Process Development for Oxidative Destruction of Tetraphenylborate
in Savannah River Site Tank 48H

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LIST OF ACRONYMS

1PB	phenylboronic acid
2PB	diphenylborinic acid
3PB	triphenylborane
AA	Atomic Absorption
ADS	Analytical Development Section
ATR	Attenuated Total Reflectance
CPP	Cyclic Potentiodynamic Polarization
Cu	Copper
DOE	Department of Energy
DWPF	Defense Waste Processing Facility
ECC	Enhanced Composition Catalyst
Fe	Iron
FTIR	Fourier Transformed Infrared Spectroscopy
GC-MS	Gas Chromatography – Mass Spectrometry
H_2O_2	hydrogen peroxide ("peroxide")
HPLC	High Performance Liquid Chromatography
IC	Ion Chromatography
ICP-ES	Inductively Coupled Plasma – Emission Spectroscopy
INEEL	Idaho National Engineering and Environmental Lab
ITP	In-Tank Precipitation
KTPB	potassium tetraphenylborate – $[K][B(C_6H_5)_4]$
LPR	Linear Polarization Resistance
MST	monosodium titanate
NaOH	sodium hydroxide
NaTPB	sodium tetraphenylborate – $[Na][B(C_6H_5)_4]$
NETL	National Energy Technology Laboratory
OSHA	Occupational Safety and Health Administration
SRS	Savannah River Site
SRTC	Savannah River Technology Center
TAML	Tetra-Amido Macrocyclic Ligand
TPB	Tetraphenylborate

1.0 EXECUTIVE SUMMARY

This study investigated oxidative options to remediate the contents of Tank 48H. Parallel studies by AEA Technologies Inc. and Oak Ridge National Laboratory examined "out of tank" processes – ones that utilize conditions hostile to the tank infrastructure – for chemical destruction of the organic material. The authors investigated "in-tank" processes using hydrogen peroxide and each of three metal catalysts: Fenton (iron), Fenton (copper), or Tetra-Amido Macrocyclic Ligand (TAML®). The results of the experiments indicate that the oxidative destruction is a viable in-tank option, but several limitations need to be addressed.

- The experiments tested five oxidative catalyst systems under a variety of conditions; hydrogen peroxide plus any of: Fenton (iron), Fenton (copper), Fenton (iron + copper), TAML®, and TAML® + Fenton (copper) catalyst systems. We found that under comparable conditions (pH 11, 25 ºC, 5 hours, using 30 mL of 50 wt% H_2O_2) TAML® gave the highest average KTPB destruction (55%).[a] In contrast, under the same conditions, Fenton (iron + copper) gave a 35% destruction, while Fenton (copper) yielded an average 46% destruction and Fenton (iron) yielded an average of 33% destruction. We did not conduct a comparable reaction using the TAML® + Fenton (copper) catalyst system. Other than phenylborates or phenol, analyses did not identify any other organic products.

- Nominally, the H_2O_2 serves as the species that performs the oxidative destruction of the organics. Decreasing the H_2O_2 addition rate, or stopping it entirely, serves as the primary oxidation reaction control. pH control serves as the hydrolysis reaction control.

- The single best KTPB destruction (95%) occurred at 45 ºC, pH 11, using a 47.6:1 molar ratio of H_2O_2 to TPB, and using approximately 500 mg/L of Fenton (copper) catalyst.

- From the results of the experiments we recommend the following actions be taken in the next round of testing.
  - Improve testing by controlling pH, temperature, etc., more precisely
  - Measure off-gas byproducts
  - Measure liquid and solid decomposition products and establish a carbon balance
  - Measure nitrite destruction in experiments with TAML®
  - Continue attempts to limit or eliminate foaming

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[a] The % TPB destruction is defined as the percent of TPB converted to any other species.

2.0 INTRODUCTION

This report documents the results of an SRTC proposal, funded by the EM Office of Cleanup Technologies[1] concerning Tank 48H. Tank 48H is a "unique tank waste that poses problematic operational processes for which there is no available technology". These experiments help develop a process for destroying Tank 48H's "legacy tetraphenylborate organic waste". Tank 48H will serve as the feed tank for the Actinide Removal Process, which will treat low curie waste. 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 non-radioactive, simulated waste. For those processes that prove most attractive, personnel will later demonstrate process viability through pilot scale and actual waste testing.

The overall program includes five parallel areas of research performed in an attempt to develop processing alternatives for Tank 48H.
1. AEA Technologies Inc. performed research to develop a low pH, boiling Fenton's Reagent process for the destruction of tetraphenylborate (TPB).[2]
2. WSRC Closure Engineering requested Savannah River Technology Center (SRTC) and Idaho National Engineering and Environmental Laboratory (INEEL) to examine the viability of steam reforming for treating the Tank 48H waste. Jantzen (SRTC) completed laboratory testing with simulated waste as defined in the Task Plan for this work.[3] A separate report documented those findings.[4] Similarly, INEEL personnel conducted pilot-scale demonstrations based on the SRTC work and a separate report covers that study.[5]
3. Other SRTC researchers completed corrosion testing to examine corrosion rates applicable for any in-tank processing alternatives. A separate report describes those results.[6]
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. Task Technical Requests [7,8] issued by Closure Engineering provided the requirements of the testing for FY03. SRTC documented the agreed upon experimental design in a Task Plan.[9] A report describes those results.[10] SRTC also documented a separate report of the flowsheet analysis, [11] the cost estimates,[12,13,14] and the risk assessments of the in-tank options.[15,16,17]
5. The DOE funded testing to develop an in-tank and out-of-tank Fenton Process. A separate Task Plan defines the experimental design.[18] This report describes those results.

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 Fenton's processing alternatives.[19] The second is a SRTC proposal awarded funds from the EM-21 Office of Cleanup Technologies to develop in-tank and out-of-tank Fenton's processes for Tank 48H.[20] We developed the testing to minimize any duplication of effort between the two tasks so to better utilize resources. This report documents testing in support of the NETL funded tasks.

2.1 Alternative Technologies for Destruction of the Tetraphenylborate in Tank 48H
SRTC researchers served as members of a Tank 48H team chartered in FY02 to identify options, evaluate alternatives and recommend selected alternative(s) for processing Tank 48H contents to a waste form capable of being processed or stored by existing or planned facilities. The Savannah River Site (SRS) project team included subject matter experts from WSRC and its partners. The team documented all ideas in the Phase 1 report.[21] SRTC conducted testing of the most favored options as described in Section 7 of the SRS Tank 48H Team's report.[22]

In Tank 48H testing, Fenton's Reagent showed the 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 became the primary focus of a large portion of the experimental study for the Tank 48H work, and received further investigation in the more recent laboratory waste disposal[23] and Tank 50H solids destruction[24] testing. The copper catalyst and acid hydrolysis options also showed good decomposition rates, but produced benzene as the main byproduct. Lastly, permanganate treatment showed some degree of success, but had the disadvantage of producing a large amount of solid byproduct manganese dioxide, which would go to DWPF for glass production. The project team elected to not pursue this last option. Parallel experiments examined steam reforming, a technology under study at Hanford,[25] so as to determine its efficiency in destroying TPB-laden waste. The current work scope assists the project team in selecting preferred options based on technical viability.

2.2 Fenton's Reagent Background
Fenton's Reagent is an oxidation process developed by H.J.H. Fenton in 1894.[26] Fenton's Reagent is used to degrade the organic components of a variety of industrial wastes such as wastewaters, sludges, and contaminated soils.[27] Fenton's Reagent has been used in a collaborative effort between Geo-Cleanse International, Inc., and WSRC in 1997.[28] 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 that makes the operation complex with respect 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.[29] TAML® offers organic destruction at higher pH ranges than a Fenton's Reagent reaction. The TAML® catalyst is used interchangeably with iron in the conventional Fenton's reactions in our work. Both reactions result in oxidations of the organic.

The test program examined five oxidative catalyst systems under a variety of conditions; hydrogen peroxide plus any of: Fenton (iron), Fenton (copper), Fenton (iron + copper), TAML®, and TAML® + Fenton (copper) catalyst systems. The tests demonstrated the effectiveness of the various reactions 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.

2.3 Risk Assessment for Fenton's In-Tank Process
While a complete document details the results of the Fenton's In-Tank risk assessment, it is relevant to give here an overview of the conclusions of that report. The risk assessment team identified twelve risks. After factoring in the risk handling strategies, these risks varied from not applicable to high in residual risk level. The conclusion of the risk assessment team was that further corrosion, Fenton, and actual waste testing was required.

2.4 Corrosion
A separate document details the results of a battery of corrosion testing. We summarize the results from that report here.

Linear polarization resistance (LPR) and cyclic potentiodynamic polarization (CPP) tests occurred on specimens of Type III waste tank steel, ASTM A537 class 1 in simulated waste solutions. The simulated waste also contained hydrogen peroxide and the catalysts ferric ion (Fenton's reagent) or TAML®. In the ferric ion tests at pH 11 and temperatures between 32 and 65°C, a relatively low general corrosion rate of 5 mils per year (0.005 inches per year – 1 mil equals $1/1000^{th}$ of an inch) occurred. However, the general corrosion rate could exceed 100 mils per year (0.10 inches per year) as revealed in tests at pH 7. Pitting occurred on all but two specimens.

In the tests with the TAML® catalyst present, testing occurred at pH 9 and 11 and at temperatures of 45 and 65 °C. The pH 11 tests produced general corrosion rates of 1.7 to 7.6 mils per year (0.0017 to 0.0075 inches per year), similar to those measured with ferric ion at pH 11. At pH 9 the general corrosion rates ranged from 2.1 to 36 mils per year. Pitting also occurred in these tests.

These experiments indicate that a decomposition process based on Fenton's reagent may not be excessively corrosive if performed at pH 11. However, the LPR tests occurred under conditions not at chemical equilibrium, as a result of the periodic additions of hydrogen peroxide and catalyst. To confirm these initial short-term electrochemical test results, long-term (2 to 4 months' duration) coupon immersion tests are recommended. In addition to supplying accurate general corrosion rate data, coupon tests provide a means of quantifying the pitting susceptibility.

2.5 Cost Analysis
A detailed breakdown of the cost structure for the Fenton In-Tank option is detailed in another document. This document estimates the total cost of the Fenton In-Tank option as $5,710,000. An estimate of the direct costs for the Fenton process is estimated at $2,090,000 and is detailed in Appendix I. The costs are subject to change [30] as program needs change, and not all project costs are listed in the Appendix information.

2.6 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 contains a boron atom surrounded by four phenyl ($-C_6H_5$) groups.

Personnel added the tetraphenylborate to Tank 48H during the demonstration and startup of the In-Tank Precipitation Facility. An unplanned catalytic reaction occurred that resulted in release of benzene at higher rates than could be accepted for the target processing rate. 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 to allow the slated use of the tank. 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 vol % in air.[31] Benzene is also a carcinogen with an Occupational Health and Safety Administration (OSHA) Permissible Exposure Limit of 1 ppm.[32] As a result of the benzene issues, processing that completely oxidizes TPB to carbon dioxide and water is less troublesome with respect to the potential benzene hazard.

3.0 EXPERIMENTAL SETUP

3.1 Experimental Plans

Personnel performed all experiments with Tank 48H simulated waste. The waste composition matched either exactly as written in Table 2 or slight variations from it. Furthermore, all of the tests added the components listed in Table 3. The added components were derived from an earlier recipe called the Enhanced Comprehensive Catalyst (ECC) elements.[33,34,35] These metals represent the approximate composition of the various metals as measured in Tank 48H samples. Personnel conducted each of the reactions in a custom made, 250 or 500 mL reactor (Figure 1). Technicians added Tank 48H waste to the reactor along with a stir-bar, followed by the additional components and any other additives. They then attached a condenser to the vessel and circulated cold tap water through for cooling. Personnel delivered hydrogen peroxide through the side arm port. An additional side arm port allowed for temperature or pH measurements or TAML[®] catalyst delivery. Temperature control and stirring used a hot-plate stirrer unit.

Table 2. Tank 48H Composition

Component	M
KTPB	0.0728 (2.32 wt %)
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

Table 3. Added Components

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 [a]	Sludge	500 [b]
MST [c]	MST	500 [b]

[a] The sludge was a PUREX recipe, see analysis in Appendix III.

[b] MST and sludge concentrations proved lower than desired due to an error in specifying the composition. It should have been 0.2 wt % not 500 mg/L. A PIR was created to investigate this problem and is detailed in SRT-LWP-2003-00115.

[c] The MST came from the "TNX" batch.

Figure 1. Custom Reactor
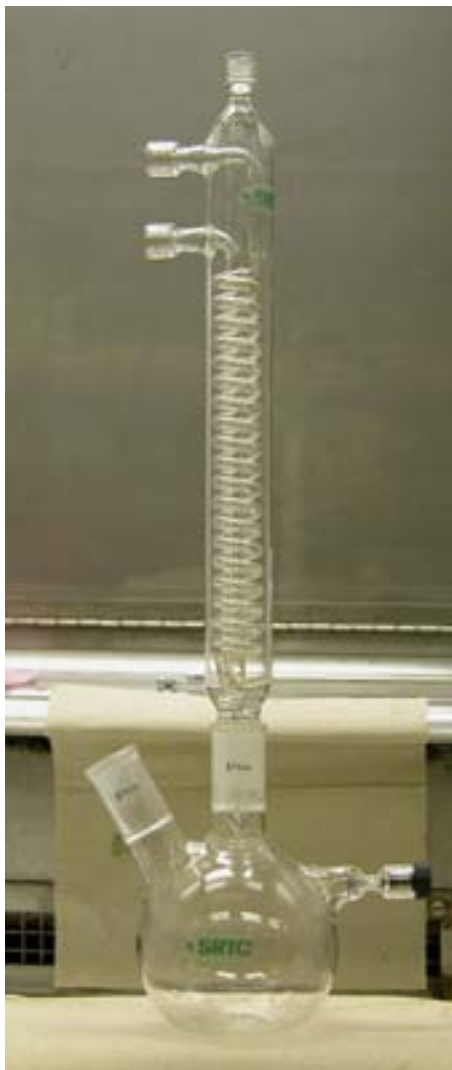
The standard method of product analysis used High Performance Liquid Chromatography (HPLC). This involved extracting the entire remaining contents of the reaction vessel and using that extract for analysis. Potassium analysis by Inductively Coupled Plasma Emission Spectroscopy (ICP-ES) or Atomic Absorption (AA) occurred at the conclusion of some of the reactions in an attempt to monitor KTPB destruction by a second method (see Appendix II). Approximately 30% variation existed between the HPLC analysis of TPB and ICPES/AA potassium analyses (as a whole), most likely due to sample heterogeneity and non-representative sampling.   Due to the fact that the HPLC results tended to be more conservative, and the fact that HPLC also provided analysis of 3PB, 2PB, 1PB, and phenol, we report only the HPLC results.

3.1.1 Proof-of-Concept Reactions

To confirm the efficacy of oxidation reactions in destroying TPB, we performed a series of proof-of-concept reactions using NaTPB instead of the KTPB found in Tank 48H. Using the much more soluble NaTPB allowed us to remove the mass transfer variable from these experiments. We used the simulant recipe listed in Table 2, as well as the additional components in Table 3. For these experiments, we omitted the potassium nitrate in the simulant recipe to avoid forming KTPB. Although tests did not add KNO_3, enough tramp potassium existed in the other materials to form white precipitated KTPB. We performed 8 experiments, varying the temperature, catalyst, and pH. Each experiment operated for five hours, and used 30 mL of 50 wt % H_2O_2 as the oxidant.

Technicians prepared the precipitate by combining a stock precipitate simulant (omitting the KNO_3) with the added components (Table 3). 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 additional components and adjusted the pH to a prescribed condition using 70 wt % nitric acid, followed by the adding the iron, copper, or TAML® 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 five hours. Technicians added the peroxide to the syringe pump and inserted the needle into the septum on the side of the flask. Figure 2 contains a photo of the flask during a typical experiment.

Figure 2. Typical Foaming Fenton Reaction.

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.

At the completion of the experiment, technicians submitted the contents of the entire flask to ADS for HPLC extraction and analysis.

3.1.2 Scouting the Operating Conditions

SRTC performed a series of 14 experiments to establish basic operating conditions required for successful KTPB destruction. The experiments used varying types of catalyst (iron, copper, iron with copper, TAML®), temperature (25, 45, 60 °C), and hydrogen peroxide (0 or 30 mL of 50 wt % H_2O_2 – 30 mL of water was added to maintain equivalent volume in Tests 9 and 21 and 90 mL of water was added in Test 22). Each of the reactions occurred at pH 14, 11 or 9, for five hours and used the Tank 48H simulant recipe listed in Table 2, as well as the additional components in Table 3. The experimental protocol (other than recipe) and post reaction analysis were identical to that of the Proof-of-Concept reactions.

3.1.3 Stoichiometry Reactions

SRTC determined that the H_2O_2 stoichiometry (0, 2.9, 8.7 moles H_2O_2 per mole of carbon) deserved a more detailed investigation before optimization of the process. We performed a series of seven reactions that used a constant temperature (45 °C), pH (11), and catalyst (TAML® at 100 mg/L) but varied the amount of H_2O_2 (0, 30 or 90 mL of 50 wt % H_2O_2 – 90 mL of water was added to maintain equivalent volume in Test 29) and reaction time (5, 29, 53 hours). The experimental protocol (other than recipe) and post reaction analysis were identical to that of the Proof-of-Concept reactions.

3.1.4 Optimization Reactions

The largest series of experiments, 26 in all, attempted to optimize the oxidation conditions. Experiments varied the pH (9, 11, 12), reaction temperature (25, 45 °C), volume of peroxide added (0, 20, or 30 mL of 50 wt % H_2O_2 – water was added to those tests without H_2O_2 to maintain equivalent), and catalyst type and amount. The tests also examined the effects of reaction scale and subsurface H_2O_2 addition. The experimental protocol (other than recipe) and post reaction analysis were identical to that of the Proof-of-Concept reactions.

3.1.5 Competitive Reactions in Tank 48H

SRTC performed six experiments designed to provide insight as to whether other species in Tank 48H compete with the oxidative destruction of KTPB. Researchers examined the effects of a Fenton (copper or TAML®) reaction on nitrite (NO_2^-), oxalate ($C_2O_4^{2-}$), formate (HCO_2^-) and biphenyl ($C_{12}H_{10}$). The experimental protocol (other than recipe) was similar to that of the Proof-of-Concept reactions except the experiments did not

include TPB. Post reaction analysis included ion chromatography (IC) for nitrite, oxalate and formate anions, and HPLC for biphenyl.

3.1.6 TAML® Solution Stability Testing

The TAML® catalyst is known to have a limited pH operating range. SRTC performed a study of TAML® in caustic solution to determine the approximate lifetime. All Fourier Transformed Infrared Spectroscopy (FTIR) data were collected on a Nicolet 210 spectrometer. The solutions were placed on an Attenuated Total Reflectance (ATR) crystal (ZnSe) that allowed the infrared beam to bounce ten times from the solution. The digital resolution of each spectrum was 4 cm^{-1}. The spectra were collected every minute with 32 scans. The spectrometer was under dried nitrogen purge during the collection. The samples were exposed to air and humidity via tubing. No mixing of the solution occurred during collection. The housing that hosted the solution was made of 314 stainless steel material.

Solutions consisted of simulated Tank 48H solution, pH adjusted to the correct value (7 or 11). Solution pH was verified with pH paper.

4.0 EXPERIMENTAL RESULTS

4.1 Proof-of-Concept Reactions

In these reactions, SRTC examined the effects of three variables – pH (7, 9, or 11), temperature (45 or 60 °C), and catalyst: Fenton (iron), Fenton (copper), Fenton (iron + copper), TAML® – on the oxidative degradation of NaTPB. Table 4 lists the parameters of the different experiments. Hydrogen peroxide (30 mL of 50 wt %) was kept constant

Table 4. Conditions of the Proof-of-Concept Reactions

Experiment #	pH	Temp (°C)	Catalyst	Target Catalyst Amount (ppm)
1	11	45	Iron	500
2	9	45	Iron	500
3	7	45	Iron	500
4	7	45	Iron/Copper	250/250
5	11	45	Iron/Copper	250/250
6	7	60	Iron/Copper	250/250
7	9	45	Iron/Copper	250/250
8	11	45	TAML®	100

Table 5 summarizes the HPLC results of each reaction. We determined the percentage NaTPB destroyed by comparing NaTPB present at the end of the reaction to the amount added to each reaction.

Table 5. Proof-of-Concept Reaction HPLC Results

Experiment #	Starting NaTPB Concentration (ppm)	Final Phenylborate Concentrations (ppm)					% TPB Destruction
		TPB	3PB	2PB	1PB	Phenol	
1	18,228	2307	852	102	<100	5,860	87
2	18,061	< 100	<100	<100	<100	5,538	> 99
3	17,954	< 100	<100	<100	<100	3,156	> 99
4	18,030	< 100	<100	<100	<100	1,046	> 99
5	18,192	< 100	<100	<100	<100	<100	> 99
6	17,962	< 100	<100	<100	<100	<100	> 99
7	17,942	9729	<100	<100	<100	2,414	46
8	18,191	9440	<100	<100	<100	<100	48

Analytical uncertainty for the HPLC results is 10%.

In general, the reactions almost completely destroyed the NaTPB to the limit of analytical detection (100 ppm). From the results of the above tests, we can draw several conclusions. First, the lower the pH, the more complete the reaction, not only in terms of NaTPB destruction, but in the amounts of phenylborate and phenol byproducts. Experiments #3, #4, #6, each at pH 7, completely destroyed the NaTPB. Experiment #2 at pH 9, gave complete NaTPB destruction, while experiment #7 (also pH 9) gave 46% destruction. Experiments #1 and #5, at pH 11, gave 87% and > 99% NaTPB destruction, respectively. Experiment #1 produced more 3PB and 2PB than any of the other reactions. Experiment #7 at pH 9 yielded only a 46% TPB destruction in comparison to >99 % reported for Experiments # 4 and 5 (conducted with the same catalyst and conditions other than pH) at pH 7 and 11. The results suggest another variable (e.g., foaming or the heterogeneous character of the material) also impacts reactivity.[b]

Temperature had a beneficial effect in reducing the amount of phenol byproduct. Experiment 4 at 45 ºC generated phenol, while experiment #6 at 60 ºC did not produce phenol.

Experiment #8, the only reaction using TAML®, gave incomplete NaTPB destruction. However, the researchers noted that this reaction had severe foaming problems which most likely hindered the oxidation reaction and lowered the overall NaTPB destruction.

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[b] We found no evidence of potassium contamination in experiments 7 and 8.

The different catalysts also gave different distributions of phenylborate and phenol byproducts. The TAML® reaction gave neither. The Fenton (iron + copper) gave no phenylborates and an average of 915 ppm of phenol per reaction. The Fenton (iron) reactions were the only reactions that evidenced phenylborate production, and they also gave an average of 4,851 ppm of phenol. It appears that phenol is produced during the destruction, and it accumulates; the last to be destroyed in the oxidation reaction. This would seem to indicate that the Fenton (iron) catalyst system is generally not fast enough to finish the oxidative destruction of all organics (at least the ones we can see by HPLC) in 5 hours. The other catalyst systems are in some cases able to completely destroy all the organics.

From these results, we conclude that either a Fenton or TAML® reaction is capable of destroying TPB from a thermodynamic standpoint and that the Fenton (iron) is somewhat slower overall in the destruction of all (not just the TPB) organic species.

4.2 Scouting the Operating Conditions

For these tests, SRTC examined the effects of amount and type of catalyst, temperature, amount of peroxide, and reaction duration. All reactions occurred at pH 14, 11 or 9. Table 6 lists the different experiments.

Table 6. List of Scouting Reactions

Experiment #	pH	mL 50 wt % H_2O_2 Added	Temp (°C)	Catalyst	Target Catalyst Concentration (mg/L)[c]
9	14	0	25	Iron	500 mg/L
10	14	30	25	Iron	500 mg/L
11	11	30	25	Copper	500 mg/L
12	11	30	25	Iron/Copper	250/250 mg/L
13	11	30	25	Iron	500 mg/L
14	9	30	25	Iron	500 mg/L
15	11	30	25	TAML®	100 mg/L
16	11	30	45	TAML®	100 mg/L
17	11	30	60	TAML®	100 mg/L
18	11	30	45	TAML®	100 mg/L
19	11	30	45	TAML®	25 mg/L
20	11	30	45	TAML®	400 mg/L
21	11	0	45	TAML®	100 mg/L
22	11	0	45	TAML®	100 mg/L

Table 7 summarizes the results of each reaction. The data shows that, in general, the destruction efficiency was lower in these experiments than observed in the

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[c] Concentration before addition of H_2O_2

Table 7. Scoping Reaction Results

Experiment #	Starting KTPB Concentration (ppm)	Final Phenylborate Concentrations (ppm)					
		TPB	3PB	2PB	1PB	Phenol	% KTPB Destruction
9	17,833	19,692	<100	<100	<100	<100	0
10	18,157	18,896	<100	<100	<100	<100	0
11	18,157	9,677	<100	<100	<100	1,179	47
12	18,136	11,709	<100	<100	<100	1,788	35
13	18,221	12,202	689	1775	167	118	33
14	18,411	15,865	<100	<100	<100	2,128	14
15	18,023	8,015	<100	<100	<100	<100	56
16	18,051	11,484	<100	<100	94	313	36
17	18,044	5,869	<100	89	<100	140	67
18	18,030	6,679	<100	107	<100	168	63
19	18,044	10,377	<100	<100	110	489	42
20	18,030	9,264	<100	215	<100	133	49
21	18,065	9,016	188	2887	497	303	50
22	12,699	4,650	<100	780	214	179	63

Analytical uncertainty for the HPLC results is 10%.

Proof-of-Concept reactions (Section 4.1, above). The lower destruction efficiencies reflect the much less soluble KTPB as harder to destroy under the heterogeneous reaction conditions (i.e., mass transfer barriers). The more numerous appearance of hydrolysis products (again, we assume the hydrolysis products are solely due to hydrolysis and not the oxidation reaction) may be tied to the lower solubility of the KTPB.

Quantities of TPB hydrolysis products are present (3PB, 2PB, 1PB and phenol) at the end of the reactions; more quantities than observed in the Proof-of-Concept reactions. The reactions using iron as the sole catalyst produced the most TPB hydrolysis products (especially phenol), while the TAML[®] catalyst generally (with experiment #21 as an exception) produced the least amount (although this could be a temperature effect). Experiments #21 and 22 omitted H_2O_2 but still resulted in an oxidation reaction. This may be due to an oxidation reaction using air instead of H_2O_2 as the oxidizer. On the other hand, the presence of notable quantities of phenylborates and phenol would seem to indicate hydrolysis is occurring in the experiment. At this time, we cannot discern the two different mechanisms due to the lack of a true blank (no TAML[®], no peroxide) reaction, with which we could subtract the background hydrolysis reaction. Duplicate Experiments # 16 and 18 show a wide variance in reactivity (36% and 63% TPB decomposition, respectively). This result again supports the theory that foaming and heterogeneity of the material affects reactivity.

4.2.1 Issues Identified During Oxidative Destruction Testing

Personnel made several observations (e.g., regarding foaming, mixing, acid addition, and temperature variance) during testing that are important considerations in future testing.

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.[36] 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. Some of the experiments used an alternate precipitation method to produce a denser, foamless precipitate. However, foaming did occur during the peroxide addition even with the alternate slurry preparation method. Reactions involving TAML® seemed to exhibit more foaming than the Fenton reactions. Future work should include attempts to limit or control the foam. Such attempts may include use of antifoam agents or delivering the peroxide below the reaction surface. Ideally, researchers will perform tests using actual waste to determine the tendency to foam.

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 – see Figure 3). For Tank 48H, the best addition strategy would add the acid through a downcomer under the liquid level while mixing the tank.

Figure 3. Hydrolysis Resulting in Byproducts
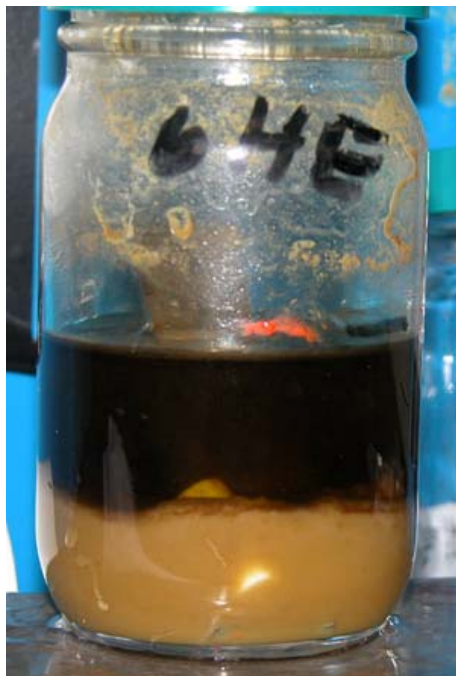
Temperature Control – Temperature control with the hot plate proved inadequate to control the temperature within 1 °C. Throughout the course of the experiments, the researchers and technicians had to adjust the heat flow to the reactors while attempting to maintain the desired temperature. This caused temperature spikes as high as 32 ℃ (worst case, Experiment #34) over the target temperature. However, these maximum values were not sustained over-temperatures. In fact, the average maximum over-temperature was 7.6 ℃. 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 experiments with better mixing would likely lead to more complete destruction.

4.3 Stoichiometry Reactions

SRTC performed a series of seven reactions to examine the effects of varying the amount and rate of added H_2O_2. Researchers performed all the experiments at pH 11 and 45 ℃, using 100 mg/L of TAML® as the catalyst. Table 8 lists the experimental conditions of these experiments.

Table 8. Reaction Conditions for the Stoichiometry Reactions

Experiment #	mL 50 wt % H_2O_2 Added	Reaction Time (h)
23	30	5
24	30	29
25	90	5
26	30	53
27	90	29
28	90	53
29	0	53

Table 9 lists the results of each reaction. Compared to the prior reactions, these tests generally showed increased KTPB destruction. At the same time, the KTPB hydrolysis

product production proved lower than in the prior tests. Only experiment #29 showed any TPB hydrolysis product formation. It appears from results that the TAML[®] catalyst is destroying any hydrolysis products that are formed, or it is destroying the KTPB before hydrolysis can take place.

Table 9. Stoichiometry Reaction Results

Experiment #	Starting KTPB Concentration (ppm)	Final Phenylborate Concentrations (ppm)					
		TPB	3PB	2PB	1PB	Phenol	% KTPB Destruction
23	18,051	1,180	<100	<100	<100	<100	93
24	18,037	4,011	<100	<100	<100	<100	78
25	12,708	6,550	<100	<100	<100	<100	48
26	12,713	3,170	<100	<100	<100	<100	75
27	18,023	5,715	<100	<100	<100	<100	68
28	12,703	4,010	<100	<100	<100	<100	68
29	12,699	9,280	<100	152	226	1080	27

Analytical uncertainty for the HPLC results is 10%.

4.4 Optimization Reactions

These reactions represent the single largest battery of experiments that SRTC performed. These reactions examined the effects of pH (see section 4.7.3 for direct comparisons), reaction temperature (section 4.7.6), catalyst amounts (section 4.7.5), reaction scale (section 4.7.8), and subsurface H_2O_2 addition (section 4.7.11). Table 10 lists the reaction conditions. Each of these reactions operated for five hours. Table 11 provides the results of each reaction.

Table 10. Reaction Conditions for the Optimization Experiments

Experiment #	pH	mL 50 wt % H_2O_2 Added	Temp (ºC)	Catalyst	Target Catalyst Concentration (mg/L)
30	11	0	25	Iron	500
31	11	0	25	TAML®	100
32	11	30	45	TAML®	25
33	11	30	45	TAML®	100
34	11	30	45	TAML®	400
35	11	30	45	TAML®	100
36	9	30	45	TAML®	100
37	9	0 [d]	45	TAML®	100
38	12	30	45	TAML®	100
39	12	0 [c]	45	TAML®	100
40	11	30	25	Iron	500
41	11	30	25	TAML®	100
46	11	20	45	Copper	500
47	11	20	45	TAML®	100
48	11	30	25	Copper	500
49	11	30	25	TAML®	100
50	9	30	45	TAML®	100
51	9	30	45	TAML®	100
52	9	30	25	Copper	500
53	9	30	25	TAML®	100
54	11	30 [e]	25	Copper	500
55	11	30 [d,f]	25	Copper	500
56	11	20 [d]	25	Copper	500
57	11	20 [d]	25	Copper	500
58	11	30 [e]	25	Copper/ TAML®	500/100
59	11	30 [e]	25	TAML®	100

[d] no H_2O_2 or H_2O was added to these reactions
[e] amount of copper catalyst was ~10% higher than planned
[f] H_2O_2 added subsurface

Table 11. Optimization Results

Experiment #	Starting KTPB Concentration (ppm)	Final Phenylborate Concentrations (ppm)					
		TPB	3PB	2PB	1PB	Phenol	% KTPB Destruction
30	18,579	18,279	409	194	<100	<100	2
31	19,445	19,957	366	142	<100	<100	0
32	14,409	8,123	<100	<100	<100	<100	44
33	13,515	8,672	<100	<100	<100	<100	36
34	18,058	8,811	<100	<100	<100	<100	51
35	18,079	7,172	<100	<100	<100	<100	60
36	18,157	10,384	<100	<100	<100	<100	43
37	22,924	11,808	<100	1,904	543	392	48
38	18,510	15,600	<100	<100	<100	<100	16
39	23,592	22,300	<100	1,690	5,450	4,120	5
40	17,167	11,600	<100	<100	<100	<100	32
41	17,038	10,500	<100	<100	<100	<100	38
46	18,237	945	<100	<100	<100	<100	95
47	18,162	6,695	<100	<100	<100	<100	63
48	16,994	9,360	<100	<100	<100	<100	45
49	16,872	5,020	<100	<100	<100	<100	70
50	17,050	12,600	<100	<100	<100	<100	26
51	17,050	16,400	<100	<100	<100	<100	4
52	16,934	11,700	<100	<100	<100	<100	31
53	16,806	11,000	<100	<100	<100	<100	35
54	17,057	17,600	<100	<100	<100	<100	0
55	17,050	16,800	<100	<100	<100	<100	1
56	17,182	19,800	<100	<100	<100	<100	0
57	17,161	18,700	<100	<100	<100	<100	0
58	18,849	19,600	<100	<100	<100	<100	0
59	18,864	17,800	<100	<100	<100	<100	6

Analytical uncertainty for the HPLC results is 10%.

This set of experiments provided a wide variety of KTPB destruction results. Both the lowest (0%) and highest (95%) observed KTPB destructions were noted in this test set. In general, no or little phenylborates or phenol formed in these reactions. Only experiments #37 and #39 showed large quantities of phenylborates or phenol at the end of the reaction. In the case of experiment #37, the low pH of 9 may have effectively shut down the TAML® aided oxidative destruction, which would leave hydrolysis to account for the KTPB destruction and the phenylborate and phenol production. Experiment #39 showed the highest level of phenylborates out of any of the tests SRTC performed. The high pH (12) may have shut down the TAML® aided oxidative destruction. The lack of KTPB destruction and presence of phenylborates and phenol may indicate a hydrolysis reaction that has not proceeded to the same extent as experiment #37.

4.5 Competitive Reactions in Tank 48H

There are a number of chemical species in the Tank 48H simulant and in Tank 48H that could interfere with the oxidation reactions. Species subject to oxidative attack such as nitrite, oxalate, formate or biphenyl could compete with the TPB and reduce the overall TPB destruction results. SRTC performed a series of six experiments to examine whether this competition occurs. These reactions occurred under a variety of conditions, but all occurred during a five hour reaction time. Starting concentrations of the species were: formate, 460 mg/L; oxalate, 460 mg/L; nitrite, 21700 mg/L; biphenyl, 1030 mg/L. Table 12 lists the reaction conditions. Table 13 lists the results from these experiments.

Table 12. Reaction Conditions for the Competitive Reactions

Experiment #	pH	mL 50 wt % H_2O_2 Added	Temp (°C)	Catalyst	Target Catalyst Concentration (mg/L)
42	3.5	30	100	Copper	500
43	3.5	30	100	Copper	500
44	11	30	25	Copper	500
45	11	30	25	Copper	500
60	11	20	25	TAML®	100
61	11	20	25	Copper	500

Table 13. Competitive Reaction Data

Experiment #	% Formate Destruction	% Oxalate Destruction	% Nitrite Destruction	% Biphenyl Destruction
42	NA	> 78	> 99	NA
43	> 79	NA	> 99	NA
44	NA	11	30	NA
45	14	NA	28	NA
60	NA	NA	NA	0
61	NA	NA	NA	0

Analytical uncertainty for the HPLC (biphenyl) results is 10%. Analytical uncertainty for the formate, oxalate, and nitrite results is 10%. NA = not measured.

Researchers found that nitrite was completely destroyed by the reaction conditions at low pH, where nitrite is already known to undergo decomposition. (At this time we cannot discern what caused the decomposition, the oxidation reaction or acid-side decomposition). Note that the conditions employed for Experiments 42 and 43 (pH 3.5 and 100 °C) are not feasible for Tank 48H. At higher pH, a moderate (~30%) amount of nitrite destruction occurred. Most nitrite salts are thermally stable, so heat alone should not be the reason for the decomposition. Reactions at low pH also decomposed the majority of the oxalate, while only 11% oxalate decomposition occurred at the higher pH. At low pH, the reaction completely consumed the formate. At higher pH only a slight amount (14%) of formate decomposed.

Two experiments examined whether biphenyl, a common TPB hydrolysis product, is attacked by the oxidation reactions. We found that neither a copper nor TAML® catalyst had any noticeable effect on decomposing biphenyl. (The biphenyl concentration actually increased slightly.) This is somewhat surprising since benzene and other aromatic compounds are readily attacked by Fenton's reagent.

4.6 TAML® Solution Stability Testing
Simulant solutions with TAML® were tested at three different pH values (7, 11, and 14). After the simulant solution was adjusted to the proper pH, researchers added TAML® and observed the resulting solution over time via infrared spectroscopy.

pH 7

The FTIR spectrum of TAML® in a pH 7 solution is shown in Figure 4. For visual clarity, Figure 4 only presents the TAML® spectrum at every hour. The first FTIR spectrum at the bottom of the figure is the spectrum of dried TAML® for comparison. Looking at this figure, it can be said that after 13 hours of spectroscopic monitoring, no

spectral changes are seen. This leads us to conclude that TAML® did not structurally change over time in this solution.

Figure 4. TAML in pH 7 Adjusted Tank 48H Simulant
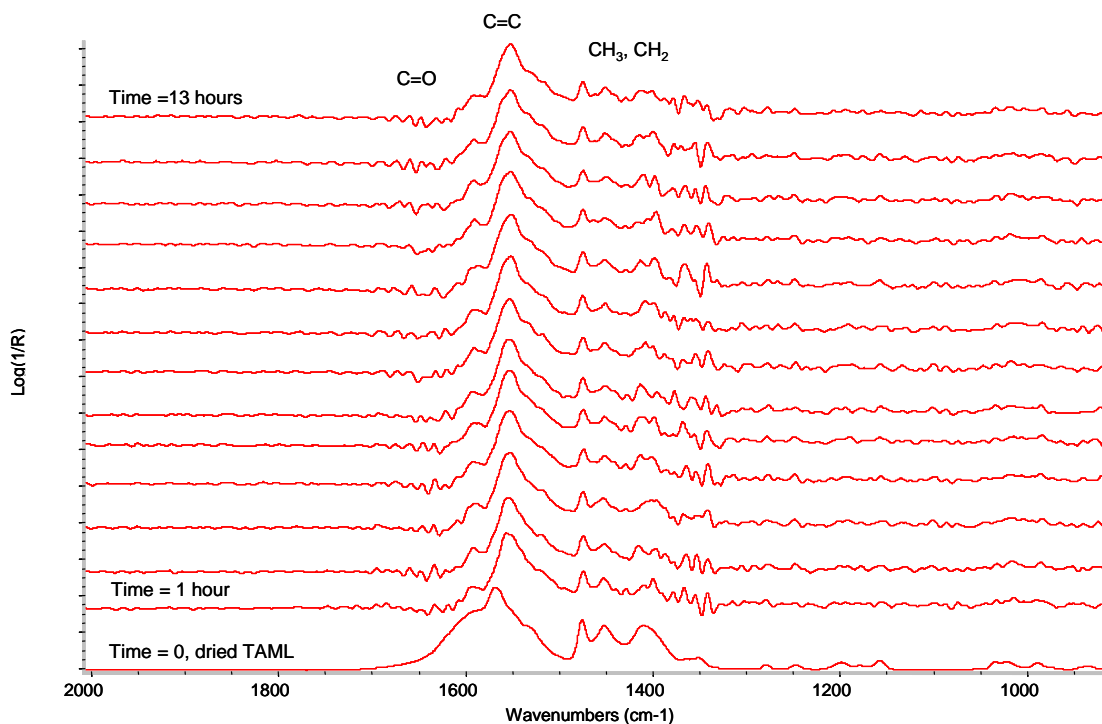
pH 11

The FTIR spectrum of TAML® in a solution at pH 11 is shown in Figure 5. Inspection of Figure 5 reveals new spectral features 14 hours after TAML® was placed in solution. This seems to indicate a possible structural change in the TAML® structure after 14 hours at pH 11. We attribute the new spectral feature at 1370 cm^{-1} to some sort of nitrate functionality and we suspect the nitrate is conjugated to the Fe as the peak intensity is large relative to the remaining features of the spectrum.

pH 14

The FTIR spectrum of TAML® in a solution of pH 14 is shown in Figure 6.   Inspection of Figure 6 reveals that spectral features of TAML® in this solution are different from the spectrum at pH 7 and the initial spectra of Figure 5 (pH 11). The spectra seems to indicate that an immediate structural change. This is noted by the intense peak at 1370 cm^{-1}. The spectra did not change with time in this solution.

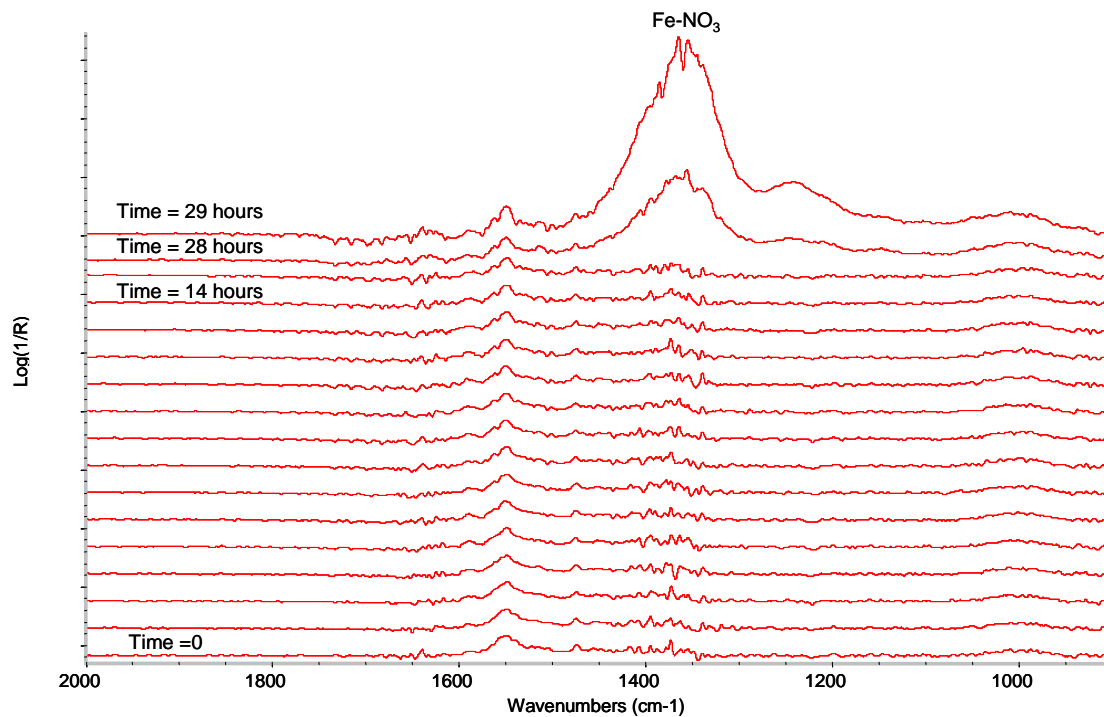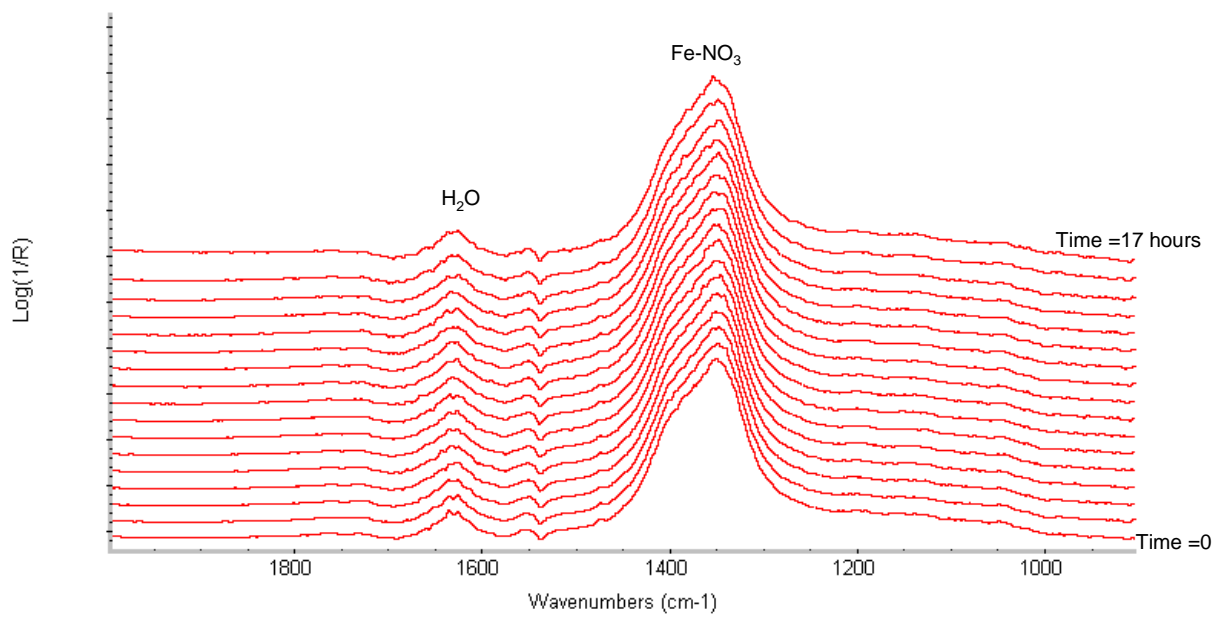**Figure 5. TAML in pH 11 Adjusted Tank 48H Simulant**

Figure 6. TAML in pH 14 Tank 48H Simulant

In total, this study indicates that in Tank 48H simulant, TAML® is indefinitely stable at pH 7, stable up to 14-28 hours at pH 11, and unstable at pH 14.

4.7 Examination and Comparisons of the Results
SRTC performed 61 experiments involving oxidation (Fenton or TAML®) catalysts. Fifty-five of these reactions involved the oxidative destruction of TPB. These experiments provide a number of single variable comparisons to determine the effect on TPB destruction. Considering that some of these comparisons are from single data points, and that there is a fair degree of variability due to foaming, the reader should consider the conclusions as preliminary.

4.7.1 Experimental Reproducibility
Virtually every reaction in the series of 61 experiments exhibited a degree of foaming, although the TAML® reactions tended to give most foaming. The presence of foam obfuscates the extent of the chemical reactions occurring in the flask due to removal of KTPB solids from the reaction liquor. This in turn tends to give a wider range of reaction results. There are four sets of experiments that were performed multiple times.

A review of duplicate experiments (Table 14) shows the degree of variability.

Table 14. Experimental Reproducibility for Duplicate Experiments

Duplicate Experiments	Average % KTPB Destruction	Standard Deviation	% Standard Deviation
13,40 (500 mg/L iron, pH 11, 5 hours, 25 ℃, 30 mL H_2O_2)	33	0.707	2.18
11,48 [g] (500 mg/L copper, pH 11, 5 hours, 25 ℃, 30 mL H_2O_2)	46	1.41	3.07
15,41,49 (100 mg/L TAML®, pH 11, 5 hours, 25 ℃, 30 mL H_2O_2)	55	16.0	29.3
16,18,23,33,35 (100 mg/L TAML®, pH 11, 5 hours, 45 ℃, 30 mL H_2O_2)	58	23.6	40.9

Analytical uncertainty for the HPLC results is 10%.

[g] Experiment 54 was also a duplicate of these two reactions. However, we discarded (from a Q-test) the result as a duplicate due to a statistical outlier result (0% destruction). The Fenton reactions always give a non-zero %TPB destruction, and the blanks give 0% destruction. From this we assume that water was used in the place of H_2O_2.

The resulting data reveals that the Fenton (iron) and Fenton (copper) experiments had less variability; this supports our observations that the Fenton reactions did not foam as much as the TAML® reactions. Conversely, while the TAML® reactions had greater variability, they appeared to provide better TPB destruction (see section 4.7.4).

4.7.2 Baseline Reaction Comparisons
The first comparison involves the blank reactions (H_2O in place of H_2O_2) to their non-blank equivalents. A total of four comparisons (Table 15) can be made from reactions at pH 11.

Table 15. Blank vs. Non-Blank Reactions

Experimental Conditions	Experiment #	H_2O_2	H_2O	% KTPB Destruction
100 mg/L TAML®, 45 ℃, 5 hour reaction time	21	None	30 mL	50
	Avg. of 16, 18, 23, 33, 35	30 mL	None	58
100 mg/L TAML®, 45 ℃, 5 hour reaction time	22	None	90 mL	63
	25	90 mL	None	48
100 mg/L TAML®, 45 ℃, 53 hour reaction time	29	None	90 mL	27
	28	90 mL	None	68
Fenton, 500 mg/L iron, 25 ℃, 5 hour reaction time	30	None	19 [h] mL	2
	Avg. of 13, 40	30 mL	None	33

Analytical uncertainty for the HPLC results is 10%.

In the first three cases (using the TAML® catalyst) we noted an appreciable degree of KTPB destruction even without added H_2O_2. In the second case (TAML® reaction using 100 mg/L TAML®, at 45 ℃ for 53 hours), the KTPB destruction proved greater for the blank than the non-blank. We hypothesize two possible reasons for this finding. First, the TAML® catalyst itself may promote a hydrolysis reaction. Second, the Carnegie-Melon personnel who synthesized the TAML® catalyst theorized that TAML®, in the

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[h] Due to a technical error, only 19 out of 30 mL of water was added to the reaction. However, the lesser amount of water should not have affected the TPB destruction.

presence of oxygen (with no H_2O_2 necessary) can promote an oxidative destruction of organics. We cannot prove or disprove these theories at this time, but will consider them in future work. In the case of the single Fenton comparison, the blank clearly showed virtually no reaction at all compared to the 33% KTPB destruction of the non-blank equivalents.

4.7.3 Effect of pH

The experiments include four different pH solutions (7, 9, 11, and 12). To reveal the effect of pH on the oxidation reactions, we examined a series of five comparisons (each reaction lasted five hours). Table 16 lists all five comparisons.

Table 16. Comparable Reactions in a Study of pH Effects

Experimental Conditions	Experiment #	pH	% KTPB Destruction
Fenton, 500 mg/L iron, 25 ºC, 30 mL H_2O_2	Avg. of 13, 40	11	33
	14	9	14
Fenton, 500 mg/L copper, 25 ºC, 30 mL H_2O_2	Avg. of 11, 48	11	46
	52	9	31
100 mg/L TAML®, 25 ºC, 30 mL H_2O_2	Avg. of 15, 41, 49	11	55
	53	9	35
100 mg/L TAML®, 45 ºC, 30 mL H_2O_2	38	12	16
	Avg. of 16, 18, 23, 33, 35	11	58
	36, 50, 51	9	24
100 mg/L TAML®, 45 ºC, 0 mL H_2O_2	39	12	5
	37	9	48

Analytical uncertainty for the HPLC results is 10%.

In the first two cases (Fenton reaction using 500 mg/L iron or 500 mg/L copper, at 25 ºC, using 30 mL H_2O_2), a decrease in pH from 11 to 9 caused a decrease in the amount of KTPB destroyed, which is the inverse of our expectations (Fenton type reactions are more favorable under lower pH conditions).

The last three cases used TAML$^®$ as the catalyst. TAML$^®$ has a more limited operational pH range that does not necessarily improve the KTPB destruction as pH decreases. In the third case (TAML$^®$ reaction using 100 mg/L TAML$^®$, at 25 ºC, using 30 mL H$_2$O$_2$), and the fourth case (TAML$^®$ reaction using 100 mg/L TAML$^®$, at 45 ºC, using 30 mL H$_2$O$_2$), decreasing the pH from 11 to 9 decreased the KTPB destruction. In the fourth case, an increase of pH from 11 to 12 also shows a decrease in the KTPB destruction. These four cases indicate a pH of around 11 is superior to pH 9 or 12 for the TAML$^®$catalyst. In the fifth and final case (TAML$^®$ reaction using 100 mg/L TAML$^®$, at 45 ºC, using no H$_2$O$_2$), was effectively a blank with no H$_2$O$_2$ used. Under these conditions, a decrease in pH of 12 to 9 gave a large increase in KTPB destruction, as well as an increase in hydrolysis products (2PB, 1PB). This likely indicates that the decrease to a pH of 9 allowed a hydrolysis mechanism to dominate the destruction pathway.

4.7.4 Effect of Type of Catalyst
In the series of 61 reactions, SRTC used five different catalyst systems: Fenton (iron), Fenton (copper), Fenton (iron + copper), TAML$^®$, and TAML$^®$+ Fenton (copper). One comparison can be made to determine the relative ability of four of the five different catalyst systems. (The TAML$^®$+ Fenton (copper) catalyst system ran under different conditions.) All of the reactions listed below in Table 17 occurred at pH 11, 25 ºC, using 30 mL of 50 wt % H$_2$O$_2$, and a reaction time of five hours.

Table 17. Catalyst Type Results of the Two Comparisons

Experimental Conditions	Experiment #	Catalyst	% KTPB Destruction
pH 11, 25 ºC, 5 hours, 30 mL H$_2$O$_2$	Avg. of 13, 40	Fenton (iron)	33
	Avg. of 11, 48	Fenton (copper)	46
	12	Fenton (iron+copper)	35
	15, 41, 49	TAML$^®$	55

Analytical uncertainty for the HPLC results is 10%.

The Fenton (iron) and Fenton (copper) reactions both showed a low experimental variability (see section 4.7.1; 2.2 and 3.1 % standard deviation, respectively). Due to this, we can definitely conclude that that Fenton (copper) is superior to the Fenton (iron) reaction in terms of KTPB destruction. Although we do not have a measure of the variability for the Fenton (iron+copper) reaction, it is likely that it, too, would have a low variability. In this case, we could then conclude that the Fenton (copper) reaction is superior to all three possible Fenton reactions. The TAML$^®$ reactions gave the highest average KTPB destruction of the comparable four catalyst types, however, there is high

variability (29 % standard deviation) associated with the TAML$^\circledR$ catalyst experiments. Due to this, the superior nature of the TAML catalyst is less certain.

4.7.5 Effect of Amount of Catalyst
For reactions using the TAML$^\circledR$ catalyst, we varied the catalyst concentration. A single comparison (Table 18) of catalyst concentration effect can be made, from reactions using 25 mg/L, 100 mg/L or 400 mg/L of TAML$^\circledR$.

Table 18. Conditions and Results of the Catalyst Amount

Experimental Conditions	Experiment #	TAML$^\circledR$ Concentration (mg/L)	% KTPB Destruction
TAML$^\circledR$, pH 11, 45 ºC, 5 hours, 30 mL H$_2$O$_2$	Avg. of 19, 32	25	43
	Avg. of 16, 18, 23, 33, 35	100	58
	Avg. of 20, 34	400	50

Analytical uncertainty for the HPLC results is 10%.

While the 100 mg/L experiments shows the greatest KTPB destruction, the differences in destruction from the other two catalyst amount is within experimental error. The relative indifference to the catalyst amount could indicate either that anything over 25 mg/L of TAML$^\circledR$ is wasted, or that the catalyst dies off fairly quickly.

4.7.6 Effect of Reaction Temperature
Temperature usually shows a strong influence on a chemical reaction. From the data we can perform a single comparison (Table 19) on the effects of temperature on a TAML$^\circledR$ reaction.

Table 19. Effect of Temperature on TAML$^\circledR$ Reactivity

Experimental Conditions	Experiment #	Temperature (ºC)	% KTPB Destruction
100 mg/L TAML$^\circledR$, pH 11, 5 hours, 30 mL H$_2$O$_2$	Avg. of 15, 41, 49	25	55
	Avg. of 16, 18, 23, 33, 35	45	58
	17	60	67

Analytical uncertainty for the HPLC results is 10%.

The KTPB destruction proved virtually identical for the 25 or 45 ºC reactions, and showed a small increase for the 60 ºC reaction. The variation is within experimental error.

4.7.7 Effect of Amount of Hydrogen Peroxide
One common feature in all of the oxidation reactions is the use of H_2O_2. One can estimate the minimum H_2O_2 required from the following reaction (Equation 1).

$$(C_6H_5)_4B^- \ + \ 60\,H_2O_2 \ \rightarrow \ 24\,CO_2 \ + \ 70\,H_2O \ + BO_2^- \qquad \text{(Equation 1)}$$
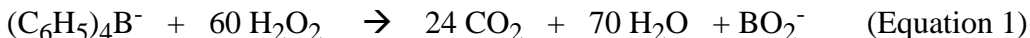
From this reaction we estimate an approximate molar ratio of H_2O_2 to TPB of 60:1.[i] So, for a clean reaction as depicted in Equation 1, 60 moles of H_2O_2 are required for every mole of TPB. In reality, this is the lower bound of H_2O_2 required due to reaction inefficiencies and H_2O_2 decomposition. In these experiments, researchers typically used ~2.5 g of KTPB and 30 mL of 50 wt % H_2O_2. This gives a H_2O_2 to TPB ratio of ~72:1, or about 20% more than required under ideal conditions. Some of the reactions used 90 mL of H_2O_2, which allows for three comparisons (Table 20) on the effect of H_2O_2 amount.

Table 20. Effect of H_2O_2 Amount on TPB Destruction

Experimental Conditions	Experiment #	mL of H_2O_2	% KTPB Destruction
TAML®, 100 mg/L, 45 ºC, pH 11, 5 h reaction	Avg. 16, 18, 23, 33, 35	30	58
	25	90	48
TAML®, 100 mg/L, 45 ºC, pH 11, 29 h reaction	24	30	78
	27	90	68
TAML®, 100 mg/L, 45 ºC, pH 11, 53 h reaction	26	30	75
	28	90	68

Analytical uncertainty for the HPLC results is 10%.

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[i] A previous document (WSRC-RP-2003-00560) quotes the molar ratio of H_2O_2 to TPB as 58:1. The ratio differences arise from slight variations in the equation used to balance the reaction of TPB with H_2O_2.

All of the reactions show a slight decline in KTPB destruction with the increased amount of H_2O_2. While the values are within experimental error of each other, at the very least the data indicates no additive value in using the greater amount of H_2O_2.

4.7.8 Effect of Reaction Scale
Towards the end of the tests the researchers decided to determine if the size of the reaction had an effect on the KTPB destruction. Smaller scale reactions allowed us to reduce waste generation, reagent use, and increase the vapor space in the reactor for the foam head. We hoped that additional headspace volume would help avoid foam formation by decreasing the air intake to the liquid. Where normally reactions would use 100 mL of Tank 48H simulant, the smaller scale reactions worked on a 2/3 scale using 67 mL of simulant. A single comparison can be made (Table 21) of otherwise identical reactions at 45 ºC, pH 11, and 5 hour reaction time.

Table 21. Effect of Reaction Size on KTPB Destruction

Experimental Conditions	Experiment #	Reaction Scale	% KTPB Destruction
100 mg/L TAML®, pH 11, 5 hours, 45 ºC	47	2/3	63
	Avg. of 16, 18, 23, 33, 35	Full	58

Analytical uncertainty for the HPLC results is 10%.

The data indicates this small change in reaction scale has no apparent effect on the KTPB destruction.

4.7.9 Effect of Hydrogen Peroxide Rate of Addition
The hydrogen peroxide serves as the source of the hydroxyl radical (·OH) which is the active species in the oxidative destruction of TPB. While adding more H_2O_2 during the reaction will increase the amount of hydroxyl radical, it also increases the amount of autodecomposition of H_2O_2 that occurs. From the data set, there are two comparisons we made (Table 22).

The data clearly shows a deleterious effect as the rate of H_2O_2 addition increases. In both comparisons, a factor of ~10 fold increase in the peroxide rate decreases the % KTPB destruction by 20%. While we cannot determine the optimal H_2O_2 addition rate, it would appear to be somewhere in the region of 1 mL/h for our experiments.

Table 22. Effect of H$_2$O$_2$ Rate on KTPB Destruction

Experimental Conditions	Experiment #	H$_2$O$_2$ Addition Rate (mL/h)	% KTPB Destruction
100 mg/L TAML$^®$, pH 11, 45 °C, 30 mL H$_2$O$_2$	26	0.60	75
	24	1.0	78
	Avg. of 16, 18, 23, 33, 35	6.0	58
100 mg/L TAML$^®$, pH 11, 45 °C, 90 mL H$_2$O$_2$	28	1.7	68
	27	3.1	68
	25	18	48

Analytical uncertainty for the HPLC results is 10%.

4.7.10 Effect of Salt Solution Changes

Throughout the entire set of experiments, researchers used the same salt solution recipe. However, after some use, it became obvious that the recipe "as made" suffered from the disadvantage of foam production even before it was used in a reaction. The more foam that is present in a reaction, the more potential there is for variation in the results of that reaction. Furthermore, we felt that pH adjusting the slurry with KTPB present could lead to hydrolysis and the production of tarry organics even before the reaction had started. We decided to slightly alter the production of the salt solution recipe to reduce foam production. In the original recipe we added the KNO$_3$ and NaTPB together and stored the resulting slurry for later use. During a reaction the slurry was pH adjusted with nitric acid. In the new recipe we did not add the KNO$_3$ and NaTPB to the salt solution. This KTPB-free solution was then pH adjusted. At the time of a reaction we added dry KNO$_3$ and NaTPB to the reaction vessel, and then slowly added the previously pH adjusted salt solution. The resulting slurry exhibited no foaming behavior before the reaction, and no discoloration from hydrolysis products. However, this did not prevent the generation of foam during the reaction due to the H$_2$O$_2$ addition. As the chemistry of the salt solution is identical between the two recipes, there should be no differences in the reactivity. A comparison of the KTPB destruction in old vs. new recipe experiments confirms this (Table 23).

In each case, the % KTPB destruction results are almost identical between the new and old simulant recipe.

Table 23. Effect of Simulant Recipe on % TPB Destruction

Experimental Conditions	Experiment #	Simulant Recipe ?	% KTPB Destruction
500 mg/L copper, pH 11, 30 mL H_2O_2, 25 ºC, 5 h reaction	11	Old	47
	48	New	45
100 mg/L TAML®, pH 11, 30 mL H_2O_2, 25 ºC, 5 h reaction	15	Old	56
	Avg. 41, 49	New	54
500 mg/L iron, pH 11, 30 mL H_2O_2, 25 ºC, 5 h reaction	13	Old	33
	40	New	32

Analytical uncertainty for the HPLC results is 10%.

4.7.11 Effect of Subsurface H_2O_2 Addition

The vast majority of the experiments delivered the H_2O_2 on top of the surface, or more precisely on top of the foam. The researchers decided to alter a few experiments to examine the effects of adding the H_2O_2 below the liquid surface. A total of three reactions (55, 58, 59) used subsurface addition of H_2O_2. All three reactions showed essentially no reaction. While we recommend examining the effect of subsurface addition under conditions with better control, at this time it appears that subsurface addition did not improve the KTPB destruction efficiency.

5.0 CONCLUSIONS

- When using a Fenton (iron) catalyst, we observed higher % KTPB destruction at pH 11 than at pH 9.

- When using a Fenton (copper) catalyst we observed higher % KTPB destruction at pH 11 than at pH 9.

- When using the TAML® catalyst we observed the following trends.
   o TAML® reactions with no H_2O_2 (control) still gave appreciable amounts of KTPB destruction; this could be due to hydrolysis or an oxidation reaction even in the absence of H_2O_2.
   o Testing at pH values of 9, 11, and 12 indicate a pH of 11 is optimal.

- While the single best result occurred with a Fenton (copper) reaction, in general, the TAML outperformed Fenton (copper) and Fenton (iron) at 25 C and pH of 11.
- Using TAML® in amounts of 25 to 400 mg/L gave only a small variation in KTPB destruction. Future testing should use the lower concentrations of TAML®.
- In tests using either 30 or 90 mL of H_2O_2, KTPB destruction decreased when using a greater rate of addition of H_2O_2.
- Scaling our typical reaction size to 2/3 scale did not change the percentage KTPB destruction.
- Subsurface addition of the H_2O_2 provided no benefit in KTPB destruction as opposed to surface addition.

- At in-tank conditions (pH 11), oxalate, and formate anions showed only slight decomposition (~10-15%) in a Fenton (copper) reaction, while nitrite showed a moderate amount of decomposition (~29%).

- Under out-of-tank conditions (pH 3.5, 100 ºC), the Fenton (copper) reactions completely destroyed the nitrite, formate, and oxalate.

- Biphenyl does not seem to be attacked in a Fenton (copper) system or in a TAML® reaction under in-tank conditions (pH 11).

From the results of the experiments we recommend the following actions for the next phase of testing.

- Improve testing by controlling pH, temperature, and mixing more precisely.

- Measure off-gas byproducts.

- Measure liquid and solid decomposition products and establish a carbon balance.

- Measure nitrite destruction in experiments with TAML®.

- Continue attempts to limit or eliminate foaming.

Appendix I. Costs Analysis of Direct Fenton Processing

Estimate Item	Cost	Assumptions
TAML® cost	$500,000	awaiting estimate
Chemical Transfer System for nitric/Fe	$30,000	Transfer system consisting of 1" piping, two control valves, and two manual shutoff valves as well as temp. dikes and spill control
Caustic - 50%	$25,000	40,000 gals. - using process flowsheet data developed by SRTC; Tanker holds 45,000 lb & cost of 50% caustic is $0.13/lb per buyer David Moss
Nitric - 50%	$18,000	23,885 gals. - using process flowsheet data developed by SRTC. Tanker holds 45,000 lb @ $0.06/lb per David Moss - chemical buyer
Fe(NO3)*9H20	$32,700	3558 kg of ferric nitrate nonahydrate per SRTC flowsheet @ $400 per 100 lb bulk from www.spectrumchemicals.com
Peroxide Storage & Delivery System	$22,000	Rental for 12 months @ ~1830/mo - per Solvay Interlox note 7/25/03
Peroxide cost	$400,000	200,000 gallons @ $2/gal - per Solvay Interlox note 7/25/03
GC sampling support	$38,808	56 days of 1 FTE @ $693/day to run/maintain and do HP coverage for 8 weeks
Liquid sampling support	$35,720	40 days of 1 FTE @ $693/day to sample and do HP coverage for 40 samples
ADS cost for liquid sampling	$68,000	40 samples for hplc, potassium, free OH-, and ICP-ES analysis in SRTC @ $1,200/sample per Tom White in SRTC, along with safety shower, etc. support at tank
Waste disposal	$17,860	20 days of 1 FTE @ $693/day to sample and HP coverage for 40 samples
N2 blanketing of Tank 48	$900,000	600 SCFM nitrogen requirements based on ITP operation; nitrogen cost ~$0.32/100f3 per buyer Royce Borden. Assumed project life = 300 days
Total Cost	$2,088,088	

Appendix II. Experimental Data Sets

This appendix, lists all of the experimental data from the 61 reactions.

Proof of Concept Reactions

Reaction Conditions

Experimental Notebook ID	Experiment #	pH	Temp (ºC)	Catalyst	Target Catalyst Concentration (mg/L)
NaTPB 1	1	11	45	Iron	500
NaTPB 2	2	9	45	Iron	500
NaTPB 3	3	7	45	Iron	500
NaTPB 4	4	7	45	Iron/Copper	250/250
NaTPB 5	5	11	45	Iron/Copper	250/250
NaTPB 6	6	7	60	Iron/Copper	250/250
NaTPB 7	7	9	45	Iron/Copper	250/250
NaTPB 8	8	11	45	TAML	100

The catalyst concentration is based on initial volume of Tank 48H simulant.

HPLC Data

Experiment #	Starting NaTPB Concentration (ppm)	Final Phenylborate Concentrations (ppm)					
		TPB	3PB	2PB	1PB	Phenol	% TPB Destruction
1	18228	2307	852	102	<100	5860	87
2	18061	< 100	<100	<100	<100	5538	> 99
3	17954	< 100	<100	<100	<100	3156	> 99
4	18030	< 100	<100	<100	<100	1046	> 99
5	18192	< 100	<100	<100	<100	<100	> 99
6	17962	< 100	<100	<100	<100	<100	> 99
7	17942	9729	<100	<100	<100	2414	46
8	18191	9440	<100	<100	<100	<100	48

Analytical uncertainty for the HPLC results is 10%.

Scoping Reactions

Reaction Conditions

Experimental Notebook ID	Experiment #	pH	mL 50 wt % H$_2$O$_2$ Added	Temp (ºC)	Catalyst	Target Catalyst Concentration (mg/L)
Blank1	9	14	0	25	Iron	500 ppm
Scope 1	10	14	30	25	Iron	500 ppm
Scope 2	11	11	30	25	Copper	500 ppm
Scope 3	12	11	30	25	Iron/Copper	250/250 ppm
Scope 4	13	11	30	25	Iron	500 ppm
Scope 5	14	9	30	25	Iron	500 mg/L
Scope 6	15	11	30	25	TAML	100 mg/L
Scope 8	16	11	30	45	TAML	100 mg/L
Scope 9	17	11	30	60	TAML	100 mg/L
Scope 10	18	11	30	45	TAML	100 mg/L
Scope 11	19	11	30	45	TAML	25 mg/L
Scope 12	20	11	30	45	TAML	400 mg/L
Blank3	21	11	0	45	TAML	100 mg/L
Blank8	22	11	0	45	TAML	100 mg/L

The catalyst concentration is based off of initial volume of Tank 48H simulant. In cases where no H$_2$O$_2$ was added, DDI water was added in its place.

HPLC Data

Experiment #	Starting KTPB Concentration (ppm)	Final Phenylborate Concentrations (ppm)					% KTPB Destruction
		TPB	3PB	2PB	1PB	Phenol	
9	17833	19692	<100	<100	<100	<100	0
10	18157	18896	<100	<100	<100	<100	0
11	18157	9677	<100	<100	<100	1179	47
12	18136	11709	<100	<100	<100	1788	35
13	18221	12202	689	1775	167	118	33
14	18411	15865	<100	<100	<100	2128	14
15	18023	8015	<100	<100	<100	<100	56
16	18051	11484	<100	<100	94	313	36
17	18044	5869	<100	89	<100	140	67
18	18030	6679	<100	107	<100	168	63
19	18044	10377	<100	<100	110	489	42
20	18030	9264	<100	215	<100	133	49
21	18065	9016	188	2887	497	303	50
22	12699	465 0	<100	780	214	179	63

Analytical uncertainty for the HPLC results is 10%.

ICP-ES Data

Experiment #	Starting K (mg/L)	Ending K (mg/L)	ICP-ES % KTPB Destruction	HPLC % KTPB Destruction
9	140	2150	101	0
10	141	1530	69	0
11	141	1330	59	47
12	141	1170	52	35
13	141	1480	66	33
14	143	1040	45	14
15	140	1480	67	56
16	140	1250	56	36
17	140	1670	76	67
18	140	NA	NA	63
19	140	NA	NA	42
20	140	1590	53	49
21	140	1180	72	50
22	98	NA	NA	63

Analytical uncertainty for the HPLC and ICP-ES results are 10%.

Stoichiometry Experiments

Reaction Conditions

Experimental Notebook ID	Experiment #	mL 50 wt % H_2O_2 Added	Reaction Time
Process 1	23	30	5
Process 2	24	30	29
Process 3	25	90	5
Process 4	26	30	53
Process 5	27	90	29
Process 6	28	90	53
Blank 7	29	0	53

HPLC Data

Experiment #	Starting KTPB Concentration (ppm)	Final Phenylborate Concentrations (ppm)					% KTPB Destruction
		TPB	3PB	2PB	1PB	Phenol	
23	18051	1180	<100	<100	<100	<100	93
24	18037	4011	<100	<100	<100	<100	78
25	12708	6550	<100	<100	<100	<100	48
26	12713	3170	<100	<100	<100	<100	75
27	18023	5715	<100	<100	<100	<100	68
28	12703	4010	<100	<100	<100	<100	68
29	12699	9280	<100	152	226	1080	27

Analytical uncertainty for the HPLC results are 10%.

ICP-ES Data

Experiment #	Starting K (mg/L)	Ending K (mg/L)	ICP-ES % KTPB Destruction	HPLC % KTPB Destruction
23	140	NA	NA	93
24	140	1100	49	78
25	98	NA	NA	48
26	98	1230	81	75
27	140	1030	45	68
28	98	1040	68	68
29	98	520	32	27

Analytical uncertainty for the HPLC and ICP-ES results are 10%.

Initial Optimization Reactions

Reaction Conditions

Experimental Notebook ID	Experiment #	pH	mL 50 wt % H_2O_2 Added	Temp (ºC)	Catalyst	Target Catalyst Concentration (mg/L)
ImpControlFe-Blank	30	11	0	25	Iron	500
ImpControlTAML®-Blank	31	11	0	25	TAML®	100
OptTAML1	32	11	30	45	TAML®	25
OptTAML2	33	11	30	45	TAML®	100
OptTAML3	34	11	30	45	TAML®	400
OptTAML4	35	11	30	45	TAML®	100
OptTAML5	36	9	30	45	TAML®	100
OptTAML6	37	9	0	45	TAML®	100
OptTAML7	38	12	30	45	TAML®	100
OptTAML8	39	12	30	45	TAML®	100
TomIron1	40	11	30	25	Iron	500
TomTAML®1	41	11	30	25	TAML®	100
Fenton-1, Fenton-2	46	11	20	45	Copper	500
TAML®-1, TAML®-2	47	11	20	45	TAML®	100
8-12-03 Fenton	48	11	30	25	Copper	500
8-12-03 TAML®	49	11	30	25	TAML®	100
OPTTAML-5	50	9	30	45	TAML®	100
OPTTAML-6	51	9	30	45	TAML®	100
A	52	9	30	25	Copper	500
B	53	9	30	25	TAML®	100
8-19-03 Small Flask	54	11	30	25	Copper	500
8-19-03 Large Flask	55	11	30	25	Copper	500
8-20-03 Cu	56	11	20	25	Copper	500
8-20-03 Cu+antifoam	57	11	20	25	Copper	500
8-21-03 TAML/Fenton sub	58	11	30	25	Copper/ TAML®	500/100
8-21-03 TAML® sub	59	11	30	25	TAML®	100

HPLC Data

Experiment #	Starting KTPB Concentration (ppm)	Final Phenylborate Concentrations (ppm)					% KTPB Destruction
		TPB	3PB	2PB	1PB	Phenol	
30	18579	18279	409	194	<100	<100	2
31	19445	19957	366	142	<100	<100	0
32	14409	8123	<100	<100	<100	<100	44
33	13515	8672	<100	<100	<100	<100	36
34	18058	8811	<100	<100	<100	<100	51
35	18079	7172	<100	<100	<100	<100	60
36	18157	10384	<100	<100	<100	<100	43
37	22924	11808	<100	1904	543	392	48
38	18510	15600	<100	<100	<100	<100	16
39	23592	22300	<100	1690	5450	4120	5
40	17167	11600	<100	<100	<100	<100	32
41	17038	10500	<100	<100	<100	<100	38
46	18237	945	<100	<100	<100	<100	95
47	18162	6695	<100	<100	<100	<100	63
48	16994	9360	<100	<100	<100	<100	45
49	16872	5020	<100	<100	<100	<100	70
50	17050	12600	<100	<100	<100	<100	26
51	17050	16400	<100	<100	<100	<100	4
52	16934	11700	<100	<100	<100	<100	31
53	16806	11000	<100	<100	<100	<100	35
54	17057	17600	<100	<100	<100	<100	0
55	17050	16800	<100	<100	<100	<100	1
56	17182	19800	<100	<100	<100	<100	0
57	17161	18700	<100	<100	<100	<100	0
58	18849	19600	<100	<100	<100	<100	0
59	18864	17800	<100	<100	<100	<100	6

Analytical uncertainty for the HPLC results is 10%.

ICP-ES Data

Experiment #	Starting K (mg/L)	Ending K (mg/L)	ICP-ES % KTPB Destruction	HPLC % KTPB Destruction
32	156	750	39	44
33	156	750	41	36
34	157	1020	44	51
35	157	840	35	60
36	157	1040	45	43
37	197	1060	34	48
38	155	720	29	16
39	197	960	29	5

Analytical uncertainty for the HPLC and ICP-ES results are 10%.

Competitive Reactions

Reaction Conditions

Experimental Notebook ID	Experiment #	pH	mL 50 wt % H_2O_2 Added	Temp (ºC)	Catalyst	Target Catalyst Concentration (mg/L)
Oxalate Out Of Tank	42	3.5	30	100	Copper	500
Formate Out Of Tank	43	3.5	30	100	Copper	500
Oxalate In Tank	44	11	30	25	Copper	500
Formate In Tank	45	11	30	25	Copper	500
8-26-03 TAML®	60	11	20	25	TAML®	100
8-26-03 Fenton Cu	61	11	20	25	Copper	500

Reaction Data

Experiment #	% Formate Destruction	% Oxalate Destruction	% Nitrite Destruction	% Biphenyl Destruction
42	NA	> 78	> 99	NA
43	> 79	NA	> 99	NA
44	NA	11	30	NA
45	14	NA	28	NA
60	NA	NA	NA	0
61	NA	NA	NA	0

Analytical uncertainty for the HPLC (biphenyl) results are 10%. Analytical uncertainty for the Ion Chromatography (formate, oxalate, nitrite) results is 10%.

NA = Not analyzed

Appendix III. PUREX Sludge Analysis

SRTC Purex simulant sludge (IDMS last batch of Purex 01-16-97 without noble metals).[37]

Notebook WSRC-NB-2002-93 p. 38
Stallings Report 7-24-2002.xls
Concentration in original sample in ug/g (ppm)

	180849	180851
Al	45100	45400
B	780	NA
Ba	3040	2800
Ca	28700	26600
Cd	<30	<30
Co	<50	<50
Cr	2900	2800
Cu	1600	1460
Fe	275000	262000
Li	<100	<100
Mg	3810	2610
Mn	56700	54100
Mo	<100	<100
Na	NA	24500
Ni	30000	28700
P	<1000	<1000
Pb	4340	4400
Si	15700	14500
Sn	<1000	<1000
Sr	583	553
Ti	<200	<200
V	<200	<200
Zn	3100	2960
Zr	NA	28300
La	<800	<800
K	NA	19000
Ag	<300	<300

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