maximum rate of gas generation values correspond to a gas generation rate of approximately 1.2 cfm in the field, which may exceed the tank’s reduced venting capacity during filtration. Additionally the reverse method promotes increased $NO_x$ generation.

## REFERENCES

1) J. H. Gray, "The Formation and Dissolution of Plutonium Oxalate Solids in HB-Line Phase II Filtrate Streams", WSRC-TR-2001-00317, July 12, 2001.
2) J. W. Ladbury, C. F. Cullis, "Kinetics and Mechanism of Oxidation by Permanganate," Chemical Reviews, 58, 403, 1959.
3) N. Askew, "Gas and Heat Generation after HB-Line Phase II Chemical Addition," X-CLC-H-00161.
4) J. H. Gray to R. Smith, "Dissolving Plutonium Oxalates (U)" SRT-ATS-2000-00130 September 29, 2000.
5) J. H. Gray to R.L. Yourchak, "Analysis of C-7B solids", WSRC-TR-2000-00140, October 27, 2000.
6) J.I. Mickalonis, "NMSS Dissolver Testing II" Linear sweep voltammetry experiments, WSRC-NB-99-00210, p84-85.
7) N. E. Bibler, J. E. Hoisington, and E.W. Holtzscheiter, "Technical Data Summary, Decomposition of Oxalic Acid by the Manganese Catalyzed Nitric Acid Reaction, Laboratory-Scale and Engineering Analysis" DPSTD-80-36, March 1981.