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W. R. Wilmarth
C. L. Crawford
R. A. Peterson

Westinghouse Savannah River Company
Savannah River Technology Center
Aiken, SC 29808

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W. R. Wilmarth, C. L. Crawford and R. A. Peterson
Waste Processing Technology Section
Savannah River Technology Center
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Abstract

This study examined decomposition of the soluble phenylborates at elevated temperature (45 °C) to determine the effects of filtering the solid tetraphenylborate, solid sludge and monosodium titanate and spiking additional levels of transition metal catalysts. Results from these tests are used to predict benzene generation rates for the aerated Tank 50H. Analysis of the results of these tests provide the following conclusions.

- Tetraphenylborate reacts in air-sealed vessels after an extended time at 45 °C.
    - Calculated rate constants resemble those for copper catalysis.
    - Further addition of copper or palladium does not increase the observed rate of decomposition.

- Triphenylborane reacted at rates similar to copper catalyzed systems in any of the tested filtrate media.

- Rate constants for the lower phenylborate species (2PB and 1PB) have been measured and reaction rates are rapid with a half life at 45 °C of ~ 100 h.

- Phenol is favored over benzene as a reaction product in the flowing air systems and would reduce the overall benzene generation if air sparging is an option.

Introduction

Over the past several months, the Waste Processing Technology Section has been investigating the decomposition of sodium tetraphenylborate and other phenylborate species in alkaline, aqueous systems in support of the resumed operations of the In-Tank Precipitation (ITP) facility.[1-3] The results of these studies has provided significant insight into the chemical processes in Tank 48H and Tank 49H which involve either the precipitation or storage of potassium and cesium tetraphenylborate solids.

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Decontaminated salt solution from this precipitation process transfers to Tank 50H. This tank differs from either Tank 48H or 49H in that the operation uses an air-based system while Tanks 48H and 49H remain inerted. This air operation in Tank 50H drives control of the safety of deflagrations and explosions to control of the fuel. The potential fuel in Tank 50H is benzene generated by the decomposition of sodium tetraphenylborate and other phenylborate decomposition products. These phenylborate compounds exhibit high solubilities[4] and react with several transition metals[5-7] under these conditions. As a result, High-Level Waste Engineering requested the Savannah River Technology Center to investigate the nature of this decomposition reaction in the absence of solids to estimate the benzene generation rate for catalyst-containing filtrate solutions.[8] The reactivity of the filtrate may prove quite lower than the slurry.[9]

Experimental

Researchers initiated the decomposition of the phenylborates in simulated Batch 2 slurries containing the Enhanced Comprehensive Catalyst (ECC). A slurry of precipitated potassium tetraphenylborate was prepared by the addition of an excess of sodium tetraphenylborate. The soluble tetraphenylborate ion was observed to react prior to filtration. Subsequently, the decomposition of the soluble phenylborate species in the filtrate was monitored as a function of time.

Personnel dissolved reagent-grade chemicals in distilled, deionized water to provide 1 L of stock solution to simulate the ITP Batch 2 composition as shown in Table 1. Sodium tetraphenylborate was added to precipitate the potassium ion and to provide an excess (~ 800 mg/L) of sodium tetraphenylborate. The slurry was stirred for three days to equilibrate. A qualitative test was performed to determine if soluble sodium tetraphenylborate existed in solution. This test consisted of adding a few drops of a potassium solution to an aliquot of filtered slurry. A positive test for soluble sodium tetraphenylborate resulted in the precipitation of potassium tetraphenylborate upon the addition of potassium ion.

Sodium tetraphenylborate was eventually added in the form of 0.55 M solution, solid (Boulder Scientific), and as a powder (Aquafine) before the qualitative test was positive. The total amount of sodium tetraphenylborate added produced a 4 wt % sodium tetraphenylborate slurry.

The ECC, as described in Table 2, was added and researchers removed aliquots (~4 mL) of the slurry or supernate and filtered using a 0.45 micron syringe filter to remove sodium/potassium tetraphenylborate solids. These filtered samples were submitted for analysis by High Performance Liquid Chromatography (HPLC) using routine quality assurance protocols.[10] This slurry preparation experiment continued for one week to allow the reaction to proceed.

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Table 1. Batch 2 Simulant

Chemical	Conc. (M)	Target(g)	Actual (g)
$Al(NO_3)_3$	0.2	75.06	75.08
KNO_3	0.036	3.64	3.63
$NaNO_2$	0.7	48.3	48.33
Na_2CO_3	0.28	34.7	34.73
NaOH	3.6	144.0	144.07

Personnel removed the slurry from the oven and filtered using a medium frit glass filter without cooling the slurry. The filtrate was then divided into four fractions for further testing. Two of these tests used glass vials as the reaction vessel as previously described,[11] and equipped to provide for flowing air. The other two reaction vessels were the standard 160-mL serum vials. Approximately 100 mL of the filtrate was added to each vial and placed at 45 °C. During this experiment, researchers removed aliquots (~ 4 mL) of the slurry or filtrate and filtered using a 0.45 micron syringe filter. These filtered samples were submitted for analysis by High Performance Liquid Chromatography (HPLC) using routine quality assurance protocols.[10]

Finally, researchers added soluble copper or palladium catalyst at 10 mg/L to each reaction vessel. Decomposition of the phenylborate species was followed for several weeks with the reaction vessels at 45 °C. In spiking the palladium-containing solutions, a different, incorrect stock solution was used and initial concentrations were only 1.3 mg/L. Later additions raised the palladium concentration to 10 mg/L. Personnel monitored the temperatures within the air space of the ovens to ± 3 °C using thermometers traceable to NIST standards. Researchers monitored the oven display and thermometer reading during the days and shift operating personnel monitored these readings during the night shifts.

Data gathered during these experiments are recorded in accordance with Procedure 4.10 of the L1 Manual, SRTC Procedures Manual. The laboratory notebook, WSRC-NB-97-61, will provide lifetime storage as a record. Furthermore, data collected and procedures used in this study were prepared in accordance with the Task Technical Plan[11] and Task Quality Assurance Plan.[12]

Table 2. Enhanced Comprehensive Catalyst

Soluble Metal Additives:		Solid Additives:	
Cu	1.7 mg/L	MST	2g/L
Ru	0.8 mg/L	Sludge Solids	2g/L yielding:
Rh	0.2 mg/L	Cu	2mg/L
Pd	0.4 mg/L	Ru	4.6 mg/L
Ag	0.6 mg/L	Rh	1.2 mg/L
Fe	2.6 mg/L	Pd	2.2 mg/L
Cr	60 mg/L	Mn	118 mg/L
Hg	2.2 mg/L	Fe	576 mg/L
Cd	0.4 mg/L	Cr	4 mg/L
Zn	8.7 mg/L	Ni	50 mg/L
Mo	12 mg/L	Al	96 mg/L
Ce	0.3 mg/L	Mg	2 mg/L
Si	16 mg/L	Zn	4 mg/L
Se	1 mg/L	Pb	6 mg/L
As	0.04 mg/L		
Pb	1.2 mg/L		
Sn	2.1 mg/L	Organic Compounds:	
Co	0.04 mg/L	Diphenylmercury	150 mg/L
Ca	12.2 mg/L	Benzene	750 mg/L
Sr	0.1 mg/L		
La	0.05 mg/L		

Experimental Results

Where practical, the phenylborate species were analyzed as a function of time to derive pseudo-first order rate constants using Microsoft® Excel data regression function.

Slurry Preparation

To effectively simulate conditions in Tank 50H, the Batch 2 simulated slurry was prepared and determined reactive prior to filtration. Table 3 shows the concentrations of the phenylborate species as a function of time. The soluble sodium tetraphenylborate concentration remained relatively unchanged with some dissolution of the solid tetraphenylborate. The soluble concentration remained nearly constant at ~ 225 mg/L. The slurry remained unreactive for

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approximately 100 hours at 45 °C. The triphenylborane concentration increased dramatically from non-detectable at the 42 hour sample to 1270 mg/L at the 135.5 hour sample. Similarly, the diphenylborinic acid and phenylboronic acid concentrations increased in the 135.5 hour sample.

Table 3. Phenylborate Concentration (mg/L) of Reactive Slurry

Elapsed Time (h)	4PB	3PB	2PB	1PB	Phenol
0	207	10	103	126	131
21	223	10	84	124	154
42	214	10	97	124	173
135.5	256	1270	730	205	193
161	271	1434	836	203	193

Decomposition in Filtrate

Researchers followed the decomposition of the phenylborate species in filtrate from ECC-containing slurries over a period of approximately 500 hours. In the four experiments, the initial soluble concentrations for sodium tetraphenylborate, triphenylborane, diphenylborinic acid, phenylboronic acid, and phenol ranged from 204 to 232 mg/L, 1312 to 1332 mg/L, 802 to 819 mg/L, 199 to 211 mg/L, and 186 to 190 mg/L, respectively. This uncertainty represents an estimate of the analytical and sampling error. Table 4 shows the observed concentrations of the phenylborate species as a function of time in these air sealed and air sparged filtrates. In addition, researchers analyzed the filtrate using Inductively Coupled Plasma - Emission Spectroscopy (ICP-ES) and ICP-Mass Spectrometry (ICP-MS) to determine the elemental composition of the filtrate. Table 5 contains these data. The potential catalysts identified by Barnes[13] are observed at slightly lower soluble concentrations than the total amounts added to the initial slurry. In particular, copper, rhodium and ruthenium are observed at 1-4 mg/L; whereas, palladium is reduced to 0.05 mg/L.

Table 4. Phenylborate Concentrations (mg/L) in Air Sealed and Air Sparged Filtrates

Elapsed Time (h)	4PB	3PB	2PB	1PB	Phenol
Air Sealed					
Sample A					
0	220	1324	814	200	190
7	223	1353	772	234	209
28	191	1364	634	298	258
47	228	1396	552	326	286
118.5	190	1336	268	356	463
198	183	1358	104	272	531
342.5	148	1291	19	98	687
492	113	1306	13	38	808
Sample B					
0	204	1317	809	199	188
7	256	1383	794	237	212
28	199	1372	641	300	256
47	240	1352	549	331	283
118.5	214	1400	270	360	421
198	173	1338	130	287	502
342.5	166	1273	22	119	640
492	134	1257	11	43	763
Flowing Air					
Sample C					
0	229	1312	802	206	186
7	223	1359	767	240	228
28	222	1398	626	298	323
47	223	1360	528	337	401
118.5	228	1423	256	385	683
198	241	1435	93	333	893
342.5	212	1350	34	213	876
492	204	1338	12	102	1219
Sample D					
0	232	1332	819	211	188
7	227	1371	789	238	202
28	237	1428	662	307	322
47	261	1401	539	335	395
118.5	256	1416	266	381	670
198	221	1368	95	340	876
342.5	229	1347	35	220	1017
492	227	1324	16	109	1155

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Researchers regressed the data using the Microsoft® Excel regression function and obtained the calculated pseudo-first order rate constants for each of the phenylborate species. Table 6 contains these values. Figure 1 shows the behavior of sodium tetraphenylborate in these air sealed and flowing air tests. Sodium tetraphenylborate in the air sealed tests appears to slowly react over the extended ~ 500 hour test; whereas the sodium tetraphenylborate in the flowing air test does not appreciably decompose. One explanation is the air is consumed by the lower phenylborates in the air sealed test, converting the solution to an anoxic condition. This anoxic condition supports transition metals, e.g., Cu, in reduced oxidation states capable of reacting with the sodium tetraphenylborate. This atmospheric dependence has been observed previously by Hyder[6] for triphenylborane, diphenylborinic acid and phenylboronic acid. The calculated pseudo-first order rate constant for the sodium tetraphenylborate decomposition in this anoxic condition (0.0011 - 0.0013 h^{-1}) is comparable to the data from tests with real waste material from Tank 48H.[2]

Table 5. Elemental Composition (mg/L) of ECC-Containing Filtrate

ICP-ES

Ag	4.83	B	192.44	Ca	0.07
Cd	0.95	Cu	3.84	Cr	2.59
Fe	2.07	Mn	1.27	Mo	14.72
Ni	2.55	Pb	19.64	Zn	10.55

ICP-MS

Pd	0.05	Rh	1.06
Ru	1.95	Cu	1.32

Table 6. Pseudo-First Order Rate Constants (h^{-1}) of Filtered Slurry

Component	Air Sealed		Flowing Air	
Sample No.	A	B	C	D
4PB	0.0013	0.0011	0.00013^{NR}	0.00011^{NR}
3PB	0.00013^{NR}	0.00015^{NR}	NR	NR
2PB	0.009	0.009	0.0092	0.009
1PB	0.0053	0.005	0.0045	0.0048

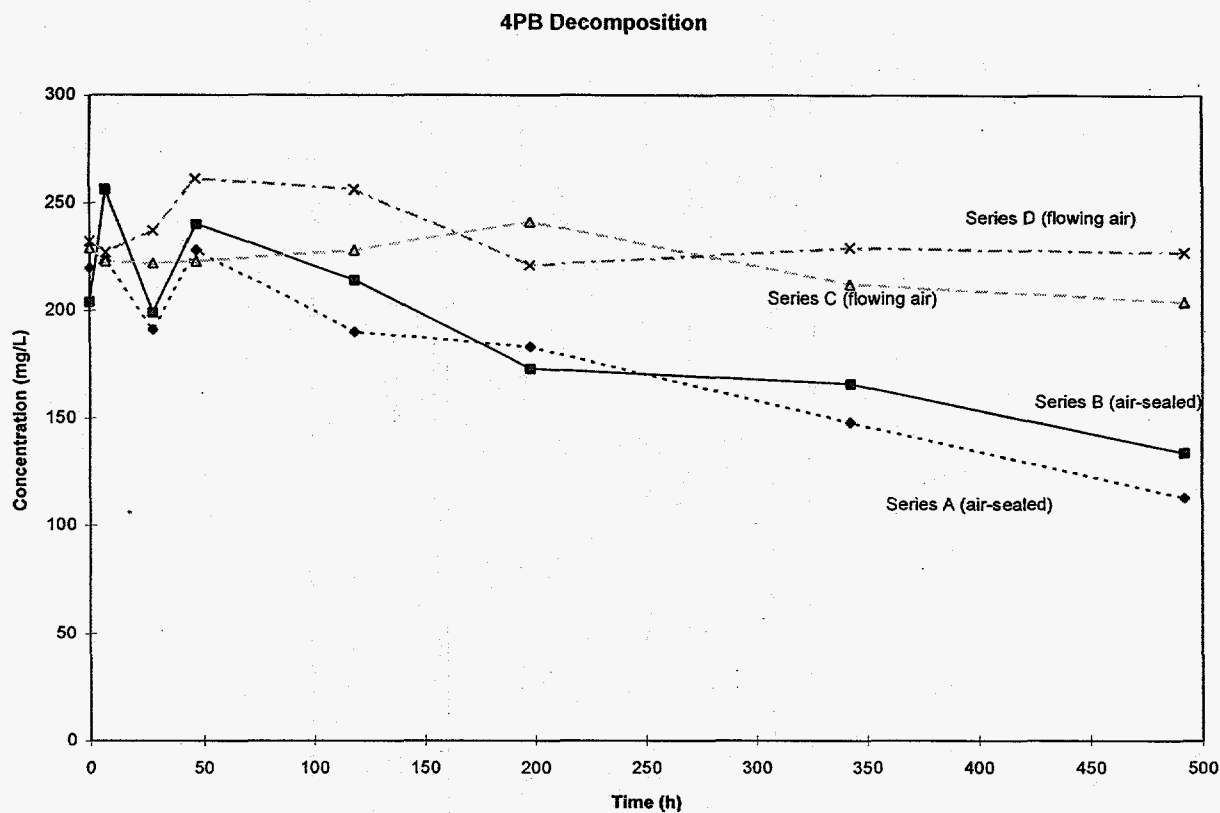NR = No Statistically Significant Reaction

4PB Decomposition

Figure 1. Sodium Tetraphenylborate Decomposition in ECC-Containing Filtrate

Figure 2 shows the behavior of triphenylborane in the ECC-containing filtrate. The triphenylborane remains relatively stable under these conditions. Attempts to regress the decomposition data did not reveal statistically significant rate constants. However, in both the flowing air and sealed experiments, the diphenylborinic acid and phenylboronic acid decompose readily as shown in Figure 3. The calculated pseudo-first order rate constants measured 0.009 h^{-1} and 0.005 h^{-1} for diphenylborinic acid and phenylboronic acid, respectively. The rate constants appear relatively independent of the oxygen content of the filtrate, exhibiting the same behavior in both systems. Phenylboronic acid showed the most dependence on atmosphere, but the dependence was not statistically significant. These rate constants are significant with a half life at 45 °C of approximately 100 hours.

3PB Decomposition
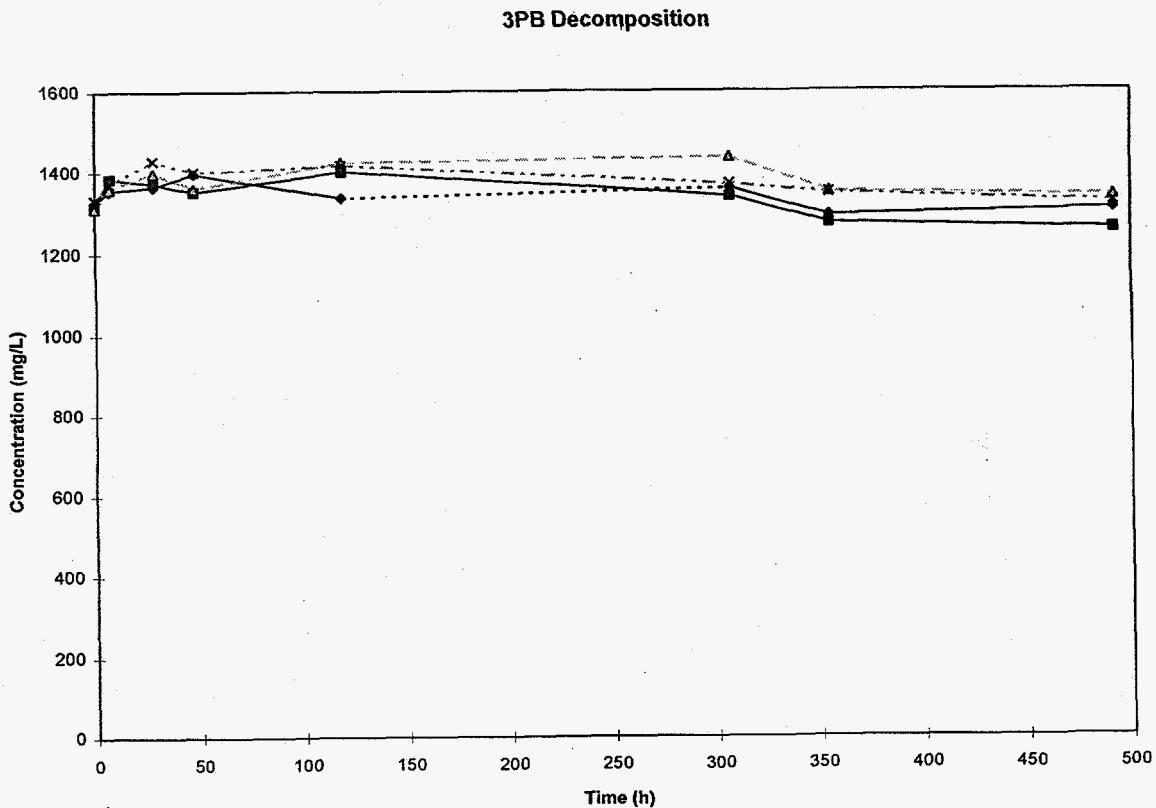

Figure 2. Triphenylborane Decomposition in ECC-Containing Filtrate

2PB and 1PB Decomposition in Filtrate
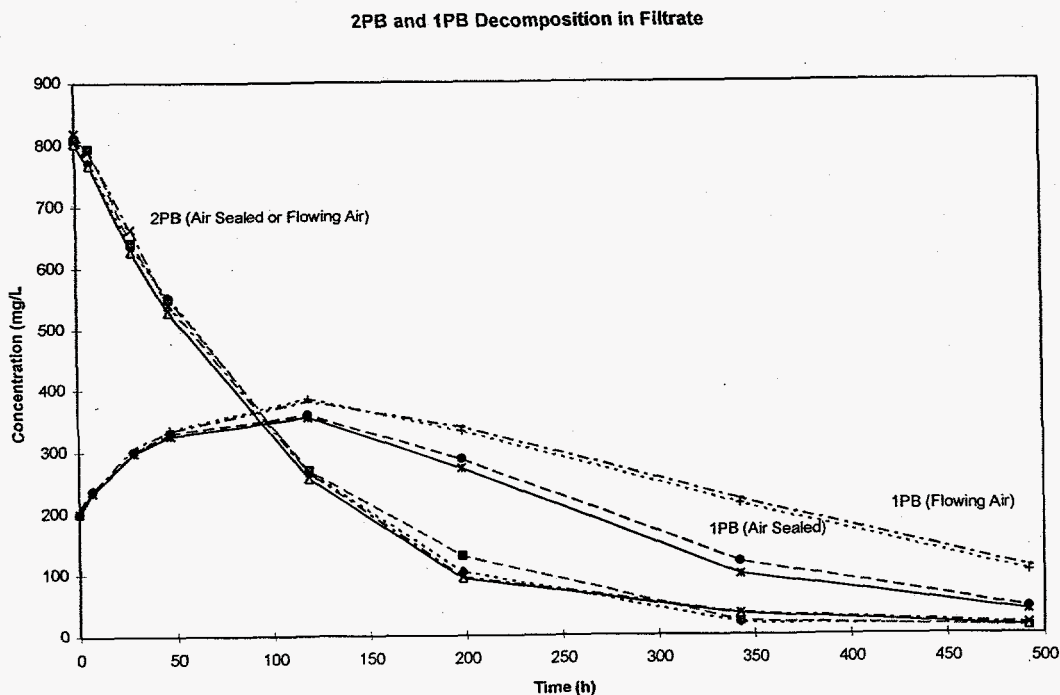

Figure 3. Diphenylborinic Acid and Phenylboronic Acid Decomposition in ECC-Containing Filtrate

Copper and Palladium Additions

Researchers placed additional copper catalyst in the ECC-containing filtrate under flowing air and sealed air conditions to determine the effect of copper concentration. Simultaneously, palladium was spiked into two other reactions vessels containing the filtrate raising the reactive catalyst concentration to nominally 10 mg/L. In the case of the palladium experiments, two separate additions were performed. The first palladium addition raised the concentration from 0.05 mg/L to 1.3 mg/L while the second addition raised the level to 10 mg/L. Visual observations revealed no evidence of precipitation of the catalyst.

Table 7 provides the concentrations of the phenylborate species and phenol observed in the catalyst addition experiments. In the case of increased copper catalyst, sodium tetraphenylborate appears relatively stable under both flowing air and sealed air conditions. Under flowing air conditions and increased copper concentration, sodium tetraphenylborate appears to react slightly faster than in the initial filtrate, very similar to the decomposition to the air sealed system. Triphenylborane decomposes faster in the air sealed system. Diphenylborinic acid and phenylboronic acid both react rapidly. Phenol production is favored in the flowing air system as expected. Figures 4 and 5 show the behavior of the phenylborate species in the air sealed and flowing air systems, respectively.

Researchers regressed the concentration data and have calculated pseudo first order rate constants for each of the phenylborate species. Table 8 lists these rate constants. The rate constant for sodium tetraphenylborate does not appear to show a dependency on the copper concentration, except in the flowing air system. However, the rate constants calculated for diphenylborinic acid and phenylboronic acid increased by a factor of 5 with the increased copper concentration indicating a first order dependency.

Table 7. Copper and Palladium Catalysis of Phenylborate Decomposition

Elapsed Time (h)	4PB	3PB	2PB	1PB	Phenol
Copper sealed in Air					
0	237	1415	410	359	508
23	223	1380	198	324	588
55.5	236	1273	69	179	626
72	191	1177	38	107	650
95	203	1185	23	59	878
167.5	181	1109	11	10	813
336	154	1003	10	10	918
527	103	859	10	10	964
Copper under Flowing Air					
0	242	1375	293	363	570
23	219	1303	128	285	1141
55.5	244	1368	37	157	1076
72	239	1355	24	111	1096
98.5	211	1309	13	50	1248
167.5	217	1316	14	10	1318
336	198	1216	10	10	1345
527	191	1147	10	10	1403
Palladium Sealed in Air					
0	251	1413	424	432	484
23	224	1388	330	373	568
55.5	227	1333	225	350	600
72*	232	1354	190	334	616
95.75	190	1201	154	280	694
167.5	176	1103	97	13	766
336	131	967	37	44	888
527	81	812	33	10	1015
Palladium in Flowing Air					
0	260	1413	426	363	517
23	213	1363	311	379	580
55.5	227	1290	197	348	630
72*	242	1347	157	340	710
95.25	210	1301	115	279	824
167.5	209	1234	63	41	943
336	204	1151	40	55	1078
527	200	1078	39	38	1159

*Second palladium addition made following the 72 hour sample.

Table 8. Pseudo-First Order Rate Constants (h^{-1}) of Catalyst Additions

Component	Copper		Palladium*	
	Air Sealed	Flowing Air	Air Sealed	Flowing Air
4PB	0.0017	0.0012	0.0014 (0.0017)	0.0018 (0.0002)
3PB	0.0012	0.0004	0.0009 (0.0011)	0.0013 (0.0005)
2PB	0.045	0.042	0.014 (0.017)	0.018 (0.012)
1PB	0.031	0.027	0.0113 (0.058)	0.010 (0.030)

*Values in () are for 10 mg/L Pd; others are for 1.3 mg/L
Note: Cu and Pd additions were to a filtrate containing 1-3 mg/L Cu and 0.05 mg/L Pd

In the case of the palladium additions, sodium tetraphenylborate does not appear to exhibit a palladium concentration dependency showing a rate constant on the order of 0.001 to 0.002 h^{-1}. The reactivity of triphenylborane with the increased palladium concentrations also resemble the reactivity in the copper catalyzed system. Figures 6 and 7 show the behavior of the palladium catalyzed systems. For diphenylborinic acid, the rate constants are increased slightly with increased palladium concentration but remain lower than the rate constants calculated for the copper system. Copper seems the dominant catalyst for the decomposition of diphenylborinic acid. The behavior of phenylboronic acid indicates a slightly faster reaction in the palladium system than the copper system. The calculated rate constant for the decomposition of 1PB nearly doubles (0.03 to 0.058 h^{-1}) in the air-sealed experiments. However, in the Flowing Air experiments, the rate constants are similar.

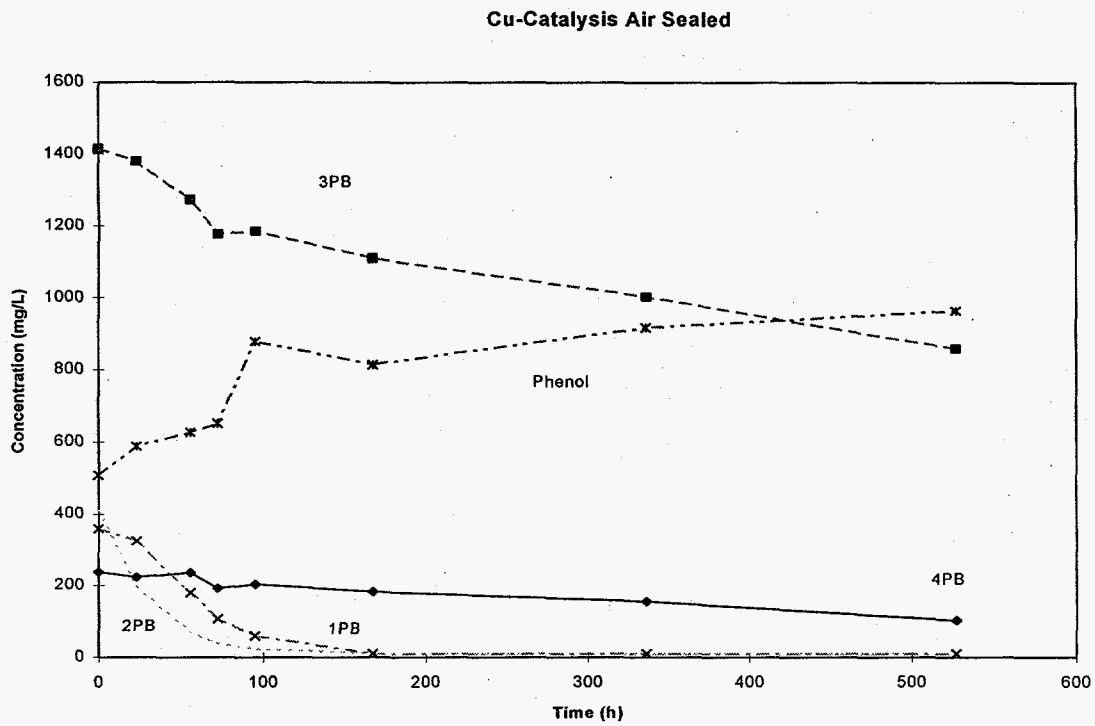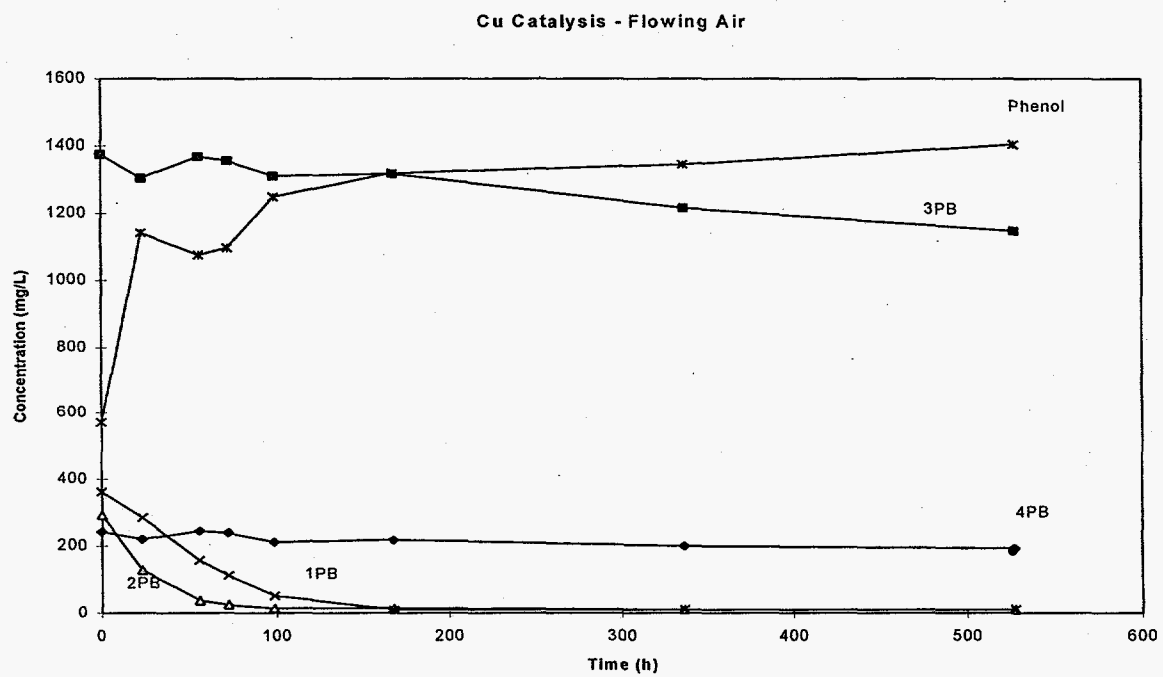**Cu-Catalysis Air Sealed**

Figure 4. Copper Catalysis of an Air Sealed System.

Cu Catalysis - Flowing Air

Figure 5. Copper Catalysis in a Flowing Air System.

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Pd Cataylsis - Air Sealed
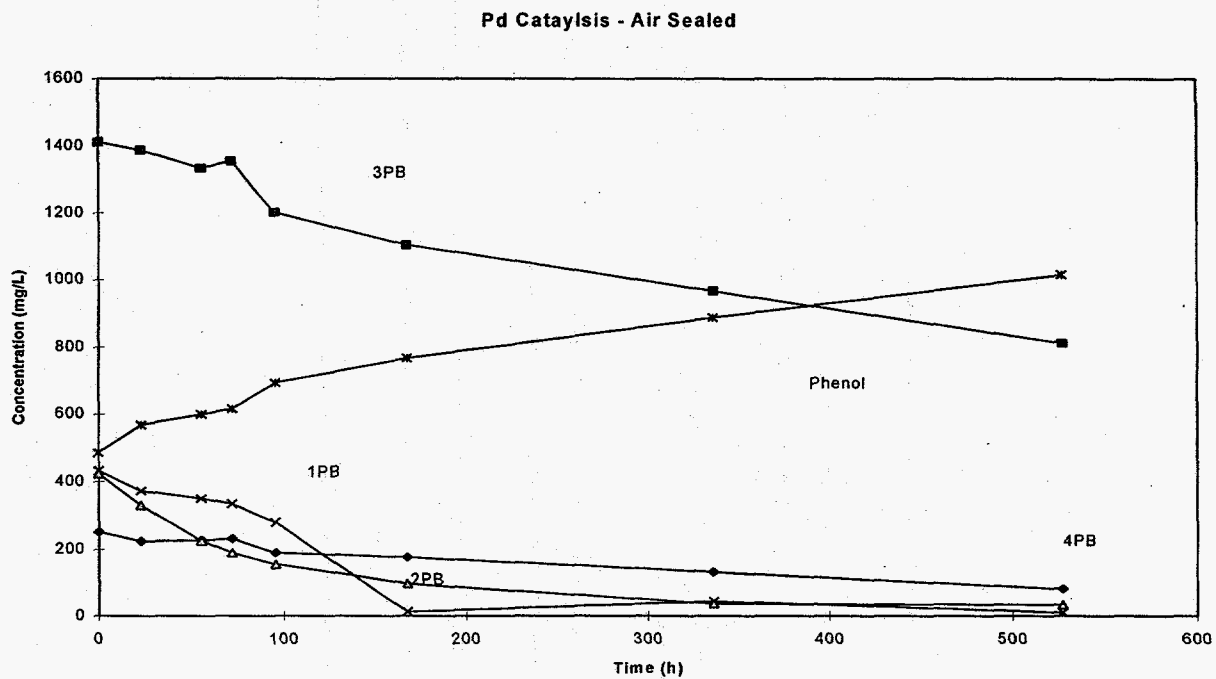
Figure 6. Palladium Catalysis in a Flowing Air System.

Pd Catalysis - Flowing Air
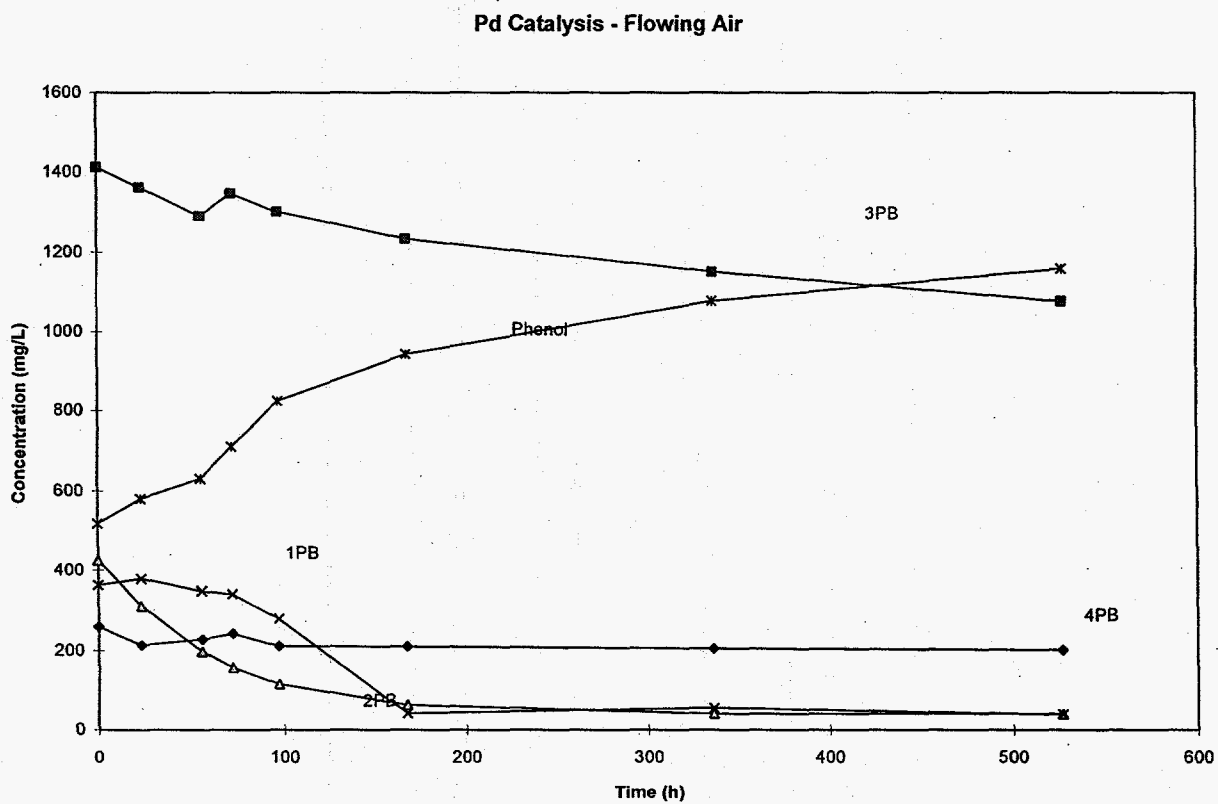
Figure 7. Palladium Catalysis in an Air Sealed System.

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Comparisons of Rate Constant for Phenylborate Species

Table 9 contains the pseudo-first order rate constants calculated from data measured by several different researchers investigating decomposition of phenylborate species in aqueous alkaline media. Most of the data is for the lower phenylborate species (2PB and 1PB). The data is for temperatures near 45 °C. It must be recognized that these data derived from different experimental conditions but trends can be observed by examination of the relative values.

Table 9. Comparison of Rate Constants (h^{-1}) for Filtrates near 45 °C

	This Study		Crawford Peterson[a]	Hyder[b]	Barnes
	Sealed	Flowing			
4PB	0.0013(f)	0.0001(f)			0.00027[c]
	0.0017(Cu)	0.0012(Cu)			0.0007[d]
	0.0017(Pd)	0.0002(Pd)			0.0003[e]
3PB	0.00014(f)	No Reaction	0.0007(1.3 mg/L)	0.003 (Air)	
	0.012(Cu)	0.004(Cu)	0.0010(3.2 mg/L)	0.013 (N_2)	Wilmarth[f]
	0.0011(Pd)	0.0005(Pd)	0.0016(10 mg/L)		Crawford Peterson
2PB	0.009(f)	0.0091(f)	0.0202(1.3 mg/L)	0.12 (Air)	0.026(Air)
	0.045(Cu)	0.042(Cu)	0.0317(3.2 mg/L)	0.03 (N2)	
	0.017(Pd)	0.012(Pd)	0.0561(10 mg/L)		
1PB	0.0053(f)	0.005(f)	0.0008(1.3 mg/L)	0.125 (Air)	0.039(Air)
	0.031(Cu)	0.027(Cu)	0.0018(3.2 mg/L)	0.012 (N2)	
	0.058(Pd)	0.030(Pd)	0.0049(10 mg/L)		

(f) = filtrate

[a]Crawford and Peterson, WSRC-TR-97-0045 [Cu-only, Air Sealed, temperature corrected to 45 °C]

[b]Hyder, WSRC-TR-97-0046 [1.0 M NaOH, Cu-only, 59 °C].

[c] Calculated from Barnes, WSRC-TR-97-0060, Test 7 [2.7 M Na+, 55 °C, Comprehensive Catalyst]

[d]Calculated from Barnes, WSRC-TR-96-0351, Test 5A [0.1 M NaOH, 1.69 mg/L Cu, 40 °C] (Note 3 other tests showed no reaction)

[e]Same as (d) but 50 °C, Tests 9A and 10A with 1.2 mg/L Cu.

fWilmarth, et al., WSRC-TR-97-0238, 40 °C, 1 M NaOH.

Barnes[14,15] studied the decomposition of sodium tetraphenylborate using either copper ion or a comprehensive catalyst mixture at temperatures between 40 °C and 55 °C. The pseudo-first order rate constants varied from 0.00027 h^{-1} to 0.0007 h^{-1}. These rate constants are similar to those calculated from the flowing air-filtrate test described in this report. However, the rate constant reported for the sealed air system (0.0013 h-1) is nominally an order of magnitude larger. Addition of copper or palladium do not significantly raise the flowing air rate of decomposition, as previously mentioned. However, addition of copper to 10 mg/L concentration, increases the rate constant in the flowing air system.

In the case of triphenylborane, the simulated Tank 50H filtrate is non-reactive. Additions of copper or palladium increase the rate constant. These values of the rate constants are approximately the same as Crawford and Peterson[5] measured but are significantly less than the values reported by Hyder.[6] The data reported herein is in agreement with Hyder that triphenylborane reacts faster in the presence of copper when oxygen is limited.

Several different studies have been performed on the decomposition of diphenylborinic acid. The pseudo-first order rate constant derived from the filtrate is lower than the results of the other experimenters. Addition of copper to the 10 mg/L level raised the reactivity to that observed by Crawford and Peterson,[5] Hyder,[6] and Wilmarth, Crawford and Peterson.[b] The rate constant calculated from the experimental data when copper is added agrees well from each researcher with a value close to 0.03 to 0.04 h^{-1} at 45 °C.

The data on phenylboronic acid appear to agree when using the reaction vessel designed by Hyder,[6] but does not agree with the filtrate experiments of Crawford and Peterson.[5] The rate constant reported by Crawford and Peterson is about an order of magnitude lower than the copper addition. The value is, however, similar to the value for the current filtrate test. As previously mention, the largest rate constant is that found in the palladium addition experiment.

Conclusions

Researchers studied the decomposition of the phenylborates in systems containing filtrate from a reacting slurry containing the Enhanced Comprehensive Catalyst. Phenylborate decomposition in both air sealed and flowing air systems have been examined. These studies were performed to determine the behavior expected for Tank 50H. Sodium tetraphenylborate and triphenylborane remain relatively stable in these conditions exhibiting reactivity similar to copper catalysis.

Diphenylborinic acid and phenylboronic acid, however, react quickly with the catalyst concentrations which passed the filter. These experiments show pseudo-first order rate constants on the order of 0.005-0.009 h^{-1} have been calculated from the experimental data.

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Approvals

Authors:

_____   11-24-97
W. R. Wilmarth, Waste Processing Technology   Date

_____   11-25-97
C. L. Crawford, Waste Processing Technology   Date

_____   11/25/97
R. A. Peterson, Waste Processing Technology   Date

Design Check

_____   11/25/97
M. J. Barnes, Waste Processing Technology   Date

Management

_____   11-25-97
S. D. Fink, Manager, Level 4 Manager,   Date
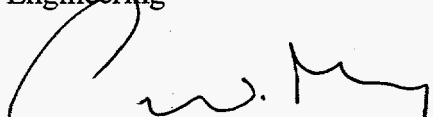Waste Processing Technology

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J. T. Carter, Leader   Date
In-Tank Precipitation Flow Sheet Team

_____   12-8-97
J. Barnes, Deputy Manager   Date
WPT Engineering

_____   12/9/97
C. W. McVay,   Date
SW&ER Engineering

_____   12/16/97
W. L. Tamosaitis, Level 3 Manager,   Date
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