Sodium Tetrphenylborate Catalyst Identification: Phase D Statistical Design Studies

by

M. J. Barnes

Westinghouse Savannah River Company

Savannah River Site

Aiken, South Carolina 29808

R. A. Peterson

DOE Contract No. **DE-AC09-96SR18500**

This paper was prepared in connection with work done under the above contract number with the U. S. Department of Energy. By acceptance of this paper, the publisher and/or recipient acknowledges the U. S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering this paper, along with the right to reproduce and to authorize others to reproduce all or part of the copyrighted paper.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

JB

DISCLAIMER

**Portions of this document may be illegible
electronic image products. Images are
produced from the best available original
document.**

RECORDS ADMINISTRATION

ABQM

**SODIUM TETRAPHENYLBORATE CATALYST IDENTIFICATION: PHASE D
STATISTICAL DESIGN STUDIES (U)**

M. J. Barnes

Publication Date: September 5, 1997

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

SAVANNAH RIVER SITE

**Sodium Tetraphenylborate Catalyst Identification:
Phase D Statistical Design Studies (U)**

Author

M. J. Barnes, Waste Processing Technology
9/5/97
Date

Design Check

R. A. Peterson, Waste Processing Technology
(per Manual E7, Procedure 2.40)
9/5/97
Date

Approvals

S. D. Fink, Level 4 Manager, Waste Processing Technology
9/5/97
Date

W. L. Tamosaitis, Level 3 Manager, Waste Processing Technology
9/5/97
Date

J. T. Carter, In-Tank Precipitation Flow Sheet Team Leader
9/15/97
Date

M. J. Montini, Deputy Manager, ITP/ESP Engineering
9-16-97
Date

1.0 Summary

The decomposition of excess sodium tetraphenylborate during startup of the In-Tank Precipitation facility in 1995 is under investigation. A primary task within this investigation involves the identification of the key catalyst system responsible for the decomposition. The final stage of this task, Phase D, finished. Observations and conclusions drawn from Phase D testing follow.

- Uranium does not catalyze decomposition under the test conditions.
- Uranium does not accelerate the previously identified palladium, diphenylmercury, benzene, and phenylborate intermediates catalytic system.
- Pre-irradiation (i.e., a 200 Mrad dose) does not accelerate catalytic decomposition.
- Continuous irradiation at a low dose rate does not accelerate catalytic decomposition.
- Testing indicates that both continuous and pre-irradiation inhibit the previously identified palladium, diphenylmercury, benzene, and phenylborate intermediates catalytic system.

This work supports resolution of DNFSB Recommendation 96-1 and the task seeking to identify the catalyst responsible for NaTPB decomposition in the In-Tank Precipitation facility.

2.0 Introduction

The decomposition of excess sodium tetraphenylborate (NaTPB) during the startup of the In-Tank Precipitation (ITP) process in 1995 is under investigation. [Ref. 1] A primary task within this investigation tries to identify the catalyst system responsible for the decomposition. [Ref. 2] Preliminary catalyst identification testing assessed the relative influence of reaction conditions (for example, reaction vessel, agitation, salt solution composition, and insoluble tetraphenylborate). [Ref. 3, 4] Statistically designed tests, to identify the key NaTPB decomposition catalysts, followed the preliminary testing. These tests evaluated 36 potential catalysts or factors. Three staged sets of tests (i.e., Phase A, B, and C) determined the key NaTPB catalyst system contained a mixture of palladium, diphenylmercury, benzene, and phenylborate intermediates (i.e., triphenylborane (3PB), diphenylborinic acid (2PB), and phenylboronic acid (1PB)). [Ref. 5, 6] Phase A tests demonstrated that a large number of the species found in ITP waste proved catalytically insignificant (relative to the aforementioned interaction). Table 1 contains a list of all active and inactive species. The concentrations listed represent values measured in samples from Tank 48H during the 1995 reaction. The inclusion of all chemical species (except oxygen) provides a "fully-loaded" simulant of the ITP waste and, thus, should mimic the observed NaTPB reaction. We term this simulant the Enhanced Comprehensive Catalyst, or ECC. Previous studies evaluated the reaction rates for this system. [Ref. 3 - 4]

The last stage of statistically designed catalyst identification tests (i.e., Phase D) examines the influence of one additional species, uranium, and one environmental factor, radiation, not included in Phases A, B, or C. Previous tests omitted the two variables to allow for experimental flexibility (and since they were not expected to provide a significant influence). Phase D testing sought to demonstrate that neither uranium nor irradiation significantly increased the rate of NaTPB decomposition. This document describes the results of Phase D tests and provides the fifth report for the task [Ref. 2] designed to identify soluble NaTPB decomposition catalysts. This task, performed as part of the Defense Nuclear Facility Safety Board (DNFSB) Recommendation 96-1 Implementation Plan [Ref. 7], completes the request by High Level Waste Engineering (HLWE) and the ITP Flow Sheet Team as defined in Task Technical Request HLW-TTR-97008. [Ref. 8]

3.0 Experimental

3.1 Statistical Design

Phase D tests address three specific potential influences (i.e., uranium, pre-irradiation, and continuous irradiation). Available equipment limited the continuous irradiation tests to a temperature of 45 °C. Therefore Phase D tests occurred in two sets (i.e., continuous irradiation tests at 45 °C, uranium and pre-irradiation tests at the prior catalyst identification testing temperature of 55 °C). Table 2 shows the Phase D statistical designs for each set of tests. Note the design includes replicates for all tests. The design looked for primary effects between the ECC system and the specific variable (i.e., either uranium, pre-irradiation, or continuous irradiation). Cross term effects between the three variables were unexpected and therefore not included as part of the test design. Tests requiring the ECC system added all of the inactive and active components listed in Table 1. The design did not include centerpoint tests. The table uses two values (1, -1) to signify inclusion or exclusion from the test, respectively.

3.2 Reaction Conditions

Tests used non-radioactive simulants, with the exception of depleted uranium. Solutions added reagent grade chemicals by weighing on calibrated balances. The accuracy of glassware used to measure volumes was verified by gravimetric methods using water as a standard. [Ref. 9] Temperature measurements used thermometers calibrated by the SRTC Standards Laboratory. Temperature monitoring occurred at least once per day. The temperature targeted ± 3 °C of the stated set point. All additional measuring and test equipment used in this task received calibration or verification for accuracy prior to use.

As noted above, Table 1 lists the concentration of ECC components. Table 2 provides the statistical design (i.e., which tests include uranium or irradiation). Typically, 55 °C tests were monitored over two weeks and 45 °C tests over four weeks. Based upon conclusions drawn from earlier tests (Ref. 3 and 4), all tests used sealed glass serum bottles with a nitrogen atmosphere. Each test used 2.7 M Na⁺, 48 g/L KTPB slurry containing only soluble NaTPB (i.e., no NaTPB solids). Each bottle was charged with the simulant slurry (see Table 3) followed by a prescribed amount of the required components (e.g., ECC or uranium). The soluble metal species came from stock solutions prepared from common salts. For the insoluble solids, the tests used simulated Purex sludge without noble metals, copper, silver, or mercury. All tests added hydrated forms of simulated sludge and MST. The soluble organic species (i.e., 3PB, 2PB, 1PB, phenol, isopropanol, and methanol) came from an alkaline stock solution. Monosodium titanate (MST), benzene, diphenylmercury, and biphenyl were added as pure compounds. Uranium, when required, was added at a target concentration of 340 mg/L in the form of depleted uranyl nitrate. The concentration is four times larger than the maximum expected (assuming 1000 mg/L sludge per batch) in any batch. [Ref. 10] Tests requiring pre-irradiation received a 200 Mrad dose followed by addition of NaTPB, benzene, diphenylmercury, and phenylborate intermediates prior to incubation at 55 °C. This addition proved necessary since the large pre-irradiation dose likely destroyed the majority of these components. A cobalt-60 source provided the continuous irradiation dose rate of $3.1 \times E4$ rad/h. A cobalt-60 source with a dose rate of $1.69 \times E6$ rad/h provided the 200 Mrad pre-irradiation dose.

In all tests, an initial filtrate sample was obtained immediately after sealing each vessel. This was analyzed by High Performance Liquid Chromatography (HPLC) to obtain starting concentrations of NaTPB, 3PB, and 2PB. No analyses for benzene, 1PB, phenol, or soluble boron occurred. Furthermore, only NaTPB, triphenylborane, and diphenylborinic acid species were monitored in subsequent samples. Filtrate was obtained for analysis by using syringe filter discs with a 0.45 μ nominal pore size to remove solids from the slurry sample. Periodic analysis of the reaction mixtures occurred during the remainder of the testing. Slurry sampling occurred after aggressive, manual shaking for approximately 15 seconds. The HPLC analysis of the filtrate from these samples allowed determination of the rate and extent of reaction. The tetraphenylborate ion (TPB⁻) reaction rate represents the TPB⁻ loss per unit time.

4.0 Results and Discussion

Tables 4 through 17 contain concentration data for NaTPB, 3PB, and 2PB for Tests 73 through 86, respectively. Sections 4.1 through 4.4 discuss the significance of the data.

4.1 Reaction Rates and Rate Constants

Reaction rates for Tests 73 through 86 were calculated based only on measured soluble NaTPB concentrations from samples taken throughout the reaction period (Equation 1). The calculations used Microsoft® Excel 5.0 for data regression analysis. Kinetic calculations yielded pseudo first-order rate constants for each reaction. Changes in the concentrations of soluble decomposition products (i.e., 3PB and 2PB) during the testing verify that differences ($\pm 10\%$) in NaTPB concentration reflect either decomposition or error in analysis. Since decomposition of NaTPB results in the production of 3PB and eventually 2PB, these measurements provide a confirmation of NaTPB decomposition (i.e., 3PB and 2PB measurements help determine if an observed change or observed variability in NaTPB reflects decomposition or analytical error). Table 18 lists pseudo first-order rate constants for Tests 73 through 86. Sections 4.2 through 4.4 provide analysis and discussion of the data.

$$\text{Rate} = -d[\text{NaTPB}]/dt = k[\text{TPB}][\text{catalyst}]^n = k'[\text{TPB}], \text{ where } k' = k[\text{catalyst}]^n \quad (1)$$

4.2 Effect of Pre-irradiation

The following summary table provides rate constants for the six tests examining the influence of pre-irradiation. Replicate tests show good agreement ($\pm 7.4\%$). Rate constants marked as NRD (i.e., no reaction detected) indicate statistically insignificant changes in NaTPB concentration and limited 3PB and 2PB concentrations. Figure 1 provides graphical evidence of NaTPB decomposition with respect to time. Despite the lower starting NaTPB concentration for the four pre-irradiated tests, the data conclusively demonstrate that the most reactive tests contained the ECC system that was not pre-irradiated. Pre-irradiated simulants without the ECC system proved unreactive. Pre-irradiation of simulants containing the ECC system resulted in reduced rate constants. The most probable cause of this observation involves palladium or diphenylmercury deactivation by reduction. Analysis of Tests 75 and 76 after an extended length of time (i.e., 6 weeks) demonstrated that the deactivation persists under reaction conditions. The slow rate of decomposition observed in Tests 75 and 76 exceed that of previously observed copper catalysis (1.7 E-4 h^{-1}). [Ref. 11] (Note that the copper rate constant was derived from tests without radiation. This rate might also decrease in the presence of radiation.)

Test	Rate Constant (h^{-1})	ECC System	Pre-irradiated
73	NRD	-1	1
74	NRD	-1	1
75	17.1 ± 9.0	1	1
76	18.0 ± 6.7	1	1
77	98.9 ± 22.6	1	-1
78	77.2 ± 22.6	1	-1

*Obtained from equation, $\text{Rate} = -d[\text{NaTPB}]/dt = k[\text{TPB}][\text{Catalyst}]^n = k'[\text{TPB}]$, where $k' = k[\text{Catalyst}]^n$

^bNRD represents "no reaction detected" and indicates [TPB] data variance not statistically significant at a 95% confidence level. 3PB and 2PB data verifies the lack of reaction.

^c-1 indicates the ECC system absent from the test. 1 indicates the ECC system present with concentrations listed in Table 1.

^d-1 indicates the test was not pre-irradiated. 1 indicates the test was pre-irradiated.

Figure 1. Demonstration of the effect of 200 Mrad pre-irradiation on tests with and without the ECC system.

4.3 Effect of Uranium

The following summary table lists rate constants obtained from tests investigating the influence of uranium. The data shows nearly the same rate of NaTPB decomposition in the four tests. Figure 2, which provides a graphical representation of NaTPB concentration with respect to time, shows the same result. Therefore, uranium appears inert in the test system and does not catalyze NaTPB decomposition under the conditions tested.

Test	Rate Constant, k'	Uranium	ECC
77	98.9 ± 22.6	1	-1
78	77.2 ± 22.6	1	-1
79	70.3 ± 4.6	1	1
80	77.5 ± 8.1	1	1

*Obtained from equation, $\text{Rate} = -d[\text{NaTPB}]/dt = k[\text{TPB}][\text{Catalyst}]^n = k'[\text{TPB}]$, where $k' = k[\text{Catalyst}]^n$

^b1 indicates the ECC system present with concentrations listed in Table 1.

^c-1 indicates uranium absent from the test. 1 indicates uranium added to the test.

Figure 2. Demonstration of the effect of uranium on NaTPB reactivity.

4.4 Effect of Continuous Irradiation

The summary table below lists rate constants obtained from continuous irradiation test program. These tests (Tests 81 through 86) occurred at 45 °C. However, Tests 81 and 82 incurred a temperature excursion to 65 °C during the early stages of testing. Records indicate the oven remained at approximately 65 °C for at least 8.5 hours but no more than 58 hours. The temperature excursion occurred between 140 and 200 hours in the reaction. Because of the temperature excursion, data from Tests 81 and 82 obtained after 138 hours of reaction does not provide reliable insight to the kinetics.

Test	Rate Constant, k (h ⁻¹)	ECC System	Irradiation
81	83.9 ± 25.8^d	1	-1
82	81.3 ± 30.1^d	1	-1
83	20.9 ± 5.2	-1	1
84	26.7 ± 7.8	-1	1
85	25.5 ± 7.9	1	1
86	24.1 ± 6.8	1	1

^aObtained from equation, $\text{Rate} = -d[\text{NaTPB}]/dt = k[\text{TPB}][\text{Catalyst}]^n = k'[\text{TPB}]$, where $k' = k[\text{Catalyst}]^n$

^b-1 indicates the ECC system absent from the test. 1 indicates the ECC system present with concentrations listed in Table 1.

^c-1 Indicates the test was not continuously irradiated. 1 indicates continuous irradiation.

^dData from Tests 81 and 82 not reliable for kinetic analysis due to a temperature excursion during testing.

Figure 3. Demonstration of the effect of 3.1 E4 rad/h continuous irradiation on tests with and without the ECC system.

Rate constants obtained from tests 83 through 86 agree within measurement error. The data indicate continuous irradiation, in the absence of the ECC system, produces a small degree of decomposition. Furthermore, comparison of Tests 83 through 86 indicate that either a slow reaction of the ECC system at 45 °C or that the continuous irradiation suppresses the ECC induced reaction. Data obtained from Tests 81 and 82 prior to the temperature excursion suggest the suppressed reaction is most likely since the initial rate of decomposition of Tests 81 and 82 exceeds that of Tests 85 and 86. Inspection of Figure 3 further highlights this conclusion. Even with the temperature excursion, the data conclusively demonstrate that continuous irradiation does not promote an accelerated catalytic NaTPB decomposition.

5.0 Conclusions

The last set, Phase D, of statistical design catalyst identification tests finished. Testing determined uranium does not influence the ECC system and does not catalyze NaTPB decomposition under the test conditions. Additionally, pre-irradiation (i.e., a 200 Mrad dose) does not promote accelerated catalytic decomposition. Data strongly suggests that pre-irradiation reduces NaTPB decomposition, most likely through catalyst deactivation. Furthermore, continuous irradiation exhibits the same trends (i.e., it does not promote accelerated catalytic decomposition and appears to suppress reactivity).

6.0 Path Forward

The program, as scheduled, does not include further catalyst identification testing. The complex catalyst system containing palladium, benzene, diphenylmercury, and phenylborates provides the most rapid decomposition of NaTPB observed. The work to date does not fully explain the role of each species in the catalyst system. For example, other work shows nearly as rapid reaction in the absence of diphenylmercury. [Ref. 6] Also, the work did not attempt to identify if only one of the added phenylborates promotes the reaction. Similarly, the earlier work shows a complex dependency on the presence of benzene. Further work could help understand these features.

7.0 Tables

Table 1. Enhanced Comprehensive Catalyst (ECC) components for Phase D statistical design catalyst identification tests with target concentrations provided in parentheses.

Inactive Components

methanol (5 mg/L)
isopropanol (50 mg/L)
phenol (125 mg/L)
biphenyl (150 mg/L)
copper (1.7 mg/L)
cadmium (0.4 mg/L)
molybdenum (12 mg/L)
cerium (0.3 mg/L)
silicon (16 mg/L)
selenium (1 mg/L)
arsenic (0.04 mg/L)
tin (2.1 mg/L)
cobalt (0.04 mg/L)
calcium (12.2 mg/L)
strontium (0.1 mg/L)
lanthanum (0.05 mg/L)
iron (579 mg/L)
chromium (64 mg/L)
zinc (12.8 mg/L)
manganese (118 mg/L)
nickel (50 mg/L)
aluminum (96 mg/L)
magnesium (2 mg/L)
zirconium (50 mg/L)
lead (6 mg/L)
monosodium titanate (2 g/L)
ruthenium (5.4 mg/L)
rhodium (1.4 mg/L)
silver (6.8 mg/L)

Active Organics

benzene (720 mg/L)
diphenylmercury (150 mg/L)
Phenylborate intermediates

- 3PB (125 mg/L)
- 2PB (125 mg/L)
- 1PB (125 mg/L)

Active Metal

palladium (2.6 mg/L)

Table 2: Phase D statistical designs for miscellaneous (i.e., pre-irradiation, uranium, and continuous irradiation) catalyst identification testing.

Part A: Pre-irradiation and uranium test design.

Test #	ECC ^a	200 Mrad Pre-irradiation ^b	340 mg/L Uranium ^c	Temperature (°C)
73	-1	1	-1	55
74	-1	1	-1	55
75	1	1	-1	55
76	1	1	-1	55
77	1	-1	-1	55
78	1	-1	-1	55
79	1	-1	1	55
80	1	-1	1	55

^a -1 indicates the ECC system absent from the test. 1 indicates the ECC system present with concentrations listed in Table 1.

^b -1 indicates the test was not pre-irradiated. 1 indicates pre-irradiation.

^c -1 indicates uranium absent from the test. 1 indicates uranium added to the test.

Part B: Pre-irradiation and uranium test design.

Test #	ECC ^a	3.1 E4 rad/h Continuous irradiation ^b	Temperature (°C)
81	1	-1	45
82	1	-1	45
83	-1	1	45
84	-1	1	45
85	1	1	45
86	1	1	45

^a -1 indicates the ECC system absent from the test. 1 indicates the ECC system present with concentrations listed in Table 1.

^b -1 indicates the test was not continuously irradiated. 1 indicates continuously irradiation.

Table 3. Standard tetraphenylborate slurry simulant for Phase D statistical design catalyst identification tests (target concentrations).

Component	2.7 M Na ⁺ Slurry Concentration
sodium ^a	2.66 M
hydroxide	1.49 M
nitrite	0.39 M
nitrate	0.38 M
aluminate	0.09 M
sulfate	0.006 M
carbonate	0.10 M
chloride	0.008 M
fluoride	0.004 M
phosphate	0.003 M
TPB ^(b)	0.02 M
NaTPB (insoluble) ^b	0 g/L
KTPB (insoluble) ^c	48 g/L

^aTheoretical (estimated from filtrate density). [Ref. 12]

^bTheoretical (calculated using sodium ion concentration). [Ref. 13]

^cInitial concentration represents ~ 4 wt % KTPB.

Table 4. Soluble sodium tetraphenylborate, triphenylborane (3PB) and diphenylborinic acid (2PB) concentrations versus time for Test 73.

Reaction Time (h)	Soluble NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)
0.0	3544	< 10	< 10
17.3	5194	9	< 10
132.5	4892	< 10	< 10
202.9	3449	20	< 10
297.1	3273	20	< 10

Table 5. Soluble sodium tetraphenylborate, triphenylborane (3PB) and diphenylborinic acid (2PB) concentrations versus time for Test 74.

Reaction Time (h)	Soluble NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)
0.0	3652	< 10	< 10
17.3	4592	3	< 10
132.5	5073	< 10	< 10
202.9	4475	13	< 10
297.1	3126	9	< 10

Table 6. Soluble sodium tetraphenylborate, triphenylborane (3PB) and diphenylborinic acid (2PB) concentrations versus time for Test 75.

Reaction Time (h)	Soluble NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)
0.0	2995	101	25
17.3	3660	235	43
132.5	3918	835	39
202.9	3209	1011	< 10
297.1	2698	1130	47
781.3	935	2006	77

Table 7. Soluble sodium tetraphenylborate, triphenylborane (3PB) and diphenylborinic acid (2PB) concentrations versus time for Test 76.

Reaction Time (h)	Soluble NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)
0.0	3206	98	42
17.3	3419	233	46
132.5	3408	684	42
202.9	3081	946	< 10
297.1	2500	1084	81
781.3	855	1835	57

Table 8. Soluble sodium tetraphenylborate, triphenylborane (3PB) and diphenylborinic acid (2PB) concentrations versus time for Test 77.

Reaction Time (h)	Soluble NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)
0.0	8948	77	114
17.3	9424	533	136
132.5	3531	2850	1305
202.9	1508	2997	2036
297.1	495	2388	2516

Table 9. Soluble sodium tetraphenylborate, triphenylborane (3PB) and diphenylborinic acid (2PB) concentrations versus time for Test 78.

Reaction Time (h)	Soluble NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)
0.0	7906	66	81
17.3	9512	308	105
132.5	4126	3099	1001
202.9	2123	3610	1561
297.1	882	3373	2098

Table 10. Soluble sodium tetraphenylborate, triphenylborane (3PB) and diphenylborinic acid (2PB) concentrations versus time for Test 79.

Reaction Time (h)	Soluble NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)
0.0	9082	80	141
18.1	8704	333	121
134.4	3625	3285	719
203.7	2294	3844	1002
298.4	1152	3806	1563

Table 11. Soluble sodium tetraphenylborate, triphenylborane (3PB) and diphenylborinic acid (2PB) concentrations versus time for Test 80.

Reaction Time (h)	Soluble NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)
0.0	9028	80	135
18.1	8465	271	123
134.4	3601	3304	775
203.7	2055	3699	1080
298.4	899	3601	2311

Table 12. Soluble sodium tetraphenylborate, triphenylborane (3PB) and diphenylborinic acid (2PB) concentrations versus time for Test 81.

Reaction Time (h)	Soluble NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)
0.0	8975	73	130
134.0	5848	2780	480
300.7	2318	3696	1422
637.5	94	2857	2270
826.1	< 10	1830	2319

Table 13. Soluble sodium tetraphenylborate, triphenylborane (3PB) and diphenylborinic acid (2PB) concentrations versus time for Test 82.

Reaction Time (h)	Soluble NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)
0.0	9308	74	133
134.0	6273	2520	397
300.7	2525	3047	1270
468.0	861	2954	1424
637.5	166	2444	1417
826.1	9	1648	1439

Table 14. Soluble sodium tetraphenylborate, triphenylborane (3PB) and diphenylborinic acid (2PB) concentrations versus time for Test 83.

Reaction Time (h)	Soluble NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)	Radiation Dose (Mrad)
0.0	9389	< 10	< 10	0.0
136.6	7440	79	997	4.2
302.8	5254	152	1503	9.4
469.8	4066	196	1891	14.6
638.0	2365	270	1917	19.8

Table 15. Soluble sodium tetraphenylborate, triphenylborane (3PB) and diphenylborinic acid (2PB) concentrations versus time for Test 84.

Reaction Time (h)	Soluble NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)	Radiation Dose (Mrad)
0.0	9253	< 10	< 10	0.0
136.6	7385	88	1048	4.2
302.8	4792	60	1565	9.4
469.8	3310	208	2087	14.6
638.0	1631	261	2048	19.8

Table 16. Soluble sodium tetraphenylborate, triphenylborane (3PB) and diphenylborinic acid (2PB) concentrations versus time for Test 85.

Reaction Time (h)	Soluble NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)	Radiation Dose (Mrad)
0.0	8802	70	132	0.0
136.6	7652	323	572	4.2
302.8	5025	680	488	9.4
469.8	3248	825	464	14.6
638.0	1759	918	439	19.8

Table 17. Soluble sodium tetraphenylborate, triphenylborane (3PB) and diphenylborinic acid (2PB) concentrations versus time for Test 86.

Reaction Time (h)	Soluble NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)	Radiation Dose (Mrad)
0.0	8896	71	133	0.0
136.6	7526	309	584	4.2
302.8	5007	485	517	9.4
469.8	3458	728	472	14.6
638.0	1901	831	466	19.8

Table 18. Kinetics data for Phase D statistical design catalyst identification Tests 73 through 86.

Test	Pseudo first Order Rate Constant ^a , k' (h ⁻¹ • 1 E-4)	Comments ^b
73	9.2 ± 26.7 ^c	no reaction detected
74	5.8 ± 26.6 ^c	no reaction detected
75	17.1 ± 9.0 ^c	
76	18.0 ± 6.7 ^c	
77	98.9 ± 22.6 ^c	
78	77.2 ± 22.6 ^c	
79	70.3 ± 4.6 ^c	
80	77.5 ± 8.1 ^c	
81	83.9 ± 25.8 ^d	Oven temperature excursion - data not reliable for kinetic analysis
82	81.3 ± 30.1 ^d	Oven temperature excursion - data not reliable for kinetic analysis
83	20.9 ± 5.2 ^d	
84	26.7 ± 7.8 ^d	
85	25.5 ± 7.9 ^d	
86	24.1 ± 6.8 ^d	

^aObtained from equation, Rate = -d[NaTPB]/dt = k[TPB][Catalyst]ⁿ = k'[TPB], where k' = k[Catalyst]ⁿ

^b"No reaction detected" indicates [TPB] data not statistically significant at a 95% confidence level. 3PB and 2PB data verifies the lack of a significant reaction.

^cTests conducted at 55 °C.

^dTests conducted at 45 °C.

8.0 Internal References

1. D. D. Walker, M. J. Barnes, C. L. Crawford, R. F. Swingle, R. A. Peterson, M. S. Hay, and S. D. Fink, "Decomposition of Tetraphenylborate in Tank 48H (U)", WSRC-TR-96-0113, Rev. 0, May 10, 1996.
2. M. J. Barnes, C. L. Crawford, C. A. Nash, and T. B. Edwards, "Task Technical Plan for Sodium Tetraphenylborate Decomposition Catalyst Identification Studies (U)", WSRC-RP-96-600, Rev. 2, June 20, 1997.
3. M. J. Barnes, C. L. Crawford, and C. A. Nash, "Sodium Tetraphenylborate Catalyst Identification: Preliminary Studies Set 1 (U)", WSRC-TR-97-0060, March 6, 1997.
4. M. J. Barnes, "Sodium Tetraphenylborate Catalyst Identification: Preliminary Studies Set 2 (U)", WSRC-TR-97-0144, Rev. 0, March 6, 1997.
5. M. J. Barnes, "Sodium Tetraphenylborate Catalyst Identification: Phase A Statistical Design Studies (U)", WSRC-TR-97-0210, Rev. 0, July 22, 1997.
6. M. J. Barnes, "Sodium Tetraphenylborate Catalyst Identification: Phase B and C Statistical Design Studies (U)", WSRC-TR-97-0230, Rev. 0, August 13, 1997.
7. "Department of Energy Implementation Plan for Defense Nuclear Facilities Safety Board Recommendation 96-1 to the Secretary of Energy", In-Tank Precipitation Facility at the Savannah River Site, October 1996.
8. A. W. Wiggins, "Soluble TPB Decomposition and Catalysis" (U), HLW-TTR-97008, November 15, 1996.
9. D. D. Walker, "Calibration of Laboratory Glassware" (U), Manual L12.1, Procedure IWT-OP-009, Rev. 3, May 8, 1995.
10. J. R. Fowler, "Sludge Composition for Each Tank and DWPF Feed Batches" (U), DPST-84-556, June 11, 1984.
11. M. J. Barnes and T. B. Edwards, "Copper Catalyzed Sodium Tetraphenylborate Decomposition Studies (U)", WSRC-TR-96-0351, November 7, 1996.
12. D. D. Walker, data contained in Laboratory Notebook WSRC-NB-95-23, p. 88.
13. M. J. Barnes, R. A. Peterson, R. F. Swingle and C. T. Reeves, "Sodium Tetraphenylborate Solubility and Dissolution Rates (U)", WSRC-TR-95-0092, March 7, 1995.

DISTRIBUTION

Amerine, D. B., 704-56H
Barnes, J. L., 704-S
Barnes, M. J., 773-A
Britt, T. E., 732-B
Carter, J. T., 704-25S
Cauthen, G. L., 241-119H
Clark, W. C., 241-119H
Crawford, C. L., 773-41A
Doughty, D. E., 704-56H
Eberlein, S. J., 704-56H
Eibling, R. E., 704-T
Elder, H. H., 241-121H
Fink, S. D., 773-A
Fowler, J. R., 704-Z
Hitchler, M. J., 992W-1
Hobbs, D. T., 773-A
Holtzscheiter, E. W., 773-A
Hsu, C. W., 773-A
Hsu, R. H., 773-43A
Hyder, M. L., 773-A
ITP Library (c/o A. G. Wiest), 241-119H
Jacobs, R. A., 704-T
Johnson, M. D., 704-56H
Keefer, M. T., 241-153H
Landon, L. F., 704-T
Lewis, B. L., 703-H
Lex, T. J., 719-4A
Lowe, P. E., 773-42A
Marek, J. C., 704-T
McCabe, D. J., 773-43A
McCullough, J. W., 703-H
Melton, W. L., 241-154H
Menna, J. D., 730-2B
Miller, M. S., 704-72S
Montini, M. J., 704-56H
Morin, J. P., 719-4A
Nash, C. A., 676-1T
Nelson, L. M., 773-43A
Norkus, J. K., 730-2B
Papouchado, L. M., 773-A
Peterson, R. A., 676-T
Pettigrew, W. H., 704-S
Piccolo, S. F., 704-56H
Randall, C. T., 704-T
Rutland, P. L., 241-152H
Satterfield, R. M., 719-4A
Suggs, P. C., 703-H
Swingle, R. F., 773-A
Tamosaitis, W. L., 773-A
Taylor, G. A., 241-121H
Thomas, J. K., 730-2B
Van Pelt, W. B., 676-1T
Walker, D. D., 773-A
Walker, W. C., 241-82H
Wiggins, A. W., 241-84H
Wooten, A. L., 732-B
Wright, G. T., 773-A
IWT-LWG Files, 773-A
TIM (4), 703-43A