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Tank 50H Tetraphenylborate Destruction Results

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List of Abbreviations

3PB	triphenyl boron
2PB	diphenylborinic acid
1PB	phenylboronic acid
ADS	Analytical Development Section
ARP	Actinide Removal Process
Cs	Cesium
DF	Decontamination Factor
ECC	Enhanced Catalyst Composition
HLW	High Level Waste
HPLC	high-pressure liquid chromatography
SRTC	Savannah River Technology Center
SWPF	Salt Waste Processing Facility
TPB	Tetraphenylborate
WPTS	Waste Processing Technology Section
wrt	with respect to

1.0 Executive Summary

We conducted several scoping tests with both Tank 50H surrogate materials (KTPB and phenol) as well as with actual Tank 50H solids. These tests examined whether we could destroy the tetraphenylborate in the surrogates or actual Tank 50H material either by use of Fenton's Reagent or by hydrolysis (in Tank 50H conditions at a maximum temperature of 50 ºC) under a range of conditions. The results of these tests showed that destruction of the solids occurred only under a minority of conditions.

- Using Fenton's Reagent and KTPB as the Tank 50H surrogate, no reaction occurred at pH ranges greater than 9.
- Using Fenton's Reagent and phenol as the Tank 50H surrogate, no reaction occurred at a pH of 14.
- Using Fenton's Reagent and actual Tank 50H slurry, a reaction occurred at a pH of 9.5 in the presence of ECC additives.
- Using Fenton's Reagent and actual Tank 50H slurry, after a thirty three day period, all attempts at hydrolysis (at pH 14) were too slow to be viable. This happened even in the case of higher temperature (50 ºC) and added (100 ppm) copper.

2.0 Introduction

Tank 50H is scheduled to return to HLW Tank Farm service with capabilities of transferring and receiving salt supernate solutions to and from the Tank Farms and staging feed for the Saltstone Facility. Before returning Tank 50H to Tank Farm service as a non-organic tank, less than 5 kg of TPB must remain in Tank 50H. Recently, camera inspections in Tank 50H revealed two large mounds of solid material, one in the vicinity of the B5 Riser Transfer Pump and the other on the opposite side of the tank.[1] Personnel sampled and analyzed this material to determine its composition.[2] The sample analysis indicated presence of a significant quantity of organics in the solid material. This quantity of organic material exceeds the 5 kg limit for declaring only trace amounts of organic material remain in Tank 50H. Additionally, these large volumes of solids, calculated[3] as approximately 61K gallons, present other obstacles upon returning Tank 50H to HLW service. The concerns include the potential for retention of flammable gases, nuclear criticality safety implications, and possible combustible solids formation. A recent document describes the initial results of that work.[4]

Additional scope was requested by the customer at a later date. The Technical Task Request HLE-TAR-2003-081 asks SRTC to perform scoping studies on the feasibility of destroying the organics in Tank 50H itself. While most of the TPB can be removed by suspending and transfer to Saltstone, the heel of material may prove problematic. Destruction in place may be required.

3.0 Experimental Detail

The Task Request specified that we should conduct scoping tests on Tank 50H organics (TPB). At that time, Fenton's Reagent appeared the most promising candidate on the horizon. As work progressed, the customer requested that we also study phenylborate hydrolysis.

3.1 Fenton's Reagent Testing

The Fenton Reagent is a "practical, inexpensive, green chemical process for degrading environmental pollutants".[5] Fenton's Reagent is used to treat a variety of industrial wastes containing a range of toxic organic compounds (e.g., phenols, formaldehyde, and complex wastes derived from dyestuffs, pesticides, wood preservatives, plastics additives, and rubber chemicals). The process has been applied to wastewaters, sludges, and contaminated soils.[6] Fenton's Reagent has been used to solve a number of environmental problems involving the destruction of organic contaminants in soil and groundwater including a collaborative effort between Geo-Cleanse International, Inc. and WSRC in 1997.[7] Fenton's Regent (a combination of iron and hydrogen peroxide) produces hydroxyl radicals known to oxidatively degrade organic materials, ideally yielding carbon dioxide. In our tests with Fenton's Reagent, we used 250 mL reaction vessels (Figure 1), set up as shown in Figure 2. Each test occurred at room

Figure 1. Glass Reaction Vessel

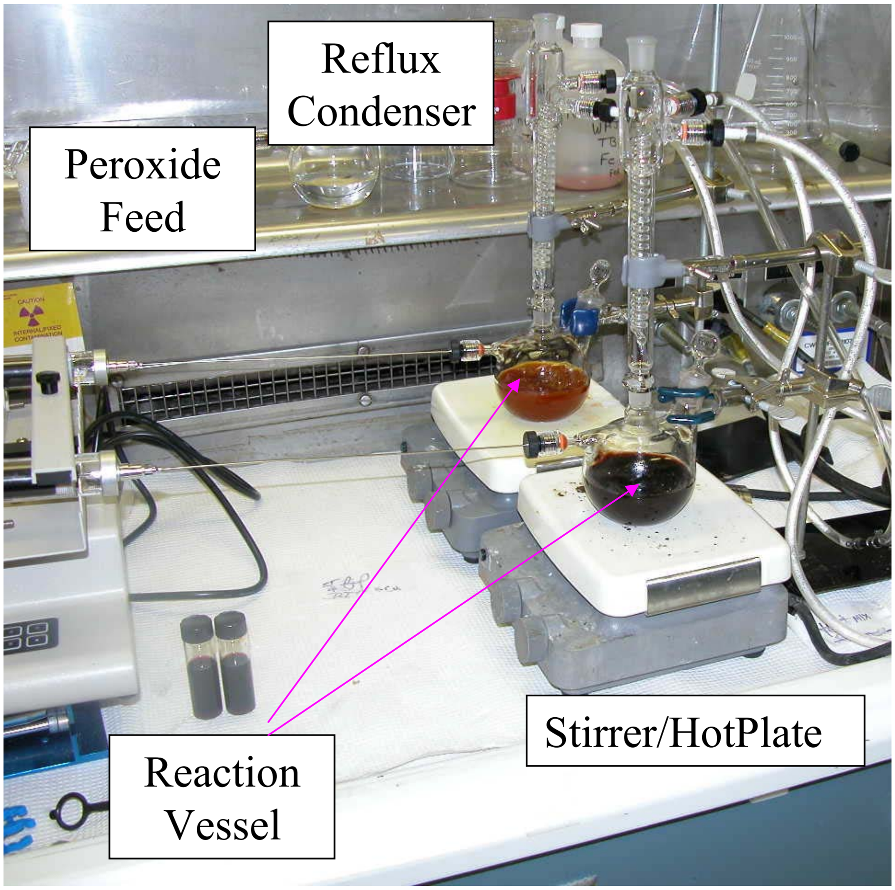

Figure 2. Experimental Setup for Fenton's Reagent Reactions

temperature with the H_2O_2 added over a four hour time period. At the end of the four hours, personnel sealed the flask and sent it to the Analytical Development Section (ADS). The analyst extracted the entire organic contents of the flask with acetonitrile and analyzed via high-pressure liquid chromatography (HPLC) for phenylborates and phenol. As a surrogate for actual Tank 50H slurry, we used either freshly precipitated KTPB or phenol.

3.2 Phenylborate Hydrolysis

Tetraphenylborate is known to undergo hydrolysis at lower pH values, and this can be accelerated by the addition of copper compounds. For example, the phenylborate contents in Tank 49H were remediated using copper aided hydrolysis in 2000.[8] For this work, researchers studied the behavior of actual Tank 50H slurry. We performed four parallel tests:

- Room temperature, no added copper, pH 14
- Room temperature, 100 ppm added copper, pH 14
- 50 ºC temperature, no added copper, pH 14
- 50 ºC temperature, 100 ppm added copper, pH 14

In each test, personnel continuously agitated five 30 mL polypropylene bottles of Tank 50H slurry for the duration of the test. We removed a bottle of each slurry 1, 2, 3, 14, and 33 days after the start of each test and sent to ADS for analysis. Personnel extracted the organic contents of each bottle with acetonitrile and analyzed via HPLC for phenylborates and phenol.

4.0 Results of Investigations

4.1 Results of Fenton's Reagent Tests

4.1.1 Test with KTPB

The first tests used KTPB as a surrogate for Tank 50H solids. We freshly precipitated the KTPB in the reactor by the reaction of equimolar amounts KNO_3 and NaTPB. 100 mL of salt solution was used in each reaction, and each reaction was done at room temperature. The target amount of KTPB equaled 500 mg. In addition to the KTPB, each reaction used one of two supernate salt solutions; "Low OH" or "High OH" (see Table 1).

Table 1. Composition of the Low and High OH Salt Solutions

Component	Low OH Molarity	High OH Molarity
Total Na	5.60	5.60
NaOH	1.17	3.05
$NaNO_3$	2.84	1.08
$NaNO_2$	0.370	0.740
$NaAlO_2$	0.320	0.270
Na_2SO_4	0.220	0.0300
Na_2CO_3	0.160	0.170
NaCl	0.0400	0.0100
NaF	0.0500	0.0100
Na_2HPO_4	0.0100	0.0080
Na_2C2O_4	0.00800	0.0080
Na_2SiO_3	0.00400	0.00400
Na_2MoO_4	0.0002	0.0002
KNO_3	0.00410	0.0300
CsCl	0.00014	0.00037

We chose these two salt solutions based on customer recommendations of the two likely end conditions of Tank 50H after addition of high sodium tank supernates: high hydroxide and high nitrate. Technicians added enough $Fe(NO_3)_3 \cdot 9H_2O$ to achieve an iron concentration of 500 ppm. They performed pH adjustment with a slow, controlled addition of 70 wt % nitric acid and confirmed by both a pH meter and colorimetric pH paper. We added enough hydrogen peroxide to provide 3 moles of H_2O_2 per moles of carbon (i.e., 5.76 mL of 50 wt %). Table 2 lists the matrix for all of the KTPB experiments. An examination of the table shows that the majority of the experiments showed essentially no reaction. While the experiment (1st in the table) with High OH and pH of 14 indicated 19% destruction of TPB, we believe that this result is false because we see detectable hydrolysis products (3, 2, 1 PB) and little phenol (which is probably a common oxidation product of TPB). It is possible this result indicates that hydrolysis occurred during the analytical preparation (part of the analysis is a pH adjustment). On the other hand, the last experiment in the table (Low OH, pH 9) does seem to show a real reaction. An apparent meaningful decrease in TPB is matched by an almost equal increase in phenol concentration. From this data, it would appear that pH values <10 are required for a noticeable Fenton's reaction to occur within four hours.

Table 2. Matrix for TPB Experiments[∂]

Supernate	pH	Start TPB (mg/L)	End TPB (mg/L)	End 3PB (mg/L)	End 2PB (mg/L)	End 1PB (mg/L)	End Phenol (mg/L)	% TPB Destr.
High OH	14	4180	3392	73	184	39	7	18.8
High OH	13	4721	4481	< 100	< 100	< 100	< 100	5.1
Low OH	13	4721	4565	< 100	< 100	< 100	< 100	3.3
Low OH	11.5	4731	4345	< 100	< 100	< 100	< 100	8.2
Low OH	11.5	4731	4701	< 100	< 100	< 100	< 100	0.7
Low OH	10	4721	4806	< 100	< 100	< 100	< 100	0
Low OH	9	4682	3951	< 100	< 100	< 100	732	15.6

1σ analytical uncertainty for HPLC is 10% for sample results > 15 ppm and 20% for results ≤ 15 ppm

4.1.2 Tests with Phenol

While KTPB is a better surrogate for actual Tank 50H solids, the insolubility of the KTPB adds mass transfer as a variable to the Fenton's reaction. The reactivity of an insoluble material can be masked by its inability to contribute to a homogenous reaction. To try and avoid this issue, we decided to try several experiments with a soluble organic

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[∂] Historically, TPB analysis is returned to us in terms of NaTPB. We have corrected results in Table 2 to reflect KTPB.

material that at least had some similarity to KTPB; phenol (Figure 3). Phenol has an aromatic character like TPB, but has appreciably greater solubility in caustic solutions. In each of the phenol reactions, our target amount of phenol equaled 524 mg. We added enough $Fe(NO_3)_3 \cdot 9H_2O$ to achieve an iron concentration of 500 ppm. We used the same two salt solutions (100 mL volume) used in the KTPB tests (see section 4.1.1, above), although the pH remained at 14 for all three tests. We performed each reaction at room temperature. Technicians added enough hydrogen peroxide to provide 3 moles of H_2O_2 per moles of carbon (i.e., 5.76 mL of 50 wt %). Table 3 lists the matrix for all of the phenol experiments.

Figure 3. Structures of TPB and Phenol

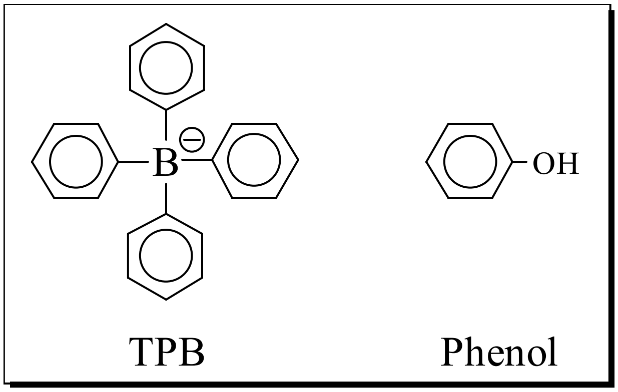

Table 3. Matrix for Phenol Experiments

Supernate	pH	Start Phenol (mg/L)	End Phenol (mg/L)	% Phenol Destr.
High OH	14	4375	4090	6.5
Low OH	14	4375	4070	7.0
Low OH	14	4383	4390	0

1σ analytical uncertainty for HPLC is 10% for sample results > 15 ppm and 20% for results ≤ 15 ppm

The results of the three tests show essentially no destruction of the phenol (analysis by HPLC) since we place the analytical variance at ~10%. As phenol is readily oxidized and is soluble, the lack of any reaction leads us to believe that at pH 14, no Fenton's reaction can occur.

4.1.3 Tests with Actual Tank 50H Material

Finally, we performed two Fenton's Reagent tests with actual Tank 50H material. While we had planned to first firmly establish a set of optimal Fenton's reaction conditions, a customer request accelerated the tests with actual waste. In these two tests, we used 100 mL of well-mixed Tank 50H slurry. Technicians added enough $Fe(NO_3)_3 \cdot 9H_2O$ to achieve an iron concentration of 500 ppm and adjusted the pH with a slow, controlled addition of 70 wt % nitric acid as confirmed by colorimetric pH paper. (We did not have a pH meter available for use in the radioactive hood.) We added the same amount of hydrogen peroxide as in the previous tests (i.e., 5.76 mL of 50 wt %), and ran each reaction at room temperature. The two experiments differed only in the addition of the ECC group of catalysts (see Table 5) to one of the experiments. Table 6 lists the matrix for all of the KTPB experiments.

Table 5. Enhanced Catalyst Composition (ECC) Set

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	$Na_2MoO_4\bullet 2H_2O$ Na_2CrO_4 $Na_2SiO_3\bullet 9H_2O$ Na_2SeO_4 As_2O_3	12 60 16 1 0.04
Zn/Pb/Fe	$Zn(NO_3)_2\bullet 4H_2O$ $Pb(NO_3)_2$ $Fe(NO_3)_3\bullet 9H_2O$	8.8 1.2 2.6
Sn	$SnCl_2$	2.1
Ca/La/Co	$Ca(NO_3)_2\bullet 4H_2O$ $La(NO_3)_3\bullet 6H_2O$ $Co(NO_3)_2\bullet 6H_2O$	12.2 0.05 0.04
Cd/Ce	$Cd(NO_3)_2\bullet 4H_2O$ $Ce(NO_3)_3\bullet 6H_2O$	0.4 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

Table 6. Matrix for Actual Tank 50H Experiments

Supernate	pH	ECC Added ?	Start TPB (mg/L)	End TPB (mg/L)	End 3PB (mg/L)	End 2PB (mg/L)	End 1PB (mg/L)	End Phenol (mg/L)	% TPB Destr.
High OH	9.5	NO	454	443	< 20	< 20	< 20	20	2.5
High OH	9.5	YES	454	378	< 20	< 20	< 20	53	16.8

1σ analytical uncertainty for HPLC is 10% for sample results > 15 ppm and 20% for results ≤ 15 ppm

The results suggest the presence of the ECC group had an appreciable effect on the reaction. With no ECC present, no effective reaction occurred. With ECC present, a 17% destruction occurred over the 4 hour time period.

When considering all the experiments, our data seems to indicate that the pH of the solution is the primary controlling factor. pH values < 10.0 are required for a Fenton's reaction to occur. A second factor is the presence of the ECC materials. Their presence appears to increase or facilitate the destruction of TPB (although we cannot discern if this is from hydrolysis or from the Fenton's reaction).

4.2 Results of Hydrolysis Tests at pH 14

We performed a series of four hydrolysis tests, each using 30 mL of well-mixed actual Tank 50H slurry (pH 14). Each experiment used five bottles under identical conditions. The only difference in any series of 5 bottles involved the time of analysis (1, 2, 3, 14, and 33 days after the start of each test) via HPLC. The starting concentration of TPB measured ~ 450 ppm.

The first test involved hydrolysis at room temperature with 100 ppm of copper (added in the form of $Cu(NO_3)_2 \cdot 2.5\ H_2O$). Table 7 lists the HPLC results from this test.

Table 7. HPLC Results From Room Temperature, 100 ppm Copper Test

Species	Day 1	Day 2	Day 3	Day 14	Day 33
TPB	471	464	493	501	452
3PB	<5.0	<5.0	<5.0	<5.0	<10
2PB	<5.0	<5.0	<5.0	<5.0	<10
1PB	<5.0	<5.0	<5.0	<5.0	<10
Phenol	31	29	30	29	28

1σ analytical uncertainty for HPLC is 10% for sample results > 15 ppm and 20% for results ≤ 15 ppm

From these results, we conclude that there is no effective destruction of the TPB. Not only does the TPB concentration show no downward trend, but there is no indication of hydrolysis products (3, 2, 1PB) being formed.

The next test occurred at room temperature with no added copper (Table 8) and served as a measure of the base stability of the Tank 50H material.

Table 8. HPLC Results From Room Temperature, No Copper Test

Species	Day 1	Day 2	Day 3	Day 14	Day 33
TPB	487	492	479	458	468
3PB	<5.0	<5.0	<5.0	<5.0	<10
2PB	<5.0	<5.0	<5.0	<5.0	<10
1PB	<5.0	<5.0	<5.0	<5.0	<10
Phenol	32	30	30	29	28

1σ analytical uncertainty for HPLC is 10% for sample results > 15 ppm and 20% for results ≤ 15 ppm

As the analogous test with added copper shows no reaction, it is not surprising that this reaction also shows no sign of hydrolysis. There is no downward trend in TPB and no hydrolysis products formed.

The third test occurred at 50 ºC with 100 ppm of added copper (Table 9). Of all the tests, this one had the best potential to show hydrolysis.

Table 9. HPLC Results From 50 ºC, 100 ppm Copper Test

Species	Day 1	Day 2	Day 3	Day 14	Day 33
TPB	469	487	481	469	410
3PB	<5.0	<5.0	<5.0	<5.0	<10
2PB	<5.0	<5.0	<5.0	<5.0	<10
1PB	<5.0	<5.0	<5.0	<5.0	<10
Phenol	32	34	36	40	51

1σ analytical uncertainty for HPLC is 10% for sample results > 15 ppm and 20% for results ≤ 15 ppm

Unfortunately, this test also showed minimal indication of TPB decomposition. Approximately 14% of the TPB decomposed over the thirty three day period.

The final test occurred at 50 ºC temperature, with no added copper (Table 10).

Table 10. HPLC Results From 50 ºC, no Copper Test

Species	Day 1	Day 2	Day 3	Day 14	Day 33
TPB	442	489	482	492	434
3PB	<5.0	<5.0	<5.0	<5.0	<10
2PB	<5.0	<5.0	<5.0	<5.0	<10
1PB	<5.0	<5.0	<5.0	<5.0	<10
Phenol	32	33	33	34	44

1σ analytical uncertainty for HPLC is 10% for sample results > 15 ppm and 20% for results ≤ 15 ppm

This last test also shows no indication of significant TPB decomposition.

5.0 Conclusions

We performed a series of scoping tests to examine reactivity – to hydrolysis, catalysis, and Fenton's reagent – of Tank 50H waste. These experiments provide the following conclusions.

- Using Fenton's Reagent and KTPB or phenol as the Tank 50H surrogate, no reaction occurred at pH ranges greater than 9.

- Using Fenton's Reagent and actual Tank 50H slurry, a reaction occurred at a pH of 9.5 in the presence of ECC additives. The ECC additives may help promote a reaction at higher pH values than normally available in a Fenton's reaction. As the current set of results cannot differentiate whether the ECC additives are causing hydrolysis or aiding the Fenton's reaction, we plan on performing a control experiment. This document will be revised when that data becomes available.

- After a thirty three day period, the hydrolysis reactions were too slow to be viable. Longer times may be required in order for significant organic destruction via hydrolysis reactions at high pH.

6.0 References

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