

## Decomposition Studies of Tetraphenylborate Slurries

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**DECOMPOSITION STUDIES OF  
TETRAPHENYLBORATE SLURRIES (U)**

RECORDS ADMINISTRATION



ABGJ

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## SUMMARY

Researchers studied the decomposition of aqueous (K,Na)TPB slurries in concentrated salt solutions containing potential catalytic additives between 40 to 70 °C. The following statements summarize the results.

- Comparison of several measures of NaTPB decomposition indicates that the present simulant recipe does result in reaction similar to that observed previously in Tank 48H. The measures include maximum amounts and rates of production for several decomposition species such as soluble boron and potassium, benzene, phenylboronic acid and phenol.
- Using a simplified kinetic analysis, researchers calculate the activation energy obtained for decomposition of NaTPB in the slurries as about  $43 \pm 20$  kJ/mole in the temperature range of 40 to 70 °C. This value remains lower than that from copper only rates and suggests another catalyst.
- Removing only solid monosodium titanate from the comprehensive recipe had no significant effects on NaTPB decomposition relative to that observed using the comprehensive recipe at 55 and 70 °C.
- Removing both solid sludge additives, which contained about 80% of the total noble metals Ru, Pd and Rh found in the comprehensive recipe, and solid monosodium titanate additives from the comprehensive recipe resulted in decreased NaTPB decomposition rates at 55 °C. Magnitudes of decomposition products were also decreased. The NaTPB decomposition decreased 15% or less, compared to average soluble boron measurements at 55 °C from duplicate tests containing the comprehensive recipe.
- Similar comparisons from removing these materials at 70 °C indicate a more significant decrease in NaTPB decomposition rates and decreased magnitudes of decomposition products. The decrease in NaTPB decomposition reached about 25% compared to soluble boron measurements at 70 °C from average duplicate tests containing the comprehensive recipe.
- Duplicate slurries tested in the temperature range of 40 to 70 °C indicate variability of 2% to 25% and 3% to 17% in measurements of phenol and soluble boron, respectively. This variability comes from relative standard deviations calculated from comparison of phenol and soluble boron concentrations at about 400, 1000 and 1600 hr of testing.
- Measurable amounts of NaTPB solids existed in all slurries tested at 40 and 55 °C for 1600 hours indicating incomplete decomposition of the initial NaTPB solids. Similar analyses indicate complete decomposition of NaTPB in certain tests at 70 °C.
- Researchers detected insignificant amounts of potassium ion in filtrates of reacted slurries containing all potential catalytic additives at 40 °C for 1600 hours, indicating no detectable dissolution of the initial KTPB solids.

- Analyses showed measurable amounts of potassium from filtrates of reacted slurries containing all potential catalytic additives at 55 and 70 °C for 1600 hours, indicating KTPB solids decomposition or dissolution of about 1,920 mg/L and 4,656 mg/L KTPB solids, respectively. These levels of KTPB solids correspond to roughly 5% and 10%, respectively, of the targeted starting 48,000 mg/L KTPB solids present initially.
- Preliminary calculations explain the levels of soluble potassium by the temperature dependent equilibrium of the KTPB and NaTPB solids, coupled with the decomposition kinetics of soluble TPB<sup>-</sup>, at the higher temperatures of 55 and 70 °C.

### Recommendations

- A complete and thorough analysis of various kinetic parameters for the data presented in Tables 1 through 10 of this study should occur. Efforts should analyze the resulting composition data of each test in a comprehensive manner to obtain kinetic data for tetraphenylborate and the intermediates triphenylborane, diphenylborinic acid and phenylboronic acid.
- Researchers should perform rigorous calculations involving the temperature dependent equilibrium of KTPB and NaTPB solids coupled with the decomposition kinetics of soluble TPB<sup>-</sup> to show that the magnitudes of soluble potassium analyzed fall within the expected dissolution of solid KTPB.

### INTRODUCTION

The In-Tank Precipitation (ITP) process started radioactive operation in Tank 48H in August of 1995. High rates of sodium tetraphenylborate (NaTPB) decomposition and benzene generation were encountered approximately 2-3 months after beginning ITP operations.<sup>1,2</sup> Sodium tetraphenylborate exhibits known instability in the presence of copper.<sup>3</sup> Recent work indicates excess sodium tetraphenylborate in Tank 48H is susceptible to decomposition, with the rate strongly influenced by temperature.<sup>4</sup>

Preliminary data reported in Ref. 1 (specifically the tests described in Series 1 and 2 Sealed Stainless-Steel Bottle Tests on pages 51-59) indicate that aqueous (K,Na)TPB slurries in concentrated salt solutions can partially decompose on time-scales of several hundred hours in the presence of simulated sludge containing noble metals, monosodium titanate (MST), various soluble metals and organic additives at temperatures of 70 °C. Decomposition of the slurries, contained in air-sealed stainless-steel bottles, was evidenced by approximate complete loss of all soluble as well as insoluble NaTPB present in the original (K,Na)TPB slurry. The calculated losses of both TPB<sup>-</sup> and solid NaTPB were based on comparison with total measured soluble boron and benzene yields. The primary decomposition product was benzene. Other products analyzed in the above tests included soluble boron, phenylboronic acid (LPB) and the relatively stable final organic product phenol.

This report details the decomposition of aqueous (K,Na)TPB slurries in concentrated salt solutions using a more complete candidate catalyst recipe, extended testing temperatures (40-70 °C) and test durations of ~1500 hours (9 weeks). This study uses recently developed High-Pressure Liquid Chromatography (HPLC) methods for analysis of tetraphenylborate (TPB<sup>-</sup>), triphenylborane (3PB) and diphenylborinic acid (2PB). All of the present tests involve non-radioactive simulants and do not include investigations of radiolysis effects. The main objectives of the tests include:

- establishing the extent of TPB<sup>-</sup> decomposition reactions at lower temperatures (i.e., at 40 and 55 °C) than previously tested,
- demonstrating that the catalyst recipe provides an all-inclusive or near-complete set of additives from which statistically designed NaTPB decomposition tests can follow,<sup>5</sup>
- verifying this simulant recipe results in a reaction that approximates the current understanding of Tank 48H behavior in December 1995,<sup>6</sup> and
- investigating the effects of both sludge solids and monosodium titanate (MST) solids on tetraphenylborate decomposition.<sup>7</sup>

The following sections discuss the results of this study. Appendix A details the overall test design and experimental methods.

## RESULTS AND DISCUSSION

The extent of tetraphenylborate decomposition in the slurries was measured by the following methods. The slurries and vapor spaces were both analyzed for benzene. Filtrates from the slurries were also analyzed for soluble organic compounds and soluble boron. Tables 1 through 12 contain data sets for all twelve tests. Figures 1 through 14 depict these results.

Figures 1 to 5 show plots of the total measured benzene versus time. Figures 6 to 14 show plots of soluble organic compounds and soluble boron versus time. Figures 6 through 8 compare average values plotted from duplicate tests at 40 to 70 °C. The plots include two different measures of boron: measured total soluble boron determined from emission spectroscopy and cumulative soluble boron based on the sum of measured TPB<sup>-</sup>, 3PB, 2PB and 1PB.

### Benzene Production

#### Complete Catalyst Systems

Figures 1 to 3 show measured benzene for the duplicate systems tested at 40, 55 and 70 °C, respectively with the complete catalyst system present (Table A-2). Benzene data for the 40 °C duplicate tests appear consistent showing a steady increase with time, reaching maximum values approaching 2,500 mg/L. Benzene data for the 55 and 70 °C tests show considerable variability, reaching maximum values approaching 6,000 mg/L. Data recorded during these tests included vessel weights before and after incubation periods and gas chromatography (GC) calibration before and after each sampling. The GC calibration data

indicate a variability of about 6% or less over the total 1600 hour duration of these tests. Analysis of the vessel weights indicate possible benzene losses during testing. Researchers measured mass losses on the order of 0.1 to 0.3 grams between successive samplings for some of the tests at the higher temperatures of 55 and 70 °C. These magnitudes of weight loss account for the various decreases in benzene (i.e., about 1000 to 3500 mg/L) plotted in Figures 2 and 3. The observed benzene measurement variability also likely results from non-representative sampling of the slurries.

#### Incomplete Catalyst Systems

Benzene data for additional tests using less complete recipes at 55 to 70 °C showed roughly the same trends as tests performed at similar temperatures of 55 to 70 °C with all additives present. Figure 4 shows benzene data plotted for these tests. These data also reflect benzene losses of about 1000 to 2000 mg/L similar to those discussed above. In all tests shown in Figure 4, the maximum amount of benzene measured reached values in the range of 4,000 mg/L to 6,000 mg/L. Benzene data for the two slurries tested at 55 and 70 °C with no additives present show little benzene produced (typically < 50 mg/L) compared to levels approaching 6,000 mg/L detected in slurries tested with additives present. Hence, these benzene measurements do not conservatively represent the total benzene produced in these tests, given the observed mass losses and measurement variability resulting from non-representative sampling.

One may also express benzene yields as generation rates. Tables 1 through 12 provide these values, expressed in units of  $\mu\text{g}/(\text{L}\cdot\text{hr})$ . The benzene generation rates result from dividing the total benzene measured at a given time by the total number of hours in that time interval from the start of the tests. The range in benzene generation rates generally increases with temperature although much scatter exists in measured benzene levels. The maximum rates ranged from 1700-1900  $\mu\text{g}/(\text{L}\cdot\text{hr})$  at 40 °C, 5500-7000  $\mu\text{g}/(\text{L}\cdot\text{hr})$  at 55 °C and 6300-15900  $\mu\text{g}/(\text{L}\cdot\text{hr})$  at 70 °C.

#### Tetraphenylborate Decomposition and Soluble Boron Production

Several trends occurred for the expected increase in the rate of NaTPB decomposition with temperature from 40 to 70 °C. As temperature increases, the rate of loss of soluble  $\text{TPB}^-$  increases, the peak concentrations of all boron-containing organic intermediates occurs earlier in time and the rate of boron appearance, measured as total soluble boron in solution, steadily increases. These trends are shown in Figures 6 through 8 and the data are contained in Tables 1 through 6. Appearance of soluble boron in the reaction mixtures in amounts greater than the initial soluble  $\text{TPB}^-$  indicates production of phenyl borate intermediates and boric acid either from decomposition of soluble  $\text{TPB}^-$  with subsequent dissolution of solid tetraphenylborates or from direct decomposition of the solid. One can measure soluble boron directly by ICP-ES (see Tables 1-12, 'Boron (ICP-ES)') or by HPLC measurements of phenyl borates (see Tables 1-12, 'Boron (from organics)'). These two methods are represented by the equations below.

- Soluble boron (ICP-ES):  $= \text{TPB}^- + 3\text{PB} + 2\text{PB} + 1\text{PB} + \text{Boric Acid}$
- Soluble boron (HPLC):  $= \text{TPB}^- + 3\text{PB} + 2\text{PB} + 1\text{PB}$

Table 13 summarizes the initial rates of NaTPB decomposition calculated from these boron measurements over the first 168 hr of testing. Note that these rates are calculated using only two data points involving measured boron concentrations at 0 and 168 hr. The two different boron rate measurement values agree reasonably well for each individual test at the lower temperatures (i.e., 40 and 55 °C). The data shown in Table 13 for the duplicate systems tested at 40 to 70 °C with all additives present (see Tests 1 through 6) indicate that the soluble boron production rates increase with temperature. Based on ICP-ES boron data, the average rates increase from about  $2.0 \times 10^{-5}$  mole/(L\*hr) to  $5.5 \times 10^{-5}$  mole/(L\*hr) to  $7.8 \times 10^{-5}$  mole/(L\*hr) for the respective temperatures of 40, 55 and 70 °C. Note that the duplicate tests at 55 °C show rather good precision. However, at 40 °C and 70 °C the range of total boron appearance rates show a relatively large variability (i.e., 0.92 to  $3.08 \times 10^{-5}$  mole/(L\*hr) at 55 °C and 4.8 to  $10.8 \times 10^{-5}$  mole/(L\*hr) at 70 °C). The lower value of  $4.8 \times 10^{-5}$  mole/(L\*hr) at 70 °C demonstrates a low bias value since this value falls below the average of about  $5.5 \times 10^{-5}$  mole/(L\*hr) at 55 °C.

Using the average rate values for the 40 and 55 °C tests and the higher rate value for the 70 °C test, these initial boron appearance rates increase by about factors of 2.7X and 2.0X, respectively, as the temperature increases from 40 to 55 °C and from 55 to 70 °C. These increases in rate resemble the standard kinetic 'rule of thumb' involving roughly a 2X increase in reaction rate for every 10 °C increase in temperature.

The boron appearance rates based on measured phenyl borates (i.e., HPLC) at 70 °C show better precision than those based on ICP-ES at 70 °C. However this HPLC-derived average rate of about  $4 \times 10^{-5}$  mole/(L\*hr) is lower than either rate calculated from ICP-ES data (i.e., 4.8 to  $10.8 \times 10^{-5}$  mole/(L\*hr)). This average rate at 70 °C based on measured phenyl borates is also lower than the average boron rate of about  $5.2 \times 10^{-5}$  mole/(L\*hr) calculated at 55 °C from the measured phenyl borates. One possible explanation for observed decrease in boron appearance rates calculated from the boron measured as the phenyl borates at 70 °C could be the accompanying relatively prompt decomposition of the intermediates 3PB, 2PB and 1PB on the time-scale of the initial 100 to 200 hours of testing. For instance, related testing on the copper catalyzed decomposition of these intermediates at 70 °C indicate all three intermediates can decompose to final organic products benzene and phenol (i.e., organic compounds not containing boron) at reaction times < 200 hours.<sup>8</sup>

Table 13 gives negative values for soluble boron appearance rates in the control samples. The two control samples maintained at 55 and 70 °C with no additives present showed a significant decrease in soluble TPB<sup>-</sup>, from an initial average value of 150 mg/L to about 60 mg/L, over the first 96 hours of testing at elevated temperatures. The soluble TPB<sup>-</sup> values were relatively constant at 60 mg/L observed from 96 hours until the end of testing (see Tables 11 and 12). Since the original analyses (i.e., the 'time zero' data) were performed on filtrates from the initial slurries immediately after slurry preparation at ambient temperatures, the observed decrease in soluble TPB<sup>-</sup> over the first 96 hours of testing at 55 to 70 °C probably represents precipitation of



soluble TPB<sup>-</sup>. The soluble boron data also reflect this interpretation. Data from Tables 11 and 12, plotted in Figures 13 and 14, indicate that soluble boron decreased in the initial 96 hr. The remaining boron data vary around  $(2.3 \pm 0.5) \times 10^{-3}$  mole/L for 55 °C and  $(2.1 \pm 0.5) \times 10^{-3}$  mole/L for 70 °C. The above results indicate that the slurries were not at equilibrium at the start of testing.

There appears a significant decrease in soluble boron for the last data set at both temperatures as shown in Figures 13 and 14. However, the TPB<sup>-</sup> data does not reflect this decrease, as was the case for the initial 96 hour time period. The variations listed above in soluble boron for these control samples at 55 and 70 °C represent much less than the total soluble boron increases observed for the tests containing all additives at 55 and 70 °C (i.e., soluble boron levels reached about  $3.5 \times 10^{-2}$  mole/L and  $4.3 \times 10^{-2}$  mole/L at 55 and 70 °C, respectively).

#### Activation Energy Determination

A simplified kinetic analysis<sup>9</sup> of the soluble boron rate data in Tables 1 through 6 was performed. A rigorous analysis of this data will follow in a subsequent report. One may estimate the average rate constant for first-order decomposition of NaTPB from the data for increasing soluble boron. Restricting the analysis to the first ~168 hr of data in a given experiment ensures the presence of solid NaTPB. Also the initial boron appearance rates are calculated over 168 hr (instead of the initial 96 hr) since the above mentioned precipitation appears to have complete by 96 hr of testing. Other assumptions in this treatment include a rapid dissolution of solids replenishes the solution with TPB<sup>-</sup> and that the decomposition of a mole of NaTPB produces a mole of soluble boron, neglecting any precipitation of the ultimate borate product. Under these assumptions, dividing the rate of increase in soluble boron by the initial (saturated) TPB<sup>-</sup> concentration yields an apparent first-order rate constant for the decomposition of NaTPB. (Note: Given the lack of knowledge of the dissolution rates of NaTPB in these static systems, the derived rate constant serves only as a crude measure for the data set. This method of calculation will provide significant negative bias in the estimated rate constants.)

Two columns of Table 13 provide estimates for these first-order rate constants for the respective sets of boron measurements (i.e., via HPLC or ICP-ES, respectively). Figure 15 shows a plot of the logs of these rate constants from the ICP-ES data versus temperature. Figure 15 indicates an activation energy for NaTPB decomposition of about  $43 \pm 20$  kJ/mole for the temperature range of 40 to 70 °C.

The value of 43 kJ/mole for the activation energy determined in this study for decomposition of NaTPB in the presence of many potential catalysts including copper, remains lower than activation energies determined from copper catalyzed TPB<sup>-</sup> decomposition in aqueous solutions.<sup>10</sup> Activation energies reported in those studies ranged between 86 kJ/mole and 140 kJ/mole. The present activation energies also remain lower than recently reported values determined for copper catalyzed decomposition of the intermediate species 3PB, 2PB and 1PB in aqueous solutions.<sup>8</sup> Activation energies reported in those studies ranged between 82 kJ/mole and 107 kJ/mole.

Several factors could contribute to the apparent reaction rates and thus affect the activation energies determined in this work. The temperature dependent tetraphenylborate rate of dissolution, the presence of both organic tetraphenylborate solids and inorganic (sludge and MST) solids, and the presence of potential catalytic species in addition to copper could all possibly contribute to the observed activation energy determination. The lower activation energy suggests presence of a more effective catalyst than copper.

The kinetic analysis of NaTPB decomposition discussed above strongly depends on the temperature dependent rate of dissolution of solid NaTPB to form soluble TPB<sup>-</sup> in these slurries.<sup>11</sup> A more complete and thorough analysis of various kinetic parameters for the data presented in Tables 1 through 10 of this study will follow.<sup>12</sup> These efforts will analyze the resulting composition data of each test in a comprehensive manner to obtain kinetic data for tetraphenylborate and the intermediates triphenylborane, diphenylborinic acid and phenylboronic acid. These analyses include an empirically derived fitting term based on the measured rate of soluble boron appearance into solution.

#### Variability of Duplicate Tests

The variability of duplicate tests in these studies establishes a basis for analysis of future catalyst identification tests conducted under similar conditions. A measure of the repeatability allows one to judge whether or not minor changes, such as removing one or more potential catalysts species from a comprehensive recipe, has a measurable effect on the observed decomposition. Note that the present tests used static conditions with minimal mixing during most of the reaction time. Continuous mixing of the slurry samples during testing would improve precision of replicate tests. Data previously shown in Table 13 representing the initial soluble boron appearance rates (i.e., rates calculated over first 168 hr) for boron indicate poor precision between duplicate tests for two of the data sets at 40 and 70 °C. Since all of these systems used predominately static environments, a better measure of the variability in these tests would consider decomposition product production rates over larger time increments more representative of the total 1600 hours of testing.

The author reports two measures of variability for duplicate tests performed at 40 to 70 °C. The final, relatively stable decomposition products phenol and soluble boron (i.e., these two product species which do not show formation and subsequent decay behavior similar to the more transient species 3PB, 2PB and 1PB) were compared from the duplicate slurries tested in the temperature range of 40 to 70 °C at various time periods (432, 1008 and 1600 hr) of the tests. Table 14 gives these comparisons. Phenol concentration levels show relative standard deviations (%RSD) in the range of 4% to 25% at 40 °C and 2% to 13% at 70 °C. The same %RSD measure is higher for the 55 °C phenol test data. The values of phenol concentrations in Test 3 at 55 °C appear possibly low-biased data considering Test 4 at 55 °C gives final phenol values that fall within the average of the 40 and 70 °C final phenol average concentrations.

Boron concentration levels show relative standard deviations in the range of 6% to 15% at 40 °C, 3% to 14% at 55 °C and 16% to 17% at 70 °C. Note that agreement of the 55 °C boron data further suggests a bias in the 55 °C data for phenol. This measure of variability involving

soluble boron likely better indicates NaTPB decomposition than the phenol measure since soluble boron directly results from decomposition. In contrast, phenol forms as a result of several intermediate decomposition steps influenced by the presence of oxygen.

#### **Influence of Solid Additives on NaTPB Decomposition**

Tests 7 to 10 investigate the influence of solid sludge additives (i.e., Tests 8 and 10) and solid sludge and monosodium titanate (MST) additives (i.e., Tests 7 and 9) on NaTPB decomposition. Tests 7 through 10 included both sets of soluble organic and metal additives shown in Table A-2 of Appendix A. Note also from Table A-2 that about 20% of the total noble metals Ru, Pd and Rh come from the soluble metal additives group (i.e., removal of sludge solids does not remove all noble metals from the comprehensive recipe). The effect of various additives discussed below derive from data shown in Tables 3 through 10 and plotted in Figures 7 through 12 and Figures 16 through 19. The initial rates of increase in soluble boron concentrations from Table 13 also aid in the discussion of these effects.

#### **Effects of Solid MST Additives**

For both the 55 and 70 °C tests, the effects of MST addition on TPB decomposition do not appear significant. Figure 16 repeats some of the data from Figure 10 (Test 8, no MST added) and Figure 7 (Tests 3 and 4, all additives present) for the 55 °C tests for comparison. Figure 16 shows little difference in the kinetic behavior and concentration magnitudes of both total soluble boron (ICP-ES) and the phenyl borates (HPLC). Figure 17 repeats some of the data from Figure 12 (Test 10, no MST added) and Figure 8 (Tests 5 and 6, all additives present) for the 70 °C tests for comparison. Figure 17 shows little difference in the kinetic behavior and concentration magnitudes of both total soluble boron (ICP-ES) and the phenyl borates (HPLC).

Recall that data plotted as solid squares and open squares in both Figures 16 and 17 represent average values from duplicate samples with some associated variability at each point in time. The data from each test without MST solids at 55 °C (Test 8) and 70 °C (Test 10) fall within the range of the comparable average (plus or minus one standard deviation) calculated from the duplicate tests. Table 15 gives the comparisons suggested above using total soluble boron data at various time intervals. Removal of the solid MST additive does not significantly alter these boron concentration levels.

Similar conclusions to those reached above arise from visual inspection of the concentration plots and by comparison of the kinetic data shown in Table 13. (Table 15 also provides this data for comparison.) Initial boron production rates appear similar, though higher, for Test 8 (no MST added) compared to the average of duplicate Tests 3 and 4 (all additives present) for the 55 °C tests. Soluble boron production rates seem similar, and also higher, for Test 10 (no MST added) compared to the average from duplicate Tests 5 and 6 (all additives present) for the 70 °C tests.

Processes involving energy deposition into systems containing certain titanate materials can produce catalytically active surfaces on the titanate solids. The forms of energy deposition most often studied include either photolytic or radiolytic. As indicated in the

introduction of the present study, this study did not allow for any synergistic activity due to presence of monosodium titanate in a radiation field.

#### Effects of Solid Sludge Additives

For the 55 °C tests, the effects of solid sludge additives on NaTPB decomposition do not appear significant. Figure 18 repeats some of the data from Figure 9 (Test 7, soluble additives only) and Figure 7 (Tests 3 and 4, all additives present) for the 55 °C tests for comparison. Figure 18 shows insignificant differences in the kinetic behavior and concentration magnitudes of both total soluble boron (ICP-ES) and the phenyl borates (HPLC). Recall that data plotted as solid squares and open squares Figures 18 are average values from duplicate samples with some associated variability at each point in time. Table 15 provides the comparisons of soluble boron concentrations at various time intervals and initial appearance rates. Removal of solid additives from the comprehensive recipe had the effect of decreasing the final soluble boron levels at 55 °C by only about 15% or less when compared to the average values from the comprehensive catalyst systems at 55 °C.

For the 70 °C tests, Figure 19 repeats some of the data from Figure 11 (Test 9, soluble additives only) and Figure 8 (Tests 5 and 6, all additives present) for comparison. Figure 19 shows measurable differences in the concentration magnitudes of total soluble boron (ICP-ES). (Table 15 also provides the comparisons above using boron (ICP-ES) data.) Removal of solid additives from the comprehensive recipe had the effect of decreasing soluble boron levels at 70 °C by about 25%, when compared to the average values from the comprehensive catalyst systems at 70 °C. Comparison of the phenyl borate data plotted in Figure 19 also indicate that phenyl borate species persisted at longer times in Test 9 with soluble additives only. This indicates a less reactive system compared to the Tests 5 and 6 that contained the comprehensive catalyst system.

Similar conclusions to those reached above, arising from visual inspection of the concentration plots, can be reached by comparison of the kinetic data shown in Table 13 (or Table 15). A soluble boron production rate of  $4.8 \times 10^{-5}$  mole/(L\*hr) at 55 °C for Test 7 (soluble additives only) is only slightly lower compared to the average rate of  $5.5 \times 10^{-5}$  mole/(L\*hr) from duplicate Tests 3 and 4 containing all additives at 55 °C. A soluble boron production rate of  $3.8 \times 10^{-5}$  mole/(L\*hr) at 70 °C for Test 9 (soluble additives only) is lower compared to the average rate of  $7.8 \times 10^{-5}$  mole/(L\*hr) from duplicate Tests 5 and 6 containing all additives at 70 °C.

From the above discussion, effects observed in the absence of solid additives (i.e., less overall NaTPB decomposition as concluded from comparison of soluble boron values) are shown to be only marginally significant in the 55 °C data and significant in the 70 °C data when sludge solids were excluded. It follows that this effect results from the lack of sludge solids instead of the lack of MST solids.

## Analyses of Slurries for NaTPB Solids and Potassium Ion

### Initial Attempts to Analyze for NaTPB Solids

Researchers analyzed slurry samples at the completion of the decomposition tests for the presence of both NaTPB solids and soluble potassium ion. The original slurry used for all test samples was also analyzed. This original slurry was maintained at ambient temperature for the duration of the tests. NaTPB solids were analyzed by diluting a small amount of (K,Na)TPB slurry with deionized water (about 1 gram of slurry mixed with 5 mL of water), followed by agitation, filtration and analysis of the resulting filtrate for TPB<sup>-</sup>. Dilution of the (K,Na)TPB slurry with water would allow the more soluble NaTPB to readily dissolve leaving the much less soluble KTPB as solid. Results from these tests indicate that not all of the solid NaTPB was dissolved. For instance, the original slurry tested in the procedure above indicated only about one third of the targeted amount of NaTPB was found to be present in the slurry. Table 16 reports the results of these slurry dissolution tests in a qualitative manner only (i.e., dissolved NaTPB present (yes) or not present (no) above HPLC analytical detection limits of about 20 mg/L).

### Repeat Analyses for NaTPB Solids from Original Batch Slurry

The dissolution testing was repeated in duplicate with the original slurry. Unfortunately, the reacted slurries from Tests 1 to 12 had been disposed at the time of this follow-up analysis. A larger volume of dilution water, 40 mL compared to 5 mL previously, was used in dissolving the 1 gram slurry portions. As shown in Table 16, this increased dilution measure of NaTPB solids indicates  $12,300 \pm 600$  mg/L NaTPB solid present in the original slurry (compared to only 7,200 mg/L NaTPB solids measured from the previous single analysis of original slurry). This latter measure appears more accurate since a larger dilution water volume was used and the diluted slurries were stirred for at least 12 hours before filtration and submission for TPB<sup>-</sup> analysis.

The last column of Table 16 also shows the calculated equivalent amounts of NaTPB represented by the soluble boron measured via ICP-ES in the filtrates. These calculations indicate that 6,240 mg/L at 40 °C, 10,560 mg/L at 55 °C and 13,680 mg/L at 70 °C solid NaTPB decomposed during testing. Comparing these values to the experimentally determined value of about 12,300 mg/L NaTPB solids in the original slurry indicates that about 50%, 85% and 100% of the NaTPB solids decomposed at 40, 55 and 70 °C, respectively. Note that the 13,320 mg/L to 13,680 mg/L NaTPB solids calculated to have dissolved/decomposed in the 70 °C tests slightly exceeds the calculated  $12,300 \pm 600$  mg/L total NaTPB solid experimentally determined (based on soluble TPB<sup>-</sup> data) in the repeat analyses of the original slurry. This difference may reflect additional dissolution of KTPB solids at the higher temperatures of 55 and 70 °C (see below).

### Potassium Analyses from Slurry Filtrates

Researchers also obtained potassium analyses from filtrates of the fully reacted slurries with no dilutions involved. The original slurry was also tested. Table 17 shows the results from these analyses in the first column of numerical data. The second column of numerical data indicate the corresponding amounts of equivalent KTPB dissolved during testing. Table 17 also repeats some of the data shown previously in

Table 16 for equivalent NaTPB dissolved based on final soluble boron data for comparison. Data shown in Table 17 indicate very little soluble potassium ion present in the original slurry, the control test slurries at 55 and 70 °C containing no additives, and the slurries tested at 40 °C with additives present. As shown in Table 17 these low levels of soluble potassium of less than about 3.7 mg/L in the slurry filtrates indicate that less than 36 mg/L of the original targeted 48,000 mg/L KTPB solids dissolved over the 1600 hours of testing in either the control test slurries at 55 and 70 °C containing no additives, or the slurries tested at 40 °C with all additives present. Recall data in Table 16 show that there was excess NaTPB also present in these slurries.

Potassium data for all final test samples with additives present at temperatures of 55 and 70 °C indicate that varying amounts of the targeted original 4.0 wt % KTPB solids (or 48,000 mg/L KTPB solids) dissolved during testing. These values approached 1,920 mg/L KTPB at 55 °C and 4,656 mg/L KTPB solids at 70 °C. Note from Tables 3 through 10 that the soluble TPB<sup>-</sup> values for these final test samples were all below the HPLC detection limits of about 20 mg/L. The amounts of potassium found in the filtrates (ranging from 6.6 to 506 mg/L) exceed the equilibrium values calculated from the KTPB solubility product constant ( $K_{sp}$ ) at 55 and 70 °C.<sup>11</sup> Using the temperature dependent equation for calculation of  $K_{sp}$  for KTPB and the experimentally determined activity coefficients found in Ref. 11, one can show based on KTPB solubility alone that less than 2 mg/L of soluble potassium would be expected in these slurries. These calculations assume that all NaTPB has been decomposed. Table 17 shows that measured values of potassium approached about 209 mg/L and 506 mg/L, respectively, at 55 to 70 °C.

The presence of soluble potassium at the measured levels in these slurries indicates either solid KTPB decomposition or decomposition of essentially all excess NaTPB with subsequent dissolution of KTPB solids. Preliminary calculations involving the temperature dependent dissolution equilibrium of KTPB and NaTPB solids<sup>11</sup> coupled with the decomposition kinetics of soluble TPB<sup>-</sup> indicate that the magnitudes of soluble potassium analyzed fall within the expected dissolution of solid KTPB. Dissolution of solid KTPB would occur as the solid NaTPB fully depletes from these slurries by decomposition of soluble TPB<sup>-</sup> in solution. Note that the two tests showing highest amounts of NaTPB decomposition (i.e., Tests 5 and 10 at 70 °C in Table 16) also show the highest amounts of analyzed soluble potassium (i.e., Tests 5 and 10 in Table 17).

#### **Comparison of Present (K,Na)TPB Slurry Decomposition Tests with Previous Tank 48H Data**

The main objectives of the present study were to establish the extent of tetraphenylborate decomposition reactions in the temperature range of 40 to 70 °C over about 1500 hours of testing, and to demonstrate that the catalyst recipe tested provides an all-inclusive or near-complete set of additives from which statistically designed catalyst identification tests could follow.<sup>5</sup> The present tests were conducted to verify this simulatant recipe results in a reaction that approximates current understanding of Tank 48H behavior in December of 1995. Comparison of several measured decomposition products in the present tests with similar measurements from Tank 48H provide verification that the present

simulant recipe does indeed result in reaction similar to that observed previously in Tank 48H.

Table 18 shows a comparison of relevant data from the present tests at 40 to 55 °C to data obtained from Tank 48H. All Tank 48H data shown in Table 18 come from a previous report (see specifically Figure 3 and Table 2 from Ref. 1). Data in the present study were collected over a testing period of about 1600 hours or 66 days. The Tank 48H data was collected over an approximate time period of six months or 180 days from October 12, 1995 until April 15 of 1996 (see Table 2 of Ref. 1). The magnitudes of all species shown in Table 18 represent maximum amounts produced over the approximate time periods indicated. Table 18 also shows estimated production rates of the various species over the appropriate time periods for comparison.

The organic decomposition products benzene, 1PB and soluble boron reach comparable concentration levels when comparing data from Tank 48H to data from the present studies at constant temperatures of 40 and 55 °C. In most cases, the estimated rates of production for the various species also compare favorably. Phenol production in the laboratory tests at 40 or 55 °C, however, at least tripled that of Tank 48H. This difference presumably results from higher levels of air present in the air-sealed bottle tests relative to the more inerted atmosphere in Tank 48H (see discussion below on 'Differences in Present Tests Compared to Tank 48H').

Potassium measures are comparable for the Tank 48H data and the 40 °C tests, whereas higher potassium rates were observed in the 55 °C tests. Tank 48H recorded temperatures ranged from 33 to 52 °C from August 31, 1995 to mid-November of 1995. The tank temperatures steadily decreased to about 25 °C by mid-December and remained at the lower level until April of 1996. The time-profile of temperatures recorded in Tank 48H proves important when comparing data from Tank 48H to the present laboratory tests. Significant increases in soluble boron, 1PB and phenol existed in Tank 48H at the beginning of December, 1995 (see Table 2 of Ref. 1), indicating some decomposition. Samples obtained from Tank 48H on December 18 indicated that more than 95% of the excess NaTPB had decomposed.<sup>1</sup> Thus most of the decomposition appears to have taken place in Tank 48H during the relatively high temperature (33 to 52 °C) period preceding the mid-December (and latter) temperatures of 25 °C. Therefore this temperature range of 33 to 52 °C compares reasonably well to the two present data sets at 40 and 55 °C used in Table 18 of this report. The potassium data for the 55 °C tests especially reflect these comparisons when contrasted to the amounts of potassium produced in the Tank 48H samples or the 40 °C data. Rates in Tank 48H remained much lower because the temperature remained low after consumption of excess TPB<sup>-</sup>.

#### Differences in Present Tests Compared to Tank 48H

Although the present tests simulate the slurries and additives thought present in Tank 48H, there exists several differences in the present studies and the conditions of Tank 48H. The present investigation did not involve any radiation effects on the thermal catalytic NaTPB decomposition. The radiation field calculated in Tank 48H, about 24,000 rad/day, would contribute some  $7.25 \times 10^5$  rads of accumulated dose over each month.<sup>1</sup> The effects of these levels of ionizing radiation on the chemical decomposition involving potential catalytic species present in

current tests has yet to be studied in the temperature range of 40 to 55 °C. Previous testing<sup>1</sup> at 70 °C concluded that simulated doses did not have significant effects on NaTPB decomposition using a potential catalyst recipe nearly identical to the one used in this most recent work (see Table A-2).

Another difference in these tests was the relative abundance of oxygen from air contained within the sealed slurries in the laboratory tests. About 5 to 10 cc of air was introduced into these systems each time an analysis was performed. In contrast, Tank 48H atmosphere was predominately inerted with nitrogen to attain a nominal 5 vol% oxygen. During the time period from early October 1995 to April 1995, air was present in Tank 48H for only two relatively brief ~ 5 day periods. During these two periods in which nitrogen ventilation was halted, the atmosphere was measured to contain 20 vol% and 10 vol% oxygen, respectively. At all other times the atmosphere was measured to contain about 5 vol% oxygen (see Figure 4 of Ref. 1). The effects of oxygen on the copper catalyzed decomposition of TPB<sup>-</sup> in homogeneous aqueous solutions have recently been reported.<sup>10,13</sup> Oxygen was found to inhibit the overall decomposition of TPB<sup>-</sup> in the copper-only studies.

The specific preparation of the mixed (K,Na)TPB slurry systems also differed in these investigations compared to Tank 48H processes. This study involved preparation of the mixed (K,Na)TPB solids in alkaline solution by adding concentrated soluble TPB<sup>-</sup> solutions to a potassium-containing caustic solution, thereby forming the slurry targeted to contain approximately 5.5 wt % (K,Na)TPB solids. The slurry preparation was complete in about one hour. The remaining salts were then mixed into the slurry within about one hour. Finally, the various potentially catalytic additives (see Table A-2) were added in just prior to testing. In Tank 48H a concentrated caustic soluble TPB<sup>-</sup> solution is typically added to an existing slurry containing approximately 1 wt % (K,Na)TPB solids, in the waste tank containing all of the potential catalytic additives.<sup>1</sup> The tank contents are then mixed to promote precipitation. The details of addition and mixing order related to these two different procedures, and any effects this order might have on the onset and rate of TPB<sup>-</sup> decomposition in the presence of potential catalytic species, have not been studied.

## CONCLUSIONS

Researchers studied the thermal catalytic decomposition of tetraphenylborate in mixed (K,Na)TPB slurries contained in concentrated salt solutions between 40 and 70 °C. The slurries contained additives thought to comprehensively represent feeds to Tank 48H. Comparison of several measures of tetraphenylborate decomposition for this study and previous Tank 48H activities indicates that the present simulant recipe does result in reaction similar to that observed previously in Tank 48H. The activation energy for decomposition of NaTPB in the slurries is  $43 \pm 20$  kJ/mole in the temperature range of 40 to 70 °C.

Removing both solid sludge additives and solid monosodium titanate additives from the comprehensive potential catalytic recipe resulted in lower decomposition rates and decreased magnitudes of soluble boron products at 70 °C. The decreases in NaTPB decomposition were found less significant (i.e., effects less than 15%) at 55 °C. The effects were about 25% at 70 °C when compared to the averages of duplicate tests



containing all additives. When only solid monosodium titanate was removed from the comprehensive potential catalytic recipe, no significant effects on decomposition were observed relative to decomposition observed using the comprehensive potential catalysts recipe at 55 and 70 °C.

Thus the present tests suggest that solid MST additives do not contribute significantly to NaTPB decomposition. From these preliminary tests, it can be assumed that solid sludge additives used in these particular experiments, which contained portions of the total noble metals and a portion of the total copper, do increase NaTPB decomposition. The effects were less apparent at 55 °C. It remains to be seen whether these effects observed with the solid sludge are due to the increased amounts of copper, increased amounts of noble metals, or whether the sludge solids provide a heterogeneous catalysis reaction site. Current catalyst identification tests using sludges formulated without copper present will address these questions.<sup>5</sup>

Duplicate slurries tested as static, unstirred systems with the comprehensive catalyst recipe in the temperature range of 40 to 70 °C indicate variability of 2% to 25% and 3% to 17% in measurements of phenol and soluble boron, respectively. This level of variability can be used to judge in future decomposition tests the relative effects of specific additives on the catalytic chemical processes. As suggested in the text, boron analyses are considered a better measure of decomposition since phenol production is influenced by oxygen content.

Measurable amounts of NaTPB solids were detected in slurries tested at 40 and 55 °C for 1600 hours, indicating incomplete decomposition of the targeted starting 18,000 mg/L NaTPB solids. Similar analyses indicate possible complete decomposition of NaTPB at 70 °C in certain tests. Theoretical amounts of decomposed NaTPB based on soluble boron analyses in the fully reacted 70 °C tests approached 13,680 mg/L, which were slightly higher than the measured amounts of NaTPB equal to  $12,300 \pm 600$  mg/L determined from dissolution of the original slurry.

Insignificant amounts of potassium ion were detected in filtrates of reacted slurries containing potential catalytic additives at 40 °C for 1600 hours and in filtrates of reacted slurries containing no additives at 55 and 70 °C for 1600 hours. This is consistent with the presence of excess NaTPB. Similar analyses showed measurable amounts of potassium from filtrates of reacted slurries containing potential catalytic additives at both 55 and 70 °C for 1600 hours, indicating a maximum KTPB concentration of about 1,920 mg/L and 4,656 mg/L KTPB, respectively. These potassium amounts result from either decomposition of KTPB solids or TPB<sup>-</sup> decomposition and subsequent KTPB dissolution. These tests suggest that about 4% and 10% of the theoretical 4.0 wt % KTPB solids (or 48,000 mg/L KTPB solids) decomposed after 1600 hours of testing at the respective test temperatures of 55 and 70 °C. Preliminary calculations involving the temperature dependent solubility equilibrium of KTPB indicate that decomposition of TPB<sup>-</sup> and KTPB dissolution processes may adequately explain the observed concentrations of soluble potassium at these higher temperatures of 55 and 70 °C.

## APPROVALS

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(per Manual E7, Procedure 2.40)

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Table 1 Test 1: 40 °C, Soluble organics and metals, Solid sludge and MST additives

Reaction Time (hr)	Benzene (mg/L)	Benzene Rate ( $\mu\text{g}/(\text{L}\cdot\text{hr})$ )	TPB- (mole/L)	3PB (mole/L)	2PB (mole/L)	PBA (mole/L)	Phenol (mole/L)	Soluble Boron (mole/L) Boron(KP-ES)	Boron (mole/L) (from organics)	Equivalent NaTPB(mg/L)
0	45	—	4.78E-04	2.64E-04	1.42E-04	1.64E-04	7.23E-04	4.18E-03	1.05E-03	1431
96	39	0	3.20E-04	5.53E-04	9.86E-04	1.16E-03	1.93E-03	4.71E-03	3.02E-03	1813
168	379	1988	2.51E-04	1.42E-03	3.33E-03	2.51E-03	2.94E-03	9.36E-03	7.51E-03	3203
288	325	972	1.57E-04	1.23E-03	3.49E-03	4.41E-03	4.32E-03	1.04E-02	9.29E-03	3552
432	348	701	8.14E-05	1.16E-03	2.21E-03	4.97E-03	6.28E-03	1.31E-02	8.43E-03	4498
672	862	1216	7.52E-05	9.54E-04	1.24E-03	3.81E-03	8.85E-03	1.74E-02	6.08E-03	5957
1008	1274	1219	4.39E-05	4.71E-04	8.53E-04	2.46E-03	9.90E-03	2.00E-02	3.83E-03	6829
1296	2165	1636	0.00E+00	2.48E-04	7.77E-04	1.62E-03	1.33E-02	2.22E-02	2.64E-03	7613
1608	2034	1237	1.25E-05	1.11E-04	4.53E-04	9.43E-04	1.43E-02	2.26E-02	1.52E-03	7735
Rate Data			-1.63E-06	mole/(L·hr)			96 hrs	5.53E-06	2.05E-05	mole/(L·hr)
			-1.34E-06	mole/(L·hr)			168 hrs	3.08E-05	3.85E-05	mole/(L·hr)
			-1.11E-06	mole/(L·hr)			288 hrs	2.15E-05	2.86E-05	mole/(L·hr)

Table 2 Test 2: 40 °C, Soluble organics and metals, Solid sludge and MST additives

Reaction Time (hr)	Benzene (mg/L)	Benzene Rate ( $\mu\text{g}/(\text{L}\cdot\text{hr})$ )	TPB- (mole/L)	3PB (mole/L)	2PB (mole/L)	PBA (mole/L)	Phenol (mole/L)	Soluble Boron (mole/L) Boron(KP-ES)	Boron (mole/L) (from organics)	Equivalent NaTPB(mg/L)
0	45	—	4.78E-04	2.64E-04	1.42E-04	1.64E-04	7.23E-04	4.18E-03	1.05E-03	1431
96	68	240	3.54E-04	4.96E-04	3.42E-04	4.84E-04	1.19E-03	4.19E-03	1.68E-03	1434
168	247	1202	3.20E-04	8.22E-04	1.26E-03	1.26E-03	1.90E-03	5.72E-03	3.66E-03	1958
288	280	816	1.82E-04	9.95E-04	2.99E-03	2.88E-03	2.84E-03	8.69E-03	7.05E-03	2973
432	512	1081	1.83E-04	1.07E-03	2.44E-03	4.03E-03	4.39E-03	1.06E-02	7.71E-03	3633
672	1182	1692	1.13E-04	9.08E-04	1.51E-03	3.96E-03	7.23E-03	1.56E-02	6.49E-03	5322
1008	1519	1462	5.64E-05	4.63E-04	8.31E-04	2.47E-03	9.19E-03	1.73E-02	3.82E-03	5936
1296	2271	1718	2.82E-05	2.48E-04	6.40E-04	1.60E-03	1.21E-02	2.01E-02	2.51E-03	6876
1608	1343	807	0.00E+00	1.07E-04	4.13E-04	9.19E-04	1.34E-02	2.07E-02	1.44E-03	7069
Rate Data			-1.27E-06	mole/(L·hr)			96 hrs	8.67E-08	6.55E-06	mole/(L·hr)
			-9.32E-07	mole/(L·hr)			168 hrs	9.17E-06	1.56E-05	mole/(L·hr)
			-1.02E-06	mole/(L·hr)			288 hrs	1.56E-05	2.08E-05	mole/(L·hr)

Table 3 Test 3: 55 °C, Soluble organics and metals, Solid sludge and MST additives

Reaction Time (hr)	Benzene (mg/L)	Benzene (ug/L*hr)	TPB- (mol/L)	3PB (mol/L)	2PB (mol/L)	PBA (mol/L)	Phenol (mol/L)	Soluble Boron (mole/L) Boron(OP-ES)	(mole/L) Boron (from organics)	Equivalent NaTPB(mg/L)
0	45	-	4.76E-04	2.64E-04	1.42E-04	1.84E-04	7.23E-04	4.18E-03	1.05E-03	1431
96	89	458	1.82E-04	1.52E-03	3.58E-03	3.42E-03	2.92E-03	9.70E-03	8.70E-03	3320
168	976	5542	1.32E-04	1.18E-03	3.98E-03	5.83E-03	4.09E-03	1.34E-02	1.11E-02	4589
288	1046	3476	3.45E-05	5.24E-04	2.89E-03	9.09E-03	4.88E-03	1.67E-02	1.25E-02	5700
432	1165	2593	0.00E+00	1.65E-04	1.27E-03	1.11E-02	5.59E-03	1.95E-02	1.26E-02	8886
672	353	458	0.00E+00	0.00E+00	4.13E-04	8.84E-03	7.41E-03	2.89E-02	9.05E-03	9222
1008	524	475	0.00E+00	0.00E+00	2.27E-04	7.09E-03	7.34E-03	2.96E-02	7.31E-03	10143
1296	4980	3808	0.00E+00	0.00E+00	7.11E-05	1.57E-03	9.34E-03	3.99E-02	1.85E-03	11600
1608	2279	1389	0.00E+00	0.00E+00	4.89E-05	3.12E-04	1.04E-02	3.50E-02	3.61E-04	11976
Rate Data										
96 hrs			-3.07E-06	mole/(L*hr)			96 hrs	5.75E-05	7.97E-05	mole/(L*hr)
168 hrs			-2.05E-06	mole/(L*hr)			168 hrs	5.49E-05	6.00E-05	mole/(L*hr)
288 hrs			-1.53E-06	mole/(L*hr)			288 hrs	4.33E-05	3.99E-05	mole/(L*hr)

Table 4 Test 4: 55 °C, Soluble organics and metals, Solid sludge and MST additives

Reaction Time (hr)	Benzene (mg/L)	Benzene (ug/L*hr)	TPB- (mol/L)	3PB (mol/L)	2PB (mol/L)	PBA (mol/L)	Phenol (mol/L)	Soluble Boron (mole/L) Boron(OP-ES)	(mole/L) Boron (from organics)	Equivalent NaTPB(mg/L)
0	45	-	4.76E-04	2.64E-04	1.42E-04	1.84E-04	7.23E-04	4.18E-03	1.05E-03	1431
-96	72	281	2.26E-04	1.19E-03	1.99E-03	2.33E-03	2.64E-03	8.74E-03	5.73E-03	2990
168	842	4744	9.71E-05	1.59E-03	2.88E-03	4.05E-03	4.45E-03	1.36E-02	8.62E-03	4660
288	1252	4191	5.84E-05	1.20E-03	1.83E-03	4.12E-03	7.09E-03	1.78E-02	7.20E-03	6027
432	1577	3546	0.00E+00	4.58E-04	1.00E-03	2.62E-03	9.12E-03	2.04E-02	4.08E-03	6990
672	1660	2403	0.00E+00	0.00E+00	1.11E-04	9.10E-04	1.28E-02	2.66E-02	1.02E-03	8776
1008	1031	978	0.00E+00	5.37E-05	1.24E-04	3.36E-04	1.21E-02	2.85E-02	5.14E-04	9072
1296	5282	4041	0.00E+00	0.00E+00	1.84E-04	3.53E-04	1.43E-02	2.95E-02	5.17E-04	10098
1608	1959	1190	0.00E+00	0.00E+00	1.02E-04	0.00E+00	1.47E-02	2.85E-02	1.02E-04	9741
Rate Data										
96 hrs			-2.61E-06	mole/(L*hr)			96 hrs	4.74E-05	4.88E-05	mole/(L*hr)
168 hrs			-2.26E-06	mole/(L*hr)			168 hrs	5.61E-05	4.51E-05	mole/(L*hr)
288 hrs			-1.46E-06	mole/(L*hr)			288 hrs	4.66E-05	2.14E-05	mole/(L*hr)

Table 5 Test 5: 70 °C, Soluble organics and metals, Solid sludge and MST additives

Reaction Time (hr)	Benzene (mg/L)	Benzene Rate (ug/(L*hr))	(mol/L) TPB	(mol/L) 3PB	(mol/L) 2PB	(mol/L) PBA	(mol/L) Phenol	Soluble Boron (mole/L) Boron(ICP-ES)	Boron (mole/L) (from organics)	Equivalent NaTPB(mg/L)
0	45	--	4.76E-04	2.84E-04	1.42E-04	1.84E-04	7.23E-04	4.18E-03	1.05E-03	1431
96	47	21	9.71E-05	7.89E-04	2.67E-03	5.81E-03	4.76E-03	1.59E-02	9.38E-03	5427
168	1684	9756	1.57E-05	2.81E-04	1.67E-03	6.75E-03	7.75E-03	2.23E-02	8.72E-03	7617
288	1471	4951	0.00E+00	0.00E+00	4.62E-04	3.93E-03	1.04E-02	2.75E-02	4.39E-03	9412
432	1271	2838	0.00E+00	0.00E+00	1.38E-04	2.55E-03	1.08E-02	2.89E-02	2.69E-03	9882
672	348	451	0.00E+00	1.11E-04	2.31E-04	1.03E-03	1.14E-02	3.59E-02	1.37E-03	12277
1008	398	350	0.00E+00	0.00E+00	8.44E-05	9.92E-04	1.29E-02	3.72E-02	1.08E-03	12725
1296	3338	2541	0.00E+00	0.00E+00	5.78E-05	8.81E-04	1.49E-02	4.18E-02	7.38E-04	14305
1608	4423	2723	0.00E+00	0.00E+00	3.11E-05	7.87E-04	1.62E-02	4.33E-02	8.18E-04	14813
Rate Data			96 hrs 168 hrs 288 hrs	-3.95E-08 mole/(L*hr) -2.74E-08 mole/(L*hr) -1.65E-08 mole/(L*hr)				1.22E-04 1.08E-04 8.10E-05	8.89E-05 4.57E-05 1.16E-05	mole/(L*hr) mole/(L*hr) mole/(L*hr)

Table 6 Test 6: 70 °C, Soluble organics and metals, Solid sludge and MST additives

Reaction Time (hr)	Benzene (mg/L)	Benzene Rate (ug/(L*hr))	(mol/L) TPB	(mol/L) 3PB	(mol/L) 2PB	(mol/L) PBA	(mol/L) Phenol	Soluble Boron (mole/L) Boron(ICP-ES)	Boron (mole/L) (from organics)	Equivalent NaTPB(mg/L)
0	45	--	4.76E-04	2.84E-04	1.42E-04	1.84E-04	7.23E-04	4.18E-03	1.05E-03	1431
96	20	0	2.69E-04	5.53E-04	5.02E-04	6.48E-04	1.50E-03	6.08E-03	1.97E-03	2080
168	494	2673	9.08E-05	9.33E-04	2.54E-03	3.56E-03	4.18E-03	1.22E-02	7.12E-03	4192
288	1296	4344	1.67E-05	4.67E-04	1.00E-03	2.35E-03	6.53E-03	1.76E-02	3.84E-03	6039
432	1553	3491	0.00E+00	1.24E-04	3.91E-04	1.33E-03	9.05E-03	2.27E-02	1.84E-03	7762
672	1260	1808	0.00E+00	4.54E-05	2.49E-04	4.51E-04	1.16E-02	2.70E-02	7.45E-04	9256
1008	891	839	0.00E+00	0.00E+00	2.89E-04	1.06E-03	1.28E-02	2.98E-02	1.35E-03	10208
1296	4427	3381	0.00E+00	0.00E+00	8.88E-05	7.79E-04	1.45E-02	3.45E-02	8.68E-04	11800
1608	3114	1909	0.00E+00	0.00E+00	3.11E-05	2.05E-04	1.57E-02	3.46E-02	2.36E-04	11837
Rate Data			96 hrs 168 hrs 288 hrs	-2.15E-06 mole/(L*hr) -2.29E-06 mole/(L*hr) -1.60E-06 mole/(L*hr)				1.97E-05 4.80E-05 4.67E-05	9.65E-06 3.62E-05 9.68E-06	mole/(L*hr) mole/(L*hr) mole/(L*hr)

Table 7 Test 7: 55 °C, Soluble organics and metals additives

Reaction Time (hr)	Benzene (mg/L)	Benzene Rate ( $\mu\text{g}/(\text{L}\cdot\text{hr})$ )	TPB- (mol/L)	3PB (mol/L)	2PB (mol/L)	PBA (mol/L)	Phenol (mol/L)	Soluble Boron (mol/L) Boron(ICP-ES)	Boron (mol/L) (from organics)	Equivalent NaTPB(mg/L)
0	45	—	4.78E-04	2.64E-04	1.42E-04	1.84E-04	7.23E-04	4.18E-03	1.05E-03	1431
96	118	780	2.57E-04	2.13E-03	2.44E-03	1.76E-03	4.18E-03	1.05E-02	6.59E-03	3807
168	938	5315	1.79E-04	2.83E-03	3.01E-03	2.55E-03	5.57E-03	1.17E-02	8.57E-03	3989
288	1502	5059	1.13E-04	3.14E-03	2.95E-03	3.30E-03	7.73E-03	1.33E-02	9.50E-03	4555
432	1726	3891	7.20E-05	2.81E-03	2.42E-03	3.58E-03	9.62E-03	1.77E-02	8.87E-03	6073
672	2569	3756	2.82E-05	1.88E-03	1.77E-03	3.09E-03	1.34E-02	2.42E-02	6.75E-03	8284
1008	1874	1814	0.00E+00	7.68E-04	1.52E-03	1.88E-03	1.58E-02	2.48E-02	4.17E-03	8474
1296	4635	3542	0.00E+00	4.21E-04	3.02E-04	3.85E-04	1.91E-02	2.85E-02	1.11E-03	9748
1608	3061	1878	0.00E+00	2.89E-04	0.00E+00	1.84E-04	1.99E-02	2.86E-02	4.53E-04	9089
Rate Data										
96 hrs			-2.28E-06	mole/(L·hr)				6.82E-05	5.77E-05	mole/(L·hr)
168 hrs			-1.77E-06	mole/(L·hr)				4.45E-05	4.48E-05	mole/(L·hr)
288 hrs			-1.26E-06	mole/(L·hr)				3.17E-05	2.93E-05	mole/(L·hr)

Table 8 Test 8: 55 °C, Soluble organics and metals additives, Solid sludge Additives

Reaction Time (hr)	Benzene (mg/L)	Benzene Rate ( $\mu\text{g}/(\text{L}\cdot\text{hr})$ )	TPB- (mol/L)	3PB (mol/L)	2PB (mol/L)	PBA (mol/L)	Phenol (mol/L)	Soluble Boron (mol/L) Boron(ICP-ES)	Boron (mol/L) (from organics)	Equivalent NaTPB(mg/L)
0	45	—	4.78E-04	2.64E-04	1.42E-04	1.84E-04	7.23E-04	4.18E-03	1.05E-03	1431
96	101	583	1.72E-04	1.45E-03	4.09E-03	3.49E-03	3.00E-03	1.20E-02	9.21E-03	4111
168	1230	7054	5.95E-05	1.23E-03	4.99E-03	5.93E-03	5.27E-03	1.67E-02	1.22E-02	5706
288	1682	5884	9.40E-06	2.89E-04	3.81E-03	9.73E-03	6.08E-03	1.98E-02	1.38E-02	6785
432	1147	2551	0.00E+00	3.72E-05	9.84E-04	1.16E-02	7.23E-03	2.15E-02	1.26E-02	7368
672	845	1190	0.00E+00	0.00E+00	2.04E-04	8.04E-03	8.73E-03	2.95E-02	8.24E-03	10104
1008	752	701	0.00E+00	0.00E+00	1.11E-04	4.67E-03	9.52E-03	3.28E-02	4.79E-03	11158
1296	5359	4100	0.00E+00	0.00E+00	6.68E-05	9.19E-04	1.12E-02	3.71E-02	9.85E-04	12681
1608	3981	2435	0.00E+00	0.00E+00	4.89E-05	5.25E-04	1.20E-02	3.51E-02	5.74E-04	12028
Rate Data										
96 hrs			-3.17E-06	mole/(L·hr)				9.16E-05	8.50E-05	mole/(L·hr)
168 hrs			-2.48E-06	mole/(L·hr)				7.44E-05	6.65E-05	mole/(L·hr)
288 hrs			-1.62E-06	mole/(L·hr)				5.43E-05	4.44E-05	mole/(L·hr)

Table 9 Test 9: 70 °C, Soluble organics and metals additives

Reaction Time (hr)	Benzene (mg/L)	Benzene Rate (ug/(L*hr))	TPB- (mol/L)	3PB (mol/L)	2PB (mol/L)	PBA (mol/L)	Phenol (mol/L)	Soluble Boron (mole/L)	Boron (mole/L)	Equivalent NaTPB(mg/L)
0	45	--	4.76E-04	2.64E-04	1.42E-04	1.64E-04	7.23E-04	4.18E-03	1.05E-03	1431
96	67	229	2.29E-04	1.89E-03	1.43E-03	9.10E-04	2.58E-03	7.81E-03	4.46E-03	2673
168	1110	6339	1.91E-04	2.77E-03	1.60E-03	1.57E-03	4.41E-03	1.05E-02	6.14E-03	3594
288	1763	5965	1.25E-04	3.25E-03	1.54E-03	1.88E-03	6.02E-03	1.27E-02	6.79E-03	4342
432	2100	4757	5.64E-05	2.73E-03	1.63E-03	2.03E-03	8.32E-03	1.63E-02	8.45E-03	5569
672	2496	3647	0.00E+00	1.07E-03	1.86E-03	2.22E-03	1.08E-02	2.36E-02	5.15E-03	8082
1008	1299	1244	0.00E+00	1.73E-04	9.46E-04	1.60E-03	1.24E-02	2.65E-02	2.72E-03	9066
1296	5943	4551	0.00E+00	5.37E-05	1.95E-04	0.00E+00	1.47E-02	3.12E-02	2.49E-04	10887
1608	3606	2215	0.00E+00	0.00E+00	1.51E-04	0.00E+00	1.51E-02	2.94E-02	1.51E-04	10056
Rate Data			-2.68E-06	mole/(L*hr)				3.78E-05	3.56E-05	mole/(L*hr)
			-1.70E-06	mole/(L*hr)				3.76E-05	3.03E-05	mole/(L*hr)
			-1.22E-06	mole/(L*hr)				2.95E-05	1.99E-05	mole/(L*hr)

Table 10 Test 10: 70 °C, Soluble organics and metals, Solid sludge additives

Reaction Time (hr)	Benzene (mg/L)	Benzene Rate (ug/(L*hr))	TPB- (mol/L)	3PB (mol/L)	2PB (mol/L)	PBA (mol/L)	Phenol (mol/L)	Soluble Boron (mole/L)	Boron (mole/L)	Equivalent NaTPB(mg/L)
0	45	--	4.76E-04	2.64E-04	1.42E-04	1.64E-04	7.23E-04	4.18E-03	1.05E-03	1431
96	571	5479	2.38E-04	7.14E-04	1.44E-03	2.56E-03	3.69E-03	1.18E-02	4.95E-03	4042
168	2723	15940	4.39E-05	8.51E-04	3.13E-03	5.18E-03	6.51E-03	1.99E-02	9.05E-03	6815
288	2331	7938	0.00E+00	7.85E-05	1.34E-03	6.99E-03	7.10E-03	2.52E-02	6.79E-03	8614
432	827	1810	0.00E+00	0.00E+00	3.78E-04	6.77E-03	7.99E-03	2.86E-02	6.14E-03	9782
672	917	1298	0.00E+00	0.00E+00	1.55E-04	2.98E-03	8.70E-03	3.51E-02	3.12E-03	12001
1008	591	542	0.00E+00	0.00E+00	5.39E-05	1.78E-03	9.45E-03	3.89E-02	1.83E-03	13297
1296	5994	4590	0.00E+00	0.00E+00	2.67E-05	1.18E-03	1.03E-02	4.45E-02	1.21E-03	15227
1608	3949	2428	0.00E+00	0.00E+00	0.00E+00	8.12E-04	1.06E-02	4.41E-02	8.12E-04	15103
Rate Data			-2.48E-06	mole/(L*hr)				7.95E-05	4.07E-05	mole/(L*hr)
			-2.57E-06	mole/(L*hr)				9.36E-05	4.77E-05	mole/(L*hr)
			-1.22E-06	mole/(L*hr)				7.29E-05	1.99E-05	mole/(L*hr)





Table 13. Preliminary Kinetics Data for (K,Na)TPB Slurries Tested at 40 to 70 °C.

Test #	Temp. (°C)	Additives	Cumulative <sup>a</sup> Boron Rate (mole/(L*hr)) (x10 <sup>-5</sup> )	Pseudo first <sup>b</sup> Order Rate Constant, k' (hr <sup>-1</sup> )	Total Soluble <sup>c</sup> Boron Rate (mole/(L*hr)) (x10 <sup>-5</sup> )	Pseudo first <sup>b</sup> Order Rate Constant, k' (hr <sup>-1</sup> )
1	40	d	3.85	0.0808	3.08	0.0579
2	40	d	1.56	0.0327	0.92	0.0199
3	55	d	6.00	0.1260	5.49	0.1003
4	55	d	4.51	0.0946	5.61	0.1025
5	70	d	4.57	0.0959	10.80	0.1930
6	70	d	3.62	0.0759	4.80	0.0882
7	55	e	4.48	0.0941	4.45	0.0820
8	55	f	6.65	0.1396	7.44	0.1345
9	70	e	3.03	0.0637	3.76	0.0699
10	70	f	4.77	0.1001	9.36	0.1685
11 <sup>g</sup>	55	h	-0.16	<0.0001	-0.66	<0.0001
12 <sup>g</sup>	70	h	-0.16	<0.0001	-0.81	<0.0001

<sup>a</sup> Cumulative boron initial production rates calculated from boron produced in first 168 hours as boron-containing organics from HPLC analyses of the slurry filtrates. Note rates are based on only two data points (time = 0 and 168 hr).

<sup>b</sup> Obtained from equation,  $\text{Rate} = k[\text{TPB}^-][\text{Catalyst}]^n = k'[\text{TPB}]$ , where  $k' = k[\text{Catalyst}]^n$  using data from the first 168 hours. Note: This method of calculation provides a significant negative bias in the estimated rate constants.

<sup>c</sup> Total soluble boron initial production rates calculated from boron produced in first 168 hours as total soluble boron from ICP-ES analyses of the slurry filtrates. Note rates are based on only two data points (time = 0 and 168 hr).

<sup>d</sup> Soluble organics, soluble metals, solid sludge and solid MST added.

<sup>e</sup> Soluble organics, soluble metals.

<sup>f</sup> Soluble organics, soluble metals and solid sludge added (NO MST).

<sup>g</sup> The negative values for soluble boron appearance rates in these control samples result from the observed decrease in soluble TPB<sup>-</sup> over the initial 96 hours of testing.

<sup>h</sup> Control samples containing NO additives.

Table 14. Reproducibility of Duplicate Tests.<sup>a</sup>

Test #	Temp. (°C)	Additives	Phenol (mg/L)			Boron (mg/L)		
			(432)	Time, hr (1008)	(1608)	(432)	Time, hr (1008)	(1608)
1	40	b	589	932	1346	142	215	244
2	40	b	413	865	1264	114	187	223
Average			501	898	1305	128	201	233
Standard Deviation			124	47	57	20	20	14
%Relative Standard Deviation			25	5	4	15	10	6
3	55	b	526	691	981	210	320	378
4	55	b	858	1142	1381	220	286	307
Average			692	916	1181	215	303	343
Standard Deviation			234	319	282	7	24	49
%Relative Standard Deviation			34	35	24	3	8	14
5	70	b	1020	1217	1520	312	402	468
6	70	b	852	1202	1482	245	322	374
Average			936	1209	1501	279	362	420
Standard Deviation			119	11	26	47	57	66
%Relative Standard Deviation			13	1	2	17	16	16

<sup>a</sup> Data shown comes from previous Tables 1 through 6 for final 1600 hours of testing. Standard deviations represent 1 sigma value at 95% confidence level as calculated by Microsoft<sup>®</sup> EXCEL Version 4.0 spreadsheet function. Relative Standard Deviation defined as ((Standard Deviation/Average) x 100).

<sup>b</sup> Soluble organics, soluble metals, solid sludge and solid MST added.

Table 15. Effects of Removing Solid MST Additives or Removing Solid Sludge and Solid MST Additives on NaTPB Decomposition.

Test #	Temp. (°C)	Missing Additives	Boron (ICP-ES, mg/L)			Boron Rate <sup>a</sup> (mole/(L*hr)) (x10 <sup>-5</sup> )
			Time, hr (432)	(1008)	(1608)	
3	55	(all present)	210	320	378	5.5
4	55	(all present)	220	286	307	5.6
8	55	w/o MST	233	352	380	7.4
7	55	w/o sludge and MST	192	268	287	4.8
5	70	(all present)	312	402	468	10.8
6	70	(all present)	245	322	374	4.8
10	70	w/o MST	309	420	477	9.4
9	70	w/o sludge and MST	176	286	317	3.8

<sup>a</sup> Total soluble boron initial production rates calculated from boron measured in first 168 hours as total soluble boron from ICP-ES analyses of the slurry filtrates.

Table 16. NaTPB Solids Based on Soluble TPB<sup>-</sup> Analyses and Soluble Boron Analyses.

Test #	Temp. (°C)	Additives	Final NaTPB <sup>a</sup> Present in Slurry	Equivalent <sup>b</sup> NaTPB Dissolved (mg/L)
1	40	c	yes	6,240
2	40	c	yes	5,640
3	55	c	yes	10,560
4	55	c	yes	8,280
5	70	c	no	13,320
6	70	c	yes	10,440
7	55	d	yes	7,680
8	55	e	yes	10,560
9	70	d	yes	8,640
10	70	e	no	13,680
11	55	f	yes	(g)
12	70	f	yes	(g)
			NaTPB (mg/L)	Equivalent <sup>j</sup> NaTPB Dissolved (mg/L)
Original Slurry <sup>h</sup>			1185 <sup>a</sup>	7,200
Original Slurry <sup>h</sup>			242 <sup>i</sup>	11,880
Original Slurry <sup>h</sup>			282 <sup>i</sup>	12,720

- a. Determined from HPLC analyses of filtrates obtained from mixing 1 gram slurry amounts with 5 mL of deionized water.
- b. Based on ICP-ES analyses of soluble boron in filtrates using a nominal slurry density of 1.2 g/mL. These values represent amount of equivalent solid NaTPB dissolved during testing.
- c. Soluble organics, soluble metals, solid sludge and solid MST added.
- d. Soluble organics, soluble metals.
- e. Soluble organics, soluble metals and solid sludge added (no MST).
- f. Control samples containing no additives.
- g. Soluble boron analyses in these two samples indicate no significant change (about  $704 \pm 170$  mg/L equivalent NaTPB) from 96 hr to the end of testing.
- h. Obtained from excess slurry used in original tests preparation stored at ambient temperature for the duration of testing.
- i. Determined from HPLC analyses of filtrates obtained from mixing 1 gram slurry amounts with 40 mL of deionized water after stirring in sealed containers for 12 hours.
- j. Based on HPLC analyses of filtrates. These values represent amount of equivalent solid NaTPB in the (K,Na)TPB slurries.

Table 17. Analyses for Soluble Potassium Ion from (K,Na)TPB Slurries Tested at 40 to 70 °C.

Test #	Temp. (°C)	Additives	Final Potassium <sup>a</sup> in Filtrates (mg/L)	Equivalent <sup>b</sup> KTPB Dissolved (mg/L)	Equivalent <sup>c</sup> NaTPB Dissolved (mg/L)
1	40	d	2.7	36	6,240
2	40	d	2.2	24	5,640
3	55	d	144.0	1,320	10,560
4	55	d	6.6	60	8,280
5	70	d	420.0	3,984	13,320
6	70	d	209.0	1,920	10,440
7	55	e	8.9	84	7,680
8	55	f	209.0	1,920	10,560
9	70	e	48.0	444	8,640
10	70	f	506.0	4,656	13,680
11	55	g	3.5	36	(h)
12	70	g	2.7	24	(h)
Original Slurry <sup>i</sup>			0.2	<2	NA <sup>j</sup>

a Determined from Atomic Absorption analyses of slurry filtrates.

b Based on Atomic Absorption analyses for soluble potassium ion in filtrates using a nominal slurry density of 1.2 g/mL. These values represent amount of equivalent solid KTPB that was dissolved during testing.

c Data repeated from Table 16 based on ICP-ES analyses of soluble boron in filtrates using a nominal slurry density of 1.2 g/mL. These values represent amount of equivalent solid NaTPB dissolved during testing.

d Soluble organics, soluble metals, solid sludge and solid MST added.

e Soluble organics, soluble metals.

f Soluble organics, soluble metals and solid sludge added (no MST).

g Control samples containing no additives.

h Soluble boron analyses in these two samples indicate no significant change (about  $704 \pm 170$  mg/L equivalent NaTPB) from 96 hr to the end of testing.

i Obtained from excess slurry used in original tests preparation stored at ambient temperature for the duration of testing.

j Soluble boron was not analyzed from the excess slurry used in the original tests.

Table 18. Comparison of Previous Tank 48H Data with Present (K,Na)TPB Slurry Decomposition Data

		Tank 48H <sup>a</sup> (25-52 °C) <sup>b</sup>	Present Tests <sup>c,d</sup> (40 °C) (55 °C)	
Benzene	Amounts (mg/L)	6300	2200	5200
	Time Period (hours)	2160	1600	1600
	Rate (mg/(L*hr))	2.92	1.37	3.25
Potassium	Amounts (mg/L)	1-6	2-3	6-209
	Time Period (hours)	1968	1600	1600
	Rate (mg/(L*hr))	(0.5-3.0)E-3	(1.2-1.9)E-3	0.004-0.130
Phenol	Amounts (mg/L)	1000	1200-1300	1000-1800
	Time Period (hours)	4320	1600	1600
	Rate (mg/(L*hr))	0.23	0.75-0.81	0.63-1.12
1PB	Amounts (mg/L)	1900	600	1400
	Time Period (hours)	2280	432	432
	Rate (mg/(L*hr))	0.83	1.39	3.24
Boron	Amounts (mg/L)	500	220-240	300-370
	Time Period (hours)	1584	1600	1600
	Rate (mg/(L*hr))	0.32	0.14-0.15	0.19-0.23

<sup>a</sup> Data for Tank 48H obtained from Figure 3 (temperature range) and Table 2 (species concentrations) in Ref. 1. The magnitudes of all species represent maximum amounts produced over the approximate time periods indicated.

<sup>b</sup> Tank 48H recorded temperatures ranged from 25 to 52 °C from August 31, 1995 to April 27, 1996. Note however, from Ref. 1 that Tank 48H temperatures ranged from 33 to 52 °C from August 31, 1995 to mid-November of 1995.

<sup>c</sup> Data for the 40 °C studies obtained from Tables 1 and 2 for tests containing full set of additives. The magnitudes of all species represent maximum amounts produced over the approximate time periods indicated.

<sup>d</sup> Data for the 55 °C studies obtained from Tables 3 and 4 for tests containing full set of additives. The magnitudes of all species represent maximum amounts produced over the approximate time periods indicated.

Figure 1. Benzene Production for Tests 1 and 2 at 40 °C with All Additives.

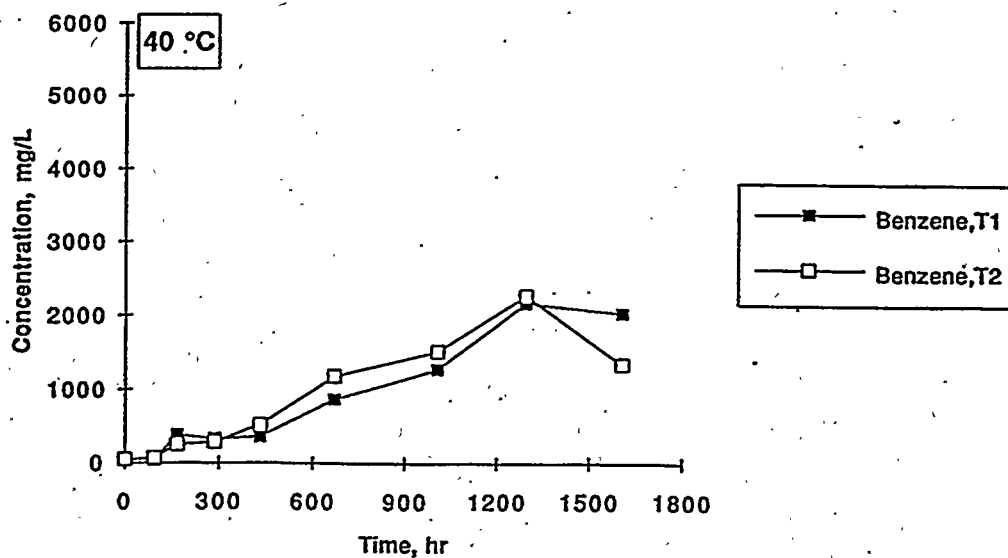


Figure 2. Benzene Production for Tests 3 and 4 at 55 °C with All Additives.

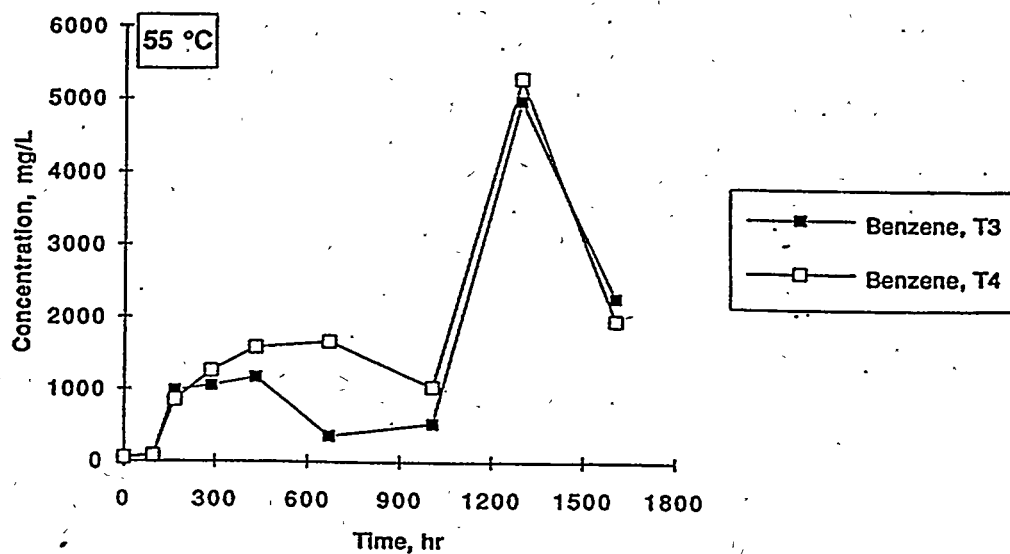


Figure 3. Benzene Production for Tests 5 and 6 at 70 °C with All Additives.

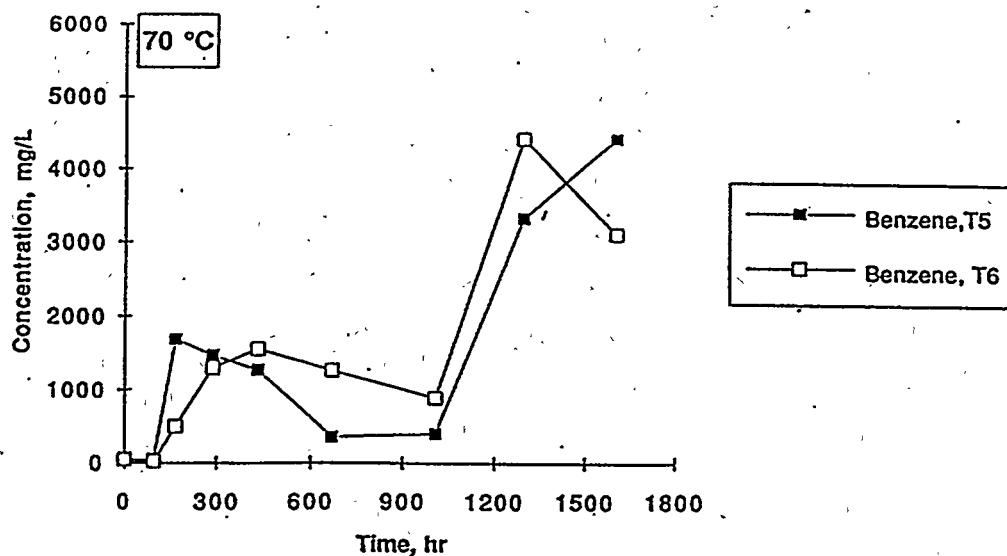


Figure 4. Benzene Production for Tests at 55 and 70 °C with Either Soluble Additives Only (i.e., Test 7 and Test 9) or Soluble Additives plus Sludge Solids (i.e., Test 8 and Test 10).

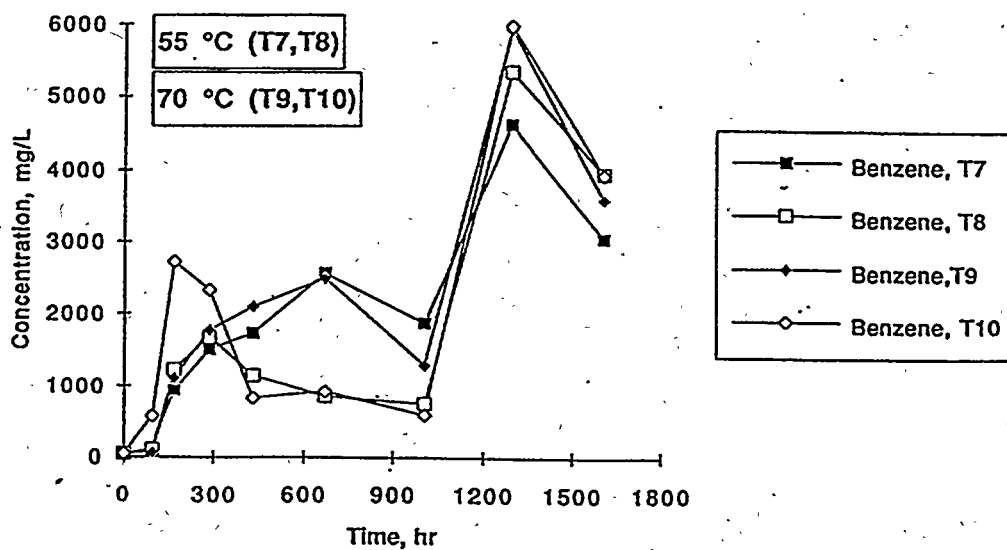




Figure 5. Benzene Production for Control Sample Tests 11 and 12 at 55 and 70 °C, respectively, with No Additives Present.

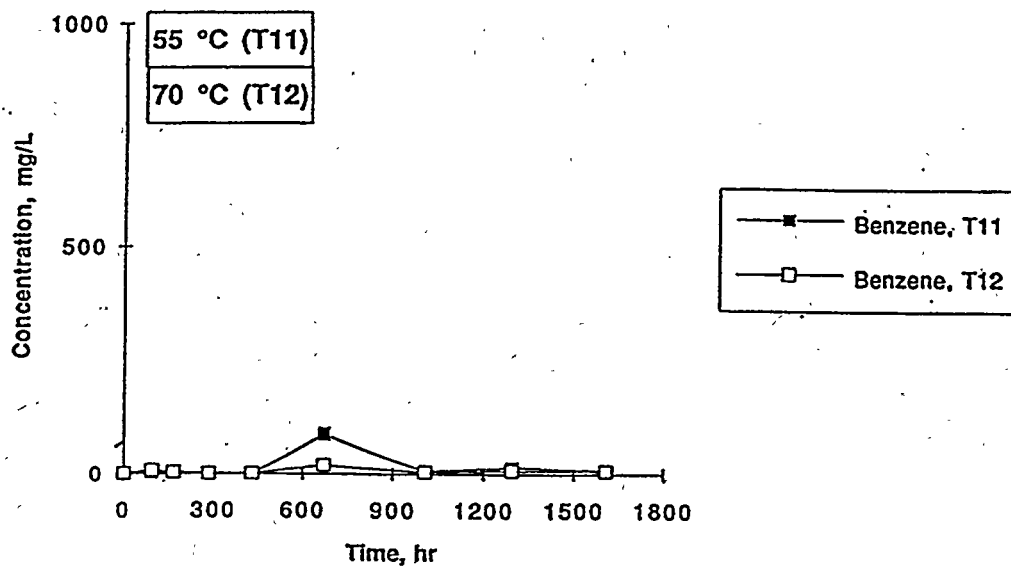




Figure 8: Average Tetraphenylborate, Intermediates and Product Concentrations versus Time for Duplicate Tests 5 and 6 at 70 °C with All Additives.

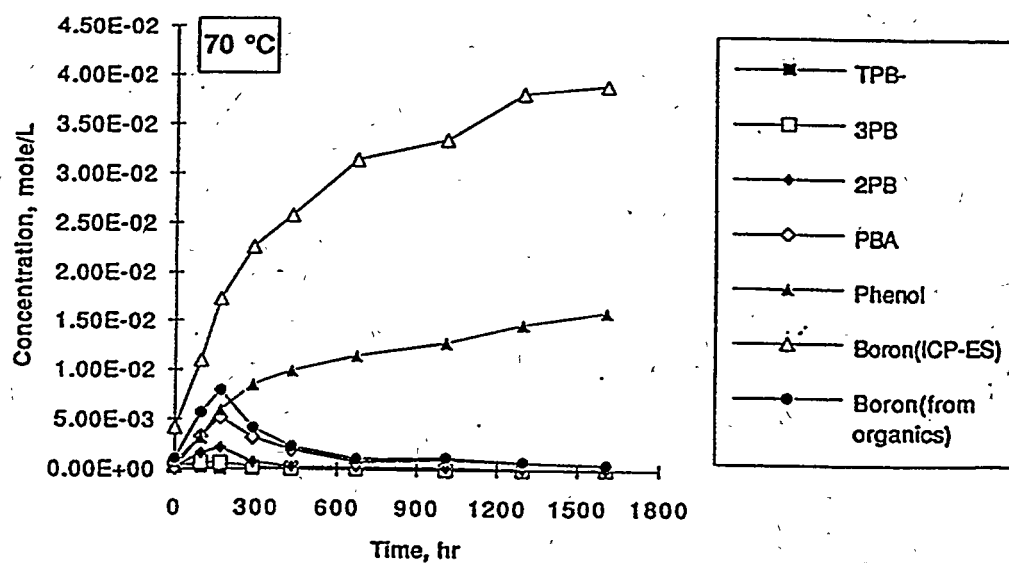


Figure 9. Tetraphenylborate, Intermediates and Product Concentrations versus Time for Test 7 at 55 °C with Soluble Additives Only.

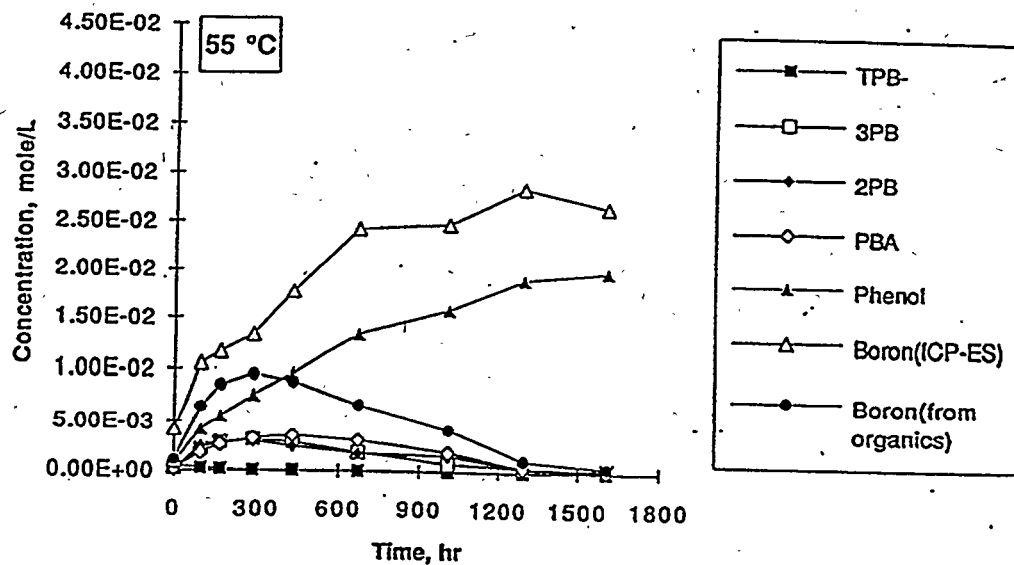


Figure 10. Tetraphenylborate, Intermediates and Product Concentrations versus Time for Test 8 at 55 °C with Soluble Additives Plus Sludge Solids.

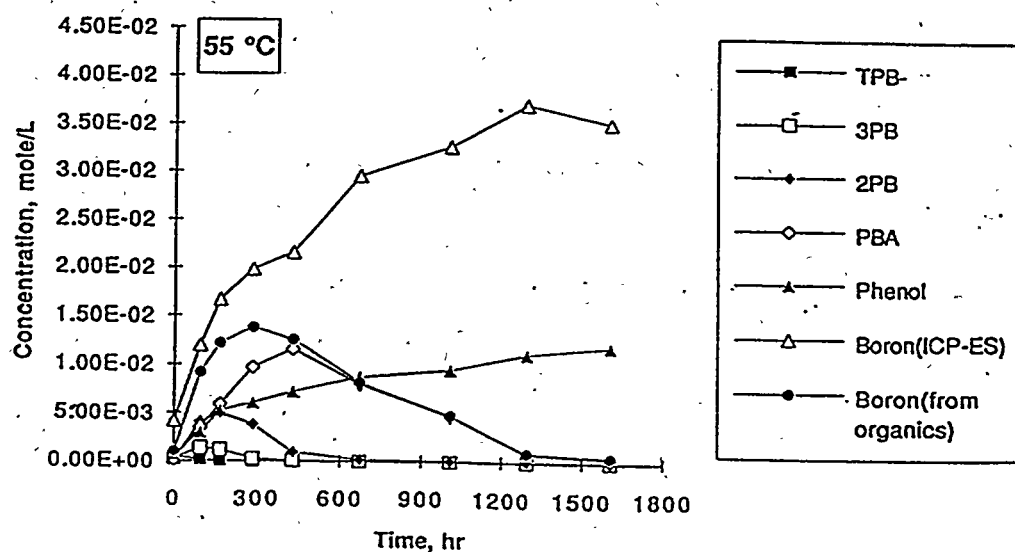


Figure 11. Tetraphenylborate, Intermediates and Product Concentrations versus Time for Test 9 at 70 °C with Soluble Additives Only.

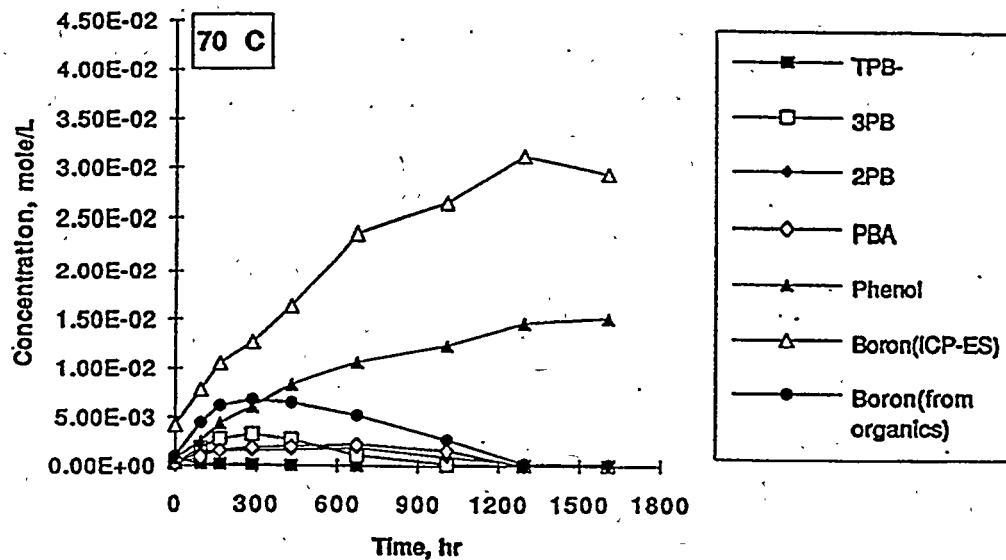


Figure 12. Tetraphenylborate, Intermediates and Product Concentrations versus Time for Test 10 at 70 °C with Soluble Additives Plus Sludge Solids.

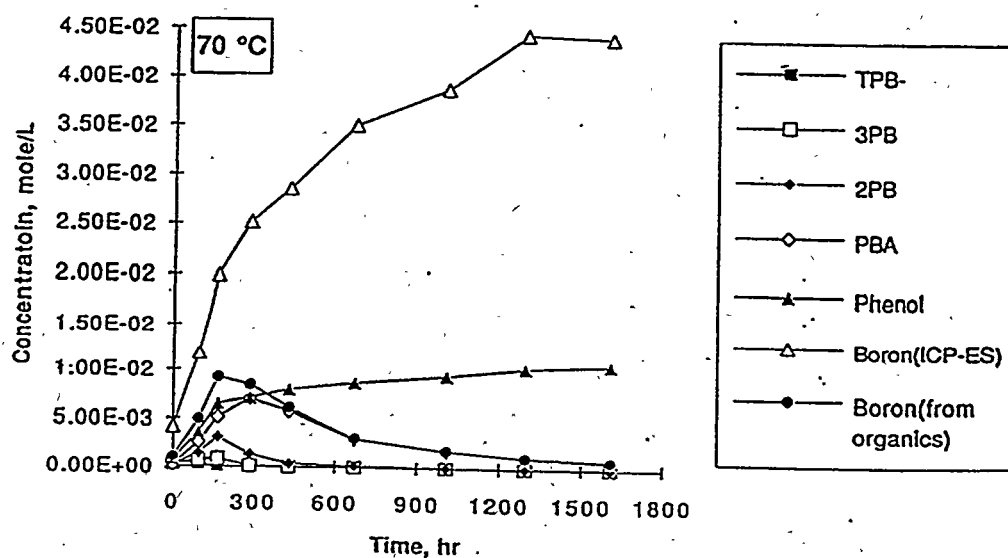


Figure 13. Tetraphenylborate, Intermediates and Product Concentrations versus Time for Control Sample Test 11 at 55 °C with No Additives.

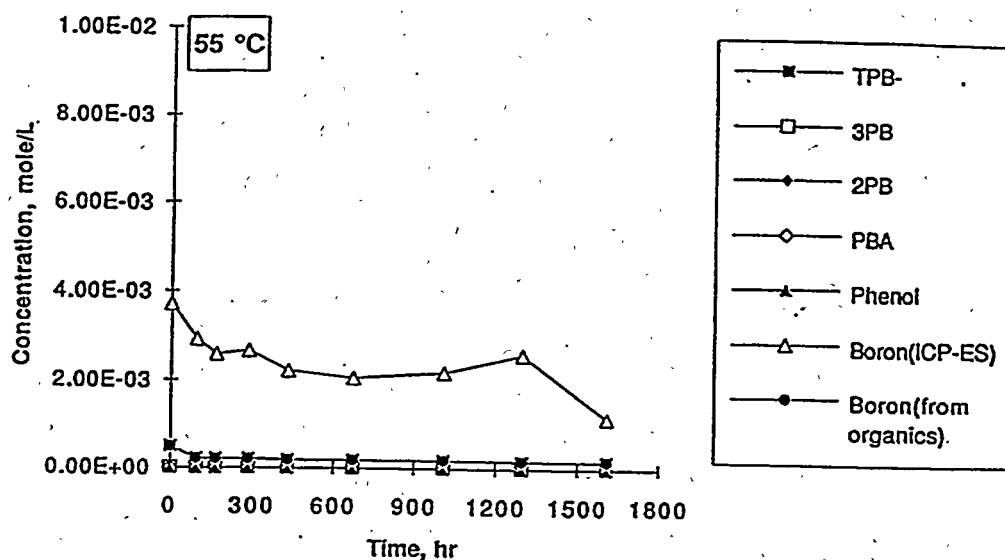


Figure 14. Tetraphenylborate, Intermediates and Product Concentrations versus Time for Control Sample Test 12 at 70 °C with No Additives.

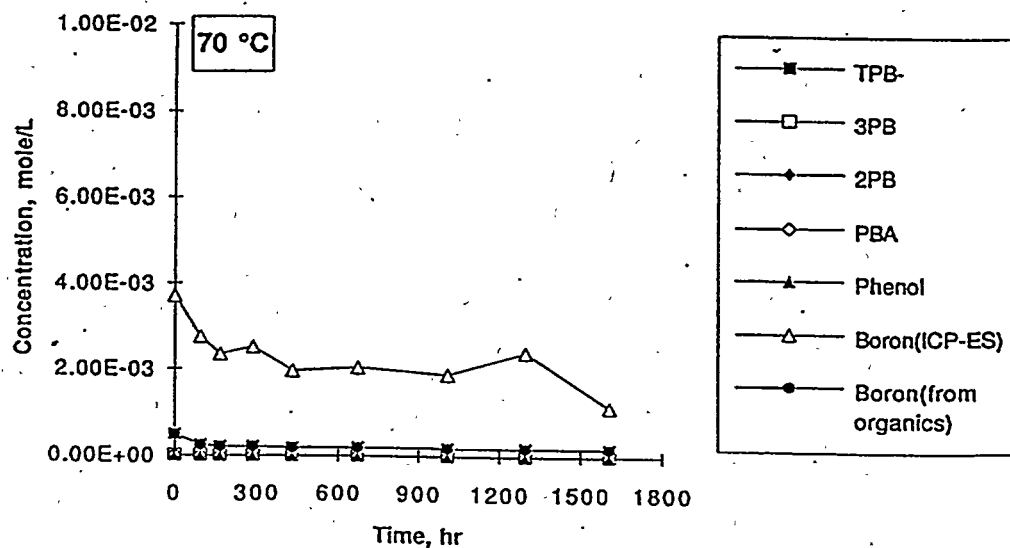


Figure 15. Arrhenius Plot of  $\ln(\text{initial soluble boron rate})$  versus Inverse Temperature.

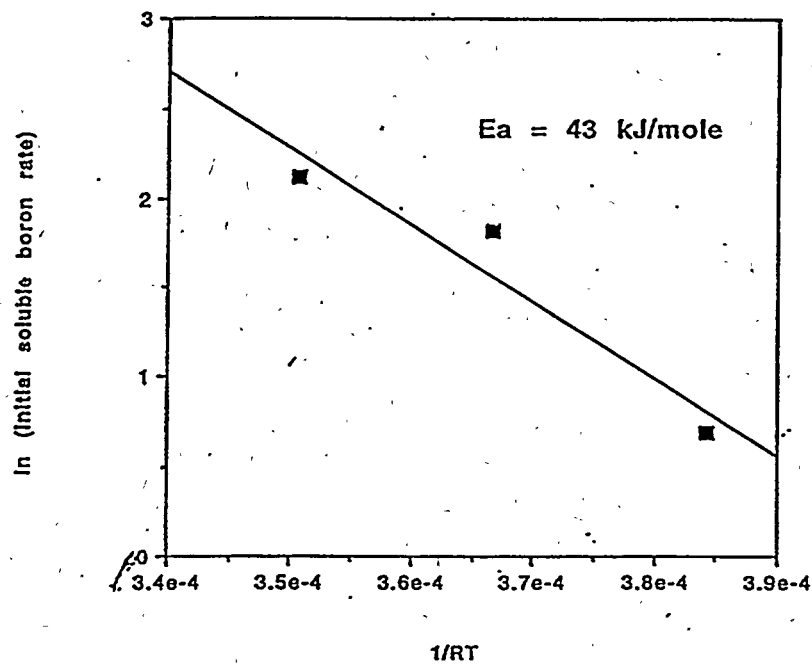


Figure 16. Soluble Boron (ICP-ES) and Phenyl Borate (HPLC) Concentrations versus Time for Test 8 at 55 °C with Soluble Additives Plus Sludge Solids (w/out MST) Compared to Averages from Duplicate Tests 3 and 4 at 55 °C with All Additives.

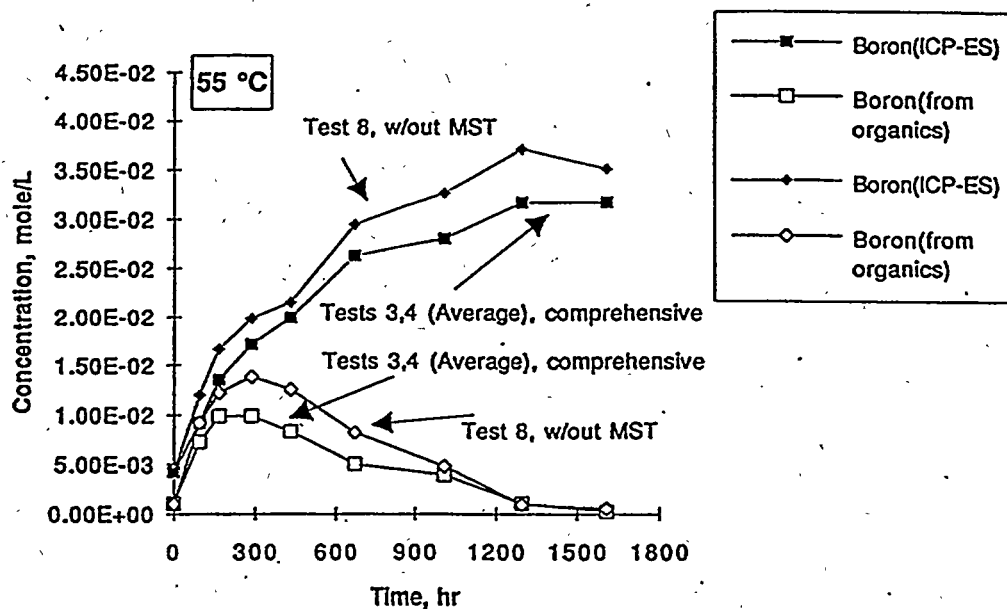


Figure 17. Soluble Boron (ICP-ES) and Phenyl Borate (HPLC) Concentrations versus Time for Test 10 at 70 °C with Soluble Additives Plus Sludge Solids (w/out MST) Compared to Averages from Duplicate Tests 5 and 6 at 70 °C with All Additives.

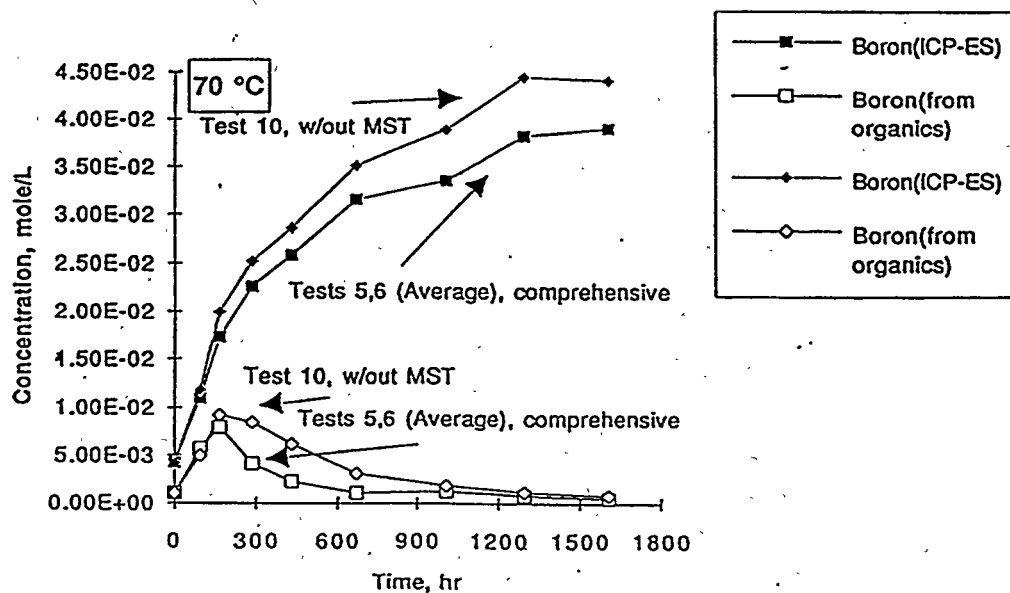




Figure 18. Soluble Boron (ICP-ES) and Phenyl Borate (HPLC) Concentrations versus Time for Test 7 at 55 °C with Soluble Additives (w/out sludge and MST) Compared to Averages from Duplicate Tests 3 and 4 at 55 °C with All Additives.

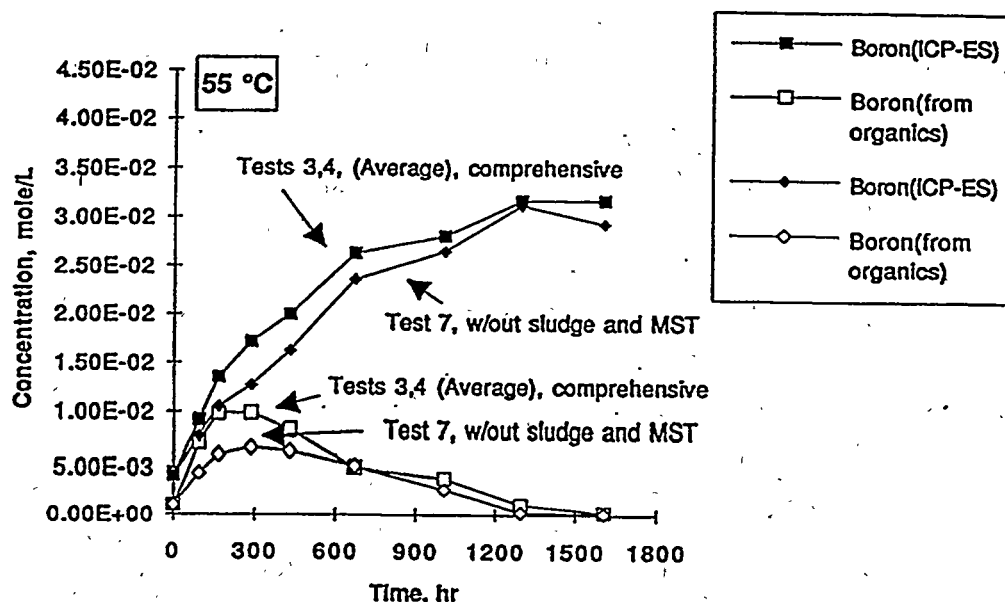
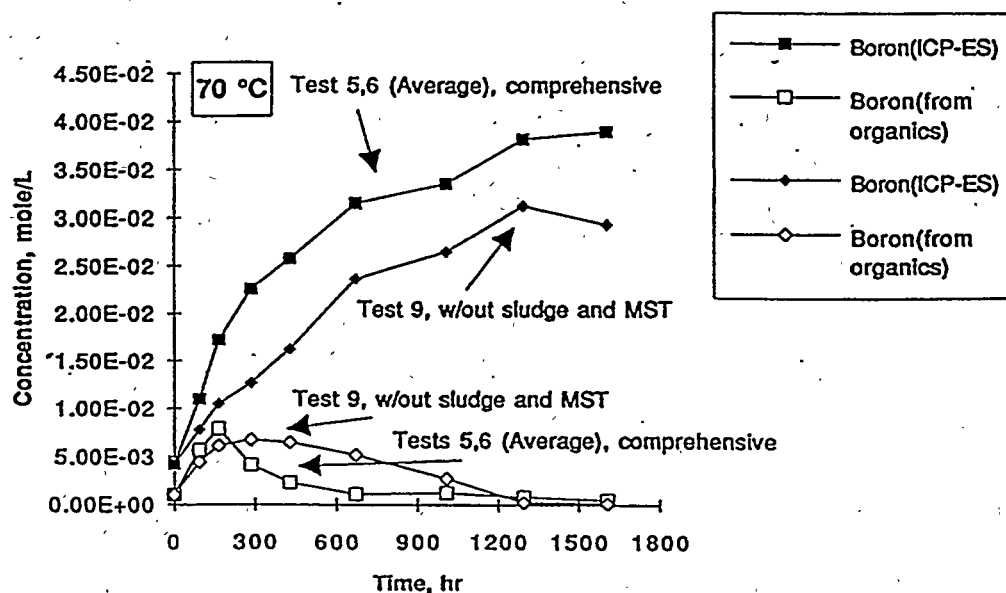


Figure 19. Soluble Boron (ICP-ES) and Phenyl Borate (HPLC) Concentrations versus Time for Test 9 at 70 °C with Soluble Additives (w/out sludge and MST) Compared to Averages from Duplicate Tests 5 and 6 at 70 °C with All Additives.



## QUALITY ASSURANCE

The experimental methods and results were recorded in laboratory notebook WSRC-NB-95-308. The task plan and quality assurance plans are:

C. L. Crawford, "Task Technical Plan for Decomposition Studies of Tetraphenylborate Slurries (U)", WSRC-RP-96-549, Rev. 0, October 23, 1996.

C. L. Crawford, "Task Quality Assurance Plan - Decomposition Studies of Tetraphenylborate Slurries (U)", WSRC-RP-96-550, Rev. 0, October 23, 1996.

## REFERENCES

1. D. D. Walker, M. J. Barnes, C. L. Crawford, R. F. Swingle, R. A. Peterson, M. S. Hay and S. D. Fink, "Decomposition of Tetraphenylborate in Tank 48-H (U)", WSRC-TR-96-0113, May 10, 1996.
2. "Department of Energy Implementation Plan for Defense Nuclear Facilities Safety Board Recommendation 96-1 to the Secretary of Energy, In-Tank Precipitation Facility at the Savannah River Site", A. Lee Watkins, DNFSB 96-1 Implementation Plan, Rev. 0, October 21, 1996.
3. M. J. Barnes, "Decomposition of Sodium Tetraphenylborate (U)", WSRC-RP-90-465, May 10, 1990.
4. D. D. Walker and C. A. Nash, "Results from Tank 48H Slurry Decontamination and Decomposition Experiments in Support of ITP Process Verification Testing (U)", WSRC-TR-96-0190, September 6, 1996.
5. M. J. Barnes, C. L. Crawford, C. A. Nash and T. B. Edwards, "Task Technical Plan for Sodium Tetraphenylborate Decomposition Catalyst Identification Studies (U)", WSRC-RP-96-600, Rev. 0, December 10, 1996.
6. J. E. Marra and J. T. Carter, "Soluble TPB Decomposition and Catalysis", HLE-TTR-97008, November 14, 1996.
7. J. E. Marra and J. T. Carter, "Effect of Sludge Solids and ST on TPB Decomposition", HLE-TTR-97012, November 14, 1996.
8. C. L. Crawford and R. A. Peterson, "Decomposition Studies of Triphenylboron, Diphenylborinic Acid and Phenylboric Acid in Aqueous Alkaline Solutions Containing Copper (U)", WSRC-TR-97-0045, Rev. 0, February 11, 1997.
9. P. W. Atkins, Physical Chemistry, Chapter 27 - "The Rates of Chemical Reactions", pp 920-968, W. H. Freeman and Co., San Francisco, CA, 1982.
10. M. J. Barnes and T. B. Edwards, "Copper Catalyzed Sodium Tetraphenylborate Decomposition Kinetic Studies (U)", WSRC-TR-96-0351, Rev. 0, November 7, 1996.

11. D. J. McCabe, "Cesium, Potassium, and Sodium Tetraphenylborate Solubility in Salt Solution (U)", WSRC-TR-96-0384, Rev. 0, December 16, 1996.
12. D. D. Walker, M. L. Hyder, M. J. Barnes, C. L. Crawford and R. A. Peterson, "Intermediate Decomposition Rates", SRP-LWP-97-0021, Rev. 0, February 26, 1997.
13. M. L. Hyder, "The Role of Oxygen in the Copper-Catalyzed Decomposition of Phenyl Borates in Aqueous Alkaline Solutions (U)", WSRC-TR-97-0069, Rev. 0, March 17, 1996.
14. a) Analytical Development Section, QA Implementation Manual, 1Q31-3.  
b) Analytical Development Section, Analytical Operating Procedures Manual, L16.1.
15. C. L. Crawford, "Preliminary High-Pressure Liquid Chromatography (HPLC) Analyses of Composite Mixtures of Tetraphenylborate, Triphenylboron, Diphenylboronic Acid, Phenylboric Acid and Phenol in Aqueous Alkaline Salt Solutions (U)", WSRC-TR-96-0364, Rev. 0, December 18, 1996..

APPENDIX A  
TEST DESIGN AND EXPERIMENTAL METHODS AND ANALYSES

A total of 12 slurry samples were tested. The test matrix, sample preparations and analytical methods are described below.

The test matrix for six slurry plus additive samples (V1-6) was identical except for the different temperatures of 40, 55 and 70 °C (see V1-6 of Table A1). Each (K,Na)TPB slurry consisted of the simulated slurry in concentrated salt solution containing the soluble metal, soluble organics, and solid sludge and MST additives shown in Table A2. The non-radioactive recipe given in Table A2 best approximates the Tank 48H radioactive slurry (See specifically Tables 2, 8, 9 and 12 of Ref. 1). As noted in Table A2, the NaTPB fraction of the (K,Na)TPB solids is purposely made higher (targeted to contain 1.5 wt % NaTPB solids or about 18,000 mg/L NaTPB solids) relative to the measured 0.6 wt % NaTPB value in Tank 48H slurry. This was done to assure an adequate amount of excess NaTPB so the extent of reaction can be monitored in the planned decomposition tests. These samples, v1-6, were tested in duplicate at each temperature. Tests were conducted in unstirred 160 mL carbon-steel air-sealed containers (i.e., static systems). All vessels initially contained 100 mL of slurry.

Additional slurries in concentrated salt solution, one containing only soluble metal and organic additives of Table A2 (no sludge nor MST solids present) and one containing all additives of Table A2 except MST, were tested at the higher temperatures of 55 and 70 °C (see V7-10 of Table A1). These tests were designed to provide information on the effects of solid additives on the extent of TPB reaction.

Single (K,Na)TPB slurries in concentrated salt solution sample containing no potential soluble (metals or organics) nor solid (sludge or MST) additives shown in Table A2, i.e., 'control samples', were included for comparison purposes at the two higher temperatures of 55 and 70 °C (see V11-12 in Table A1).

All containers were cleaned before testing by rinsing with deionized water, contacting with ~ 1% nitric acid for ~ 1 hr, rinsing with deionized water, heat treating to ~ 580 °C for at least 8 hr, and lastly soaking in 0.5 M NaOH for at least 8 hr.

Table A-1. Reaction Conditions of (K,Na)TPB Slurry  
Decomposition Studies<sup>a</sup>

Test #	Temperature	Soluble Organics	Soluble Metals	Solid Sludge	Solid MST
1	40	yes	yes	yes	yes
2	40	yes	yes	yes	yes
3	55	yes	yes	yes	yes
4	55	yes	yes	yes	yes
5	70	yes	yes	yes	yes
6	70	yes	yes	yes	yes
7	55	yes	yes	no	no
8	55	yes	yes	yes	no
9	70	yes	yes	no	no
10	70	yes	yes	yes	no
11	55	no	no	no	no
12	70	no	no	no	no

<sup>a</sup> All tetraphenylborate slurry prepared to be 5.5 wt % total (K,Na)TPB solids with 4.0 wt % KTPB (or 48,000 mg/L KTPB) and 1.5 wt % NaTPB (or 18,000 mg/L NaTPB).

Table A-2. Tank 48H Non-Radioactive Simulant Test Matrix for (K,Na)TPB Slurry Decomposition Studies<sup>a</sup>

Salt Content (M)	Soluble Metal Additives (mg/L)		Solid Additives (wt %)
4.7 M Na <sup>+</sup>	1.7 Cu(II)	0.8 Ru(III)	0.2 wt % Sludge
2.7 M OH <sup>-</sup>	12 Mo(VI)	0.4 Pd(II) <sup>b</sup>	0.2 wt % MST
0.70 M NO <sub>2</sub> <sup>-</sup>	60 Cr(VI)	0.2 Rh(III) <sup>b</sup>	
0.69 M NO <sub>3</sub> <sup>-</sup>	16 Si(IV)	0.6 Ag(I)	
0.17 M AlO <sub>2</sub> <sup>-</sup>	0.4 Cd(II)	0.04 Co(II)	
0.01 M SO <sub>4</sub> <sup>2-</sup>	1 Se(VI)	2.2 Hg(II)	
0.19 M CO <sub>3</sub> <sup>2-</sup>	0.04 As(IV)	12.2 Ca(II)	
0.014 M Cl <sup>-</sup>	8.8 Zn(II)	0.1 Sr(II)	
0.008 M F <sup>-</sup>	1.2 Pb(II)	0.05 La(III)	
0.006 M PO <sub>4</sub> <sup>3-</sup>	2.6 Fe(III)	0.3 Ce(IV)	
0.003 M TPB <sup>-</sup>	2.1 Sn(II)		
Pre-dried			
Organic Additives	Sludge Simulant <sup>c</sup>		
(mg/L)	Component	(wt % of dry sludge)	Concentration <sup>d</sup> (mg/L)
720	Benzene	Al	4.8
150	Diphenylmercury	Fe	28.8
125	Triphenylboron	Mn	5.9
125	Diphenylboronic Acid	Ru	0.23
125	Phenylboronic Acid	Pd	0.11
125	Phenol	Rh	0.06
150	Biphenyl	Cr	0.2
50	Isopropanol	Cu	0.1
5	Methanol	Mg	0.1
		Ni	2.5
		Pb	0.3
		Zn	0.2
		Zr	2.5

<sup>a</sup> Tetraphenylborate slurry prepared to be 5.5 wt % total (K,Na)TPB solids with 4.0 wt % KTPB (or 48,000 mg/L KTPB) and 1.5 wt % NaTPB (or 18,000 mg/L NaTPB).

<sup>b</sup> Palladium and rhodium soluble metal additives were not included as soluble additives in any of the previous TPB sealed-bottle catalyst tests reported in Ref. 1. Note that inclusion of these metal additives as soluble species in the present tests increases their magnitudes by:

$$[(0.4 \text{ mg/L(soluble)} + 2.2 \text{ mg/L(solid)}) / 2.2 \text{ mg/L(solid)} - 1] \times 100 = 18\% \text{ for Pd, and}$$

$$[(0.2 \text{ mg/L(soluble)} + 1.2 \text{ mg/L(solid)}) / 1.2 \text{ mg/L(solid)} - 1] \times 100 = 17\% \text{ for Rh.}$$

<sup>c</sup> Sludge composition originally reported in Ref. 1.

<sup>d</sup> These concentrations for sludge components based on presence of solid sludge at 0.2 wt % in the simulated slurries.

Samples from all slurries were analyzed to provide measurements of various components initially present. Subsequent sampling of the slurries was performed on a frequency of approximately every 2-3 days. All vessels were removed from the controlled temperature environments and immersed in water baths to cool them to ambient temperature immediately before sampling. The slurries were mixed by vigorous shaking immediately prior to gas-phase and slurry sampling. All test-vessels containing the slurry samples were weighed prior to and immediately after sampling.

A typical sampling extracted  $\leq 0.5$  cc gas sample of the vapor-space within the sealed vessel and removed approximately 4 mL of slurry (~ 1 mL analyzed for liquid benzene and ~ 3 mL filtered -- 0.45  $\mu$ m filter -- to provide filtrate for soluble organics, soluble boron, and possible soluble metal analyses). Ambient air, approximately equal to the gas or liquid amount withdrawn, was introduced into the sealed vessels immediately before each sampling. This was to prevent any depressurization of the sealed vessels due to multiple gas and slurry removals over the duration of the tests.

The experimental program to measure the decomposition of NaTPB in slurries used the following critical measurements.

Mass and volume Solutions were made from reagent grade chemicals by weighing on calibrated balances checked daily before use (WPTS Operating Procedure #IWT-OP-011). The weights used for balance checks were calibrated at the SRTC Standards Laboratory. Volume measurements were made with glassware with accuracy verified by gravimetric methods using water as a standard (WPTS Operating Procedure #IWT-OP-009).

Temperature Samples were maintained at the specified testing temperatures by placement in laboratory ovens. Temperatures within the air-space of the ovens were determined by thermometers constantly kept in place within the ovens in very close proximity to the set of test vessels. Thermometers used were calibrated by SRTC Standards Laboratory using NIST-traceable procedures. The oven display temperature and thermometer temperatures were recorded on appropriate data sheets located at each oven. These temperature data sheets were kept upon completion of the tests as a permanent record in laboratory notebooks. The frequency of temperature monitoring and control was adequate during normal daily laboratory hours to assure a constant thermometer temperature reading within the range of  $\pm 2$  °C of the specified test temperature. Temperature monitoring and control during normal laboratory daily hours was conducted by researchers and technicians. Temperatures were also recorded on night-shift and weekend-shifts by SRTC Control Room personnel as requested by a 'night-sheet' records request that was officially filed with SRTC Control Room staff.

High-Performance Liquid Chromatography (HPLC) Organic components were measured by HPLC methods from aqueous portions of the filtrate (0.45  $\mu$ m filter). These analyses were performed by the Analytical Development Section (ADS) of SRTC. ADS activities were controlled in accordance with the ADS QA program.<sup>14</sup>

Researchers used the following sample preparation and HPLC analysis procedure.<sup>15</sup>

A 1 mL aliquot of each caustic solution to be analyzed was buffered with ~2.5 mL of potassium phosphate buffer solution, and then diluted to 10 mL with acetonitrile. The resulting mixture was mixed (inverted several times) for several minutes to facilitate the extraction of the organic components into the acetonitrile. Aliquots (5-10  $\mu$ L) of the organic-phase were then injected into two different HPLC units (HPLC #1 and HPLC #2).

- HPLC #1 (TPB<sup>-</sup>, 3PB and 2PB Analysis): TSP LC, acetonitrile-ammonium phosphate buffer eluent, Whatman ODS-2 column (TPB<sup>-</sup> retention  $\approx$  5.5 minutes, 3PB retention  $\approx$  11.5 minutes, 2PB retention  $\approx$  7.8 minutes).
- HPLC #2 (1PB and Phenol Analysis): Hewlett Packard LC, acetonitrile-water eluent, Chemco-5-ODS column (1PB retention  $\approx$  10.5 minutes and phenol retention  $\approx$  14.6 minutes).

Benzene Measurements Benzene was measured by gas chromatography (GC). The GC instruments was calibrated for benzene with gravimetrically prepared standards from reagent grade benzene (WPTS Operating Procedure #IWT-OP-007). Both gas-phase (from within the sealed carbon-steel vessels) and liquid-phase (from small,  $\leq$  1-mL, aliquots of the mixed slurries) benzene were measured. Gas-phase benzene measurements were estimated by transferring a known volume of gas from within the sealed carbon-steel vessels to a sealed secondary container (typically 20-60 mL glass vials) of known volume. Injections from the secondary container were made directly into the GC instrument.

Liquid-phase benzene measurements were conducted by transferring a 4-mL aliquot of the mixed slurry from the carbon steel vessels into a sealed secondary container. This container was a 4-mL glass vial fitted with a screw-top lid. The slurry was transferred in the 4-mL sealed glass vial to a separate laboratory containing the GC instrument. The 4 mL slurry sample was then mixed by shaking, uncapped and sampled by transferring a small  $\leq$  1-mL portion via a calibrated micro-pipette to a sealed 1.0 L glass bulb container. This bulb was agitated/swirled to ensure complete liquid 'coating' of the inner vessel walls to promote maximum liquid/vapor surface area within the bulb. From this sealed bulb a  $\leq$  0.250 cc gas aliquot was injected into the GC for benzene analysis. All benzene measurements were typically performed within 4 to 8 hours of slurry sampling.

Soluble Boron Species The filtrates of selected samples were analyzed for total soluble boron content to determine the extent of (K,Na)TPB solids (NaTPB and possibly KTPB solids) decomposition in the slurries. Total soluble boron was determined by ICP-ES. All filtrates were diluted by a factor of six with deionized water. A single standard boron sample was submitted with each set of boron analyses. This multi-element, high purity boron-containing standard contained boron at (20 mg/L  $\pm$  0.5%) in a 2 % HNO<sub>3</sub> aqueous solution and was analyzed undiluted. The analyzed boron content for this standard was consistently biased high by about 15% (average analysis from 9 samples = (23.1  $\pm$  1.8 mg/L)).

#### NaTPB Determination from Dissolution of Slurries

An initial batch slurry and final test sample slurries were analyzed for solid NaTPB by mixing about 1 gram of well mixed slurry with 5 mL of deionized water. The 1-gram slurry samples were obtained from the



slurries as they were being stirred (reacted slurries were transferred from the carbon steel reaction vessels into glass beakers) in attempts to obtain a representative sample. The resulting diluted slurry, after being stored for about 24 hours unstirred, was filtered and analyzed for soluble  $\text{TPB}^-$  by HPLC analysis. These analyses were performed to measure both the initial (from the original batch slurry) and final amounts of solid  $\text{NaTPB}$  in the slurries. After review of the results from these tests, the analyses were repeated in duplicate for the batch slurry only, using a larger dilution volume of 40 mL deionized water and stirring of the diluted slurry for about 18 hours in a sealed container before filtration and HPLC analysis for  $\text{TPB}^-$ .

#### Soluble Potassium

An initial batch slurry filtrate and all final test sample filtrates were analyzed for soluble potassium ion content using Atomic Absorption Spectroscopy to determine the extent of  $\text{KTPB}$  solubility in the aqueous phase of the slurries. These slurry samples were also obtained from the slurries as they were being stirred in attempts to obtain a representative sample.

## DISTRIBUTION

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