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# Tank 48H Tetraphenylborate Mitigation: Simulant Studies using Sodium Permanganate

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# Tank 48H Tetraphenylborate Mitigation: Simulant Studies using Sodium Permanganate

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# EXECUTIVE SUMMARY

Three experiments were performed to determine the efficacy of using sodium permanganate for the destruction of tetraphenylborate (TPB) in Tank 48H simulants at 40 °C. The intent was to identify a set of conditions for in-tank or out-of-tank processing consistent with returning Tank 48H to service. Sodium permanganate was added over 14 days to Tank 48H simulants prepared at varying initial pH values: 1) pH 11 for comparison with previous experiments at room temperature, 2) pH 10 as the minimum pH recommended by the Corrosion Control Program for in-tank processing, and 3) pH 8 to determine the effectiveness of TPB destruction at near neutral pH where the permanganate reaction is more favorable.

TPB destruction was monitored indirectly by measuring boron (B) and potassium (K) ingrowth in filtrate samples and directly by measuring TPB and TPB byproducts in unfiltered samples. A summary of the results are shown in the table below and indicate the destruction of TPB increases as a function of time and permanganate addition.

**Summary of TPB Destruction Results After 1 and 2 Weeks of Permanganate Oxidation**

| | % Destruction Week 1 | | | % Destruction Week 2 | | |
|---|---|---|---|---|---|---|
| | B | K | TPB | B | K | TPB |
| pH 8 | 7% | 49% | 30% | 34% | 96% | 84% |
| pH 10 | 8% | 43% | 94% | 26% | 93% | -- |
| pH 11 | 7% | 43% | 73% | 24% | 89% | 96% |

Challenges were noted in the acidification and maintenance of pH values owing to the large buffering capacity provided by the high (i.e., 1.0 M) carbonate concentration in the initial simulant. Additionally, a side reaction that increases pH via oxidation of nitrite to nitrate was observed at lower pH values.

Also described in this document is the observation that free-flowing simulants appeared to solidify several months after the permanganate oxidation reaction. While the exact cause is unknown, it is postulated the $MnO_2$ solids aged to form a thick slurry.

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| | |
|---|---|
| 1-PB | Phenylboronic Acid |
| 2-PB | Diphenylborinic Acid |
| 3-PB | Triphenylborane |
| B | Boron |
| $BO_3^-$ | Perborate |
| CCP | Corrosion Control Program |
| CsTPB | Cesium Tetraphenylborate |
| HPLC | High Performance Liquid Chromatography |
| IC | Ion Chromatography |
| KTPB | Potassium Tetraphenylborate |
| FT | Fourier-Transform |
| FTIR | Fourier-Transform Infrared Spectroscopy |
| ICP-ES | Inductively Coupled Plasma Emission Spectroscopy |
| ITP | In-Tank Precipitation |
| K | Potassium |
| KTPB | Potassium Tetraphenylborate |
| PSAL | Process Science Analytical Laboratory |
| SRNL | Savannah River National Laboratory |
| SRS | Savannah River Site |
| TPB | Tetraphenylborate |

## 1.0 Introduction

Tank 48H currently holds legacy material containing organic tetraphenylborate (TPB) compounds from the operation of the In-Tank Precipitation (ITP) process.[1,2] TPB was added during the ITP process to precipitate the otherwise soluble cesium as insoluble cesium TPB (CsTPB), but excessive benzene generation from TPB degradation curtailed this treatment method. The contents of Tank 48H, which include approximately 26,000 kg of potassium TPB (KTPB) and trace CsTPB, are not compatible with the waste treatment facilities at the Savannah River Site (SRS) since the organic content and the associated flammability issues pose a challenge to the salt processing and sludge processing facilities within the liquid waste system. An in-tank process to remove (or decompose) TPB safely would be of great value.[3]

Previous testing at Savannah River National Laboratory (SRNL) demonstrated the destruction of glycolate via chemical oxidation using sodium permanganate with simulated and radioactive waste.[4-7] Scoping tests were performed to study the destruction of TPB to determine if the contents of Tank 48H would be amenable to the same type of destruction.[8] Partial destruction of TPB was observed in Tank 48H simulants under mild conditions (e.g., pH 11, room temperature) with no definitive indication of benzene generation. To build upon the success of the scoping tests, an additional study was requested to provide a better understanding of the underlying chemistry for Tank 48H content destruction using sodium permanganate.

Three experiments were performed with Tank 48H simulants at 40 °C to determine the efficacy of using sodium permanganate for TPB destruction. Three starting pH values were selected: 1) pH 11 for comparison with the previous work at room temperature, 2) pH 10 as the minimum pH recommended by the Corrosion Control Program (CCP) for in-tank processing, and 3) pH 8 to determine the effectiveness of TPB destruction at near neutral pH. While below the allowable pH for the CCP,[9] the experiment at pH 8 was performed to study the TPB-Permanganate reaction under more extreme conditions and further verify the potential for out-of-tank processing.

## 2.0 Experimental Procedure

### 2.1 Simulant Preparation

The Tank 48H simulant composition shown in Table 2-1 was modified from the recipe used in the previous scoping study.[7] TPB was added as the potassium salt in contrast to the sodium form to reduce foaming and mitigate concerns over uncertainty of potassium content in time zero samples. Other changes were made to accommodate lower pH solutions: sodium nitrite was added in-lieu of sodium hydroxide to account for hydroxide neutralization by nitric acid, and sodium aluminate was not included due to the precipitation of aluminate solids at lower pH values.

**Table 2-1. Base Simulant Composition**

| Chemical Name | Formula | Molarity |
|---|---|---|
| Sodium Carbonate | $Na_2CO_3$ | 1.00 |
| Sodium Nitrite | $NaNO_2$ | 0.62 |
| Sodium Nitrate | $NaNO_3$ | 1.83 |
| Potassium Nitrate | $KNO_3$ | 0.012 |
| Nitric Acid | $HNO_3$ | 0.18* |
| Potassium Tetraphenylborate | $KC_{24}H_{20}B$ | 0.028 |

**Molarity of nitric acid in pH 10 simulant.*

KTPB was prepared by the reaction of potassium nitrate and sodium TPB in deionized water. The precipitate was collected by filtration, washed with deionized water, and air dried to constant weight.

Simulant solutions were prepared by adding the sodium salts to a volumetric flask and diluting with deionized water to 250 mL. The solutions were then transferred to poly bottles where concentrated nitric acid was added dropwise until the target pH (i.e., pH 8, 10, or 11) was achieved. The addition of nitric acid increased the adjusted simulant volumes to 278.6, 266.3, and 252.1 mL for the pH 8, 10, and 11 simulants respectively. After the pH had stabilized, KTPB was added to produce a final concentration of 0.028M. Addition of TPB after acid addition eliminated TPB destruction facilitated by localized regions of low pH during the addition of concentrated nitric acid.

### 2.2 Experimental Apparatus and Parameters

Experiments were performed in an apparatus similar to the apparatus used for the prior scoping study.[8] 250 mL of base simulant was added to 2.0 L borosilicate glass reactors and mixed with a Teflon coated stir-bar until a vortex was maintained. 20 wt% (1.6 M) sodium permanganate solutions were added to the reaction vessels using a syringe pump at 2.5 mL/hr for 8 hours per day of addition. Temperature control was provided by circulating heated water through the jacketed reaction vessels. The test solution remained stirring at 40 ºC for the duration of testing; including times where no permanganate was being added (e.g., overnight and on weekends). Deionized water was periodically added to replace evaporated water and maintain a volume of approximately 250 mL. A photograph of the equipment is shown in Figure 2-1.

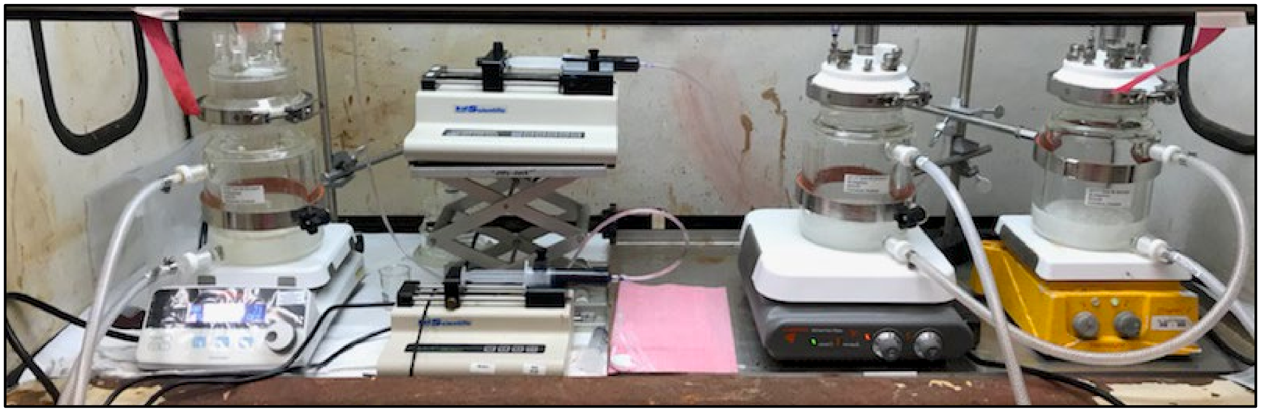

**Figure 2-1: Photograph of the experimental setup showing syringe pumps interfaced with three glass reactors on stir plates.**

Three tests were performed simultaneously on Tank 48H simulants having an initial pH of 8, 10 and 11. The testing parameters for all three tests were as follows:

- Vessel volume: 2 L
- Initial simulant volume: 250 mL
- Reaction temperature: 40 ºC (non-insulated)
- 20 wt% sodium permanganate (1.6 M)
- $NaMnO_4$ addition rate: 2.5 mL/hr (8 hr/day, 160 mL or 0.256 mols total)
- Duration: 14 days, with $NaMnO_4$ additions on days 1-4 (80 mL) and days 8-11 (80 mL)
- Samples acquired:
    - Time 0
    - End of Week 1 (7 days)
    - End of Week 2 (14 days)

All samples were quenched with sodium sulfite shortly after being pulled to remove unreacted permanganate and stop any additional reactions.

### 2.3 Sample Analysis

Inductively Coupled Plasma Emission Spectroscopy (ICP-ES) analysis for boron (B) and potassium (K), and Ion Chromatography (IC) measurements for nitrite and nitrate were provided by SRNL's Process Science Analytical Laboratory (PSAL). Prior to analysis, samples were filtered with a 0.45 um syringe filter.

High Performance Liquid Chromatography (HPLC) was used to measure TPB, and TPB byproducts.[10] The byproducts are a series of boric acid compounds ranging from 3 to 1 phenyl moieties termed triphenylborane (3-TB), diphenylborinic acid (2-TB), and phenylboric acid (1-TB). In addition, phenol was analyzed.

### 2.4 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2. Information from the experiments was posted in Electronic Laboratory Notebook: C8102-00273-02.

## 3.0 Results and Discussion

### 3.1 Visual Observations

Distinct colors exist for many relevant species in the KTPB/Permanganate system that allow for colorimetric detection. Relevant colors include: KTPB (white), manganese dioxide (black/brown), and permanganate (purple). A visual depiction of the first twenty minutes of the permanganate reaction with Tank 48H simulants is shown in Figure 3-1. Addition of KTPB to the base simulant solutions resulted in all simulants having an initial milky-white color. Soon after the addition of permanganate, deviations in color were noted between the three pH simulants. The simulant with a starting pH of 8 changed from pink to brown, suggesting formation of manganese dioxide solids. The simulant with a starting pH of 11 changed from light to dark purple indicative of unreacted permanganate. The simulant with a starting pH of 10 had colors in-between those of the pH 8 and 11 simulants.

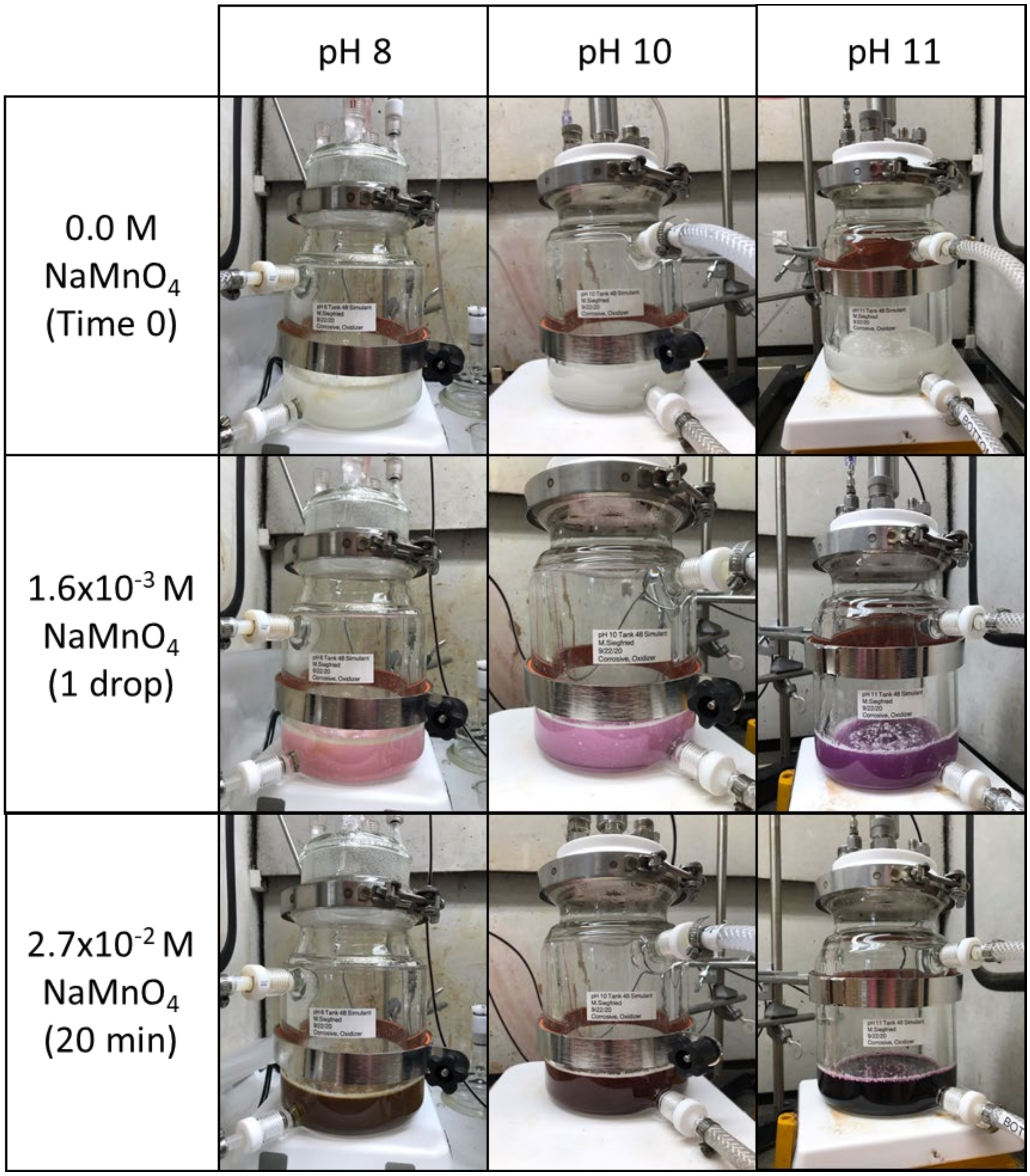

**Figure 3-1: Photographs of simulant solutions in the first 20 minutes of the reaction showing simulant color as a function of initial simulant pH and permanganate concentration.**

Simulant color became difficult to ascertain after about 20 minutes of permanganate addition due to the formation of solids and the high permanganate concentration. Photos of back-lit samples acquired at the end of week 1 are shown in Figure 3-2. Care was taken to pull samples from the center of the stirred mixtures to obtain representative samples. Only the filtered pH 10 simulant was semi-transparent, with all others being opaque. This may suggest the pH 10 sample had less unreacted permanganate. The subsequent sulfite-quench resulted in all samples containing brown solids and clear supernate indicative of a permanganate quench.

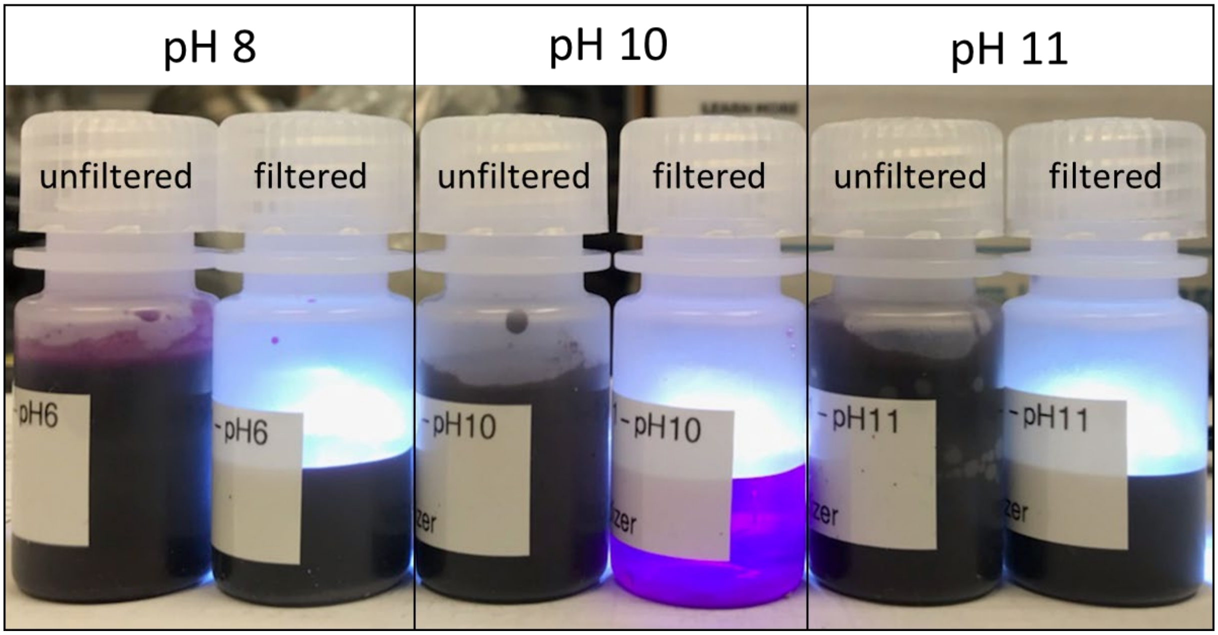

**Figure 3-2: Photographs of filtered and unfiltered samples taken at the end of week 1.**

Figure 3-3 shows top-down photos of all three reaction vessels at the conclusion of the second week of testing. A film of fine solid particles appeared to float on the surface of the initial pH 8 and 11 simulants. The initial pH 10 simulant had no such film on the surface.

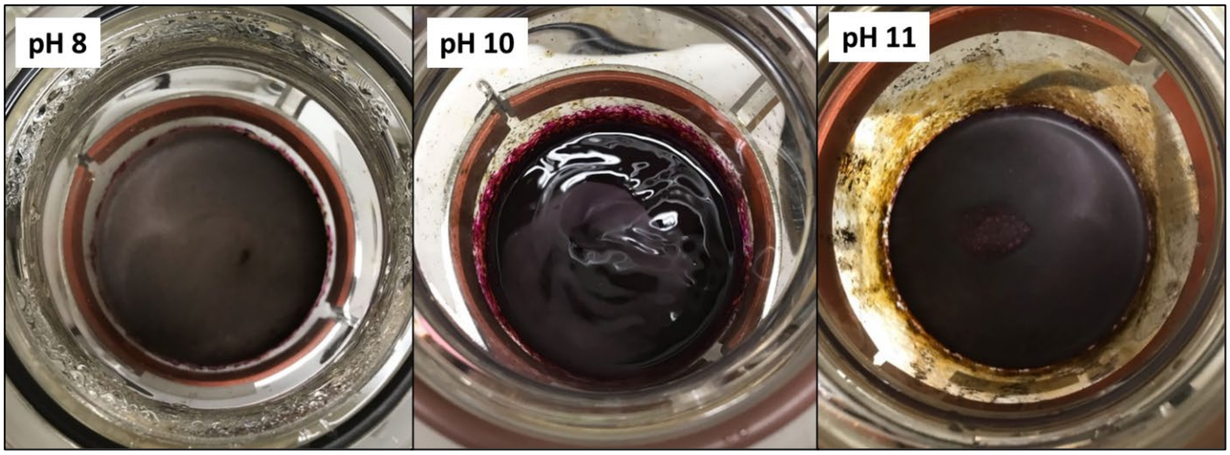

**Figure 3-3: Photographs of the surface of simulant mixtures at the end of week 2.**

Figure 3-4 shows the pH 8, 10, and 11 simulants after being transferred to 500 mL poly bottles at two weeks and six months after the start of permanganate addition. After two weeks, the simulants were free flowing liquids with settled (presumably $MnO_2$) solids. The final color of all three simulant solutions remained purple, indicating the presence of unreacted permanganate. White solids appeared to cling to poly bottles of the initial pH 8 and 11 simulants, but not pH 10. After 6 months of sitting at room temperature, the initial pH 10 simulant appeared to completely solidify, and the initial pH 8 and 11 simulants partially solidified. The poly bottles were inverted in the photograph labeled "6 months" to demonstrate the extent of solids formation.

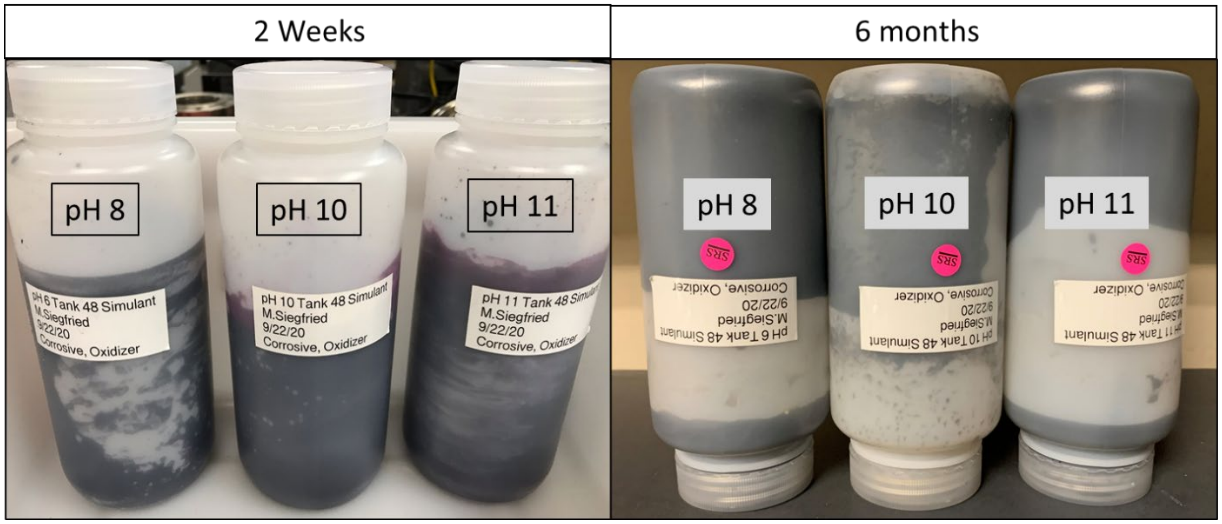

**Figure 3-4: Photographs of initial pH 8, 10, and 11 simulants in 500 mL poly bottles *(left side)* two weeks and *(right side)* 6 months after permanganate addition. Note: The poly bottles are inverted in the right photo to illustrate the extent of solidification.**

### 3.2 Proposed Reaction Mechanisms and pH

Carbonate in Tank 48H can be significant with the current concentration being 1.43 M (WCS Online, accessed 6/9/2021). Total carbonate will increase pH, and precise pH control is complicated by the high carbonate/bicarbonate buffering capacity in this system (carbonic acid is a diprotic acid with a $pKa_1$ of 6.4 and $pKa_2$ of 10.3). More complexity is introduced below pH 8.4 with the evolution of carbon dioxide. Consequently, potentially significant amounts of acid will need to be introduced to both lower and maintain a near neutral pH in this system.

A proposed reaction for the oxidation reaction of TPB and any TPB biproducts with permanganate is shown in Equation (**1**) below. While it is unlikely TPB was fully decomposed in this experiment, Equation (**1**) does suggest the oxidation of TPB will generate hydroxide ions at a ratio of nearly 40:1 and increase the system pH as a function of TPB destruction.

$$122MnO_4^- + 3BC_{24}H_{20}^- + 31H_2O = 72CO_2 + 122MnO_2 + 3BO_3^- + 122OH^- \qquad (\mathbf{1})$$

In the range of pH 3-12, permanganate will oxidize nitrite and result in the generation of manganese dioxide solids and nitrate as shown in Reaction (**2**) below. In addition, this reaction will generate 2 mols of hydroxide for every 3 mols of nitrite reacted. Assuming 100% conversion of the 0.62 M nitrite in the Tank 48H simulant to nitrate, hydroxide content would increase by 0.42 M. In the absence of carbonate, 0.42 M hydroxide would increase the simulant pH to > 13.

$$2MnO_4^- + 3NO_2^- + H_2O = 2MnO_2 + 3NO_3^- + 2OH^- \qquad (\mathbf{2})$$

### 3.3 Volume Determinations

The reactor vessels were open systems and deionized water was periodically added to compensate for loss due to evaporation to maintain a volume of approximately 250 mL. ICP-ES provides data in mg/L or parts per million (ppm). To calculate the total mass of boron and potassium in the reactor using ICP-ES data, an accurate volume measurement is needed. Two methods were used to determine total simulant volume in the reactor at the times samples were acquired.

The volume of the entire contents of the reaction vessels were measured at the conclusion of the experiment. This allowed for a direct measurement, but included uncertainty from loss due to sub-sampling, rinsing, solids formation, and transfer of material out of the reactor vessel. Additionally, volume determinations were not possible for the intermediate samples.

Alternatively, volumes were estimated by comparing the amount of nitrite and nitrate added to the initial simulant to the measured amounts of nitrite and nitrate in subsequent samples. Assuming the total moles of nitrite and nitrate are constant and there are no other side reactions, Equation (**2**) predicts a 1:1 conversion of nitrite to nitrate. Consequently, the sum of the moles of nitrite and nitrate should be constant and any deviations in concentration can be attributed to a change in volume. While this method allows for a total reactor volume to be approximated for any sample with measured nitrite and nitrate concentrations, there is added uncertainty from each ICP-ES measurement. It should also be noted that no off-gas measurements were performed in this study and this method does not account for any nitrite converted to $NO_x$ gas or any other species.

### 3.4 Results

The simulant recipe shown in Table 2-1 provides a KTPB concentration of 10,000 mg/L (0.028 M). 0.256 mols of permanganate were added over the course of two weeks resulting in a 1.02 M permanganate solution. According to Equation (**1**), a concentration of 1.14 M permanganate would be required to fully oxidize TPB to carbon dioxide and perborate ($BO3^-$). Assuming 100% completion of both reactions (**1**) and (**2**), a 1.56 M solution of permanganate would be required. While the reaction may not go 100% to completion (even with excess permanganate), larger quantities of permanganate may be required to fully decompose TPB.

destruction of TPB was monitored indirectly by measuring boron and potassium content in simulant filtrate by ICP-ES. Complete destruction of TPB entails the removal of phenyl groups from boron making it available for analysis. Potassium can also be used to indirectly monitor TPB destruction as TPB forms a complex with potassium rendering it unmeasurable in filtrate samples. As the complexing TPB is destroyed, potassium is liberated and accessible in the filtrate. However, an increase in potassium may not correspond to the complete destruction of TPB since it provides no indication of TPB byproducts.

Table 3-1 and Table 3-2 list summaries of results obtained by monitoring boron and potassium using ICP-ES. The mass of each species is reported to account for changes in concentration due to evaporation and the addition of permanganate and nitric acid. Results from the time zero and week two data sets were calculated using measured volumes. Results for week 1 were approximated by normalizing measured data to nitrite and nitrate content. "<" values denotes the mass is below the listed reportable limit.

**Table 3-1: Results Derived from ICP-ES Measurements of Boron in Filtered Samples**

| | Measured pH | Measured B | Added from KTPB | TPB Destruction |
|---|---|---|---|---|
| | | mg/L | mg/L | % |
| Time 0 | 7.8 | <1.00 | 0.0 | 0.0% |
| | 9.6 | <1.00 | 0.0 | 0.0% |
| | 10.7 | <1.00 | 0.0 | 0.0% |
| Week 1 | 11.8 | 18.2 | 261 | 7.0% |
| | 10.5 | 21.3 | 278 | 7.7% |
| | 11.9 | 19.9 | 298 | 6.7% |
| Week 2 | 11.7 | 87.9 | 261 | 33.7% |
| | 10.8 | 71.6 | 278 | 25.7% |
| | 11.6 | 71.9 | 298 | 24.2% |

*ICP-ES measurement uncertainty is 10%

**Table 3-2: Results Derived from ICP-ES Measurements of Potassium in Filtered Samples**

| | Measured pH | Measured K | From KNO3 | From KTPB | KTPB Added | TPB Destruction |
|---|---|---|---|---|---|---|
| | | mg/L | mg/L | mg/L | mg/L | % |
| Time 0 | 7.8 | 420 | 420 | 0 | 0 | 0.0% |
| | 9.6 | 439 | 439 | 0 | 0 | 0.0% |
| | 10.7 | 464 | 464 | 0 | 0 | 0.0% |
| Week 1 | 11.8 | 884 | 420 | 464 | 947 | 49.0% |
| | 10.5 | 876 | 439 | 437 | 1010 | 43.3% |
| | 11.9 | 930 | 464 | 465 | 1080 | 43.1% |
| Week 2 | 11.7 | 1330 | 420 | 913 | 947 | 96.4% |
| | 10.8 | 1370 | 439 | 935 | 1010 | 92.5% |
| | 11.6 | 1430 | 464 | 962 | 1080 | 89.0% |

*ICP-ES measurement uncertainty is 10%

It should be noted the target values for the time zero samples were pH 6, 10 and 11. The pH of solutions changed in the time between simulant preparation (where a pH probe was used) and the time pH measurements were performed by PSAL a few days later. By the end of the first week of testing, all simulants had a pH of approximately 11-12, further illustrating the difficulty of precise pH control in this system. A likely explanation for this increase can be found in Section 3.2.

All time zero samples in both tables show no reportable boron and only the potassium nitrate added to the initial base simulant. The slight decrease in potassium at lower pH is attributed to dilution resulting from nitric acid addition during acidification. No destruction of TPB or loss of potassium from complexed TPB or residual from KTPB preparation is indicated.

After two weeks of permanganate addition, TPB destruction was approximately the same for all initial starting pH depending on the measured species. TPB destruction calculated from measured potassium was approximately 90% and from measured B was 24-39%. While the TPB destruction determination for week 1 is only an approximation, the data does show ingrowth of both boron and potassium. It is likely potassium and boron would continue to increase if the reaction duration was longer and/or more permanganate was added to the system.

TPB and the TPB degradation products triphenylborane (3-PB), diphenylborinic acid (2-PB), phenylboronic acid (1-PB), and phenol were measured directly using HPLC. Results for both Week 1 and Week 2 samples are shown in Table 3-3 and Table 3-4 respectively. "<" values denote measurements below the listed reportable limit. Week 1 sample masses were determined by the nitrite and nitrate mass balance, whereas Week 2 sample masses were determined using direct volume measurements. Insufficient sample volume remained for HPLC analysis of the 2$^{nd}$ week pH 10 simulant as solids formation prevented a representative sample from being obtained at a later date.

**Table 3-3: HPLC Analysis of TPB and Byproducts for Week 1 Samples**

| Week 1 - TPB in Simulant (mg/L) | | | | | |
|---|---|---|---|---|---|
| | TPB | 3-TPB | 2-TPB | 1-PB | Phenol |
| pH 8 | 5560 | < 54 | < 54 | < 54 | < 54 |
| pH 10 | 487 | < 56 | < 56 | < 56 | < 56 |
| pH 11 | 2360 | < 52 | < 52 | < 52 | < 52 |

**Table 3-4: HPLC Analysis of TPB and Byproducts for Week 2 Samples**

| Week 2 - TPB in Simulant (mg/L) | | | | | |
|---|---|---|---|---|---|
| | TPB | 3-TPB | 2-TPB | 1-PB | Phenol |
| pH 8 | 1640 | < 79 | < 90 | < 90 | < 90 |
| pH 11 | 385 | < 79 | < 79 | < 79 | < 79 |

*Note: HPLC analysis of pH 10 sample not performed due to insufficient sample volume*

No measurable TPB byproducts from hydrolyzing TPB (3-PB, 2-PB, and 1-PB) were detected in any sample acquired during the reaction. This may indicate that either the 3-PB, 2-PB, and 1-PB are quickly consumed after creation, or are not created in this reaction. It also may indicate other unknown decomposition products were formed. Similar to the ICP-ES measurements of boron and potassium, results from HPLC measurements suggest TPB is destroyed by chemical oxidation via permanganate. In both cases, TPB destruction increased as a function of time and permanganate addition. Whereas boron and potassium measurements indicate destruction was similar for Tank 48H simulant in all experiments, HPLC measurements suggest TPB destruction is highest in the initial pH 10 simulant and the lowest in the initial pH 8 simulant. While changes in reactions may initially occur at differing pH, the system pH rapidly changes from initial values becoming similar for all three experiments. Conditions would need to be modified to allow for continual addition of acid and monitoring of pH to maintain stability. A summary of all TPB destruction results is shown in Table 3-5.

**Table 3-5: Summary of all TPB Destruction Results Derived from B, K, and TPB measurements**

| | % Destruction Week 1 | | | % Destruction Week 2 | | |
|---|---|---|---|---|---|---|
| | B | K | TPB | B | K | TPB |
| pH 8 | 7% | 49% | 30% | 34% | 96% | 84% |
| pH 10 | 8% | 43% | 94% | 26% | 93% | -- |
| pH 11 | 7% | 43% | 73% | 24% | 89% | 96% |

### 3.5 Solids Formation

All three simulant solutions were transferred to 500 mL poly bottles and left sealed and undisturbed on a laboratory bench at room temperature. Unexpectedly, approximately six months after the completion of the experiment, it was discovered the formerly free-flowing simulant solutions had formed into a gel-like solid as noted in Figure 3-4. The exact duration of this transition is unknown, as well as the chemistry behind the apparent change in state.

During the two-week experiment, 0.26 mols of sodium permanganate was added to each simulant. Assuming 100% conversation of permanganate to manganese dioxide and accounting for sample dilutions, the resulting initial pH 8, 10, and 11 simulants would contain 5.1, 6.3, and 5.6 wt% manganese dioxide respectively. It is likely manganese dioxide solids aged (e.g., Ostwald ripening, etc.) to form a thick slurry. It was noted the slurry dispersed into a dark brown powder when added to DI water.

Another possibility is a the formation of a polymer by an oxidative coupling reaction that commonly uses a copper catalyst.[11] Manganese dioxide has been shown to catalyze the oxidative coupling of phenols to form poly(phenylene ethers).[12] Appendix A shows Fourier-Transform Infrared Spectroscopy (FTIR) and Raman spectra of the pH 10 simulant that appears to show some evidence of carbon chains, but predominantly manganese oxides.

## 4.0 Conclusions and Recommendations

Three experiments were performed to determine the efficacy of using sodium permanganate for the destruction of tetraphenylborate (TPB) in Tank 48H simulants at 40 °C. Sodium permanganate was added over 14 days to simulants with three initial pH values: 1) pH 11 for comparison with previous experiments at room temperature, 2) pH 10 as the minimum pH recommended by the CCP for in-tank processing, and 3) pH 8 to determine the effectiveness of TPB destruction at near neutral pH where the permanganate reaction is more favorable.

TPB destruction was monitored indirectly by measuring boron and potassium ingrowth in filtrate samples and directly by measuring TPB. Results indicate destruction of TPB in Tank 48H simulants that increases with time with no measurable 3-TB, 2-TB, 1-TB or phenol observed.

Results were inconsistent regarding the effectiveness of initial pH on TPB destruction: boron and potassium measurements suggesting little-to-no effect, TPB measurements indicated destruction was heavily favored in the initial pH 10 simulant. Challenges were noted in the acidification and maintenance of pH values at near neutral pH owing to the large buffering capacity provided by the high (i.e., 1.0 M) carbonate concentration in the initial simulant. In addition to hydroxide being a potentially significant byproduct of TPB oxidation, a side reaction that produces NaOH and increases pH via oxidation of nitrite to nitrate is favorable at reduced pH. It is probable the initial pH had an effect on the reaction, but any effect was mitigated by the resulting pH increase. Future studies on the effect of pH at neutral or acidic pH should incorporate steps to incorporate acid additions to maintain a stable value.

An unexpected observation was noted after the simulants sat undisturbed for several months at room temperature: the formerly free-flowing simulants appeared to have solidified. While the exact cause is unknown, it is postulated the $MnO_2$ solids may have aged to form a thick slurry.

This study demonstrated promise for using oxidation of TPB with sodium permanganate as a method for Tank 48H organics mitigation. Since TPB destruction was noted to increase with time under all conditions evaluated, longer reaction durations are recommended to determine the extent of TPB destruction with time. Future efforts will ideally include an evaluation of reaction stoichiometry to more adequately determine the volume of sodium permanganate required to destroy TPB and minimize solids formation.

## 5.0 References

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# Appendix A:

Figure A-1 below shows overlayed Fourier-Transform Infrared Spectroscopy (FTIR) and Raman spectra of the initial pH 10 simulant at approximately 6 months after completion of the experiment. In the Raman spectrum, the broad peak around 1345 $cm^{-1}$ appears to confirm -C=C- (as in fused rings) and graphite-like carbon at 1345 cm-1, some carbon chains and Mn oxides. The FTIR spectrum indicates carbon-oxygen bonds and carbon chains, but -C=C- should appear around 1600 to 1500 $cm^{-1}$ and would be masked by the large nitrate and carbonate peaks.

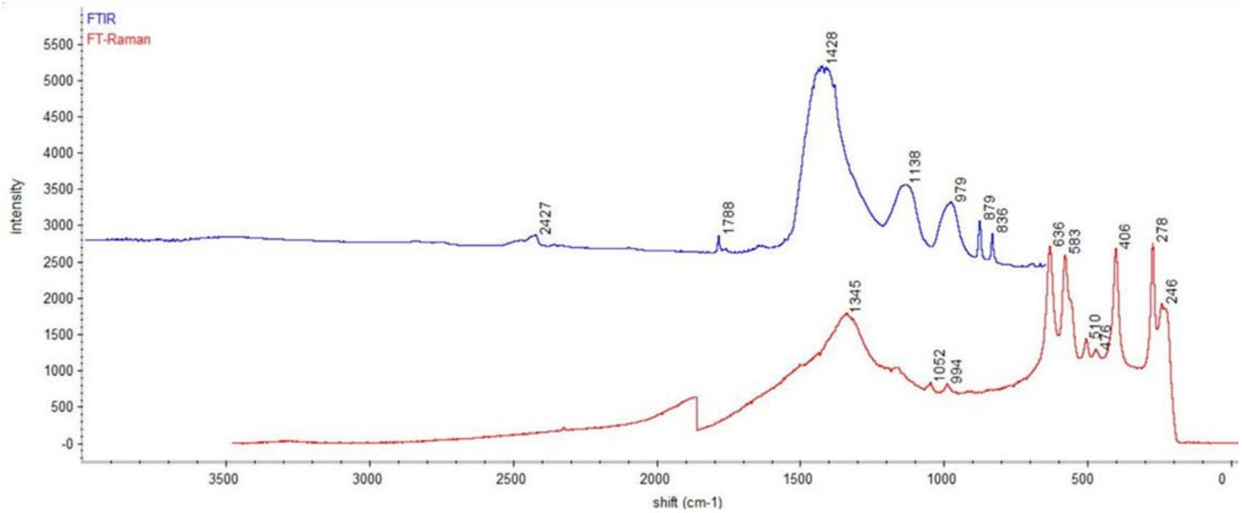

**Figure A-1: FTIR and FT-Raman spectra of the initial pH 10 Tank 48H solid simulant**

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