

JUL 17 1998

The Honorable John T. Conway  
Chairman, Defense Nuclear Facilities Safety Board  
625 Indiana Avenue, N.W., Suite 700  
Washington, D.C. 20004

Dear Mr. Chairman:

SUBJECT: Defense Nuclear Facilities Safety Board (DNFSB) Recommendation 96-1  
Deliverables - July 1998

REFERENCE: 1. Ltr, Schepens to Conway, "Defense Nuclear Facilities Safety Board  
(DNFSB) Recommendation 96-1 Deliverables", 5/27/98  
2. Ltr, Schepens to Conway, "Defense Nuclear Facilities Safety Board  
(DNFSB) Recommendation 96-1 Implementation Plan - Suspension of  
Restart Activities at the In-Tank Precipitation (ITP) Facility", 3/3/98

The following enclosed documents are submitted in accordance with the Implementation Plan for  
DNFSB Recommendation 96-1 and with Reference 1:

1. Soluble Tetraphenylborate Decomposition Studies – Final Report (Milestone # 5.2.2-1)
2. Page Change Revision - Studies on the Stability of Solid Tetraphenylborate Compounds  
(Milestone # 5.2.2-2)
3. Summary of the In-Tank Precipitation Chemistry Program

Enclosure 1 provides the final deliverable for Milestone # 5.2.2-1 and completes the milestone  
deliverables identified under Commitment # 3 of the Implementation Plan. Also, the final  
milestone deliverables identified under Commitment # 4 of the Implementation Plan were  
completed and transmitted to you in Reference 1. Accordingly, the Department of Energy has  
completed the actions identified under Commitment # 3 and Commitment # 4, and proposes  
closure of these commitments.

Enclosure 2 is provided for your information to correct a hydroxide concentration value that was  
incorrectly reported in the original issue of the report. This change only affects one page and has  
no impact on the conclusions of the report.

Enclosure 3 provides the summarized results of the ITP chemistry program, addresses the overall  
safety of the tetraphenylborate chemistry products remaining in Tanks 48 and 49, and identifies  
the outstanding issues which remain open. In Reference 2, you were informed that this summary  
report would provide a basis for closure of Recommendation 96-1; however, this summary report  
is being issued only as a status of activities to date. The Department of Energy believes that it  
would be premature to propose closure of Recommendation 96-1 prior to completing the ongoing  
High Level Waste (HLW) Salt Disposition Alternatives Evaluation. Until that time, no further  
action will be taken to resolve the remaining Recommendation 96-1 open issues.

John T. Conway

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A status of the HLW Salt Disposition Alternatives Evaluation and Recommendation 96-1 implementation activities will be discussed with you in a briefing scheduled for July 21, 1998. This status and the enclosed reports have been previously discussed with your staff.

Please direct any questions to me or W. F. Spader at (803) 208-7409.

Sincerely,

*Original Signed By:  
Roy J. Schepens*

Roy J. Schepens  
Acting Assistant Manager  
for High Level Waste

ED:JWM:kl

PC-98-0051

3 Enclosures:

1. Soluble Tetraphenylborate Decomposition Studies – Final Report
2. Page Change Revision - Studies on the Stability of Solid Tetraphenylborate Compounds
3. Summary of the In-Tank Precipitation Chemistry Program

bcc w/Enclosures:


G. Rudy, Manager, SR  
M. W. Frei (EM-30), HQ  
R. E. Erickson (EM-32), HQ  
A. B. Poston, AMESHQ, 703-47A  
M. B. Whitaker, Jr., (S-3.1), HQ

bcc w/o Enclosures:

AMHLW Rdg. File  
ED Rdg. File  
Manager's Rdg. File  
L. Adams, PGSD, 703-A

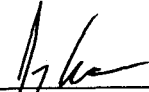
**Soluble Tetrphenylborate Decomposition Studies  
Final Report**

Prepared by:

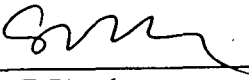
  
\_\_\_\_\_  
Paul L. Rutland  
Senior Technical Advisor, WPE  
ITP Flow-Sheet Task Team

Date 7/8/98

Approved by:

  
\_\_\_\_\_  
J. T. Carter  
Leader, ITP Flow-sheet Task Team

Date 7/8/98

  
\_\_\_\_\_  
S. F. Piccolo  
Manager, Waste Pretreatment Program

Date 7/15/98

Enclosure 1: Letter, Schepens to Jol  
Conway, "DNFSB Recommendation  
Deliverables - July 1998", dated 7/17/98

## 1.0 Executive Summary

The soluble tetraphenylborate (primarily NaTPB) decomposition studies were conducted in three phases. The first set of tests was completed prior to the issuance of DNFSB Recommendation 96-1. The second set of tests was conducted as a part of the Implementation Plan for 96-1. The last set of tests, completed as a part of the 96-1 resolution, was conducted to increase the understanding of the soluble TPB mechanism, to identify the intermediate required for the catalytic decomposition, identify inhibitors and "scram" agents to avoid the catalytic reaction, scoping tests to determine the plausibility of a benzene phase reaction, determine the solubility of tetraphenylborate salts in high ionic strength salt solutions, and identify an "operating window" that would allow operation of the In-Tank Precipitation (ITP) process within the current system configuration.

This report will discuss all of the tests that were conducted and present the results and conclusions of these experiments. Note that as the experimental program developed some conclusions from earlier tests were revised based on subsequent tests. The original conclusions from each set of experiments are presented to demonstrate the development of the program over time. These conclusions, in some cases, resulted in changes of scope and direction for the experimental program.

All of the testing for soluble tetraphenylborate decomposition has been completed. The final conclusions drawn from the soluble testing program are outlined below. These conclusions represent the current level of understanding of the soluble decomposition of tetraphenylborate.

- Copper catalyzed decomposition of tetraphenylborate and the phenylborate intermediates occurs in the systems of interest. This Copper catalysis appears to occur via homogeneous reactions that depend upon the soluble catalyst (Cu) concentration, the concentration of the organic species of interest, and the ionic strength of the solution (the sodium and/or hydroxide concentration). The presence of dissolved oxygen increases the rate of reaction likely by oxidizing the Cu to the preferred valence state and changes the product of the decomposition reaction from benzene to primarily phenol.
- Pd also catalyzes tetraphenylborate and triphenylborane (3PB) decomposition. Initial testing indicated these reactions required the presence of tetraphenylborate solids, diphenylmercury, benzene, and at least one of the phenylborate intermediates. Subsequent testing suggests no need for diphenylmercury, benzene, or added intermediates.
- Statistical analysis of the experimental data, results from the solids decomposition testing, and results from the radioactive real waste tests leads to questions about the validity of the mechanism used in earlier kinetic modeling.
- The filtrate studies show that the TPB and 3PB decomposition rates are extremely slow in solutions without potassium tetraphenylborate (KTPB) and sludge solids. These studies also show decomposition rates of diphenylborinic acid (2PB) and phenylboronic acid (1PB) similar to those observed in Tank 48H slurry conditions. These tests also indicate that 2PB and 1PB are more strongly catalyzed by copper. Soluble Pd does indicate a catalytic influence on 1PB. In aerated systems, Pd appears to show nearly equal catalytic activity as copper for 1PB decomposition.
- A distinction about which phenylborate intermediate was crucial to the reaction could not be made. All of the phenylborates appeared capable of performing the role that the intermediate plays in establishing the catalytic sequence. In addition, elevated concentrations of the intermediates do not accelerate the decomposition rate for NaTPB for palladium-catalyzed reactions or the reactions without palladium. Rapid decomposition of NaTPB, in the presence of palladium, occurs with initial concentrations of the phenylborate intermediates below 10 mg/L.
- The solubility of NaTPB in benzene appears too low to support a benzene phase reaction mechanism.
- In the operating window tests, a large number of tests exhibited an induction period prior to the onset of the accelerated decomposition. None of the controlled experimental variables correlated with the variability in the observed induction times.
- The solubility of TPB salts in high ionic strength salt solutions is lower than predicted by previous models. The "missing TPB" reported previously is explained by the new data on TPB solubility.

Difficulties in achieving the required decontamination factor in some tests are also explained by these results.

- Three inhibitors or moderators were identified that would halt or slow the decomposition reaction. These were Agent 1, Agent 2, and Agent 3. Agent 2 also works better as reaction "scram" agents. The actual compounds can be found in Reference 9.
- Based on the results of the inhibitor tests, the source of the active Pd in the simulant tests is likely soluble Pd. The active form of the catalyst is likely reduced Pd<sup>0</sup>.
- Only simulant tests conducted at Pd concentrations greater than 0.5 mg/L and at temperatures equal to or greater than 35 °C produced benzene generation rates that were beyond the limits of the current ITP configuration.
- Initial benzene concentration does not correlate with the decomposition rate or the observed induction period. Continuously stirred, nitrogen ventilated tests exhibit rates of TPB decomposition similar to those conducted in sealed, static vessels. These results indicate that benzene is not a part of the catalytic sequence for decomposition of TPB.
- No tests at 25 °C showed appreciable benzene generation rates.
- The rate of decomposition in simulants correlates with Pd concentration.
- The rate of decomposition seems to correlate with temperature. Current analysis also indicates the operating window tests at 25 °C never activated the Pd catalyst cycle.

In conclusion, the soluble decomposition tests coupled with information from the "Real Waste" tests and solids decomposition tests indicate that the current basis for benzene generation rates could be exceeded if processing at ITP was continued using the current plant configuration. The plant has no mechanism to remove entrained solids or metals from entering the ITP process. Control of the amount of excess NaTPB, purification of the NaTPB feedstock, limiting the benzene concentration of the slurry, or controlling ionic strength of the waste mixture have been shown by these tests to be insufficient means for controlling benzene generation rates.

The soluble TPB currently stored in Tank 49 is stable. No solid TPB (required for the decomposition of TPB) is present in Tank 49. In addition, the temperature will be controlled to less than 35 °C. The material in Tank 49 was filtered prior to introduction to Tank 49; therefore, significant levels of the catalyst should not be present. These factors and temperature control (<35 °C) will prevent any catalytic decomposition of the TPB in Tank 49.

## 2.0 Introduction

As a part of the initial startup program for ITP, a series of tests were planned to investigate various impacts on the time to composite lower flammability limit (CLFL) for Tank 48H. These tests are described in the Radioactive Operations Commissioning Test Plan (ROCTP)(Ref. 1). As a part of this plan, special instrument poles with gas sampling ports were installed in Tank 48H. The instrument poles allowed the Tank 48H vapor space to be sampled at 8 levels and the temperature of the vapor at these levels to be measured. Some tests were completed prior to commencing radioactive operations at ITP.

ITP began operations on September 2, 1995 with the initial addition of sodium tetraphenylborate (NaTPB). NaTPB additions were completed on September 29, 1995. 80,648 g-moles of NaTPB were added to Tank 48H. This amount was calculated to include approximately 50% excess NaTPB above that required to precipitate all of the cesium, potassium, and other species that precipitate with tetraphenylborate. Subsequent investigations indicated that the excess was actually approximately 66 % (Ref. 2). Sodium titanate (ST) was subsequently added on September 30. Filtration, deliberately conducted in three stages to observe mixing behavior of the Tank 48H slurry, was completed November 11. Per the ROCTP, pump run tests were completed at various tank volumes after the chemical additions to Tank 48H were complete. During these runs the benzene evolution rate was higher than would have been expected based on the 1995 level of understanding of benzene generation for the ITP process. The calculated amounts of benzene in

solution at this time were not enough to challenge the safety envelope for Tank 48H. Some explanations were derived that seemed to explain the higher levels of benzene.

Additional ROCTP tests were completed between November 11 and November 30. These tests included two loss of ventilation tests that were run at elevated liquid phase temperatures (~40 and 55 °C). On December 1, a significantly higher benzene concentration than had been previously observed was seen in the vapor space while operating slurry pumps in preparation for sampling Tank 48H. The pumps were shut down and an investigation was conducted.

Between December 8, 1995 and January 3, 1996 a program began to deplete the benzene from Tank 48H by operating slurry pumps. Pump operations were halted due to questions concerning the adequacy of the Tank 48H time to CLFL safety basis. Benzene depletion runs resumed on March 5 and were completed in May. SRTC analysis indicates that 95 % of the excess NaTPB had decomposed by as early as December 18. Approximately 8300 kg of benzene were accounted for during the benzene depletion runs.

An investigation of the cause of the decomposition was initiated in early December. DOE-SR halted ITP operations. In August, the Defense Nuclear Facility Safety Board (DNFSB) issued Recommendation 96-1 to the Secretary of Energy that outlined specific concerns that needed to be addressed prior to restarting the ITP process.

The DNFSB recommended that operation and testing in the ITP Facility be discontinued until development of an improved understanding of the mechanisms for benzene generation, retention, and release. The Department of Energy (DOE) developed its approach to resolving the issues raised by the DNFSB in the 96-1 Implementation Plan (Ref. 3).

Implementation Plan Commitment # 3 states that an overall bounding benzene generation rate will be determined and documented based on the understanding of all major generation mechanisms. Milestone # 5.2.2-1 provides the results of testing to understand catalytic decomposition of soluble tetraphenylborate (TPB), including identification of primary catalysts, decomposition mechanisms, and rate constants.

This document provides summarizes current knowledge regarding Milestone # 5.2.2-1.

### 3.0 Objectives

In association with the Implementation Plan, a chemistry program was outlined to investigate benzene generation. The program was divided into three distinct elements:

- Develop and test an essentially complete simulant for test program use, which produces decomposition rates similar to or greater than those observed in Tank 48H (~ 12-25 mg/L-hr) to provide the basis for further testing with simulants.
- Identify the primary catalyst or group of catalysts.
- Determine the primary reaction mechanisms and the rate constants for TPB decomposition including the intermediate reactions.

A Test Plan (Ref. 4) was written to develop a fundamental and quantitative understanding of the decomposition of soluble TPB and the subsequent generation of benzene. The specific tasks described in this test plan were:

- Perform tests to demonstrate a Tank 48H, Batch 1 simulant, which produces rates similar to or greater than those observed in Tank 48H.
- Determine significant reaction mechanisms and rate constants with soluble copper catalyst as a function of temperature, hydroxide concentration, reactant and intermediates concentrations.
- Perform preliminary testing to develop candidates for catalyst identification (ID) testing; include trace soluble species, sludge solids, sodium titanate, and organics.

- Based on preliminary catalyst ID testing, perform statistically designed experiments to identify the primary catalyst(s).
- Determine the effect of active catalysts on decomposition rates of TPB and the reaction intermediates.
- Provide correlations and rate constants for use in modeling the decomposition reactions and the process flow sheet.

#### **4.0 Experimental Program**

This report discusses all of the tests that were conducted and presents the results and conclusions of these experiments. Note that as the experimental program developed some conclusions derived from earlier tests were revised based on subsequent tests. The original conclusions from each set of experiments are presented to demonstrate the development of the program over time. These conclusions, in some cases, resulted in changes of scope and direction for the experimental program.

#### **4.1 Pre-96-1 Recommendation Testing and Results**

Testing was initiated at SRTC in December 1995. The scope of this testing is outlined below:

- Develop a quantitative description of the expected reaction products of NaTPB decomposition and the relative amounts of each product.
- Develop a qualitative description and understanding of the physical and chemical phenomena occurring in the liquid, solid, and gas phases of Tank 48H.
- Develop alternative chemical reaction pathways that are plausible explanations for the reaction products.

The complete results of this investigation are reported in Reference 5 and are briefly summarized below.

The testing was initiated to attempt to understand the excessive benzene generation that occurred during Batch 1 at ITP. The initial test results were instrumental in outlining the chemistry program to resolve the 96-1 benzene generation concerns. The program was initially directed at defining the rate of benzene generation that occurred in Tank 48H and developing conditions that would reproduce or exceed that rate. Additional tests investigated the impact of the source of the NaTPB, atmospheric impacts, the contribution of sludge and mono-sodium titanate (MST), the reaction stoichiometry, the role of known catalyst concentrations ( $\text{Cu}^{2+}$ ), and the dependency on chemical composition (OH).

This initial investigation resulted in the following conclusions about the decomposition that occurred in ITP Batch 1:

- Benzene was the major product of the decomposition. Phenol and biphenyl were minor products, and phenyl boric acid is a semi-stable intermediate.
- The product stoichiometry depends strongly on oxygen availability.
- The average rate of benzene generation in Tank 48H may have reached 12.5 - 25 mg/L/hr during the rapid decomposition. (The lack of frequent samples and the inability to measure the reaction byproducts prevented reliable estimation of the rate.)
- The reaction consumed all of the available NaTPB solids in Tank 48H, but no significant amount of insoluble potassium or cesium tetraphenylborate.
- The rate of reaction, stoichiometry, and extent of reaction were reproduced in the laboratory using simulants.

Additional observations derived from this test program are outlined below:

- Increasing the copper ion and sludge solids concentration increases the rate of decomposition of TPB.

- The presence or absence of oxygen changes the decomposition mechanism. The presence of oxygen results in an induction period not seen when tests are run under a nitrogen atmosphere.
- The source of the NaTPB used in Batch 1 cannot account for the rapid rate of decomposition observed in Tank 48H during Batch 1.
- The rate of NaTPB decomposition is temperature dependent.
- Increasing hydroxide concentration delays decomposition of NaTPB.
- The rate of NaTPB decomposition is proportional to the soluble tetraphenylborate ion concentration.

Reaction mechanisms and kinetics were postulated in consultation with the ITP Process and Mechanisms Panel. The reaction appeared to be a first order catalytic reaction of soluble tetraphenylborate. Decomposition intermediates were thought to be triphenylborane (3PB), diphenylborinic acid (2PB), and phenylboric acid (1PB). The proposed mechanism and reaction sequence is discussed more fully in Section V and Appendix P of Reference 5.

Subsequent testing was completed to verify that the rate of tetraphenylborate decomposition observed in ITP Batch 1 could not be explained by copper catalysis alone. This work is documented in Reference 6. The experimental design was developed to determine the primary effects associated with tetraphenylborate, hydroxide concentration, temperature, and reaction atmosphere. Note that analytical methods for measuring triphenylborane or diphenylborinic acid were not available for these tests or the tests described previously. The primary conclusions derived from the results of these tests were:

- The decomposition rate correlates directly with soluble TPB ion concentration.
- Temperature significantly influences the rate of reaction.
- Hydroxide concentration is not a key parameter in the copper catalyst system.
- The rate expression derived for these tests indicates only soluble tetraphenylborate concentration and temperature are critical. However, this rate expression (and the corresponding rate constants) still under predicts the observed Tank 48H rate by approximately 3 orders of magnitude.

Some of the conclusions outlined above were modified by subsequent tests. Therefore, conclusions presented for each series of tests may conflict with conclusions from later tests. The final set of conclusions for all of the tests discussed in this report are found in Section 7.0.

These tests confirmed that copper-catalysis alone could not explain the rates of decomposition observed in Tank 48H and that an alternate catalyst system needed to be investigated to explain the decomposition in Tank 48H.

These two sets of initial tests indicated that the potassium and cesium tetraphenylborate solids were stable. Subsequent testing indicated that this might not be the case (Reference 7). The DNFSB issued Recommendation 96-1, and further research into the decomposition reaction was conducted as discussed below.

#### **4.2 Soluble TPB Decomposition Program**

The initial testing was used to help formulate the ITP 96-1 Chemistry program. The program was divided into three discreet parts: soluble tetraphenylborate decomposition testing, solid decomposition testing, and real waste testing to verify simulants testing produced bounding generation rates. The latter two programs are covered in other reports. The soluble program is discussed in this report.

Testing for this part of the program was performed under three Technical Task Plans (TTPs) prepared by the performing organization. The TTPs contain detailed information on methods, temperatures, compositions, test conditions, and analytical requirements. The testing performed under each TTP is summarized below. The results for these tests are presented in Section 4.



#### **4.2.1 Decomposition Studies of Tetraphenylborate Slurries (Reference 8)**

A catalyst system was proposed based on the history and contents of Tank 48H, Tank Farm material inventory analysis, analysis of existing literature, discussions with NaTPB vendors, consultation with the ITP Process and Mechanisms Panel, and SRTC experience. This simulated catalyst system called the Enhanced Comprehensive Catalyst (ECC) was developed to maximize the probability that simulants would produce rates of tetraphenylborate decomposition comparable to that observed in Tank 48H during ITP Batch 1. The ECC contains soluble NaTPB and KTPB, soluble metal ions, organic species, simulated sludge solids, and MST. (Reference 8 has a complete recipe for the ECC.) The ECC (or small variations of that recipe to determine the influence of individual components) was used for all of the tests described in this test plan.

The primary objective of these tests was to demonstrate that the ECC produces a rate of decomposition that simulates the behavior of Tank 48H during ITP Batch 1. Additionally, these tests were to demonstrate that the full potential catalyst recipe found in the ECC provided an all-inclusive or near complete set of additives from which future 'blocking' or statistically designed TPB decomposition tests could be designed.

The tests were performed at three temperatures to determine temperature dependence. The important parameters controlled were the starting simulant compositions and the test temperatures.

Additional scoping tests were conducted to obtain an early indication of the effect of removing insoluble solids from the salt solution. Slurries without sludge and/or MST were tested.

#### **4.2.2 Sodium Tetraphenylborate Decomposition Catalyst Identification (Reference 9)**

The catalyst identification tests were completed in phases. The phases were delineated as Preliminary Tests Sets 1 and 2 and statistically designed test Phases A, B, C, and D. The Test approach is described below for each phase of testing.

##### **4.2.2.1 Preliminary Sets 1 and 2**

The first set of preliminary testing included cross check tests of previous experiments, individual condition tests to determine the influence of experimental test conditions and to verify the test conditions chosen for the catalyst identification testing, and tests to check for catalytic activity of selected noble metals. Conditions tested include reaction vessel type (glass versus carbon steel), mixing (agitated versus unagitated), and atmosphere (purged versus sealed). The last variable mentioned; not only examines oxygen - as planned for the design - but also changes the concentration of benzene in the solution which subsequent testing showed played a role in governing reaction rates. A screening test to determine if noble metals might be the principal catalysts was completed in this phase also.

The second phase of preliminary tests studied the effect of KTPB solids concentration and hydroxide concentration on catalytic activity, catalytic effect of noble metals alone, and the impact of MST and sludge form (hydrated versus dehydrated).

Based on the results of these experiments, the task plan was revised, and the statistical catalyst identification tests were designed.

#### **4.2.2.2 Phase A Statistically Designed Tests**

Phase A blocked the potential catalyst into groups. A statistical design was used to eliminate groups of potential catalysts. Potential catalyst splitting blocks were established. Based on the results of the preliminary test results, these tests were conducted at the following conditions: 55 °C, 2.7M Na<sup>+</sup>, 48 g/L KTPB slurry containing a high soluble concentration of NaTPB. All tests used glass serum bottles without continuous agitation or ventilation. Sludge and MST, where required, were used in the hydrated form. Researchers monitored tetraphenylborate ion, triphenylborane, and diphenylborinic acid species. No benzene, 1PB, or soluble boron analyses were performed.

#### **4.2.2.3 Phase B and C Statistically Designed Tests**

The Phase A experiments indicated the interaction of two groups: the combination of suspect active organics and suspect active metals produced the highest catalytic activity. The suspect active organics group included benzene, tetraphenylborate decomposition intermediates (3PB, 2PB, and 1PB), and diphenylmercury. The suspect active metals group contained palladium, rhodium, ruthenium, and silver.

Phase B tests attempted to determine which active organics were influential in the catalytic system. Phase C tests were conducted to determine which active metals were influential in the catalytic system.

#### **4.2.2.4 Phase D Statistically Designed Tests**

Previous tests omitted the presence of uranium and the effect of radiation to allow for experimental flexibility. Phase D tests were designed to determine if these factors had any effect. The impact of both pre-irradiation and continuous radiation was examined in these experiments.

#### **4.2.2.5 Special Tests**

Two additional series of tests were conducted to study the role of oxygen and the interaction of the phenylborate species on the reaction system.

##### **4.2.2.5.1 Impact of Oxygen on Tetraphenylborate Decomposition (Reference 10)**

These tests studied the impact of oxygen on the copper catalyzed decomposition of tetraphenylborate.

##### **4.2.2.5.2 Interaction of 2PB and Tetraphenylborate Ion (Reference 11)**

During the discussions on potential reaction mechanisms, a reaction between 2PB and tetraphenylborate ion was proposed. This set of experiments was designed to determine if such a reaction exists. 2PB concentration, TPB solids concentration, benzene concentration, and sludge concentration were varied.

#### **4.2.3 Decomposition Studies of 3PB, 2PB, and 1PB**

##### **4.2.3.1 Copper Catalyzed Decomposition of 3PB, 2PB, and 1PB (Reference 12)**

The purpose of these experiments was to determine individual reaction rates and the decomposition products for the intermediates outlined above in the presence of soluble copper ion. Temperature, organic reagent (3PB, 2PB, or 1PB), hydroxide concentration, and copper concentration were varied to obtain the kinetic information desired. All of the tests in this series were conducted in air-sealed, non-agitated, carbon-steel containers. A simple system was chosen to initiate the intermediates studies to provide clarity for comparison with future experiments.

#### **4.2.3.2 Decomposition of 3PB, 2PB, and 1PB Using Potential Catalysts (Reference 13)**

This series of experiments were developed to determine the kinetics of copper catalyzed decomposition of the intermediates in caustic solutions with a nitrogen atmosphere and to determine comparative overall decomposition rates and products of the intermediates decomposition in inerted aqueous solution in the presence of potential catalysts including copper.

The first series of tests varied temperature, intermediate species, hydroxide concentration, and copper concentration to develop the kinetic expressions for comparison with previous air-sealed systems. In the second set of tests, the ECC was prepared without the normal copper and noble metals. These species were added separately as soluble species. These tests were conducted to compare with results derived from the copper only series of tests.

#### **4.2.3.3 Decomposition of 3PB Using the ECC (Reference 14)**

These experiments were developed to determine the decomposition rate for 3PB as a function of ECC concentration, atmosphere (air versus nitrogen), temperature, and hydroxide concentration. These experiments were conducted with KTPB solids present.

A second set of experiments was designed to provide direct bench-marking of the results with experiments previously discussed (Sec 3.2.2.5.1).

#### **4.2.3.4 Filtrate Studies**

As a part of the tests outlined in Reference 14, some filtrate studies were completed. These experiments were designed to determine the rates of decomposition if the solids were filtered from the system. This information was obtained to aid in developing the Tank 50 Authorization Basis.

### **5.0 Results**

#### **5.1 Pre-96-1 Testing Results**

The results of the Pre-96-1 testing were discussed previously.

#### **5.2 Soluble TPB Decomposition Program Results**

##### **5.2.1 Tetraphenylborate Decomposition Studies (Reference 15)**

Tests of TPB decomposition with the ECC simulant showed that the simulant produced decomposition rates of the same magnitude as those estimated for Tank 48H. A comparison of results from Tank 48H and the TPB Decomposition studies show rate of growth in soluble boron to be comparable (See Table 18 of reference). Although the contents of Tank 48H were simulated as close as possible for these tests, some differences in the experimental environment from Tank 48H may explain any small differences in the exact absolute values of the rates. In addition, the activation energy for the ECC was significantly lower than for copper catalyzed systems suggesting that an additional catalyst was present in the ECC. The conclusion from this experimental work was that the ECC provided an adequate catalyst makeup to pursue catalyst identification studies based on the ECC recipe.

The removal of the MST from the catalytic system had no impact on the reaction rates. However, removal of the sludge solids dramatically reduced the decomposition rates.

These studies did indicate solid tetraphenylborate decomposition was occurring. The rate of decomposition could not be explained by the dissolution of KTPB and subsequent decomposition of the associated soluble TPB.

## **5.2.2 Tetraphenylborate Catalyst Identification Studies**

The catalyst identification studies were broken down into various phases as previously reported. The results of these various phases are discussed in the following paragraphs.

### **5.2.2.1 Preliminary Sets 1 and 2 (References 16 and 17 Respectively)**

Preliminary Set 1 experiments confirmed that the ECC system rates of reaction are comparable to the rates observed in Tank 48H in December 1995 based on the length of time required to decompose all of the NaTPB and the product distribution obtained. These tests also demonstrated the reproducibility of the reaction system.

The tests demonstrated that tetraphenylborate solids were required to obtain high rates of decomposition, carbon steel does not significantly catalyze the decomposition reaction, sodium or hydroxide concentration impact reaction rate constants, continuous stirring resulted in a small increase in the rate of decomposition, and noble metals alone (i.e., no other potential catalysts present) indicated low decomposition rates.

Preliminary Set 2 experiments probed the boundaries found in Set 1. The primary finding from this set of experiments is that the interaction of a noble metal or silver with other components of the ECC strongly contributes to the observed decomposition.

In addition, Set 2 experiments demonstrated that the hydroxide concentration was not a factor in the decomposition reaction, the form of MST (hydrated or dehydrated) does not influence the rate of reaction, and the hydrated form of sludge exhibited a minimal increase in reactivity.

Finally, experiments demonstrated that although tetraphenylborate solids facilitate the decomposition reaction, the rate is independent of the tetraphenylborate solids concentration between 1 and 8 wt % solids.

Based on the results of these experiments, the test conditions that were used for the remainder of the catalyst identification studies were 55 °C, 2.7 M Na<sup>+</sup> concentration, 48 g/L KTPB slurry containing a soluble concentration of NaTPB. All subsequent tests in this portion of the Chemistry program were conducted in glass serum bottles without continuous agitation or ventilation. In addition, only tetraphenylborate ion, triphenylborane, and diphenylborinic acid were monitored in the catalyst identification tests.

### **5.2.2.2 Phase A Statistically Designed Test Results (Reference 18)**

The Phase A tests indicated that the suspect organics (benzene, decomposition intermediates, and diphenylmercury) and suspect active metals (palladium, rhodium, ruthenium, and silver exhibited primary influences on the decomposition reaction. The interaction of the two groups provided the dominant decomposition of NaTPB. Copper, as well as other species tested, does not promote a significant reaction in relation to the reaction catalyzed by the interaction of the suspect active organics and metals groups.

### **5.2.2.3 Phase B and C Statistically Designed Test Results (Reference 19)**

The Phase B and C tests demonstrated that all species (benzene, diphenylmercury, and the phenylborate intermediates) in the suspect organics grouping are required to facilitate the rapid decomposition of soluble sodium tetraphenylborate. The decomposition reaction appears to be zero order with respect to the organics; however, the large molar ratio (with respect to palladium) prevents determining this value with any certainty. Benzene appeared to have a required threshold value that was not determined in these experiments.

Palladium was shown to be the noble metal species responsible for the observed rapid decomposition. Rhodium, ruthenium, and silver proved to be inactive. Limited data suggested that the reaction order for palladium is less than unity. (Subsequent testing indicates the reaction is first order in palladium.)

#### **5.2.2.4 Phase D Statistically Designed Test Results (Reference 20)**

The Phase D experiments demonstrated that uranium does not enhance the reaction rate previously identified for systems containing palladium, diphenylmercury, and phenylborate intermediates.

Neither, pre-irradiation nor continuous irradiation accelerates the catalytic decomposition. These experiments indicate that both pre-irradiation and continuous irradiation inhibit the previously identified catalyst system.

None of the catalyst identification tests indicated solid tetraphenylborate decomposition. This could have been a result of the length of the tests or that the conditions were not present for solids decomposition. In addition, all of these tests appeared consistent with a reaction in the aqueous phase.

#### **5.2.2.5 Special Test Results**

The following paragraphs describe results of the tests examining the role of oxygen and the potential interaction of the decomposition organics with tetraphenylborate.

##### **5.2.2.5.1 Impact of Oxygen on Tetraphenylborate Decomposition (Reference 21)**

The results of this investigation indicate that NaTPB reacts more slowly in an oxygen environment and that oxygen may induce an induction period for the decomposition reaction. The results of the experimental work for the phenylborate intermediates was not completely conclusive and was studied further in subsequent experimental work. (See Section 5.2.3)

##### **5.2.2.5.2 Interaction of 2PB and Tetraphenylborate Ion (Reference 22)**

The experiments demonstrated that 2PB does not react directly with tetraphenylborate anion. The reaction proposed was not present in Tank 48H in December 1995 since the precipitate remained stable after the excess NaTPB decomposed. The reaction also does not enhance the reaction identified by the catalyst identification investigation.

#### **5.2.3 Intermediate Decomposition Studies**

Studies of the decomposition of the phenylborate intermediates (3PB, 2PB, and 1PB) were conducted to determine the impact the less phenylated species may have on the overall benzene generation rates for Tank 48H. The results of these experiments are presented below.

##### **5.2.3.1 Results of Copper Catalyzed Decomposition of 3PB, 2PB, and 1PB (Reference 23)**

The copper catalyzed experiments resulted in the following conclusions.

Copper catalyzes decomposition of all of the phenylborate intermediates. All of the decomposition reactions are temperature dependent.

The 2PB and 1PB rates of decomposition were consistent with the rates observed in Tank 48H. This indicates that copper alone catalyzes the compounds.

However, the decomposition rate of 3PB was lower than those seen in Tank 48H measurements. This indicated either the conditions were not optimum for this decomposition or an additional catalyst is involved in this decomposition sequence.

Oxygen appears to be an important factor in the decomposition of the phenylborate intermediates; however, these experiments were not designed to completely illuminate its role.

#### **5.2.3.2 Decomposition of 3PB, 2PB, and 1PB Using Potential Catalysts (Reference 24)**

The results of this series of tests confirmed the decomposition of 2PB and 1PB is more strongly catalyzed by copper than palladium. In addition, the copper only tests completed in this set demonstrated that the rates of decomposition in nitrogen inerted systems are significantly slower for all of the phenylborate intermediates.

The rate of decomposition of 3PB was increased significantly by the addition of additional soluble potential catalysts. The rate was not impacted by the addition of MST or sludge solids containing the insoluble potential catalysts. These experiments also demonstrated that the copper only catalyzed system does not reproduce the rates of 3PB decomposition observed in Tank 48H.

Additional tests were completed for 2PB and 1PB using copper alone as a catalyst (Ref.25). These experiments showed that the decomposition of these two intermediates was much faster in aerated systems than in inert systems.

#### **5.2.3.3 Results of Decomposition of 3PB Using the ECC (Reference 26)**

This series of experiments confirmed the previous test results. Oxygen inhibits the decomposition of 3PB, and the reaction is temperature dependent. In addition, the experiments showed that the presence of tetraphenylborate solids enhances the decomposition of 3PB as it does with NaTPB.

#### **5.2.3.4 Results of Filtrate Studies (Reference 27)**

The results of the filtered slurries confirmed previous work completed in this program. The results that follow are for systems that had been part of a complete active (decomposing) catalytic system and then filtered. Soluble tetraphenylborate remaining after filtration reacted in air-sealed vessels. The rate constants resemble those for copper catalysis. Further addition of either palladium or copper does not increase the observed rate of decomposition.

3PB reacted at rates similar to copper catalyzed systems in any of the tested filtrate media. Palladium additions did not impact the reaction rate.

2PB and 1PB reacted quickly with the soluble catalysts that passed through the filter. The primary catalyst for these phenylborates was copper. These phenylborates appear to be first order with respect to copper. The decomposition reaction in flowing air systems produces primarily phenol and not benzene as in previous inerted system tests. In addition, these tests indicate that Pd shows an apparent catalytic influence on 1PB. The rates remain small relative to those for the slurry system but may provide a challenge for Tank 50 if high concentrations of these intermediates pass forward.

### **5.3 Impact of Other Experimental Programs on the Soluble TPB Program**

The overall benzene generation rate is a function of the combined decomposition rates of tetraphenylborate and each phenylborate intermediate. Rate constants were developed for TPB and each intermediate assuming a aqueous catalyzed reaction. These rate constants are reported in the associated reports for each species. These rate constants were used to calculate bounding decomposition rates and benzene generation

rates for tests that were to be conducted using radioactive waste to predict the behavior of the remainder of ITP Cycle 1 (Reference 28). The decomposition rates that were observed in the radioactive real Waste tests could not be explained by this method of calculation.

#### **5.4 Statistical Review of the Soluble Experimental Data**

A statistical review of all of the soluble data available at this point in the test program was conducted to provide a basis for calculating a bounding benzene generation rate. The results were expected to determine the impact of the key factors controlling the generation rate.

The results of the statistical analysis of the soluble experimental data are reported in its entirety in Reference 29. The results of this review for tetraphenylborate and each of the phenylborate intermediates are presented below.

##### **5.4.1 Tetraphenylborate**

Decomposition of tetraphenylborate is catalyzed by Pd. Cu is a much less active catalyst. The rate constant has a near unity dependence with respect to the Pd concentration. This suggests that the rate-limiting step involves the reaction of TPB with the active Pd species.

As expected from fundamental principles, the rate constant also has a strong dependence on temperature and sodium ion concentration (likely ionic strength).

The fit achieved by the statistical analysis resulted in an  $R^2$  of 88.3%. This result also indicates that the mechanism for tetraphenylborate decomposition (soluble TPB with soluble catalyst) may not be the primary route by which the tetraphenylborate decomposes.

##### **5.4.2 Triphenylborane**

Both Cu and Pd catalyze decomposition of the 3PB. The rate constants indicate a less than unity relationship with Cu concentration indicating that the regeneration of the active species may play an important role in the Cu catalyzed decomposition. The Cu catalyzed reaction also depends on the hydroxide (ionic strength) concentration.

The Pd catalyzed 3PB reaction exhibits a lower activation energy indicating Pd is a more active catalyst and like for tetraphenylborate depends upon the Pd concentration. The near unity dependence on Pd indicates a direct 3PB - Pd catalyst reaction and that the catalyst regeneration is fast compared to the decomposition reaction. Temperature also influences the reaction. The kinetic fit to the data was poor, indicating additional factors which are not accounted for in the model influence the reaction. The Pd fit to this data had an  $R^2$  of 74.5%.

A subsequent model for the Cu catalysis of triphenylborane resulted in a  $R^2$  of 65.6 %.

##### **5.4.3 Diphenylborinic Acid**

Copper catalyzes the decomposition of 2PB. The rate constant exhibits a less than unity relationship with the Cu concentration indicating that the regeneration of the catalyst plays an important role in the decomposition sequence for 2PB.

As was presented in Reference 5, the active catalyst is likely a Cu+2 species that gets reduced to Cu+1 when reacted with 2PB. The catalyst is regenerated when the Cu is re-oxidized to the +2 valence state by

reaction with dissolved oxygen. Since dissolved oxygen is an uncontrolled variable in the tests (the atmosphere above the liquid is controlled), the kinetic review for 2PB resulted in large variances for the statistical correlation ( $R^2 = 69.6\%$ ).

#### 5.4.4 Phenylboronic Acid

Cu also catalyzes the decomposition of 1PB. In this case the copper dependency is near unity suggesting that the regeneration of the copper species is fast. The 1PB reaction is the slowest in the decomposition chain as evidenced by the highest activation energy (75 kJ/mol). The 2PB rate is nearly 5 times the 1PB rate.

Dissolved oxygen plays a similar role in the 1PB reaction as was described in the 2PB reaction. For both 2PB and 1PB, the dissolved oxygen shifts the reaction product from benzene to phenol. No credit for this is currently taken in the Authorization Basis for ITP. For Authorization Basis purposes the product yield is assumed to be 100% benzene. The  $R^2$  for the copper reaction was 65%. The Pd contribution was not analyzed in this study.

#### 5.5 Conclusion

The results of the testing to this point indicated, under certain conditions, the benzene generation was too high for the proposed authorization basis. The data from the program indicated that conditions did exist where the soluble or more correctly the excess tetraphenylborate decomposition produced benzene generation rates that were acceptable under the proposed authorization basis.

The strategy for 96-1 closure, up to this point, was based upon using the simulated waste program results to construct a model to calculate a bounding benzene generation rate, which would subsequently be confirmed by real radioactive waste tests at SRTC. Due to the limitations associated with the kinetic model, based on the statistical analysis, the closure approach was revised. First, additional testing was outlined to better understand the impact of the key factors that control benzene generation. It was expected that operating limits could be developed that would produce benzene generation rates which would have been acceptable under the current ITP plant configuration and proposed authorization basis. Confirmation tests at SRTC would have then been conducted using real waste that simulates the next batch of ITP to verify that the next batch was within the operating window developed from the new test program. In-plant testing which would be required to open the operating window for benzene depletion would be used to verify no scale up issues exist within the generation program. The new tests constitute the third series of tests in the experimental program and are discussed below.

#### 6.0 Revised 96-1 Testing

The soluble tetraphenylborate (excess NaTPB hereafter) program identified variables that impacted the decomposition of tetraphenylborate and the phenylborate intermediates. The factor, believed influence, and an expected range are presented in Table 1 below. In addition, some comments are presented that indicate whether the variable may be controlled in the actual ITP process environment. These variables were used to develop the continued 96-1 testing.



Table 1: Factors Affecting Decomposition of Excess NaTPB

Factor	Influence	Range	Comment
Temperature	The impact of temperature is thought to follow the Arrhenius equation; however, there is little data below 45 °C to quantify this behavior.	25 - 45 °C Maximum temperature is the proposed authorization basis limit	Can be controlled above 30 °C by slurry pump operation and cooling coils in Tanks
[Benzene]	A threshold of 300 - 400 mg/L has been indicated in tests, however, no data is available for systems with less than threshold amount.	0 - 0.04 M	Slurry pumps can be used to strip benzene from slurry. May not be effective at high levels or high solids content. No plant controls are planned for this variable.
[Palladium]	highly dependent	0 - 3.6 mg/L The maximum Pd concentration is based on the worst case sludge concentration with entrained sludge limited to 400 mg/L.	Sludge portion may be controlled by settling prior to transfer to Tank 48H.
[Sodium Ion]	highly dependent	0.25 - 5.5 M Normal Operating Range	Can be controlled effectively if required.
[Excess NaTPB]	large influence	0 - 0.01 M The proposed A. B. will limit to 0.0024 M. Testing will be completed at 4X this value	Excess NaTPB concentration can be controlled but will always be present in ITP process.
[Diphenyl-mercury]	dependence unknown	0 - 590 mg/L	Same as Pd.
[Phenylborates ]	dependence unknown	0 - 0.01 M Expected Range	If decomposition occurs, the intermediates will be formed.
[Oxygen]	large influence	satd. soln - inert	The oxygen content of the aqueous phase cannot be controlled.
[MTPB solids]	large influence	0.5 - 10 wt%	Solid MTPB concentrations can be controlled but will always be present. The type of MTPB solid may have an impact on the decomposition rate.
[Copper]	some influence	0 - 3.7 mg/L	Same as Pd.
[Hydroxide]	small influence	0.01 - 3 M	Can be controlled by caustic addition.

The factors shown above have been examined and certain factors have been chosen on which to concentrate the continued tests.

## **6.1 Testing to Define Operating Window (Reference 30)**

### **6.1.1 Introduction**

The data from the initial soluble test program results indicated that an acceptable operating window existed. A group of personnel from the SRTC and the Flow-sheet Team analyzed the potential variables that are associated with the decomposition reaction. Table 1 (shown above) is a product of those reviews.

Two criteria were used to select the variables from Table 1 that would be adjusted in the tests to define an acceptable operating window. First, the variables that would be tested needed to be parameters that had a reasonable level of control within the ITP facility. The second criterion was the potential impact the variable had on the decomposition rate in previous tests. The variables chosen from this review were benzene concentration, sodium concentration, palladium concentration, and temperature. Sodium concentration, palladium concentration, and temperature can be controlled in the ITP facility to some extent, and all can have significant impact on the decomposition rate. Benzene, although not controllable in the ITP facility, was chosen for its impact on the decomposition rate and importance to understanding.

The remaining parameters will be fixed in these tests except in specific tests where a single parameter is being tested. The test descriptions and matrix are shown in the following sections.

### **6.1.2 Scope of Testing to Define Operating Window**

The testing to define an acceptable operating window attempted to establish boundaries for the variables for temperature, sodium concentration, and palladium concentration that would limit the benzene generation to less than 7 mg/L-hr.

### **6.1.3 Objective of Testing to Define Operating Window**

The objective of the operating window tests was to define boundaries for sodium concentration, temperature, and palladium concentration that will produce benzene generation rates that are within the bounds of the proposed authorization basis. It was expected that a window could be found inside which safe operation of the plant could commence. This window may be small compared to the window described in previous flow-sheets.

### **6.1.4 Test Methodology**

As was discussed above, key parameters were selected for this series of tests. The test variables have been discussed above. The control (fixed) parameters and variables were selected for this series to maximize the potential for meeting the objectives of this test series.

### **6.1.5 Test Descriptions**

The test series was a 43 test modified 4 variable Box-Behnken test design. The matrix is shown in Table 2. Table 3 provides the level for each variable associated with Table 2. The first 27 tests were designed to identify the boundaries of the operating window in terms of the four variables selected for study. Tests 28 - 43 are single variable tests and will be described more fully later.

Table 2. Test Matrix for Operating Window Test Series

Test	Temperature	Benzene	Na <sup>+</sup>	Palladium	
1	-1	-1	0	0	
2	-1	1	0	0	
3	1	-1	0	0	
4	1	1	0	0	
5	0	0	-1	-1	
6	0	0	-1	1	
7	0	0	1	-1	
8	0	0	1	1	
9	-1	0	0	-1	
10	-1	0	0	1	
11	1	0	0	-1	
12	1	0	0	1	
13	0	-1	-1	0	
14	0	-1	1	0	
15	0	1	-1	0	
16	0	1	1	0	
17	-1	0	-1	0	
18	-1	0	1	0	
19	1	0	-1	0	
20	1	0	1	0	
21	0	-1	0	-1	
22	0	-1	0	1	
23	0	1	0	-1	
24	0	1	0	1	
25	0	0	0	0	
26	0	0	0	0	
27	0	0	0	0	
28	0	-1	0	1	duplicate - #22
29	0	-1	0	1	stirred &
30	0	-1	0	1	ventilated
31	0	10 x 1	0	1	4000 mg/L benzene
32	0	0	washed Na <sup>+</sup>	-1	Compare to
33	0	0	washed Na <sup>+</sup>	1	# 5-8
34	0	0	0	5 x 1	also use increased sludge
35	0	0	0	5 x 1	& compare to # 25 - 27
36	0	0	-1	-1	use
37	0	0	-1	1	0.005 M NaTPB
38	0	0	1	-1	compare w/
39	0	0	1	1	# 5 - 8 & 40 - 43
40	0	0	-1	-1	use
41	0	0	-1	1	0.0025 M NaTPB
42	0	0	1	-1	compare w/
43	0	0	1	1	# 5 - 8 & 36 - 39

Table 3. Test Variable Levels for Operating Window Tests

Variable	Level		
	-1	0	1
Temperature (°C)	25	35	45
[Benzene] (mg/L)	0	200	400
[Na <sup>+</sup> ] (M)	3.5	4.5	5.5
[Pd] (mg/L)	0.1	0.5	3.6

The parameters that were held constant for these tests unless otherwise noted in Table 2 are as follows:

- The ECC was used except that the diphenylmercury concentration was increased to 590 mg/L. The phenylborate intermediate concentrations were increased to 0.0025 M for each intermediate. The new diphenylmercury concentration will bound the amounts that might be transferred to Tank 48H. The intermediate concentrations are the maximum that could be generated should all of the 0.01 M excess NaTPB decompose.
- The excess NaTPB was held constant at 0.01 M unless otherwise noted in Table 2. This excess is significantly higher than that called for in the proposed authorization basis (0.0024M). This value was selected so that reaction progress can be monitored with the current analytical uncertainties associated with determining the generation rate.
- The slurries were 4 wt % KTPB slurries.
- The tested were conducted under a nitrogen blanket using unstirred, glass vessels unless otherwise noted in Table 2.

The single parameter tests were incorporated into the plan to study the impact of certain variables that could also impact decomposition rates in the ITP facility.

Test 28 is a replicate test of Test 22.

Tests 29 and 30 are tests that would simulate the impact of continuous slurry pump operation in Tank. These tests simulated maintaining the benzene inventory in the system as low as possible.

Test 31 was included to bound the benzene concentration for future batches. Previous tests have indicated that this condition will not impact the decomposition rate.

Test 32 and 33 were designed to obtain information on the rate of decomposition of washed precipitate. These tests will be compared directly with Tests 5 - 8.

Tests 34 and 35 were designed to obtain additional information on the relationship of palladium concentration and sludge on the rate of decomposition. These tests bound the Tank Farm composition at 1000mg/L of sludge. These tests will be compared to Tests 25 - 27 and the solids stability program.

Tests 37 - 43 were designed to determine the impact of the initial excess NaTPB concentration on the decomposition rate. These tests can be used to interpret data that was obtained for tests with the 0.01 M excess.

A minimum of 5-7 samples was pulled for each of the described tests over 3 - 7 weeks. HPLC analysis for NaTPB, 3PB, 2PB, 1PB, and Phenol was completed. Soluble boron results were obtained for all tests with insoluble NaTPB.

## **6.2 Testing for Understanding of Decomposition**

### **6.2.1 Introduction**

The testing to continue to improve the understanding of the decomposition reactions attempted to better define the role of some of the parameters listed in Table 1. The tests were conducted based on the knowledge and information that had been obtained previously in the program to understand the decomposition mechanism.

### **6.2.2 Scope of Additional Testing for Understanding of Decomposition Mechanism**

This work included testing to identify the phenylborate intermediate required for the decomposition reaction, catalyst inhibitor tests to improve the understanding of the decomposition mechanism, and scoping tests to determine the feasibility (i.e., analytical techniques) of studying a benzene phase decomposition reaction mechanism, and tetraphenylborate solubility studies.

### **6.2.3 Objectives**

#### **6.2.3.1 Identification of Active Intermediate (Reference 30)**

The objective of the intermediate test program was to determine the phenylborate intermediate required for the rapid decomposition of excess NaTPB. Knowing the specific intermediate may provide insight into the role of the intermediate in the decomposition sequence. High concentration tests were performed to determine if the phenylborate intermediates lead to an auto-catalytic decomposition of soluble NaTPB

#### **6.2.3.2 Catalyst Inhibition Tests (Reference 31)**

The catalyst inhibition tests were conducted to identify agents that may be added to the system to prevent catalyst activation and therefore the rapid decomposition. Also, the tests will attempt to determine if an inhibiting agent can be added to a reactive system to "scram" the reaction. The type of agent that would inhibit the catalyst activation may provide additional information on the reaction mechanism and catalyst form.

#### **6.2.3.3 Scoping Tests for Benzene Phase Reaction (Reference 32)**

The scoping test for a benzene phase reaction was to develop analytical techniques and test strategy should additional testing of this type be deemed necessary in the future.

#### **6.2.3.4 Solubility of TPB Salts in High Ionic Strength Salt Solutions (Reference 33)**

The purpose of these tests was to determine the solubility of tetraphenylborate in high ionic strength salt solutions in order to explain previously reported "missing TPB".

### **6.2.4 Test Methodology**

Key parameters were selected for all of the tests discussed above. The key parameters were temperature, composition, and test conditions. The variables for each of test series have been selected from the list found in Table 1. The control (fixed) parameters and variables have been selected for each series to maximize the potential for meeting the objectives of each test series and will be discussed in the next section.

### **6.2.5 Test Descriptions**

The tests for each series of understanding tests are discussed in the following paragraphs.

### 6.2.5.1 Identification of Active Intermediate (Reference 31)

The test conditions for the intermediate tests were selected to be similar to the catalyst identification tests so the results could be compared. The test conditions to be held constant are outlined below:

- A modified ECC was used in these tests. Copper was not added so as to isolate the influence of palladium as a catalyst. Also, the intermediate composition was varied from that found in the ECC.
- The tests were nitrogen blanketed.
- The tests were completed at 2.7 M Na+ to allow for high NaTPB solubility and to simplify comparisons to the catalyst identification tests.
- The tetraphenylborate was in the range of 6,000-10,000 mg/L. This value represents the solubility of NaTPB at the test conditions and again simplifies comparisons with the catalyst identification tests.
- The tests were completed at 4 wt % KTPB and 55 °C in unstirred, glass vessels for comparison to previous tests.

A test matrix which varies the intermediate composition in order to identify the active intermediate was developed. The matrix is shown in Table 4.

Table 4. Active Intermediate Test Matrix

Test	3PB	2PB	1PB	
1	1	1	1	All
2	1	1	-1	Leave 1 Out
3	1	-1	1	
4	-1	1	1	
5	-1	-1	1	Add Only 1
6	-1	1	-1	
7	1	-1	-1	
8	-1	-1	-1	None
9	10x1	10x1	10x1	1250 mg/L each
10	10x1	10x1	10x1	Same without Pd
11	10x1	32x1	32x1	Similar to Test 10 without Pd

The matrix was designed to identify an active intermediate and determine if an interaction existed between the intermediates (more than one required for tetraphenylborate decomposition). The levels represented in the matrix are the ECC levels of the intermediate, and none.

A minimum of 5 samples were taken over 5 weeks. The samples were analyzed by HPLC for NaTPB, 3PB, 2PB, 1PB and phenol.

### 6.2.5.2 Catalyst Inhibition Tests – Reference 31

Three types of tests were conducted in this test sequence.

The first series of tests (Method 1) were designed to add a catalyst inhibitor to waste simulant containing the ECC that would mimic waste being transferred to Tank 48H. This waste would be approximately 8 M Na+. After the catalyst addition, the waste would be diluted, NaTPB added, and monitored for the decomposition reaction. This series of tests simulates the sequence that could be followed if Tank 42 were used as a feed tank to ITP.

The second series of tests (Method 2) would add the inhibitor to a simulant that would simulate Tank 48H after the precipitation process has taken place (4.5 M Na<sup>+</sup>) with the ECC present. The tests would be monitored for the decomposition reaction.

The third series of tests would add the inhibitor to an actively decomposing system to attempt to "scram" the decomposition reaction.

Three types of potential inhibitors have been identified: oxidizing agents, reducing agents, and precipitating agents. These agents are identified in Reference 37.

#### **6.2.5.3 Scoping Tests for Benzene Phase Reaction (Reference 32)**

These tests are scoping in nature. At the present, the tests are primarily concerned with determining analytical techniques for monitoring a reaction in the benzene phase. Additionally, some testing on the solubility of species such as tetraphenylborate in benzene is planned. If this work proceeds beyond the scoping stage, another Task Technical Plan will be prepared by SRTC describing the continued testing.

#### **6.2.5.4 Solubility of TPB Salts in High Ionic Strength Salt Solutions (Reference 33)**

The purpose of these solubility studies was to evaluate the applicability of current models based on research by McCabe and Siska (References 34 and 35 respectively), and to better understand the solubility of TPB in more complex systems. Tests were conducted at 25 °C. Variables examined in these tests were NaTPB source and form, TPB-/K<sup>+</sup> ratios, and TPB- equilibrium kinetics. Salt solutions were used that simulated actual salt waste. Specific compositions and experimental procedure are reported in Reference 33.

### **6.3 Results**

#### **6.3.1 Excess Sodium Tetraphenylborate Testing (Operating Window Tests) (Reference 36)**

A statistical analysis was completed on the data for these experiments. The analysis results in the following observations.

Palladium concentration and, to a lesser degree, temperature were shown to correlate with benzene generation rate in these tests. Benzene concentration and sodium concentration did not appear to impact the reaction rates in these tests. The effects of excess NaTPB tests were inconclusive due to problems with the test solution makeup. Agitation and ventilation did not show any signs of slowing the reaction rate in comparison with tests that were sealed and unagitated.

A large number of tests exhibited an induction period prior to the onset of the accelerated decomposition. The induction period did not correlate to any of the variables controlled in these experiments.

Tests conducted at Pd concentrations greater than 0.5 mg/L and at temperatures equal to or greater than 35 °C produced benzene generation rates beyond the limits of the current ITP plant configuration and authorization basis.

Tests at 25 °C exhibit very little decomposition. The rate of decomposition seems to correlate with temperature. Current analysis also indicates the tests at 25 °C never activated the Pd catalyst cycle.

### **6.3.2 Testing for Understanding of Decomposition**

#### **6.3.2.1 Intermediates Testing (Reference 36)**

The results of these tests indicate that the presence of any of the intermediates is not required to activate the catalyst system. The decomposition occurs and the catalyst system is activated without any of the intermediates.

Elevated concentrations of phenylborate intermediates do not catalyze the decomposition of NaTPB in the absence of either palladium or copper. The influence of elevated levels of phenylborate intermediates was not evaluated in the standard ECC formulation containing both Pd and Cu. The data suggest that elevated concentrations of the intermediates inhibit palladium-catalyzed decomposition.

#### **6.3.2.2 Inhibitors and/or "Scram" Agents (Reference 37)**

The results of the Method 1 inhibitor tests indicated that Agent 1 and Agent 3 significantly inhibited the rate of reaction (4 and 1.6 mg/L/hr benzene, respectively, versus the control of 12 mg/L/hr benzene). Two forms of Agent 2, Form 1 (~ 8 mg/L/hr) and Form 2 (5 mg/L/hr) showed some inhibiting ability.

In Method 2, Agent 1 and Agent 3 continue to show significant inhibiting properties. Agent 2, Form 1 (4 mg/L/hr) and Form 2 (4.7 mg/L/hr) performance improved.

In the "scram" tests, the two forms of Agent 2 stop the decomposition of tetraphenylborate. Agent 1 and Agent 3 show no sign of stopping the reaction.

Examination of the relative influence of various chemical additives on the decomposition behavior suggests the catalyst is a reduced species such as Pd<sup>0</sup> derived from soluble Pd. A complete discussion of this is presented in the referenced report.

#### **6.3.2.3 Plausibility of a Benzene Phase Reaction (Reference 32)**

The solubility of TPB salts in benzene is so low that a reaction occurring in the benzene phase seems implausible. The solubility of sodium and potassium tetraphenylborate is less than or equal to 3E-6 moles per liter of benzene. The solubility of 3PB in benzene when in contact with an alkaline aqueous phase is about 1.2E-5 moles per liter of benzene. (Reference 4)

#### **6.3.2.4 Solubility of TPB Salts in High Ionic Strength Salt Solutions (Reference 33)**

Previous work (References 34 and 35) did not cover the high ionic strengths present in the ITP process and the laboratory experiments. This resulted in the data being extrapolated into the high ionic strength regime. The correlation's previously used to predict the solubility of potassium tetraphenylborate over-predict the solubility in high ionic strength salt solutions. The TPB-/K+ ratio had the largest affect on TPB- solubility. TPB- solubility is depressed in the range of TPB-/K+ ratios of 1 to 10. Above a ratio of 10 the TPB- solubility appears independent of the TPB-/K+ ratio and consistent with solubility controlled by the NaTPB phase.

The TPB that seemed to be missing in PVT-1 and some laboratory experiments is in the solid phase. The reduced solubility explains why less TPB- was appearing in solution than was expected.



## 7.0 Conclusion

All of the testing for soluble tetraphenylborate decomposition has been completed. The final conclusions drawn from the soluble testing program are outlined below. These conclusions represent the current level of understanding of the soluble decomposition of tetraphenylborate.

- Copper catalyzed decomposition of tetraphenylborate and the phenylborate intermediates occurs in the systems of interest. This Copper catalysis appears to occur via homogeneous reactions that depend upon the soluble catalyst (Cu) concentration, the concentration of the organic species of interest, and the ionic strength of the solution (the sodium and/or hydroxide concentration). The presence of dissolved oxygen increases the rate of reaction likely by oxidizing the Cu to the preferred valence state and changes the product of the decomposition reaction from benzene to primarily phenol.
- Pd also catalyzes tetraphenylborate and triphenylborane (3PB) decomposition. Initial testing indicated these reactions required the presence of tetraphenylborate solids, diphenylmercury, benzene, and at least one of the phenylborate intermediates. Subsequent testing suggests no need for diphenylmercury, benzene, or added intermediates.
- Statistical analysis of the experimental data, results from the solids decomposition testing, and results from the radioactive real waste tests leads to questions about the validity of the mechanism used in earlier kinetic modeling.
- The filtrate studies show that the TPB and 3PB decomposition rates are extremely slow in solutions without KTPB and sludge solids. These studies also show decomposition rates of diphenylborinic acid (2PB) and phenylboronic acid (1PB) similar to those observed in Tank 48H slurry conditions. These tests also indicate that 2PB and 1PB are more strongly catalyzed by copper. Soluble Pd does indicate a catalytic influence on 1PB. In aerated systems, Pd appears to show nearly equal catalytic activity as copper for 1PB decomposition.
- A distinction about which phenylborate intermediate was crucial to the reaction could not be made. All of the phenylborates appeared capable of performing the role that the intermediate plays in establishing the catalytic sequence. In addition, elevated concentrations of the intermediates do not accelerate the decomposition rate for NaTPB for palladium-catalyzed reactions or the reactions without palladium. Rapid decomposition of NaTPB, in the presence of palladium, occurs with initial concentrations of the phenylborate intermediates below 10 mg/L.
- The solubility of NaTPB in benzene appears too low to support a benzene phase reaction mechanism.
- In the operating window tests, a large number of tests exhibited an induction period prior to the onset of the accelerated decomposition. None of the controlled experimental variables correlated with the variability in the observed induction times.
- The solubility of TPB salts in high ionic strength salt solutions is lower than predicted by previous models. The "missing TPB" reported previously is explained by the new data on TPB solubility. Difficulties in achieving the required decontamination factor in some tests are also explained by these results.
- Three inhibitors or moderators were identified that would halt or slow the decomposition reaction. These were Agent 1, Agent 2, and Agent 3. Agent 2 also works better as reaction "scram" agents. The actual compounds can be found in Reference 9.
- The source of the active Pd in the simulant tests is likely soluble Pd. The active form of the catalyst is likely reduced Pd<sup>0</sup>.
- Only simulant tests conducted at Pd concentrations greater than 0.5 mg/L and at temperatures equal to or greater than 35 °C produced benzene generation rates that were beyond the limits of the current ITP configuration.
- Initial benzene concentration does not correlate with the decomposition rate or the observed induction period. Continuously stirred, nitrogen ventilated tests exhibit rates of TPB decomposition similar to those conducted in sealed, static vessels. These results indicate that benzene is not a part of the catalytic sequence for decomposition of TPB.
- No tests at 25 °C showed appreciable benzene generation rates.
- The rate of decomposition correlates with Pd concentration.

- The rate of decomposition seems to correlate with temperature. Current analysis also indicates the operating window tests at 25 °C never activated the Pd catalyst cycle.

In conclusion, the soluble decomposition tests coupled with information from the "Real Waste" tests and solids decomposition tests indicate that the current basis for benzene generation rates could be exceeded if processing at ITP was continued using the current plant configuration. The plant has no mechanism to remove entrained solids or metals from entering the ITP process. Control of the amount of excess NaTPB, purification of the NaTPB feedstock, limiting the benzene concentration of the slurry, or controlling ionic strength of the waste mixture have been shown by these tests to be insufficient means for controlling benzene generation rates.

The soluble TPB currently stored in Tank 49 is stable. No solid TPB (required for the decomposition of TPB) is present in Tank 49. In addition, the temperature will be controlled to less than 35 °C. The material in Tank 49 was filtered prior to introduction to Tank 49; therefore, significant levels of the catalyst should not be present. These factors and temperature control will prevent any catalytic decomposition of the TPB in Tank 49.

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Westinghouse Savannah River Company  
High Level Waste Engineering  
Aiken, SC 29808

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July 15, 1998

To: Distribution List for WSRC-RP-98-00130, Rev. 0

From: J. R. Fowler

Page Replacement for WSRC-RP-98-00130, Rev. 0

Please replace page 19 of the WSRC-RP-98-00130, rev. 0, entitled **Studies on the Stability of Solid Tetraphenylborate Compounds** with the attached page. A typographical yields a technical inaccuracy (0.5 M should be 0.6 M in the last sentence on the page).

Enclosure 2: Letter, Schepens to Jol  
Conway, "DNFSB Recommendation  
Delivered to J. R. Fowler

Increase in  $K^+$  was monitored to establish the rate of solids decomposition in these tests, similar to the method previously described.<sup>5,7</sup>

Results from Operating Window Tests

All sample results were evaluated to provide chemical decomposition rates for solid KTPB in the projected operating range for the ITP process. Results from these latest tests are summarized in Table 4.3-3. Results from previous tests run under comparable conditions (from Table 4.3-1) are also included in Table 4.3-3 for comparison. Of particular interest with respect to catalytic activity, the observed rate of chemical degradation in this latest set of tests are about a factor of 2 to 5 times faster than expected, based on predictions from previous tests, summarized in Table 4.3-1. Results from "Operating Window" tests are summarized below:

- The measured rates of increase in  $[K^+]$  ranged from 5.8 to 27 mg/L-day in these additional tests to better define an acceptable process operating window, corresponding to benzene generation rates ranging from 2 to 9 mg/L-h due to degradation of KTPB solids at 45 °C.
- Using a dilution method more closely resembling actual tank operations (Set B in Table 4.3-3), measured rates of increase in  $[K^+]$  range from 5.8 to 19 mg/L-day, corresponding to benzene generation rates ranging from 2 to 6 mg/L-h due to degradation of KTPB solids at 45 °C. This result suggests at least a portion of the catalytic species in the slurry is removed using conditions that simulate washing operations.
- Because of the differences in the method of adding Pd in these tests compared to other solid stability tests, a separate test was completed to establish differences, if any, between these two sources of sludge and Pd catalyst. In separate analysis for the distribution and solubility of Pd after 2 weeks at 45 °C, the soluble Pd concentration was about a factor of two lower in the aged slurry (4.8 mg/L) used in previous tests than the soluble Pd concentration found for slurries in these latest tests (9.3 mg/L) in which Pd(II) nitrate was added to slurries.
- The change in the experimental method used to add Pd to the slurry mixture is the likely source of the observed increase in reaction rates for this latest set of tests. These results suggest a reaction of soluble Pd leads to catalytically active Pd species. Furthermore, aging reduces the solubility of Pd in these test slurries, suggesting that freshly precipitated Pd(OH)<sub>2</sub> is more likely to lead to catalytic decomposition than aged Pd(OH)<sub>2</sub>.

The free hydroxide concentration in a KTPB slurry should be maintained above 0.6 M to ensure benzene generation rates are less than 7 mg/L-h.



WSRC-RP-98-00300  
Revision 0

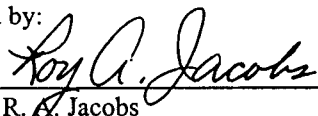
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ITP, DNFSB 96-1

Retention: Permanent

### Summary of the In-Tank Precipitation Chemistry Program (U)

July 14, 1998

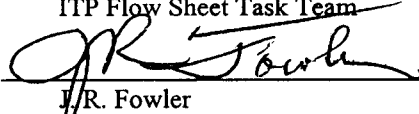
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R. A. Jacobs

Senior Fellow Engineer, SRTC  
ITP Flow Sheet Task Team

7/14/98

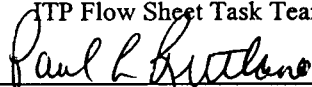
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J. R. Fowler

Senior Fellow Scientist, HLWE  
ITP Flow Sheet Task Team

7/14/98

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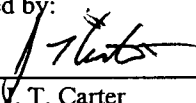
  
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P. L. Rutland

Senior Technical Advisor, HLWE  
ITP Flow Sheet Task Team

7/14/98

Date

Approved by:

  
\_\_\_\_\_  
V. T. Carter

Leader, ITP Flowsheet Task Team

7/15/98

Date

  
\_\_\_\_\_  
S. F. Piccolo

Manager, Pretreatment Program

7/15/98

Date

## Summary of the In-Tank Precipitation Chemistry Program

### 1.0 Summary

The ITP facility at the Savannah River Site began radioactive operation in September of 1995. During slurry pump operation in December of 1995, benzene evolved from Tank 48H at higher rates than expected, although the lower flammability limit for benzene in air was never approached. In August 1996, the Defense Nuclear Facility Safety Board (DNFSB) issued Recommendation 96-1 that recommended additional operation and testing not continue in the In-Tank Precipitation (ITP) facility until the mechanisms of benzene generation, retention, and release were better understood. An Implementation Plan designed to satisfy the issues raised in the DNFSB recommendation was developed by the Department of Energy (DOE) [1].

The Implementation Plan originally developed by DOE relied heavily on developing models and correlations to predict bounding benzene generation, retention and release rates. However, as experimental results accumulated from chemical studies, the reaction system was clearly more complex than originally believed. The experimental approach then evolved to one of demonstrating acceptable "operating windows" which were within the existing process capability and control. Reducing the quantity of excess sodium tetraphenylborate (NaTPB) added during precipitation has been proposed as part of normal operation to reduce the potential source of benzene during processing. For the existing plant configuration, the limitations of the Tank 48H ventilation system limits the process to a benzene generation rate no greater than 7 mg/L-hr. Remaining below this rate also ensures adequate decontamination of filtrate will be retained through precipitation and filtration operations (about 3 weeks), a key requirement for the ITP process to be viable. If the benzene generation rate holds at 7 mg/L-hr until all the excess NaTPB decomposed, additional NaTPB must then be added during the washing operation to minimize loss of  $^{137}\text{Cs}$  to the wash water storage tank.

A series of laboratory and pilot scale tests were also completed that provided key data and visual observations related to the retention and release of benzene from slurries as TPB decomposed. These studies clearly showed benzene remained associated with the TPB solids in the slurry and was released at an extremely low rate from a static system (< detection limit of ~0.5 mg/L-hr). When the slurry was left in a static state for extended periods in these tests, large globules of benzene coated with organic solids were observed to form. Retained benzene is released at a more rapid rate only when mechanical energy was added to the system. The rate of release can be controlled by simply operating the slurry pumps periodically to prevent the inventory of retained benzene from exceeding the projected peak release rates. Using a maximum benzene generation rate of 7 mg/L-hr as the basis, an operating strategy was developed that would assure safe operation and would also allow air-based mode of operation in a static system.

Subsequent results from the "operating window" tests using both simulants [2, 3] and real wastes [4] indicated the maximum benzene generation rate of 7 mg/L-hr would either be routinely challenged or possibly exceeded at the upper temperature limit of 40 °C proposed for the process, especially during the precipitation and filtration cycle when excess NaTPB is present. At generation rates approaching or exceeding 7 mg/L-hr, the overall viability of the process to always achieve the desired decontamination during the precipitation and filtration cycles may also be questionable.

On January 23, 1998, the Westinghouse Savannah River Company recommended to the DOE that facility modifications should be suspended on the In-Tank Precipitation facility, since results from chemical tests failed to resolve concerns about benzene generated by the process using the current plant configuration. The recommended suspension was accepted by the DOE to allow further review of the benzene question and to identify alternative approaches to separation, decontamination and disposal of salt wastes. Although work related to the ITP process has been suspended until alternative processes have been evaluated, sufficient understanding has been developed to address most of the issues raised in DNFSB Recommendation 96-1. This report summarizes the overall understanding obtained to date from the various elements of the chemistry program. The status of the various DNFSB milestones and deliverables specified in the Implementation Plan is included. Remaining issues that must be addressed are also identified for any of the alternative processes that use sodium tetraphenylborate (NaTPB) to precipitate KTPB and CsTPB.

The status of the various plans and reports designed to meet the milestones defined in the Implementation Plan are summarized in Section 2.0 of this report.



To investigate the generation, retention and release of benzene in the ITP process, the Chemistry Program outlined in the Implementation Plan was divided into four main elements:

- benzene generation in the presence of excess sodium tetraphenylborate (NaTPB), also known as decomposition of soluble TPB;
- benzene generation without excess NaTPB, also known as solids stability testing (KTPB/CsTPB);
- retention and release of benzene from slurries of TPB solids; and
- confirmation of benzene generation rates using actual wastes planned for the remainder of ITP Cycle 1, also known as the Real Waste Tests or the Cycle 1 Demonstration.

Results and conclusions through June 1998 for each of the elements of the chemistry program are summarized in separate reports [2, 3, 4, 5]. Results from these program elements are discussed in this report in terms of benzene generation from decomposition of both soluble and insoluble TPB compounds, the effect of inhibitors on catalytic decomposition, mechanism of benzene retention and release, identification and control of key process variables, safety issues and operating issues related to the ITP process. Remaining open issues are also summarized. Key results relative to the DNFSB recommendations in 96-1 are summarized below.

Recommendation 1: "...the planned test PVT-2 should not proceed without improved understanding..."

The proposed PVT-2 test, which involved the addition of additional salt solution and NaTPB to Tank 48H, was deferred until the mechanisms of benzene generation, retention and release were better understood. Based on the current understanding of the chemistry and the present plant configuration, this proposed test has been cancelled. Except for activities to assure continued safe conditions for Tanks 48H, 49H, 50H and saltstone, operations related to ITP processing have been suspended until the alternatives for salt processing have been evaluated.

Recommendation 2(a): "uncover the reason for the apparent decomposition of precipitated TPB in the anomalous experiment,"

In one of the early laboratory tests with real waste, results from the first two samples indicated that solid KTPB and CsTPB may also be decomposing, based on the rate of change in potassium ( $K^+$ ) concentrations. The rate of K increase was 15 mg /L-day in the first 24 hrs, corresponding to a maximum benzene rate from KTPB decomposition of 5 mg/L-hr. Although rates of  $K^+$  increase even higher than this were observed in subsequent tests on solid stability, attempts to reproduce these results at conditions recorded for the first 24 hrs of this test proved unsuccessful. Continued monitoring of this test for KTPB decomposition ultimately yielded a rate of  $K^+$  increase of only 0.2 mg/L-day after the second day, which is consistent with other test data for radiolytic decomposition of KTPB for the conditions used in this test (40 °C, 1.6 M hydroxide concentration,  $[OH^-]$ ) [2].

One possible explanation for the "unexplained anomaly" in the initial phase of this test is the occurrence of an undetected high temperature excursion, since the temperature in this test was not monitored continuously. A temperature excursion to 60-70 °C for a few hours during the first 24 hrs would have caused rapid decomposition of the NaTPB (but still within rates observed in later tests). The recorded temperatures for the first two days were 45 °C and 47 °C, respectively. After the first 2 days, the temperature stabilized at 40 °C for the remainder of the test. In addition, the results for the sample taken the second day were not internally consistent, since an increase in  $^{137}Cs$  was observed even though a relatively high TPB<sup>-</sup> concentration of 78 mg/L was measured. An error in either in sampling or in subsequent analysis is another possible cause.

Although subsequent experimental results show that NaTPB, KTPB and CsTPB are subject to chemical decomposition under adverse conditions (temperature  $\geq 45$  °C,  $[OH^-] \leq 0.6$  M; sludge concentration  $> 1$  g/L), the preponderance of data shows that solid KTPB and CsTPB do not chemically decompose to generate benzene at rates exceeding 5 mg/L-hr under less adverse conditions (temperature  $< 40$  °C,  $[OH^-] > 0.6$  M). However, temperatures greater than 35 °C yield benzene generation rates beyond the capabilities of the current tank ventilation system (7 mg/L-hr) when excess NaTPB is also present. If conditions are maintained that assure the benzene generation rate from decomposition is always within a safe operating range when excess NaTPB is present, then a substantial margin of safety is provided when only solid KTPB and CsTPB are present (the present condition in Tank 48H) [2, 3].

Solution containing NaTPB that is stored in Tank 49H was filtered before transferring it to Tank 49H. Sludge or KTPB solids are absent. Benzene generation and retention mechanisms are not operative in Tank 49H [2].

*Recommendation 2(b): "...identify the important catalysts...and develop quantitative understanding of the action of these catalysts,"*

Palladium(0) and copper(II) have been identified as important catalysts in simulant tests. Extensive data has been developed that enhances the understanding of the action and mechanism for these two metals. Cu(II) functions as a homogeneous catalyst, while Pd(0) on a solid support (sludge, undissolved NaTPB or precipitated KTPB) functions as a heterogeneous catalyst. Cu functions through a redox mechanism by shifting between Cu(II) and Cu(I). Soluble Pd(II) is apparently activated at a temperature in excess of 40 °C by first being reduced to Pd(0) in the presence of suspended solids. Thus redox activity is required for these two metals to be catalytically active. However, tests with radioactive waste do not correlate well with the measured concentrations of Pd and Cu, suggesting other waste components may be functioning as catalysts for the decomposition [2, 3].

An induction period before rapid reaction began was observed in several simulant and real waste tests. Dissolved oxygen, which was initially present in many of the tests, apparently inhibits the catalytic activity of both Pd and Cu catalysts, and may be the source of the induction period that was observed in many of the tests with simulants and radioactive waste. Although tests were run in sealed vessels, oxygen in the solution or vapor phase was monitored only in a few tests. Attempts to correlate the observed induction period with other variables proved unsuccessful. Since the ITP process vessels are purged with nitrogen to minimize flammability concerns, the possible inhibiting affect of oxygen would be limited in Tanks 48H and 49H.

At least 3 chemical additives have been identified that apparently inhibit the catalytic reaction of TPB with either Cu or Pd. Although these results are encouraging, additional work is needed (including tests with radioactive waste) to determine if the use of an inhibitor is viable.

*Recommendation 2(c): "establish ...mechanisms that determine how and to what extent benzene is retained in waste slurry, why it is released during mixing..., and any additional mechanisms that might lead to rapid release of benzene,"*

The observed behavior of benzene in a series of retention and release tests is consistent with a physical mechanism. As benzene is generated, it preferentially migrates to the TPB solids, since these solids are more organic in nature than the aqueous solution containing a high concentration of inorganic salts. Benzene associated with the solids is released from the slurry only when mechanical energy is added to the system, such as when the slurry pumps are operated. If the slurry is held static for a sufficient length of time (1 to 2 months, for example), globules of benzene coated with a layer of insoluble solids were observed to form. If globules are present near the surface of the slurry, very low energy input is needed to break the barrier to benzene release that the solid coating provides, leading to the rapid release of benzene [5].

In addition to evaluating the effect of agitation on benzene (and hydrogen) release, a seismic event and episodic release due to rolling over of the solids layer (similar to Hanford's SY-101) were evaluated. During a seismic event, the maximum sloshing would be about 26 inches in height. Sloshing would decay away exponentially in about 10 minutes, and energy input would be approximately equal to the operation of a single slurry pump at full speed. An episodic hydrogen release could occur if sufficient hydrogen were allowed to accumulate under a stagnant slurry. Mixing the slurry periodically to minimize the benzene and hydrogen inventory stored in the slurry will prevent conditions that could lead to an unsafe condition due to either of these events [5].

*Recommendation 2(d): "affirm the adequacy of existing safety measures or devise such additions as may be needed."*

Several changes to the ITP process and plant configuration have been identified that could significantly improve both process safety and process flexibility. Based on laboratory tests at lower temperature, increasing the capacity of the cooling system for Tanks 48H and 49H to assure process temperatures are always controlled to less than 35 °C would markedly reduce the rate of catalytic decomposition. Filtering the salt solution before adding it to Tank 48H would remove sludge and reduce the source of potential catalysts, while the addition of an inhibitor identified in related work would further minimize the contribution of catalytic

decomposition. These changes, when combined with the existing nitrogen purge system and agitation to release any benzene generated during processing and storage, could assure a safe and viable ITP process, if proven effective on actual radioactive waste. Each of these proposed changes, either separately or in combination, are included as options for an ITP-based process as part of the evaluation of various process alternatives to treat and dispose of salt wastes stored at the SRS [2, 3, 4].

Based on periodic sampling, the KTPB solids presently stored in Tank 48H are not chemically decomposing at a measurable rate. The observed rate of increase of potassium in solution is consistent with the expected rate of decomposition from radiolysis alone ( $< 1$  mg/L-hr). Maintaining the temperature at less than 35 °C and the  $[\text{OH}^-]$  greater than 0.6 M will assure the long-term stability of stored KTPB. Presently, the slurry in Tank 48H contains  $[\text{OH}^-]$  in excess of 1 M and the temperature is less than 30 °C. The tank is sampled periodically to monitor the concentration of hydroxide. The safety of continued storage under these conditions is also supported by more than 10 years of safe storage of a KTPB slurry in Tank 48H following the 1983 demonstration [3].

To further assure the safety of storing KTPB slurry, the vapor space of Tanks 48H is ventilated and monitored for potentially flammable components (hydrogen and benzene) in either air-based or nitrogen-based (inert) ventilation modes. The slurry will also be mixed periodically to release any benzene and hydrogen that may have accumulated in the slurry since the previous mixing operation. As a further precaution, the tank ventilation must operate in the nitrogen-based mode during mixing. Elapsed time between mixing is conservatively based on assuming all hydrogen generated from radiolysis is retained by the slurry. All of the hydrogen is assumed to be released instantaneously to the vapor space when mixing starts. Using hydrogen as the basis for the time between mixing assures the benzene inventory is too low to form globules that could lead to a rapid benzene release [5].

## 2.0 DNFSB Milestones and Deliverables

The Implementation Plan [2] specified various milestones for resolution of DNFSB 96-1. A series of test plans and reports were to be delivered to the DNFSB to meet these milestones. Current status and for the test plans are listed in Table 2-1. Corresponding reports that address each milestone are shown in Table 2-2.

**Table 2-1. Test Plans for Milestones in Response to DNFSB 96-1**

Milestone Deliverable - Test Plans	No.	Current Status
Test Plan for catalytic decomposition of soluble TPB	5.2.2-1	Completed 12/96 (Appendix A, HLW-OVP-97-0009, Rev. 0)
Test Plan for decomposition of solid TPB	5.2.2-2	Completed 1/97 (Appendix B, HLW-OVP-97-0009, Rev. 0)
Test Plan for actual waste confirming studies	5.2.2-4	Completed 4/97; revised 9/97 (Appendix E, HLW-OVP-97-0009, Rev 0 & Rev 1)
Test Plan for benzene retention mechanisms and capacity	5.2.3-1 5.2.3-2	Completed 1/97 (Appendix C, HLW-OVP-97-0009, Rev. 0)
Test Plan for laboratory benzene release studies	5.2.4-1	Completed 1/97 (Appendix D, HLW-OVP-97-0009, Rev. 0)
Sampling Plan for Tank 48H benzene measurements	5.2.4-5	Vapor space and temperature monitoring and slurry sampling of Tanks 48H & 49H are addressed in this report to assure safe storage. A sampling plan for benzene measurements will not be needed if ITP does not go back into production.

Table 2-2. Reports for DOE Milestones in Response to DNFSB 96-1

Milestone Deliverable - Reports	No.	Status
Report summarizing bounding benzene generation, retention and release	5.2.1-1	Completed 7/98 by this report (WSRC-98-00300)
Report summarizing basis for selection of primary safety strategy	5.2.1-2	Completed 1/97 (WSRC-97-0003)
Report summarizing controls and engineered systems to prevent and mitigate deflagration	5.2.1-3	Interim controls and conditions for Tank 48H and 49H in standby completed 6/98; described in this report (WSRC-98-00300)
Report on catalytic decomposition of soluble TPB	5.2.2-1	Completed 6/98 (WSRC-RP-98-00298)
Report on decomposition of solid TPB	5.2.2-2	Completed 5/98 (WSRC-RP-98-00130)
Report on PVT-1 testing	5.2.2-3	Completed 3/97 (HLW-OVP-970017)
Report on actual waste confirming studies	5.2.2-4	Completed 5/98 (WSRC-RP-98-00159)
Report on Benzene retention mechanisms and capacity	5.2.3-1 5.2.3-2	Completed 5/98 (WSRC-RP-97-0989)
Report on laboratory benzene release studies	5.2.4-1	Completed 12/97 (WSRC-RP-97-0989)
Report on bounding mass transfer coefficients	5.2.4-2	Completed 5/98 (WSRC-RP-97-0989); Use described 6/98 in this report (WSRC-98-00300)
Report on benzene release rates due to liquid additions	5.2.4-3	Completed 5/98 (WSRC-RP-97-0989); Safe lay up strategy for tanks 48H & 49H described in this report includes periodic agitation to prevent accumulation of excessive benzene inventory in the slurry that could lead to rapid release (WSRC-98-00300)
Report on bounding benzene release rates	5.2.4-4	Interim report completed in 12/97 with open items (WSRC-RP-97-0989); Open items discussed in this report (WSRC-98-00300); If a modified ITP process is selected from the alternatives evaluation, bounding release rates and controls must be addressed and closed for the modified process or facility.
Closure Report		Final report will not be issued until alternatives evaluation determine if the ITP facility (or some modification thereof) will be used to process HLW salt solutions in the future.

### 3.0 Benzene Generation

Experimentally, results on benzene generation rates were generally obtained at a temperature of 45 °C to assure the proposed temperature limit of 40 °C for the process would be bounded. Some results at higher and lower temperatures were also obtained to establish the temperature dependence of decomposition. Other variables tested included ionic strength (i.e., salt concentration), hydroxide concentration, concentration of KTPB solids, concentration of excess NaTPB and sludge concentration. Temperature, ionic strength, and concentrations of hydroxide, KTPB and NaTPB can be readily controlled in the ITP process with the current plant configuration, but there is limited ability to keep the sludge concentration in incoming salt below 400 mg/L. Without modifications to the plant configuration, control of benzene generation must be achieved through control of the other variables.

#### 3.1 Catalytic Decomposition of Waste Simulants

A mixture of metal hydroxides similar in composition to stored HLW sludge was formulated and identified as the "Enhanced Catalyst Composition (ECC)." Initially, tests with waste simulants containing the ECC yielded TPB decomposition rates comparable to the rate observed in Tank 48H, thus providing a reaction system for further studies using waste simulants. These tests confirmed that excess NaTPB, which is added to suppress

cesium solubility, catalytically decomposed to produce the large quantity of benzene that was evolved in initial ITP operations [2, 6].

In higher ionic strength solutions (i.e., high sodium molarity), measured TPB<sup>-</sup> in filtrate did not agree with predicted solubility from models developed from literature values and laboratory solubility measurements [19, 20]. This result led to a concern, later shown to be in error, that most of the excess NaTPB added to Tank 48H during PVT-1 test had rapidly decomposed, since it was not dissolved in the salt solution. Subsequent experimental work using both simulants and real waste revealed the actual NaTPB solubilities at higher sodium molarities were a factor of 5 to 10 lower than predicted by the solubility models [21]. This lower solubility could impact the process cycles if decontamination is not rapidly achieved.

Tests to identify the catalytically active species in the ECC clearly show copper (Cu) and palladium (Pd) enhance the decomposition of soluble TPB and its decomposition products [triphenylboron (3PB), diphenylborinic acid (2PB) and phenylboronic acid (1PB)]; actually sodium salts of these acids are present in the solution at high pH]. Pd is a more effective catalyst for the decomposition of TPB and 3PB, while Cu is more effective for 2PB and 1PB.

Copper-catalyzed decomposition occurs via homogeneous reactions that depend upon the soluble Cu(II) concentration, the concentration of the organic species of interest, and the ionic strength of the solution. The presence of dissolved oxygen increases the rate of copper-catalyzed reactions, especially the reactions of 2PB and 1PB, and changes the product of the decomposition reactions for 1PB and 2PB from benzene to primarily phenol [2].

Although the source of the palladium catalyst in simulant tests has been identified as soluble Pd(II), additional work with various forms of Pd suggests palladium-catalyzed decomposition of TPB and its decomposition products (3PB, 2PB and 1PB) actually occurs via heterogeneous reactions. In these reactions, the Pd catalyst must first be reduced to Pd(0) before rapid reaction proceeds. Pd(0) supported on a solid surface such as sludge, KTPB or undissolved NaTPB thus functions as the active form of the palladium catalyst.

A series of simulant tests using different forms of Pd showed the most active form of Pd(0) was obtained when KTPB was precipitated in the presence of soluble Pd(II), followed by a reduction to Pd(0). As rapid decomposition began in these tests, soluble Pd(II) concentration dropped, indicating Pd became catalytically active only after it was reduced to Pd(0). A heterogeneous mode of reaction is also supported by tests that compared the rates of decomposition in the presence of insoluble zero-valent forms of Pd [Pd(0) on BaSO<sub>4</sub> and Pd(0) metal powder suspended in mercury metal were tested] and insoluble palladium(II) oxide monohydrate added as a dry powder. The insoluble forms containing Pd(0) yielded rates that were a factor of 2 to 3 lower than the rate obtained when Pd(II) was added and then reduced to Pd(0) to initiate rapid reaction. Palladium(II) oxide yielded a rate that was about a factor of 30 lower than rates obtained from Pd(0) formed *in situ* from Pd(II) [2, 3, 7]. Tests to vary the surface area of a solid Pd(0) catalyst have not been performed.

Further evidence of heterogeneous catalysis for Pd-catalyzed decomposition was obtained from tests using filtrate from reactive waste simulants. When a solution of fresh NaTPB was added to filtrate from a rapidly reacting waste simulant slurry, the added NaTPB did not decompose at a significant rate until additional soluble Pd(II) was added to provide a source for the Pd(0) catalyst. This result clearly shows the active catalyst was either insoluble or strongly associated with the insoluble solids in the reacting slurry, since it was removed by filtration [8].

Separate tests confirmed that KTPB and CsTPB are much more stable than NaTPB. The observed relative decomposition rates for the solid tetraphenylborate compounds were as follows:

$$\text{Rate}_{\text{NaTPB}} = 24 \times \text{Rate}_{\text{KTPB}} = 73 \times \text{Rate}_{\text{CsTPB}}$$

This observed order of reactivity is consistent with conditions that led to relatively rapid chemical decomposition in Tank 48H at the end of the Batch 1 precipitation when a significant quantity of NaTPB was present. This difference in reaction rate also explains the cessation of rapid reaction after the excess NaTPB was destroyed [3]. However, under adverse conditions (temperature > 40 °C, [OH<sup>-</sup>] < 0.6 M), KTPB can decompose rapidly.

An induction period was observed in many of the tests with simulants before rapid reaction began, but the length of this induction period could not be correlated with any measured or controlled variable. The presence

of dissolved oxygen may play a role in the length of the induction period for Pd-catalyzed decomposition, since its presence could prevent Pd(II) from being reduced to the catalytically active Pd(0) species. However, the role of oxygen on either the induction period or catalysis by Pd or Cu has not been proven unequivocally.

### 3.2 Inhibiting Catalyzed Decomposition

In exploratory tests with waste simulants, three agents were identified that inhibit palladium- and copper-catalyzed decomposition of TPB. Two of these agents were also shown to significantly slow the rate of decomposition in a reacting waste simulant slurry. The agents that were effective in inhibiting the reaction reduced the rates of reaction by at least a factor of 2, compared to a control without an added inhibitor [2, 9]. Additional work to test the effects of radiation and higher temperatures is in progress to define the operating range for a possible patent (or to prevent restricted use by future patents) for this promising technology. However, tests using these agents with radioactive waste must also be completed to confirm the potential usefulness of these agents for ITP processing and their impact on downstream operations (saltstone and vitrification) before their use could be adopted.

### 3.3 Tests with Radioactive Waste

Tests using radioactive materials to simulate the planned Batches 2 through 4 for Cycle 1 in the In-Tank Precipitation (ITP) facility were generally more reactive than predicted from results obtained using waste simulants. A temperature of 45 °C was used in these tests to assure the results bounded the proposed process temperature limit of 40 °C. A sludge concentration of at least 780 mg/L was present in all these tests. However, the sludge concentrations tested in Batches 3 and 4 were not bounding. In actual plant operations, sludge solids from Batch 2 would remain in the Batch 2 heel that is a component of Batch 3, and the cumulative sludge solids from Batches 2 and 3 would remain in the Batch 3 heel that is a component of Batch 4. A change in scope from the original test plan eliminated concentrating the solids at the end of Batch 2 and Batch 3 tests that would have simulated filtration operations in the plant. Consequently, the effect of concentrating sludge solids was not tested. [2, 4].

These tests demonstrated effective initial decontamination for <sup>137</sup>Cs. Results obtained from a radioactive waste mixture representing Batch 2 showed acceptably low rates of benzene generation of about 1.5 mg/L-hr. However, results that represent precipitation operations with Batches 3 (up to 8 mg/L-hr) and batch 4 (up to 15 mg/L-hr) are too high at the proposed temperature limit to restart the ITP process and complete either the PVT-2 test or Cycle 1 for the ITP process. These benzene generation rates observed in radioactive tests generally agree with rates obtained from non-radioactive slurries containing the combination of metals in the enhanced comprehensive catalyst (ECC) used in tests with waste simulants at comparable temperatures. However, these rates are not bounded by rates observed in simulant tests. The concentrations of metals in radioactive waste tests differ from those used in simulant tests. For example, Pd was about a factor of 10 to 30 lower than the typical concentration used in simulant tests, while copper was up to a factor of 5 higher. Other metals included in the ECC were higher by as much as a factor of 160, while still others were lower by as much as a factor of 250. The sludges used in these tests also contained eight metals (vanadium, technetium, tungsten, rhenium, osmium, iridium, platinum and gold) that are not included in the ECC formulation. None of these eight metals have been tested using simulants [2, 4]. These variations show the difficulty in identifying and testing the effect of all possible catalytic metal species.

Tests to measure the relative stability of K/CsTPB in the absence of excess NaTPB show that KTPB and CsTPB are also more stable in a radioactive waste environment, in general agreement with results from simulant tests on solids. At a test temperature of 45 °C and a sludge concentration of at least 780 mg/L, the KTPB/CsTPB precipitate decomposed at a benzene generation rate no greater than 4.5 mg/L-hr after all excess NaTPB had decomposed [4].

The desired correlation between radioactive waste tests and simulant tests is tentative, at best. The higher relative stability of KTPB and CsTPB, compared to NaTPB, was confirmed, although the relative differences are somewhat lower in real waste compared to simulants. The observed correlations with Pd and Cu concentrations for NaTPB decomposition in simulant tests do not appear to hold in the tests with radioactive waste. The results with radioactive waste also suggest that Pd and Cu may not be the only catalytic species present in radioactive waste [2, 4].

#### 4.0 Mechanism of Benzene Retention and Release

Best estimate and bounding mass transfer coefficients were calculated for Tanks 48H, 49H and 50H to provide a technical basis for slurry pump operations to deplete the benzene that was generated and retained in Tank 48H in early 1996 [16]. These coefficients predicted the observed behavior in Tank 50H, but they did not predict the release rates observed in subsequent Tank 48H operations and could not explain an unusually high rate (approaching 1600 g/min release rate) observed in March of 1996 (see discussion in Section 4.2). When agitation stopped, the release also stopped. This rate of release, had it continued for an extended period, could have eventually exceeded the purge capability of the ventilation system. Various studies, calculations, and data analyses were performed to develop an understanding of benzene retention in and release from TPB slurries. Studies ranged from lab scale (~ 50 ml) to bench scale (~ 1 L) to pilot scale (~ 45 L) and provided the needed understanding for the mechanisms of benzene retention and release from KTPB slurries[5].

##### 4.1 Benzene Retention [5]

As noted above, retention behavior and form were studied in both bench scale and pilot scale work. Stagnant slurries in these experiments retained from 2,000 to 5,000 mg/L benzene, and perhaps as high as 10,000 mg/L in some tests. (The estimate for Tank 48H prior to the lengthy pump depletion runs was 8,000 mg/L.) At higher benzene concentrations, benzene was observed to collect as globules coated with KTPB and biphenyl. Globules as large as 3/4 inches in diameter were observed in the pilot-scale tests. These globules form and remain dispersed in a stagnant, consolidated slurry layer. Globule formation is believed to proceed as follows:

- initially the benzene saturates the salt solution;
- after reaching the solubility limit, the benzene begins associating with the KTPB solids by coating or wetting the solids (benzene may also be produced directly on the solids); and
- as the concentration in the slurry continues to increase, benzene droplets up to 0.75 inches in diameter form which then become coated with KTPB, biphenyl and other organic byproducts.

Buoyant forces due to lower density provides a net upward force for the globules to slowly migrate to the surface of the slurry unless hindered by a solid layer. The droplets do not coalesce further, even after six months, since the yield stress of the solids layer in the slurry apparently prevents the droplets from moving through the quiescent slurry with sufficient speed to overcome the surface tension of the coating.

These test observations are consistent with the behavior observed in Tank 48H, in which a significant inventory of benzene was generated and retained by the slurry when the tank remained unagitated over periods of 1 to 2 months when rapid decomposition of excess NaTPB was apparently occurring.

##### 4.2 Benzene Release [5]

Benzene release was also extensively studied in the bench and pilot scale experiments. Extensive data on release rates, both quiescent and agitated; was collected as a function of several different variables including temperature, TPB solids concentration, sludge concentration, quiescent time, salt solution type and sodium concentration.

A number of observations on benzene release and droplet/globule behavior were noted. Globules can rise to the slurry-vapor interface when the slurry is dispersed by agitation but do not release benzene until subjected to energy input at the surface. The presence of a low-volatility, insoluble film (KTPB, biphenyl) coating the globules, or surface tension provided by the coating, is likely responsible for the energy input required for release. As droplets grow in a stagnant slurry, the energy required to break the droplet (or globule) open becomes less. The droplet becomes "readily releasable" when the energy is sufficient to break it open at the surface causing the benzene to release at a rate comparable to a small, free benzene pool. When release starts from these globules, benzene is released at rates approaching release rates from a free benzene layer but stops when energy is removed. The coated globules observed in the laboratory are a form of readily releasable benzene, but are not the same as a free benzene layer.

In the bench-scale tests, a phenomenon characterized as a "threshold concentration" of benzene was noted. Benzene at concentrations greater than the "threshold" were readily releasable; conversely, release rates were much lower below the threshold. In the bench-scale tests, the "threshold concentration" was estimated to be 1000 - 2000 mg/L benzene per wt % KTPB solids.

Benzene release from Tank 48H observed in March 1996 is consistent with readily releasable benzene followed by a much slower release from a slurry below the threshold concentration during the lengthy pump depletion runs. The concentration in Tank 48H in March 1996 has been estimated at about 2600 mg/L per wt % KTPB, though the actual threshold concentration may be lower.

The release behavior from these slurries is significantly different for the quiescent state as compared to agitated release. In the quiescent state,

- releases are dominated by the controlling liquid phase boundary layer which is depleted of benzene,
- releases increase with increasing temperature due to increasing benzene vapor pressure, generation rate, and convective mixing in the liquid phase,
- at a constant benzene generation rate, benzene accumulates until the release rate equals the generation rate, and
- quiescent release rates
  - are initially lower than generation rate resulting in accumulation of benzene,
  - increase as the benzene accumulates,
  - can exceed actual generation rate (at that time) but only after the generation rate declines significantly, and
  - never exceeded the initial (peak) benzene generation rate.

When the slurry is being agitated, the benzene release exhibits these characteristics:

- the release rate increases two orders of magnitude or more at the onset of agitation, and may exceed the generation rate initially, but rapidly drops as benzene is depleted, and eventually approaches the generation rate;
- the magnitude of increase depends on degree of mixing and the amount of retained benzene;
- the release rate decreases with increasing KTPB solids and increasing slurry volume, due to decreased slurry mixing effectiveness;
- release rate is not dependent on solution composition and sludge concentration; and
- release flux decreases rapidly on cessation of energy input or when the benzene concentration drops below the threshold concentration.

Effects of mixing and energy input were also noted. Good mixing is required to release benzene from a slurry at rates significantly above the quiescent baseline rate. In all cases, benzene flux to the vapor phase decreased rapidly when energy input was discontinued. Large dilution through subsurface water additions did not produce significant benzene release. Moderate energy water addition (spray) on floating benzene globules did produce a significant benzene release. Low energy water addition (spray) on a floating slurry produced essentially no benzene release. Water addition (jet) with sufficient energy to fully penetrate a floating slurry containing dispersed globules did produce a significant release of benzene.

These test observations are consistent with the behavior observed in Tank 48H, in which a significant concentration of benzene was detected in the vapor phase when pumps were restarted in December of 1995. The benzene inventory in the slurry was reduced through a series of operations over the next six months, in which one to four slurry pumps were operated intermittently to agitate the tank contents. During these operations, an estimated 8300 kg of benzene were vaporized from the tank.

A single event in which benzene was rapidly released into the vapor phase occurred after a 6 weeks quiescent period in March of 1996 upon the addition of about 100 gallons of water to the tank. When the water addition stopped, the release also stopped. Based on observations in the pilot-scale retention and release tests, this event is attributed to the presence of relatively large globules of free benzene near the slurry surface. Intermittent agitation with a single slurry pump that was performed several times prior to this event likely provided sufficient energy to coalesce smaller globules that were present in the tank, but agitation was insufficient to move these globules to the slurry surface that would enable benzene to be released. During the extended quiescent period, the larger globules likely gradually rose to the surface due to relative buoyancy forces. The low energy input of water falling on the surface then provided the energy needed to release the benzene from these coated globules.



## 5.0 Identification and Control of Key Process Variables

Results for the chemistry program clearly show the effect of temperature and hydroxide concentration on the degradation of TPB. Results from solids decomposition tests using simulants indicate a minimum hydroxide concentration of 0.6 M (pH = 13.8) will control the benzene generation rates to remain well within 7 mg/L-hr at 40 °C. As expected for chemical reactions, the rate of decomposition of both soluble (NaTPB) and insoluble (KTPB, CsTPB) increases with temperature over the range of 40-60 °C. More recently, tests at 25 °C with simulants containing excess NaTPB and the ECC exhibit no decomposition and similar tests at 35 °C yield rates less than 7 mg/L-hr. Analysis indicates the active palladium(0) catalyst is not activated at lower temperature [2, 3].

Reducing the concentration of entrained sludge which serves as a possible source for catalytic metal species could serve to reduce the potential for chemical decomposition of TPB. However, the present plant configuration does not allow for either extended settling or pre-filtering. Modifications to reduce or remove sludge should be considered, if ITP is retained as the process of choice for treatment of salt solution from the alternatives evaluation. The initial results on possible inhibitors are promising, but tests using real waste are needed to confirm the usefulness of inhibitors. The impact on downstream operations (i.e., saltstone production, vitrification) is also needed before an inhibitor could be incorporated as part of the ITP process.

Even if chemical decomposition does not occur, allowing the slurry to remain stagnant for extended periods could lead to accumulation of benzene and hydrogen from radiolytic decomposition of TPB and water. Based on generation and release tests, slurries should be agitated periodically to release these flammable species from the slurry to the vapor space. Purging with nitrogen during pump operations will assure the minimum oxygen content (MOC) is maintained below a flammable vapor composition.

The very low release rate from a stagnant slurry enables "air-based" operation, if conditions that minimize TPB decomposition are maintained and the slurry is not disturbed. When entry into an air-based mode of operation is planned (e.g., to obtain a dip sample or replace a failed slurry pump), agitation with nitrogen - based ventilation mode should be performed to minimize the stored inventory of flammable species in the slurry.

## 6.0 Safety Issues

### 6.1 Revised safety strategy

The summary report on benzene retention and release contained a revised safety strategy in Appendix A [5]. Based on the information available at the time, there appeared to be "operating windows" available for the precipitation, concentration, and washing steps which would permit plant operation, based on an assumed maximum benzene generation rate of 7 mg/L-hr. The strategy involved control of the composite limiting oxidant concentration (CLOC) as previously envisioned and a revised defense-in-depth control of the composite lower flammability limit (CLFL). The revised CLFL control was based on the premise that practical operating regions for each step could be found which would limit the benzene generation to < 7 mg/L-hr. This rate was based on computer modeling which indicated 400 g/min benzene could be released and still have adequate vapor space mixing to avoid a significant stratified benzene layer [17]. At this rate, the ventilation flow could always maintain the vapor space below 60% of the CLFL.

The revised strategy was expected to easily keep the accumulated benzene well below the threshold concentration for readily releasable benzene by controlling plant operating parameters to maintain benzene rates lower than 7 mg/L-hr and periodically operating pumps to release any accumulated benzene [5, 17, 18].

If an extended pump outage were to occur, the information for quiescent release indicated that at worst the benzene concentration in the stagnant slurry would build up until the release rate equaled the generation rate. If pump operations were inadvertently started at this time, the bulk fuel concentration could exceed 60 % of the CLFL. Furthermore, if readily releasable benzene was present, then the release rate would likely exceed the 400 g/min rate resulting in a stratified benzene layer. A means to quickly detect the excessive release rate would be required and would be used to interlock the pump(s) – a strategy based on rapid reduction in benzene release when energy input is stopped [5, 17, 18].

Key concerns associated with this strategy were:

- assuring the benzene generation rate does not exceed 7 mg/L-hr;
- selecting a defensible bounding release rate for readily releasable benzene;
- proving the bounding rate could be detected in time to interlock the pump(s) before a significant benzene layer develops that is above the CLFL;
- predicting the threshold concentration for Tank 48H/49H conditions;
- depleting benzene completely during pump runs, especially at higher tank levels, and
- accumulating benzene near the threshold concentration without being detected.

### 6.2 Precipitation and Concentration (*Benzene from NaTPB decomposition with KTPB present*)

Precipitation and concentration are performed at high  $[\text{Na}^+]$  and high hydroxide molarity in the presence of excess NaTPB, KTPB solids, and sludge solids. The primary processing requirement for this step is to develop and maintain Cs decontamination during the concentration step – the period when the filtrate is going to Z Area (saltstone). Excess NaTPB is required to maintain the decontamination.

Additional tests to find an “operating window” were discussed in References 2 and 3. Control of initial  $[\text{Na}^+]$  and [benzene] were shown to have essentially no effect in the ranges of practical interest. All tests at 45 °C, a temperature that bounds the proposed AB maximum of 40 °C, either exceeded 7 mg/L-hr benzene rate or had rates in the 2.5 to 5 mg/L-hr range. Actual waste confirming studies produced comparable benzene generation rates. At 35 °C, simulant tests with high [Pd] had benzene generation rates  $\geq 7$  mg/L-hr while all tests at intermediate or low [Pd] had benzene generation rates  $\leq 1$  mg/L-hr; many were below the minimum detectable rate of about 0.7 mg/L-hr. None of the tests at 25 °C exhibited a rate consistent with an activated catalyst system – indicating all were either still in the induction period after more than two months or that the catalyst simply could not be activated at this lower temperature.

The data indicate that either temperature or catalyst could be controlled to provide an operating window. However, in the current configuration these parameters cannot be sufficiently controlled to ensure benzene rates would not consistently challenge or even exceed the proposed safety envelope.

### 6.3 Washing and Storage (*Benzene from TPB decomposition without excess NaTPB*)

After decontaminated salt solution is produced, the remaining excess NaTPB either decomposes or is removed by the washing step. The principal source of benzene then becomes decomposition of KTPB solids. After washing to about 0.2 M  $\text{Na}^+$ , the KTPB slurry is stored in Tank 49H.

Additional tests to develop an operating window for these process conditions were discussed in Section 3.2 and reference 5. These tests explored the stability of KTPB solids within the anticipated operating range from pre-washing to post-washing. All tests were conducted at 45 °C with the  $[\text{Na}^+]$  and pH at values consistent with the dilution which occurs during washing. (Based on previous testing, the pH was not allowed to fall below 12.) Four of the 20 tests had benzene rates  $> 7$  mg/L-hr and the rest ranged from 2 to 6 mg/L-hr. Actual waste confirming studies produced comparable benzene generation rates for decomposition of KTPB.

Previous tests indicate that benzene generation rates decrease with decreasing temperature and that Pd is the component in the ECC that catalyzes KTPB decomposition. Removal of the catalyst or reduced temperatures could produce acceptable rates, but these parameters cannot be adequately controlled with the current plant configuration to ensure benzene rates would not exceed or consistently challenge the proposed safety envelope.

### 6.4 Decontaminated Salt Solution and Wash Water (*Benzene from phenyl borate intermediates in the absence of TPB solids*)

Decontaminated salt solution and wash water both contain soluble NaTPB and soluble catalyst species but do not have solids required for Pd catalyzed decomposition of NaTPB.

Tests show that decomposition of NaTPB essentially stops after filtration. However, if significant concentrations of intermediates are present due to active TPB decomposition prior to filtration, 2PB and 1PB can continue to produce benzene by Cu-catalyzed decomposition in filtrate. After the 2PB and 1PB decompose, the benzene rate decreases because NaTPB in a solution free of solids does not decompose at a significant rate in an air-based system, even with copper catalyst present. The temperature limit for Tank 50H

is already specified at  $< 35\text{ }^{\circ}\text{C}$  to meet waste acceptance limits for transfer to the Saltstone Production Facility located in Z Area.

Tank 50H, whether containing decontaminated salt solution or wash water, and the Z Area Salt Solution Hold Tank (SSHT) currently operate in an air-based mode. Preliminary evaluation indicates the theoretical maximum benzene rates from decomposition of 2PB and 1PB may be too high for air-based operation, although laboratory data shows phenol is the principal product from 2PB and 1PB decomposition when dissolved oxygen is present in the solution. Tank 50H is agitated prior to making a transfer to the SSHT to reduce the soluble benzene concentration below the waste acceptance limit of 3 mg/L for transfer to the SSHT. The SSHT is continuously ventilated. The contents of the SSHT are also agitated during receipt and processing of salt solution to produce saltstone.

## 7.0 Operating Issues

The information gathered thus far not only impacts the safety envelope for ITP, but also raises concerns about the viability of the process. Sustained NaTPB decomposition in Tank 48H would require frequent NaTPB additions to maintain decontamination both during concentration (to meet saltstone requirements) and during washing (to meet ITP analytical cell requirements). This would lengthen the process cycle, increase raw material costs, and increase benzene emissions.

Frequent NaTPB additions would also be required in Tank 49H to ensure that Late Wash laboratory shielding requirements are met. Furthermore, less washing in Tank 48H to keep the  $[\text{Na}^+]$  and  $[\text{OH}^-]$  high may be required to control KTPB decomposition rates in Tank 49H. Thus, more washing would be required in Late Wash, further reducing the capacity of what is very likely the bottleneck in the HLW processing system.

Finally, sustained TPB decomposition in both Tanks 48H and 49H will elevate concentrations of phenyl borate intermediates in decontaminated salt solution and wash water. They may also decompose at rates that could require an inert gas purge rather than air-based ventilation in Tank 50H and the SSHT in the Saltstone Production Facility.

## 8.0 Path Forward

If the ITP process were operated as currently configured, then (1) upgrades and changes to the inert gas and tank ventilation systems would be required to cope with baseline and bounding benzene generation rates, and (2) significant operating cost and throughput penalties would be incurred. Therefore, on January 23, 1998 the Westinghouse Savannah River Company recommended to the Department of Energy that "facility modifications be suspended on [In-Tank Precipitation] after chemical tests failed to resolve concerns about benzene generated by that process. The suspension was recommended to further review the benzene question and identify alternative approaches to separating salt wastes."

With suspension of activity, two general areas related to DNFSB 96-1 must be addressed:

- Safe storage of the existing ITP materials and
- Closure of remaining issues.

Safe storage of the current ITP inventory is discussed in Section 8.1 while the remaining issues requiring closure for a process based on ITP technology are summarized in Section 8.2.

### 8.1 Safe Lay Up of Current ITP Inventory

#### 8.1.1 General

Tank 48H contains KTPB and CsTPB precipitates from the 1983 ITP demonstration and initial Cycle 1, Batch 1 operation from 1995. Tank 49H contains wash water from the 1983 ITP demonstration. These tanks will be maintained in a "laid up" state until the salt disposition alternatives have been evaluated and an alternative is developed. While a satisfactory operating strategy and safety basis have not been developed for continued waste processing in ITP, a comprehensive program has been developed for the safe lay up of both tanks.

A consequence analysis has been performed for both tanks [10, 14]. Based on the current radionuclide inventory in the tanks, the consequences of a deflagration (which is not credible for either tank) are not

expected to exceed the Evaluation Guidelines (EG) for an anticipated event for exposure of either an offsite or an onsite individual. Thus, neither safety class nor safety significant facilities or controls will be required. Technical Safety Requirements, as specified in procedure 2.25 of the E7 manual and the associated methodology manual, are also unnecessary for safe lay up. Nonetheless, a comprehensive safety strategy is being developed for both tanks.

Maintenance of these facilities in a laid up state is inherently safer than operation. Fresh wastes and process chemicals (such as NaTPB) will not be added to the tanks. In fact, addition of fresh waste is prohibited to protect the consequence calculations. Operations which might heat the tanks will be performed only periodically and only under controls prescribed in the Authorization Basis and controlling procedures.

#### 8.1.2 Tank 48H

Tank 48H is in lay up with K/CsTPB solids but with no excess NaTPB. (Excess NaTPB from Batch 1 and PVT-1 has decomposed.) Periodic samples during the last two years have shown the rate of increase in  $K^+$  is consistent with radiolytic decomposition of the KTPB solids only [11]. Thus, no measurable chemical decomposition of TPB has been detected in Tank 48H post PVT-1.

Based on information from the Chemistry Program, limits for monitoring and surveillance procedures during lay up of Tank 48H have been specified to reduce the chance of an unexpectedly high benzene generation rate. Storage conditions to be adopted are: (1) hydroxide concentration  $\geq 1.0$  M, (2) temperature as low as possible, not to exceed 35 °C, and (3) no addition of NaTPB. These conditions are assured by monitoring the temperature daily, sampling the tank contents periodically to assure  $[OH^-]$  is  $\geq 1.0$  M (presently about 1.3 M) and preventing the addition of fresh waste or process chemicals through procedural controls. Note also that the specified temperature limit of 35 °C is conservative for slurry containing only KTPB. This temperature is specified to minimize decomposition of the more reactive NaTPB, even though the addition of NaTPB is precluded.

However small the benzene generation rate might be, it can accumulate while the tank is unagitated. Hydrogen is generated by radiolysis of water and can also accumulate within the stagnant solids. Small quantities of benzene and hydrogen will release to the vapor space as their concentrations build in the slurry. Therefore, the tank will be ventilated to prevent accumulation in the vapor. The slurry will be agitated periodically to release any benzene and hydrogen retained in the slurry. The vapor space is also monitored for the concentration of flammable species (LFL monitoring).

As noted above, the consequence analysis of a deflagration based on the present inventory in Tank 48H does not require Safety Significant Control systems [10]. However, the Tank 48H lay up conservatively includes two carefully controlled modes of tank ventilation to prevent benzene and hydrogen from approaching concentrations that are flammable – (1) air based mode to remove potential fuels from the vapor space and (2) inert mode to reduce the oxidant concentration when fuels could be released at a higher rate by agitation. Mitigative features for each of these modes are:

##### Air based mode (Static Slurry)

- Ventilation to prevent accumulation of benzene and hydrogen in the vapor space
- Emergency response procedures in case ventilation is lost
- Primary waste tank (containment/barrier)

##### Inert mode (During Agitation)

- Inert with  $N_2$  to maintain oxidant below the CLOC using the normal nitrogen supply system
- Manual initiation of the Safety Nitrogen System and automatic isolation of the tank purge exhaust
- Emergency response procedures in the event of loss of primary and backup nitrogen supplies
- Ventilation to maintain fuel concentration below the CLFL
- Primary waste tank (containment/barrier)

Two questions arise:

- (1) What if KTPB decomposition initiates during a quiescent period and benzene accumulates in the solids in spite of all these precautions? Continual monitoring for benzene has shown that at current KTPB

decomposition and corresponding benzene generation rates, the normal vapor space benzene concentration in Tank 48H is less than the detection limit – approximately 20 ppm. A concentration above the detection limit during quiescent period could indicate an unexpected chemical reaction is occurring.

- (2) How will we know if the periodic pump depletion runs adequately release the benzene produced during the quiescent period and prevent benzene from accumulating to the threshold of the readily releasable concentration? If benzene is accumulating, the peak benzene concentration during successive pump runs would increase and accumulation would thus be evident. In this case, operating requirements (e.g., pump run frequency, configuration, and/or duration) would be modified to ensure the benzene in the slurry is depleted.

In a recent 4-pump hydrogen depletion run on Tank 48H, after a 9 month quiescent period, the peak benzene concentration did not exceed the lower detection limit of 20 ppm [15]. Concentration below 20 ppm is significantly less than the peak concentrations observed during benzene depletion runs in 1996 and in the PVT-1 test. These results provide additional support that the KTPB in Tank 48H is not chemically decomposing at a significant rate and benzene will not accumulate to the point that readily releasable benzene forms. As experience and data are gained from pump runs during lay up, the bases and calculations used to estimate frequency of pump runs may be refined to reduce the present conservatism.

### 8.1.3 Tank 49H

Wash water containing approximately 0.008 M soluble NaTPB from the 1983 ITP demonstration is stored in Tank 49H. Since this material was filtered through a cross-flow filter, KTPB and sludge solids are not present and the solution cannot accumulate benzene above the solubility of benzene in the aqueous phase. It also has very little <sup>137</sup>Cs activity (~ 30 nCi/gm) and produces almost no hydrogen or benzene by radiolysis [13]. Sample results and calculations show the benzene generation rate in Tank 49H has averaged only 3 µg/L-hr since the 1983 demonstration, which is more than a factor of 2000 below the benzene generation rate that would be of concern (7 mg/L-hr) [12]. Very conservative calculations (i.e., assumes no ventilation of the tank) show the time to benzene LFL would exceed 24 days; the hydrogen rate is negligible compared to the benzene rate in Tank 49H under these conditions [14]. As with Tank 48H, additions of fresh waste and process chemicals are prohibited.

Information from the Chemistry Program is useful in judging whether Tank 49H might be vulnerable to unexpected benzene generation. Studies show that even in the presence of an active catalyst system, decomposition of TPB in filtrate which had been separated from the solids dropped almost immediately to near zero [3]. While benzene generation from filtrate was high for a period of time, the observed benzene generation was due to continued decomposition of phenyl borate intermediates by soluble Cu catalyst. After these intermediates were consumed, the benzene generation rate decreased to near zero. Samples from Tank 49H show modest but stable concentrations of phenyl borate intermediates. The same temperature conditions and monitoring specified for Tank 48H (see Section 8.1.2) will also be applied to Tank 49H.

Since solids that could accumulate benzene or hydrogen are absent in Tank 49H, agitation to deplete fuels is unnecessary. Therefore, Tank 49H will not be agitated during lay up. Tank 49H will be maintained in air based ventilation mode for the duration of the lay up. In this mode, benzene will accumulate in the liquid phase until mass transfer by diffusion or natural convection results in a release rate equal to the generation rate. (However, the lower the generation rate, the lower the steady state liquid phase concentration.)

#### Air based mode

- Ventilation to prevent accumulation of benzene and hydrogen in the vapor space
- Emergency response procedures in case ventilation is lost
- Primary waste tank (containment/barrier)

## 8.2 Open issues

While many of the issues identified in the Implementation Plan have been successfully addressed and closed, several remain open. At this time, further work to address remaining open issues has been

suspended until alternative processes for salt disposition have been evaluated. If the ITP process in some modified form is chosen as the preferred alternative, these remaining issues must be addressed:

- Either a defensible bounding release rate for readily releasable benzene must be established and used or engineered features which eliminates the safety concern (for example, safe even if only pure benzene were present) must be installed.
- If avoiding the formation of readily releasable benzene is used as the basis for the safety strategy, then a method must be established to detect the bounding release rate and interlock the pump(s) before a significant benzene vapor layer above the CLFL forms.
- The ability to predict the threshold benzene concentration for readily releasable benzene in slurries stored in Tank 48H and 49H must be developed.
- If tank 48H and 49H are used in their present configuration, the understanding of slurry mixing, benzene release rates, and benzene retention in these tanks must be improved.
- The uncertainty about how completely benzene can be depleted during pump runs must be reduced, especially at higher tank levels.
- The uncertainty about whether benzene can accumulate to near threshold concentrations without being detected must be reduced.
- For any future process using TPB precipitation, defensible peak benzene generation rates must be selected and safety envelopes for operations must be defined.
- Similarly, defensible peak benzene generation rates for Tank 50H and the SSHT in Z Area and envelopes for safe operations must be defined.
- Since  $[Na^+]$  is high during the precipitation and concentration cycle, the effect of limited NaTPB solubility at higher sodium molarity on the overall ITP process must be evaluated.

#### 9.0 Closure of DNFSB Recommendation 96-1

At this time, no further work is authorized to address the open issues discussed in Section 8.2. Except for monitoring a few tests still in the induction period, experimental activities in progress at SRTC at the time activities were suspended have been completed or terminated. These final experiments will be documented when work is completed.

Evaluation of alternative processes for salt disposition has already started. The ITP process in some modified form (e.g., small just-in-time facility, catalyst removal or lower temperature control in existing facility) could be chosen as the preferred alternative. If so, the above issues must be addressed before DNFSB Recommendation 96-1 can be closed.

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