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PROCESS DEVELOPMENT FOR DESTRUCTION OF TETRAPHENYLBORATE IN SRS TANK 48H

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REVIEWS AND APPROVALS

LIST OF ACRONYMS

1PB	phenylboronic acid
2PB	diphenylborinic acid
3PB	triphenylboron
AA	Atomic Absorbtion
ADS	Analytical Development Section
CsTPB	Cesium tetraphenylborate – $[Cs][B(C_6H_5)_4]$
DWPF	Defense Waste Processing Facility
GC-MS	Gas Chromatography – Mass Spectrometry
H_2O_2	Hydrogen Peroxide (“peroxide”)
HLW	High Level Waste
HPLC	High Performance Liquid Chromatography
IC	Ion Chromatography
ICP-ES	Inductively Coupled Plasma – Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma – Mass Spectroscopy
ITP	In-Tank Precipitation
KTPB	Potassium tetraphenylborate – $[K][B(C_6H_5)_4]$
MST	monosodium titanate
NaOH	Sodium Hydroxide
NaTPB	Sodium tetraphenylborate – $[Na][B(C_6H_5)_4]$
NETL	National Energy Technology Laboratory
ORNL	Oak Ridge National Laboratory
SRS	Savannah River Site
SRTC	Savannah River Technology Center
SVOA	Semivolatile Organic Analysis
SWPF	Salt Waste Processing Facility
TAML®	TAML® (TetraAmidoMacrocyclicLigand) activators developed by Terry Collins of Carnegie Mellon University for activation of hydrogen peroxide.
TPB	Tetraphenylborate - $[B(C_6H_5)_4]^-$
WPTS	Waste Processing Technology Section

1.0 EXECUTIVE SUMMARY

SRTC investigated several options to remediate the contents of Tank 48H. While AEA and Oak Ridge National Laboratory examined “out of tank” processes (ones that utilize conditions hostile to the tank infrastructure), SRTC investigated “in-tank” processes. Three options were examined: the Fenton reaction, Hydrolysis and Catalysis. Each option was investigated using a series of six reactions. These reactions were exploratory in nature; optimization is planned for a later date. Each experiment was conducted over a two-week period. The results of the experiments indicate that each process is a viable in-tank option, but there are limitations (discussed below) that must be addressed.

- For all three options, tetraphenylborate (TBP) destruction (i.e., conversion of TPB into any other species) efficiencies proved higher at pH 7-8 than 11. However, parallel studies show that the corrosion rate for any in-tank option increases as pH decreases.

- TBP destruction efficiency (i.e., percent conversion of TPB into other species) at pH 11 for the Fenton reactions ranged between 22% (600 mg/L TAML, 45 ºC, 30 mL H_2O_2) to 68% (100 mg/L TAML, 45 ºC, 264 mL H_2O_2).

- TBP destruction efficiency at pH 11, 45 ºC for the hydrolysis reaction measured 84%.

- TBP destruction efficiency at pH 11, 45 ºC for the 1000 ppm Pd-catalysis reaction equaled 56%.

- The TPB destruction efficiency was highest for hydrolysis, followed by catalysis, and finally the Fenton reactions.

- The catalysis and hydrolysis experiments included placement of corrosion coupons in the reaction vessel. Only a small quantity of surface loss occurred (< 10 mils per year). A more detailed corrosion study will issue soon.

2.0 INTRODUCTION

Tank 48H is needed to serve as the feed tank for the Actinide Removal Process which will process low curie waste. Closure Engineering requested research to help evaluate process alternatives for the destruction of the TPB in Tank 48H. The main objective of the research is to develop processing conditions for the safe destruction of the organic present in Tank 48H and facilitate return of the tank to routine high level waste service by August 2005. SRTC examined processing conditions using nonradioactive simulants.

For those processes that prove most attractive, personnel will later demonstrate process viability through pilot scale and actual waste testing.

Five areas of research are being performed in an attempt to develop processing alternatives for Tank 48H.

1. AEA is performing research to develop a low pH, boiling Fenton Process for the destruction of TPB. AEA is being funded by DOE. This work is being performed by Jeff Wilks in the UK.[1] This work is being documented in a separate report by AEA.
2. Closure Engineering requested SRTC and INEEL to examine the viability of steam reforming for treating the Tank 48H waste. Carol Jantzen (SRTC) completed laboratory testing with simulated waste as defined in the Task Plan for this work.[2] A separate report documented those findings.[3] Similarly, INEEL personnel conducted pilot-scale demonstrations based on the SRTC work and a separate report covers that study.[4]
3. Other SRTC researchers completed corrosion testing to examine corrosion rates applicable for any in-tank processing alternatives. A separate report describes those results.[5]
4. Closure Engineering requested SRTC to complete research to look at in-tank processes including Fenton's Reagent, catalyzed hydrolysis and thermal treatments to destroy TPB. A Task Technical Request[7] issued by Closure Engineering provided the requirements of the testing for FY03. SRTC documented the agreed upon experimental design in a Task Plan.[2] This report describes the results of that testing.
5. NETL funded testing to develop an in-tank and out-of-tank Fenton Process. A separate Task Plan defines that experimental design.[6] A future report will be published in late October containing the data from the NETL tasks.

This report documents the results of Fiscal Year (FY) 2003 testing to destroy the tetraphenylborate in Tank 48H. Two sponsors requested parallel testing on TPB destruction alternatives. The first is the request by Closure Engineering for the development of in-tank processing alternatives.[7] The second is a National Energy Technology Laboratory (NETL) grant that requests SRTC to develop in-tank and out-of-tank Fenton's processes for Tank 48H.[8] We developed the testing to minimize any duplication of effort between the two tasks so to better utilize resources.

2.1 Tank 48H Processing History and Chemical Composition

Tank 48H, a high level waste tank at SRS, contains approximately 250,000 gallons of salt waste. The waste contains approximately 22,700 kg of organic material, primarily as potassium tetraphenylborate (KTPB). The tetraphenylborate anion [9] contains a boron atom surrounded by four phenyl ($-C_6H_5$) groups.

The tetraphenylborate was added to Tank 48H during the demonstration and startup of the In-Tank Precipitation Facility. After the shutdown of the In-Tank Precipitation Process and the DWPF Salt Cell, no process existed for the destruction of the organic in Tank 48H. Plans call for Tank 48H to serve as the feed tank for the SRS Actinide Removal Process. The organic must be treated or removed prior to the tank's slated use. Most TPB decomposition processes form benzene as a byproduct, and this potential for benzene production complicates any process for TPB destruction in Tank 48H. Benzene is flammable at concentrations between 1.3 and 7.9 volume % in air.[10] Benzene is also a carcinogen with an OSHA Permissible Exposure Limit of 1 part per million.[11] As a result of the benzene issues, processing that completely oxidizes TPB to carbon dioxide and water is less troublesome as it will minimize or eliminate the benzene hazards.

2.2 Alternative Technologies for Destruction of the Tetraphenylborate in Tank 48H

SRTC researchers (Dan Lambert and Tom Peters) served as members of an SRS Tank 48H team chartered in FY02 to identify options, evaluate alternatives and recommend a selected alternative(s) for processing Tank 48H contents to a waste form capable of being processed or stored by existing or planned facilities. The SRS Tank 48H Team included subject matter experts from WSRC and its partners. All ideas were captured on information sheets in the Phase 1 report.[12] The overview of the tests is contained in Section 7 of the SRS Tank 48H Team's report.[13]

In Tank 48H testing, Fenton's Reagent showed the most promise in that it tends to destroy organic compounds with lower yields of benzene, while at the same time having water and oxygen as the major byproducts. The Fenton's Reagent was the focus of a large portion of the experimental study for the Tank 48H work, and was also studied in the more recent laboratory waste disposal [14] and Tank 50H solids destruction [15] testing. The copper catalyst and acid hydrolysis options also showed good decomposition rates, but produced benzene as the main byproduct. The current work scope includes testing of these options. Lastly, permanganate treatment showed some degree of success, but had the disadvantage of producing a large amount of solid byproduct MnO_2. The project team elected to not pursue this last option at this time; however future needs may require us to re-examine this option. Parallel experiments examine steam reforming, a technology under study at Hanford,[16] so as to determine its efficiency in destroying TPB-laden waste. The current work scope assists the Tank 48H project team in selecting preferred options based on technical viability.

2.3 Fenton's Reagent Background

Fenton's Reagent is an oxidation process developed by H.J.H. Fenton in 1894.[17] Fenton's Reagent is used to degrade the organic components of a variety of industrial wastes such as wastewaters, sludges, and contaminated soils.[18] Fenton's Reagent has been used in a collaborative effort between Geo-Cleanse International, Inc., and WSRC in 1997.[19] Fenton's Reagent, a combination of hydrogen peroxide (H_2O_2) together with a ferric iron catalyst (Fe^{+3}), produces hydroxyl free radicals (OH•). The hydroxyl radical is a powerful oxidant that has a high propensity to degrade organic materials.

The advantage of the Fenton's Reagent compared to many other TPB destruction processes is that it produces primarily carbon dioxide and water as the main decomposition product in lieu of benzene. Excess peroxide decomposes to water and oxygen. Most other decomposition reactions produce significant quantities of benzene which makes the facility much more expensive due to the toxicity and flammability concerns.

For SRTC, the Fenton's process will use either iron or copper as the catalyst. A recently discovered material, TAML® (Tetra-Amido-Macrocyclic-Ligand, a catalyst developed by Terry Collins of Carnegie Mellon University) is also under investigation. TAML offers organic destruction at higher pH ranges than a Fenton's Reagent reaction. The TAML® catalyst was discovered after this testing began, but is used interchangeably with the conventional Fenton's reactions in our work.

The test program is designed to demonstrate the effectiveness of the Fenton Process for destroying the Tank 48H organic for both in-tank and out-of-tank processing. In-tank processing is desirable because of low capital cost and complete destruction of the organic, even on the tank surfaces and the residual waste left in the tank. Out-of-tank processing is desirable because the optimum conditions for Fenton chemistry are unsuitable for a carbon steel waste tank (pH 3-5). Testing collected the data necessary to help make a decision regarding the best process for the Tank 48H waste.

2.4 Catalysis Background

SRTC studied catalysis as a TPB destruction technology.[20,21,22,23,24,25] While a number of metal species can cause catalysis of TPB, copper and palladium are the two best known species. In fact, copper catalysis of TPB was successfully utilized in the remediation of Tank 49H in 2001.[26,27] The catalysis process is identical to the hydrolysis process except for the addition of copper or palladium catalyst. Benzene is the main organic byproduct.

2.5 Hydrolysis Background

TPB will readily hydrolyze to benzene and boric acid under conditions where the solution $pH < 14$. The ability and conditions required to hydrolyze TPB under Tank 48H conditions have been extensively studied. Hydrolysis was originally chosen as the method to destroy TPB.[9,28,29,30] The hydrolysis process is similar to the catalysis process; the only difference being that there is no deliberately added additional catalyst. (Our Tank 48H simulants contain a large battery of transition metals that may function as catalysts.) In both the catalysis and hydrolysis cases, benzene is the main organic byproduct and must be dealt with accordingly.

3.0 EXPERIMENTAL SETUP

The equipment and methods used in the SRTC testing is described in sections 3.1 through 3.1.3 of this report.

3.1 Experimental Plans

All the experiments used the same Tank 48H simulant recipe. The equipment and methods for completing the testing is described in the next three subsections of this report. Table 1 summarizes the chemical composition of the simulant used in each of the experiments. The simulant recipe is based on prior analyses of Tank 48H samples.

Table 1. Tank 48H Simulant Composition

Component	M
KTPB	0.0728
NaOH	1.8425
$NaNO_2$	0.4709
$NaNO_3$	0.2753
Na_2CO_3	0.1295
$NaAlO_2$	0.1118
Na_2SO_4	0.0071
Na_3PO_4	0.0077
NaCl	0.0088
NaF	0.0059
KNO_3	0.0051
Density	1.125
KTPB	2.32 wt %

In addition to the materials listed in Table 1, each experiment also used a battery of compounds collectively called the Enhanced Comprehensive Catalyst (referred to as the "ECC Metals").[19,20,21,22,23] The ECC mixture represents a composition of metals and species present in Tank 48H when the original, rapid catalytic decomposition of the sodium tetraphenylborate occurred. These materials were added (see Table 2) to each experiment to better simulate the composition of Tank 48H.

3.1.1 In-Tank Fenton's Reagent Destruction of Tank 48 simulant

SRTC performed a series of six tests to determine whether it was feasible to destroy TPB using Fenton's reagent under in-tank conditions (high pH and salt).

Experiment 1: pH 11, 45 ºC, 30 mL H_2O_2
Experiment 2: pH 11, 45 ºC, 264 mL H_2O_2
Experiment 3: pH 7, 45 ºC, 30 mL H_2O_2
Experiment 4: pH 7, 45 ºC, 264 mL H_2O_2
Experiment 5: duplicate of #1, 30 mL H_2O_2
Experiment 6: duplicate of #1, 30 mL H_2O_2

Technicians prepared the precipitate (see Table 1) by combining a stock precipitate simulant with ECC components (Table 2). They added 100 mL of simulant to a round bottom flask, placed the flask on a stirrer/hotplate, and agitated. The stirrer speed was adjusted as needed to produce good mixing of the slurry. Technicians then added the ECC components and adjusted the pH to a prescribed condition using 70 wt % nitric acid, followed by the addition of the iron catalyst to the precipitate. Once personnel verified the pH, they added a condenser to the top middle port on the flask. Flow of tap water through the condenser prevented water loss from the precipitate slurry. Personnel heated each reaction vessel to either 45 or 60 ºC and maintained conditions for two weeks.

Table 2. EEC Composition

Component	Compound	Species Concentration in Slurry (mg/L)
Pd	$Pd(NO_3)_2$	13.0
Cu	$Cu(SO_4)\bullet 5H_2O$	3.7
Hg	$Hg(NO_3)_2\bullet H_2O$	2.2
Diphenylmercury	$(C_6H_5)_2Hg$	150
Mo/Cr/Si/Se/As	$Na_2MoO_4\bullet 2H_2O$	12
	Na_2CrO_4	60
	$Na_2SiO_3\bullet 9H_2O$	16
	Na_2SeO_4	1
	As_2O_3	0.04
Zn/Pb/Fe	$Zn(NO_3)_2\bullet 4H_2O$	8.8
	$Pb(NO_3)_2$	1.2
	$Fe(NO_3)_3\bullet 9H_2O$	2.6
Sn	$SnCl_2$	2.1
Ca/La/Co	$Ca(NO_3)_2\bullet 4H_2O$	12.2
	$La(NO_3)_3\bullet 6H_2O$	0.05
	$Co(NO_3)_2\bullet 6H_2O$	0.04
Cd/Ce	$Cd(NO_3)_2\bullet 4H_2O$	0.4
	$Ce(NO_3)_3\bullet 6H_2O$	0.3
Rh	$Rh(NO_3)_3$	1.4
Ag	$AgNO_3$	6.8
Ru	$RuCl_3\bullet xH_2O$	5.4
sludge	Sludge	500
MST	MST	500

Technicians added the peroxide to the syringe pump and inserted the needle into the septum on the side of the flask. Figure 1 contains a photo of the flask during an experiment.

Personnel heated the slurry as required for the experiment using the hotplate. Once the solution reached temperature, they began adding the peroxide. Each experiment added peroxide at its own constant rate. Each experiment lasted 2 weeks.

At the completion of the experiment, technicians pulled well mixed 5 mL samples from the flask and submitted them to the Analytical Development Section (ADS) for ICPES (Inductively Coupled Plasma Emission Spectroscopy) analysis. In addition, we submitted the (remaining) contents of the entire flask to ADS for HPLC (High Performance Liquid Chromatography) extraction and analysis.

Figure 1. Photograph of Reaction Vessel and Peroxide addition Equipment

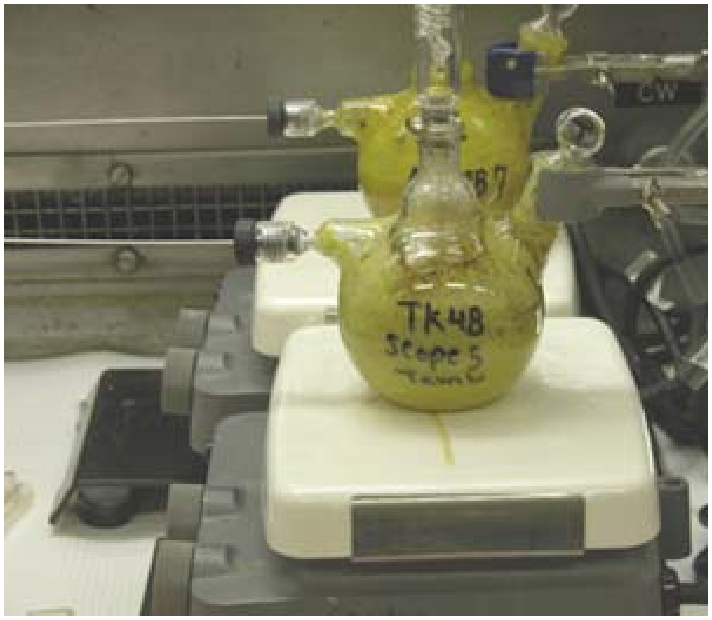
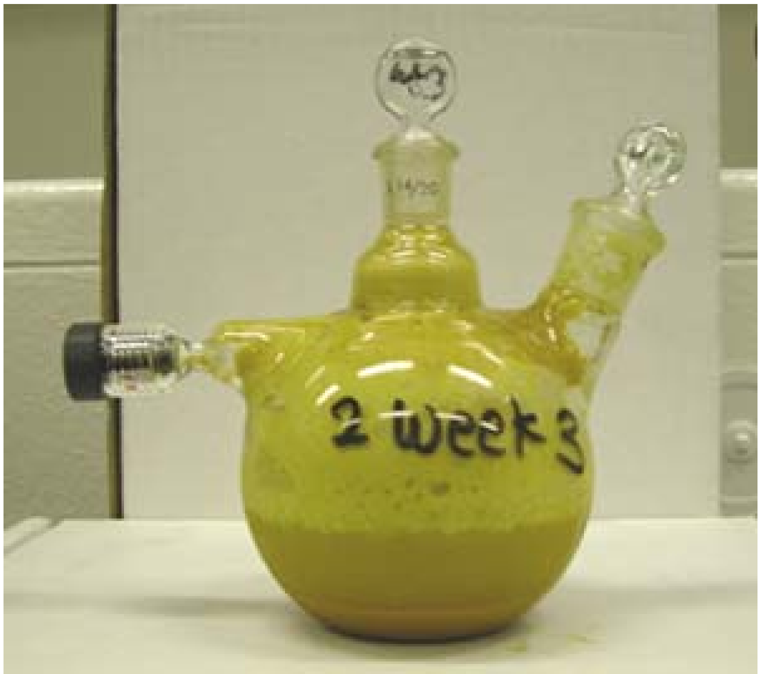


Figure 2 shows a photograph of a typical flask post reaction. Note the presence of settled solids, as well as an appreciable amount of foam in the reactor. This particular reaction is experiment 3 (see section 4.1, below).

Figure 2. Photograph of Reaction Flask Post-reaction



3.1.2 In-Tank Catalysis of Tank 48 simulant

Tetraphenylborate is known to undergo accelerated decomposition in the presence of several transition metals.[31],[32],[33],[34] SRTC performed a number of parallel tests to determine if in-tank catalysis could meet the criteria for cleaning Tank 48H, while using in-tank conditions.

The Catalysis tests involved six individual experiments.

Experiment 7: pH 8, 45 ºC, Pd catalyst
Experiment 8: pH 10, 45 ºC, Pd catalyst
Experiment 9: pH 11, 45 ºC, Pd catalyst
Experiment 10: pH 14, 45 ºC, Pd catalyst
Experiment 11: duplicate of #1, above
Experiment 12: duplicate of #1, above, but at 60 ºC

Technicians prepared six 125 mL glass bottles for these tests. They filled each bottle with 100 mL of Tank 48H simulant slurry, the requisite ECC metals and 1000 ppm of palladium catalyst (from a 15.27 wt % palladium nitrate solution). Each bottle was pH adjusted using nitric acid. Technicians added a single carbon steel coupon to the mixture. Part of the coupon resided in the slurry, and part remained suspended in the air space above the slurry. They closed each bottle and placed it into a 45 ºC or 60 ºC shaker bath, depending on the experiment. Over a two-week period, the flasks were gently agitated, and technicians pulled filtered samples once per day for potassium AA (Atomic Absorbtion) analysis. After the two week period, personnel submitted the entire contents of the flasks for HPLC analysis.

3.1.3 In-Tank Hydrolysis of Tank 48 simulant

Tetraphenylborate hydrolyzes in solutions with pH values < 14. The hydrolysis tests resembled the catalyst experiments, the only difference being the absence of the added 1000 ppm palladium catalyst.

The hydrolysis destruction tests involved six individual experiments.

Experiment 13: pH 8, 45 ºC
Experiment 14: pH 10, 45 ºC
Experiment 15: pH 11, 45 ºC
Experiment 16: pH 14, 45 ºC
Experiment 17: duplicate of #1, above
Experiment 18: duplicate of #1, above, but at 60 ºC

Technicians prepared six 125 mL glass bottles for these tests by filling each bottle with 100 mL of Tank 48H simulant and the requisite ECC metals. Each bottle was pH adjusted using nitric acid. Technicians added a single carbon steel coupon to the mixture keeping part of the coupon in the slurry, and maintaining part in the vapor space. They closed each bottle and placed into a 45 ºC or 60 ºC shaker bath, depending on the experiment. The analytical sampling for the hydrolysis experiments was identical to that of the catalysis experiments.

4.0 EXPERIMENTAL RESULTS

Experimental data from all the experiments is tabulated in Appendix I.

4.1 In-tank Fenton's Reagent Destruction of Tank 48 Simulant

Researchers performed a series of six tests (Table 3) to develop a Fenton process for Tank 48H. Typical Fenton processing performs best at pH values of 3 to 5. However, because of corrosion concerns, we sought to develop a Fenton process at a much higher pH for use in Tank 48H. The pH was not controlled during the experiment. The percent TPB destroyed was determined by HPLC analysis, which has a ±10% analytical uncertainty.

Table 3. Reaction Conditions and TPB Destruction Results

Experiment ID	Initial Catalyst Loading	Initial pH	Final pH	pH Target	Volume 50 wt%. H_2O_2 added (mL)	% TPB Destroyed
1	100 mg/L TAML®	11.1	10.6	11	30	37
2	100 mg/L TAML®	11.0	9.3	11	264	68
3	500 mg/L Fe	11.1	7.7	7	30	65
4	500 mg/L Fe	11.1	8.3	7	264	88
5	600 mg/L TAML®	11.0	NA	11	30	22
6	600 mg/L TAML®	11.0	NA	11	30	30

The initial pH of experiments 3 and 4 was intended to be 7. While the initial pH readings indicated 11.1, we know this value is incorrect. The initial pH was actually ~7 which was determined by knowing the amount of acid added. The pH readings indicate that the probe was malfunctioning after extended use. It was promptly replaced for later experiments.

The results show that as the amount of peroxide increases, there is a trend towards more complete destruction. Comparing experiments 1 and 2 shows 37% TPB destruction using 30 mL H_2O_2 versus a 68% TPB destruction using 264 mL H_2O_2. Comparing experiments 3 and 4 shows 65% TPB destruction using 30 mL H_2O_2 versus 88% TPB destruction using 264 mL H_2O_2. The additional H_2O_2 appears to insure enough hydroxyl radical is present at all times to facilitate the TPB destruction.

When comparing the amount of catalyst, it appears that higher loadings of TAML® may not be productive. A comparison of experiments 1 vs. 5 vs. 6 indicates that the higher TAML® loading provided poorer results (37% TPB destruction at 100 mg/L TAML® vs. an average of 26% TPB destruction at 600 mg/L TAML®).

The results of the six experiments indicate that as pH decreases, there is a trend towards more complete destruction; the pH 7 experiments had the best TPB destruction. However, this is not a direct comparison as the pH 7 experiments used a different catalyst as in the pH 11 experiments. Furthermore, we found that the lower pH experiments did not show any generation of phenylborate (3PB, 2PB, 1PB) compounds (i.e., almost all of 3PB, 2PB, 1PB were less than detection levels – see Appendix I). If only a simple hydrolysis reaction was occurring, there should be noticeable amounts of the hydrolysis products: 3PB, 2PB, 1PB and phenol.

While destruction efficiencies of <90% may seem low, these reactions are not optimized. The reaction times for the experiments were relatively short, and the addition of the peroxide causes additional foaming to occur (see section 4.1.1, below). Material trapped in the foam cannot react with the peroxide and so the destruction efficiencies are not optimized. As part of an attempt to control the foaming issues, the last two tests (experiments 5 and 6) used a simulant prepared in an alternate fashion. In this revised approach, personnel prepared the simulant recipe without KNO_3 or NaTPB, thus preventing the early formation of KTPB which would foam during mixing and storage. For this simulant, technicians added the KNO_3 and NaTPB as dry powders to the reaction vessel before addition of the simulant solution. The resulting mixing provided a suspension of KTPB that did not foam until the start of peroxide addition. We feel that the new simulant recipe did not invalidate the comparisons of the different experiments for two reasons. First, the new simulant recipe has the exact same ingredients in the amounts as the old recipe. Second, we observed that while the new simulant recipe did not foam during the initial stages of the reactions, it foamed to the same extent as with the old recipe after the H_2O_2 addition started (mass transfer barrier from foaming should be the same between the two recipes).

Potassium analysis by ICPES was done on a daily basis for each of the six reactions in an attempt to monitor KTPB destruction. The final ICPES results (see Appendix I) gave results that agreed fairly well with the HPLC results. However, the HPLC method analyzes the bulk of the reaction contents as opposed to a sample used for ICPES analysis. Due to this, we feel the HPLC results are more accurate; so we report only the HPLC results here.

4.1.1 Issues Identified During Fenton Testing

We identified several issues during testing that are important considerations in future testing. We describe each below.

Foaming – Foaming is common in TPB processing. The initial precipitate proved foamy as the tetraphenylborate entrained air causing it to float on the surface of the slurry. Actual Tank 48H waste shows a much-reduced tendency for foaming.[35] The foaming increased experimental variability as some experiments had more foam. Foaming TPB could lead to less efficient tetraphenylborate destruction efficiency by providing an additional mass transfer barrier. Figure 2 contains a photograph of the foamy precipitate. At the end of the Fenton’s reaction experiments, we devised a new precipitation method to produce a denser, foamless precipitate. Two of the last Fenton reactions used this improved precipitate. However, foaming did occur during the peroxide addition. Future work should include attempts to limit or control the foam. Such attempts may include the use of antifoam agents or delivering the peroxide below the reaction surface.

Acid Addition Rate – Adding acid too fast, with inadequate mixing, leads to production of tar-like organic species and a darker colored precipitate (from hydrolysis and formation of nitrogen dioxide radical). In Tank 48H the best addition strategy would add the acid through a downcomer under the liquid level while mixing the tank.

Temperature Control – Temperature control with the hot plate proved inadequate to control the temperature within 1 °C. Better temperature control can be achieved with a jacketed vessel or a water bath. Future tests should contain the glassware, or reaction vessel, in a water batch to maintain better temperature control.

Mixing Efficiency – The stir bars proved inadequate to produce good mixing of the foamy precipitate. Future testing should use baffled glassware with an agitator to improve mixing. This improved mixing may decrease test to test variability as tests with better mixing would likely lead to more complete destruction.

4.2 In-Tank Catalysis of Tank 48H Simulant

Researchers performed a series of six catalysis reactions (Table 4). Each reaction continued for two weeks at the appropriate (45 or 60 ºC) temperature. The catalyst was 1000 ppm of a solution of 15.27 wt % palladium nitrate.

Table 4. List of Catalysis Experiments

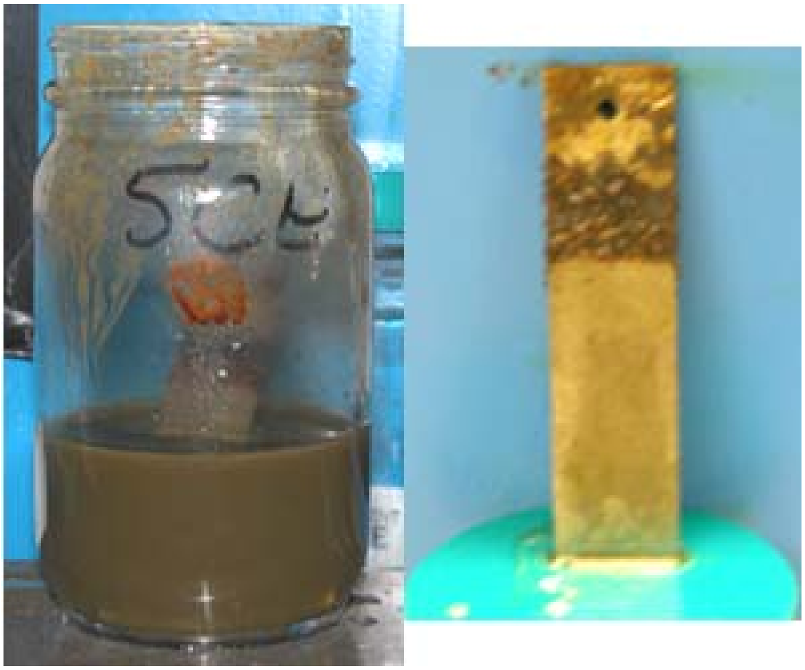
Experiment	Temp. (ºC)	Initial pH	Final pH	Target pH	% TPB Destroyed	Coupon Corrosion mils Per Year
7	45	8.1	8.9	8	99	7.87
8	45	10.0	10.3	10	75	3.53
9	45	10.7	10.3	11	56	5.06
10	45	14.0	9.8	14	10	0.00
11	45	8.1	8.7	8	>99	9.24
12	60	8.0	8.9	8	>99	7.86

From the data, the ability to destroy TPB is directly dependant on the pH. The lower the pH, the more complete the TPB destruction. The reactions at pH 8 showed essentially total TPB destruction, while the reaction at pH 14 showed virtually no reaction.

From the data, we cannot determine if using a higher temperature (60 ºC), had an effect on TPB destruction. Experiment 6, running at 60 ºC, had the same percent TPB destruction (~99%) and about the same coupon mass loss as the lower temperature analogue reactions (experiments 7 and 11).

Catalysis (or hydrolysis) under reduced alkaline (pH<14) conditions generates benzene as the main organic product. Furthermore, catalysis will inevitably produce hydrolysis byproducts (Figure 3) including aromatic compounds of various types and formulas. As the current task request did not include identification of these byproducts we did not determine the byproduct composition, although this analysis should occur in any future work.

Figure 3. Typical low pH Catalysis Experiment Residues



Each of the six experiments had a carbon steel coupon present in the reaction vessel partially submerged in the slurry at all times during each experiment. The coupons provide a measure of corrosion rates by surface area loss. After each experiment we gently scraped the coupon to remove the organic and rust deposits. In each case, we noted only a slight (< 10 mils per year) mass loss. The corrosion rate was determined by dividing the mass loss by the surface area of the submerged coupon. Not surprisingly, the highest mass losses corresponded to the pH 8 reactions. A small degree of pitting was noted on some coupons, but not quantified. A more comprehensive analysis of corrosion effects on carbon steel coupons will be presented in the near future as a separate document by Phil Zapp and John Mickalonis.

Potassium analysis by Atomic Absorbtion (AA) was done for each of the six reactions in an attempt to monitor KTPB destruction. The AA method gave results (see Appendix I) that agreed in general with the HPLC. However, we feel the HPLC method is more accurate due to the analytical methodology, and so only report the HPLC results here.

4.3 In-Tank Hydrolysis of Tank 48H simulant

We performed a series of six hydrolysis reactions (Table 5). Each reaction continued for two weeks at the appropriate (45 or 60 ºC) temperature.

Table 5. List of Hydrolysis Experiments

Experiment	Temp. (ºC)	Initial pH	Final pH	Target pH	% TPB Destroyed	Coupon Corrosion mils Per Year
13	45	8.1	8.8	8	>99	8.57
14	45	10.0	10.2	10	>99	0.00
15	45	10.7	10.3	11	84	5.83
16	45	14.0	9.9	14	0.0	0.00
17	45	7.8	8.6	8	>99	8.99
18	60	8.0	8.9*	8	>99*	0.20*

* Experiment 18 tipped over and spilled, so these results contain additional error.

As with the catalyst data, the ability to destroy TPB depends directly on the pH. The lower the pH, the more complete the TPB destruction. The reactions at pH 8 and 10 showed all but total destruction, while the reaction at pH 14 showed virtually no reaction. During the work, Experiment 18 tipped over into the water bath, lost some of the TPB slurry and took on water from the water bath (we could not quantify the exact amount). Due to this, the final pH, % TPB destroyed and coupon corrosion results contain additional error. We report the results, but we estimate they could be off by as much as ~300%.

As with the catalysis work, each of the hydrolysis experiments has a carbon steel coupon in the reaction vessel. Corrosion rates for these coupons were slight; < 9 mils per year. A more comprehensive analysis of corrosion effects on carbon steel coupons will be presented in the near future as a separate document by Phil Zapp and John Mickalonis.

As with the catalysis experiments, SRTC performed AA analyses. For the same reasons given in that section (4.2, above), we report only the HPLC results.

5.0 CONCLUSIONS

SRTC investigated three in-tank options: Fenton's reaction, hydrolysis and catalysis. In each reaction, extensive TPB destruction occurred. Each of the three options show promise as in-tank options.

For the Fenton work, the experiments provide the following conclusions.

- Fenton reactions gave TPB destruction values of 22-88% within two weeks.
- Increased amounts (264 mL vs. 30 mL) of H_2O_2 gave better TPB destruction.
- Increased amounts (600 mg/L vs. 100 mg/L) of TAML® gave a decrease in TPB destruction.
- Phenylborates (i.e., hydrolysis products) did not form from the Fenton reactions.
- We recommend that several issues discovered during Fenton testing should be examined and controlled better in any future experiments.

For the catalysis reactions, the study indicates the following.

- Catalysis reactions gave TPB destruction values of 10-99% within two weeks.
- Lower pH values gave better TPB destruction.
- Carbon steel corrosion coupons showed minimal mass loss (< 10 mils) over the entire range of experiments.

For the hydrolysis reactions, the investigation showed the following.

- Hydrolysis reactions gave TPB destruction values of 0-99% within two weeks.
- Lower pH values gave better TPB destruction.
- Carbon steel coupons showed minimal mass corrosion loss (< 9 mils) over the entire range of experiments.

Tests with the carbon steel coupons showed minimal mass loss for any of the experiments. However, the lower pH reactions (7-8) are likely to cause unacceptable corrosion rates from corrosion.

While the Fenton’s Reagent (or TAML®) gave lower overall yields than either hydrolysis or catalysis, the Fenton’s reactions showed minimal evidence of phenylborate decomposition products (3PB, 2PB, 1PB or phenol), unlike the catalysis or hydrolysis reactions. This may indicate a cleaner decomposition pathway which avoids the generation of benzene as a product than catalysis or hydrolysis. Further testing to optimize the reaction occurred within the NETL work. Further optimization should lead to improved TPB destruction. For these reasons, SRTC recommends continued studies of the Fenton reaction over hydrolysis or catalysis.

Appendix I. Summary of Experimental Data

Fenton HPLC Data

Experiment ID	Notebook Exp. Name	Initial Catalyst Loading	Initial pH	Final pH	pH Target	50 wt % H_2O_2 added (mL)
1	2week1	100 mg/L TAML®	11.1	10.6	11	30
2	2week2	100 mg/L TAML®	11.0	9.3	11	264
3	2week3	500 mg/L Fe	11.1*	7.7	7	30
4	2week4	500 mg/L Fe	11.1*	8.3	7	264
5	2week5	600 mg/L TAML®	11.0	NA	11	30
6	2week6	600 mg/L TAML®	11.0	NA	11	30

* The initial pH of experiments 3 and 4 was intended to be 7. The initial pH is actually ~7 which was determined by knowing the amount of acid that was added.

Exp. ID	Start TPB (mg/L)	End TPB (mg/L)	3PB (mg/L)	2PB (mg/L)	1PB (mg/L)	Phenol (mg/L)	% TPB Destruction
1	17255	10887	<100	110	<100	135	37
2	6512	2113	<100	<100	<100	<100	68
3	16991	5954	<100	<100	<100	556	65
4	6473	802	<100	<100	<100	<100	88
5	16870	13200	<100	<100	<100	<100	22
6	16870	11900	<100	<100	<100	<100	30

Analytical uncertainty for the results is 10%.

Fenton ICPES Data

Exp. ID	Starting K (mg/L)	Ending K (mg/L)	ICPES % TPB Destruction	HPLC % TPB Destruction
1	157	991	42	37
2	59.4	527	63	68
3	158	1700	80	65
4	60.2	703	87	88
5	154	NA	NA	22
6	154	NA	NA	30

Analytical uncertainty for the results is 10%.

The starting TPB and potassium concentration values were calculated by normalizing to the final reaction volume, which itself was dependant on the amount of H_2O_2 added (30 or 264 mL). This is why the starting concentrations varied greatly.

We did not submit ICPES samples for experiment 5 or 6. Examination of the results shows that there is a good match between the ICPES results and the HPLC. However, we feel that the HPLC results are the more accurate of the two due to the nature of the HPLC method (HPLC uses total extraction of the sample vs. sampling the reaction vessel for AA).

Catalysis HPLC Data

Experiment	Notebook Exp. Name	Temp. (ºC)	Initial pH	Final pH	Target pH	Coupon Corrosion mils Per Year
7	1-CE	45	8.1	8.9	8	7.87
8	2-CE	45	10.0	10.3	10	3.53
9	3-CE	45	10.7	10.3	11	5.06
10	4-CE	45	14.0	9.8	14	0.00
11	5-CE	45	8.1	8.7	8	9.24
12	6-CE	60	8.0	8.9	8	7.86

Exp. ID	Start TPB (mg/L)	End TPB (mg/L)	3PB (mg/L)	2PB (mg/L)	1PB (mg/L)	Phenol (mg/L)	% TPB Destruction
7	21233	222	<100	<100	1007	891	99
8	21528	5365	<100	<100	827	1073	75
9	21525	9587	102	125	854	2023	56
10	24063	21600	<100	<100	<100	358	10
11	21267	<100	<100	<100	<100	927	>99
12	21232	<100	<100	<100	<100	405	>99

Analytical uncertainty for the results is 10%.

The catalysis reactions show some amounts of phenylborate (3PB, 2PB, 1PB, and phenol) decomposition products, although less than with hydrolysis. This could be due to accelerated breakdown of the phenylborate decomposition products themselves.

Catalysis AA Data

Exp. ID	Starting K (mg/L)	Ending K (mg/L)	AA % TPB Destruction	HPLC % TPB Destruction
7	199	3510	143	99
8	199	2120	82	75
9	199	1790	68	56
10	199	736	21	10
11	199	3240	131	>99
12	199	3740	153	>99

Analytical uncertainty for the results is 10%.

Examining the results shows that there is a general match between the AA results and the HPLC. The HPLC analytical method uses a total extraction of the sample, while the AA analytical method uses a sampling of the reaction vessel. Due to this, we feel the HPLC results are the more accurate of the two analytical methods. The >100% returns in some AA results could be either due to the heterogeneous method of sampling, or the sensitivity of the analytical methods to the presence of organics.

Hydrolysis HPLC Data

Experiment	Notebook Exp. Name	Temp. (ºC)	Initial pH	Final pH	Target pH	Coupon Corrosion mils Per Year
13	1-HE	45	8.1	8.8	8	8.57
14	2-HE	45	10.0	10.2	10	0.00
15	3-HE	45	10.7	10.3	11	5.83
16	4-HE	45	14.0	9.9	14	0.00
17	5-HE	45	7.8	8.6	8	8.99
18	6-HE	60	8.0	8.9*	8	0.20*

* Experiment 18 tipped over and spilled, so these results contain additional error.

Exp. ID	Start TPB (mg/L)	End TPB (mg/L)	3PB (mg/L)	2PB (mg/L)	1PB (mg/L)	Phenol (mg/L)	% TPB Destruction
13	21218	<100	<100	<100	4005	1438	>99
14	21557	94	<100	<100	2750	2193	> 99
15	21596	3486	<100	358	2170	2881	84
16	24045	29348	<100	<100	<100	443	0
17	21150	<100	<100	<100	2888	1042	>99
18	21180	<100*	<100*	<100*	<100*	490*	>99*

Analytical uncertainty for the results is 10%.

* Experiment 18 tipped over and spilled, so these results contain additional error.

The Hydrolysis reactions show the largest amount of phenylborates (3PB, 2PB, 1PB, and phenol) of all three reactions (Fenton, catalysis, hydrolysis).

Experiment 18 (6-HE) tipped over and lost some amount of TPB slurry, while taking on water from the water bath (we could not quantify the exact amount). Due to this, the final pH, % TPB destroyed and coupon corrosion results contain additional error. We report the results, but we estimate they could be off by as much as ~300%.

Hydrolysis AA/ICPES Data

Exp. ID	Notebook Exp. Name	Starting K (mg/L)	Ending K (mg/L)	AA % TPB Destruction	HPLC % TPB Destruction
13	1-HE	199	2850	115	>99
14	2-HE	199	2760	109	> 99
15	3-HE	199	2510	98	84
16	4-HE	199	1260	41	0
17	5-HE	199	3410	139	>99
18	6-HE	199	624*	18*	>99*

Analytical uncertainty for the results is 10%.

* Experiment 18 tipped over and spilled, so these results contain additional error.

As with the catalysis experiments, there is a general match between the AA results and the HPLC. For the same reason given in the catalysis section, above, we feel the HPLC results are the more accurate of the two analytical methods.

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