Decomposition of Tetraphenylborate In Tank 48H

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I. Executive Summary

This report provides a qualitative and semiquantitative description of the chemical reaction that decomposed the excess sodium tetraphenylborate in Tank 48H during November and December 1995. A discussion of potential reaction mechanisms and implications to downstream processes are also included. This data supports development of a global model of the chemical and physical phenomena occurring in both the vapor and condensed phases in Tank 48H. It provides bounding quantities of benzene that can form in Tank 48H and provides insight into likely reaction rates. Descriptions of the physical phenomena occurring in Tank 48H (mixing, mass transfer, and adsorption) are not included. Further testing is underway to determine quantitative kinetic rate expressions for the significant benzene production mechanisms.

A rapid reaction which decomposed the excess sodium tetraphenylborate (NaTPB) in Tank 48H occurred in November and December 1995. After consuming all of the excess NaTPB, the reaction subsided and appears to have stopped. The current rate of decomposition of the potassium and cesium tetraphenylborate solids is within the expected range from previous tests. Salient points about the reaction follow.

- Benzene is the major product of the decomposition. Phenol and biphenyl are minor products, and phenylboric acid is a semi-stable intermediate.
- The stoichiometry depends strongly on the availability of oxygen, the presence of which increases the yields of the minor products. In Tank 48H, 77% of the phenyl groups on the decomposed NaTPB formed benzene, 6% formed phenylboronic acid, 4.5% formed phenol, 4% formed biphenyl, and 8.5% are unaccounted for.
- The average rate of benzene generation in Tank 48H during the rapid decomposition reaction was between 12,500 and 25,000 $\mu\text{g/L/hr}$. This was at least 1000 times faster than the current generation rate in the absence of excess.
- The reaction consumed all of the available sodium tetraphenylborate solids in the tank, but no significant amount of insoluble potassium and cesium tetraphenylborate.
- Laboratory tests with simulated waste have produced rapid decomposition of NaTPB similar to Tank 48H in stoichiometry, rate, and extent of reaction.
- Laboratory testing has demonstrated that copper ion and sludge solids increase the rate of decomposition of tetraphenylborate slurries. Additional tests in progress continue to examine the influence of other components.

- The presence or absence of oxygen changes the decomposition mechanism. At 70°C in the absence of oxygen, the reaction initiates instantaneously with benzene as the nearly exclusive product. In the presence of oxygen, an induction period is observed, benzene is the predominate decomposition product, and small quantities of phenol and biphenyl are formed.
- Under the limited range of reaction conditions tested to date, little difference in stability is observed between AFF, Boulder Scientific, and reagent grade NaTPB. Spray-drying or similar treatments appear to generate limited amounts (<1%) of decomposition impurities that increase initial benzene generation, but this does not appear to be related to the rapid decomposition reaction.

Based on the current understanding of the Tank 48H reaction, the following implications on the downstream processes are presented.

- Tank 50H benzene generation can be higher than previously predicted due to decomposition of soluble, semi-stable products from the Tank 48H reaction. Non-bounding rates as high as 300 µg/L/hr have been measured on Tank 48H filtrate.
- Saltstone prepared from a January 1996 sample of Tank 50H salt solution passed TCLP and Constituent Concentration in Waste tests.
- The rapid decomposition reaction in Tank 48H will not affect transfers to Late Wash once the reaction has subsided and the benzene inventory is reduced to less than 700 mg/L. However, the possibility of the reaction restarting when NaTPB is added in the Late Wash process cycle will limit or reduce allowable storage time.
- The implications of the rapid decomposition reaction for spent washwater storage in Tank 22H cannot be determined, because the composition of the sludge heel in Tank 22H has not been evaluated.

II. Introduction

The In-Tank Precipitation (ITP) process at the Savannah River Site (SRS) prepares high level radioactive waste for vitrification in the Defense Waste Processing Facility (DWPF). In Tank 48H of the ITP facility, cesium-137 and strontium-90 are removed from solution using two specialty chemicals, sodium tetraphenylborate (NaTPB) and monosodium titanate (MST). Sodium tetraphenylborate precipitates cesium and potassium. The titanate removes strontium through ion exchange while adsorbing uranium and plutonium. The insoluble species are concentrated and washed using crossflow filters. Decontaminated filtrate is transferred to Tank 50H for ultimate disposal by the Saltstone facility. The concentrated cesium- and strontium-containing waste is transferred to Tank 49H for storage until processed for vitrification by the Late Wash Facility and DWPF.

SRS has purchased NaTPB primarily from two vendors, AFF, Inc. and Boulder Scientific Company. AFF was selected as the primary vendor. They produced and stored NaTPB in solution with a concentration of $0.55 \pm .05$ M NaTPB and 0.10 M NaOH for stability. Boulder Scientific prepared and stored NaTPB in powder form as a back-up to AFF. During storage, AFF NaTPB solutions were observed to have varying degrees of stability. [Ref. 1,2] Decomposition studies were performed on the NaTPB solution. [Ref. 2,3] In strongly basic solutions, copper was demonstrated to promote the decomposition of dissolved NaTPB. Subsequently, AFF material was determined to be contaminated with low levels of copper. Stability studies also indicated that, in conjunction with copper, elevated temperatures (40 °C and above) or decreased hydroxide concentration increased the rate of NaTPB decomposition. Observations obtained from the various NaTPB solution studies are summarized below:

- The rate of NaTPB decomposition is dependent upon the solution temperature.
- The rate of NaTPB decomposition depends on the copper concentration of the solution. Typically, copper concentrations as low as 0.1 mg/L were capable of catalyzing the decomposition of NaTPB.
- The rate of NaTPB decomposition is proportional to the soluble tetraphenylborate ion concentration.
- Increasing hydroxide ion delays decomposition of NaTPB solutions. An increase in hydroxide concentration from 0.10 molar (typical feed solution hydroxide concentration) to 0.50 molar doubles the shelflife of a decomposing solution.

For economic reasons, the NaTPB produced by AFF was spray-dried by Aquafine, Inc. and stored as a powder. When requested, Aquafine prepared NaTPB solution with the same concentration as that prepared by AFF. Solutions of this material were observed to be unstable when exposed to elevated temperatures during storage. In addition, stability studies on the spray-dried powder indicated that the solid NaTPB was decomposing at a rate of 1% per year. [Ref. 4] During ITP

startup operations, the contract for storage and solution preparation of NaTPB changed to Holley Oak Chemicals. Sodium tetraphenylborate solutions, prepared by both Aquafine and Holley Oak, were used for ITP startup.

During September 1995, ITP began radioactive operations by adding 37,300 gallons of NaTPB solution to Tank 48H. Small amounts of benzene were detected in the tank vapor space during the addition of the NaTPB solutions. During October and early November, the slurry was filtered and tests were run to determine how well the vapor space was mixed. During each test, the maximum measured concentration of benzene in the vapor space increased from that observed in the preceding test. In part, the increase was thought to be due to the increased effectiveness of mixing and mass transfer as the liquid level was reduced. On November 13, all pumps in the tank stopped for a test of vapor space mixing with the ventilation system halted. The tank remained stagnant for 18 days. On December 1, 1995, all four slurry pumps were energized for 3.5 hours. There was a rapid increase in the benzene concentration in the tank vapor space, to concentrations that far exceeded previous levels. A few days later, elevated benzene concentrations (near 9 mg/L) were also observed in Tank 50H liquid samples.[Ref. 5] (The benzene concentration originally measured in the filtrate hold tank prior to transfer never exceeded 1.0 mg/L.) This increase suggests that NaTPB or a decomposition reaction intermediate in the decontaminated filtrate decomposed after transfer. Tests indicate that Saltstone performance was not affected by this material.

The above results were unexpected since the 1983 ITP demonstration did not produce the same effects. The 1983 demonstration differed from the 1995 startup in a number of ways. First, the majority of NaTPB used in 1983 was from Boulder Scientific.[Ref. 6] Second, the 1983 demonstration was performed in a much shorter time period and the tetraphenylborate slurry produced was washed. This washing removed excess NaTPB before decomposition could occur. Third, in 1983 the waste tank was air ventilated and not inerted as was the recent startup. Other differences between the two periods were that the amount of MST added was nearly double in the current operation, the current waste in Tank 48H had a higher plutonium activity, and there was "aged" precipitate from 1983 present in the current operation. Each of these could have contributed to the differences in behavior between the 1983 demonstration and startup in 1995.

III. Experimental

Logic Flowchart

Following the unexpected benzene evolution from Tank 48H on December 1, 1995, researchers from the Savannah River Technology Center (SRTC) met with High Level Waste Engineering personnel to consider immediate response actions. During the ensuing month, SRTC structured an integrated research program aimed at understanding the underlying chemistry. Figure 1 provides an overview of that program. (The text section titled "Tank 48H Data and Information" details the significance of the dates cited in Figure 1.) Table 1 documents progress made in understanding the chemistry as a result of the research program.

Figure 2 provides a schematic of the logic used for investigating chemical generation of benzene. This report examines those tests at length. Other reports document the remaining elements of the program. This report makes no attempt to provide a comprehensive examination of the global program.

Figure 1. Schematic describing the elements of research program supporting In-Tank Precipitation.

Researchers considered the available data for Tank 48H for the period of July 1995 through December 1, 1995. They contrasted this data with documented evidence from the 1983 demonstration of the process. This effort produced a list of known differences that may have contributed to the rapid benzene formation in 1995. No single variable was identified initially that would have produced the large amount of benzene. Hence, researchers developed a multivariate exploratory program. The program focused primarily on chemical differences between the two campaigns (e.g., metal hydroxide solids, the source of NaTPB, and the possible presence of soluble metals). Researchers designed the program to allow simultaneous study of potential interaction from perceived 'secondary' variables. These 'secondary' variables included radiation, oxygen level, and presence of organics from the decomposition.

Analysis of Benzene in Tank 48H Slurry Samples

The volume of a 50-mL Erlenmeyer flask was measured by adding distilled, deionized water, of a known temperature and density, and weighing the flask. The flask was equipped with a ground glass stopper and sidearm. A septum was placed over the sidearm. The dried flask was preweighed and 2 mL of ITP slurry was added. The flask was weighed after replacing the stopper. After stirring for 1 hour the vapor space in the flask was sampled through the septum on the sidearm using a gas tight syringe. The syringe was sealed by closing a valve at the base and removed from the Shielded Cells for analysis by gas chromatography.

Table 1. Advances in understanding causes and implications of unexpected tetraphenylborate decomposition.

<u>Date</u>	<u>Accomplishment</u>
1/19/96	Tank 48H Organic Material Balance Drafted
1/23/96	Tank 50H Generation Rates and Mass Transfer Behavior Documented
2/4/96	Complete Consumption of Excess Sodium Tetraphenylborate Documented
2/8/96	First Meeting of ITP Process Chemistry and Mechanisms Panel
2/22/96	Mass Transfer Predictions for Future Pump Operations
2/23/96	Documented Acceptable Saltstone Product
2/28/96	Documented Acceptable Benzene Generation Rates in Saltstone Process
3/25/96	Documented Minor Contribution of Mechanical Energy to Decomposition
4/1/96	Documented Waste Analyses for Potential Future Feeds
4/9/96	Documented Simulation of Waste Addition to Tank 48H
4/29/96	Documented Accepted Filter Performance for Tank 48H Contents
4/30/96	Documented Hydrogen Radiolysis Data for Authorization Bases Upgrades

Figure 2. Logic diagram for studies of chemical generation of benzene.

Hexane Extraction of Tank 48H Slurry Samples

Neutral, aqueous-insoluble organic decomposition products of tetraphenylborate were isolated from the ITP slurry by extraction with hexane. Approximately 10 mL of ITP slurry were added to a preweighed centrifuge tube. The centrifuge tube was weighed again to accurately determine the amount of slurry added. The slurry was centrifuged for 10 minutes to separate the solids. The aqueous layer was decanted from the centrifuge tube. The solids were washed three times with 10 mL portions of water using the same centrifugation and decanting technique. The washed solids were then extracted with three 15 mL portions of hexane. The decanted hexane extracts from the three extractions were combined and analyzed. A fourth hexane extraction was analyzed separately to determine the effectiveness of the first three extracts.

NaTPB Decomposition Tests

Laboratory tests of NaTPB decomposition were conducted in reaction vessels that were continuously ventilated and stirred, and also in reaction bottles that were capped, not stirred, and non-ventilated (i.e., static). Both nitrogen and air atmospheres were used during the tests. The continuously ventilated tests were performed by placing 100 mL of salt solution into a 200 mL reaction vessel. The

solution varied from test to test but was in many instances actual Tank 48H filtrate. Sodium tetraphenylborate was added to this solution. Humidified air or nitrogen was passed through the vessel at a flow rate of approximately 10 mL/min. Samples of the vapor stream were analyzed periodically for benzene by a gas chromatograph fitted with a photoionization detector.

Static bottle tests were conducted by charging either glass, stainless steel, or polyethylene bottles with a salt solution or Tank 48H simulant. The bottles were capped in the appropriate atmosphere and the gas space sampled periodically. Liquid samples from both the ventilated and non-ventilated tests were obtained to investigate the potential for forming less volatile soluble aqueous products. In some tests (i.e., static tests conducted in stainless steel vessels), the liquid phase was sampled for benzene.

Isolation of Tank 48H Insoluble, Inorganic Solids in ITP Slurry Samples

The insoluble solids entrained in ITP slurry were isolated by filtering approximately 200 mL of ITP slurry. The solids were washed with three 50-mL portions of water to remove any residual water soluble material. The remaining solids were washed with acetonitrile to remove tetraphenylborate salts. The washing continued until the filtrate was clear. The solids were air dried. The solids were divided into ~0.25 g aliquots to reduce radiation exposure during removal from the Shielded Cells.

Monosodium Titanate Simulant

Actinide-loaded monosodium titanate (MST) was prepared from a sample of the same MST batch that had been added to Tank 48H in September 1995 (Optima lots #95QAB391 and #95QAB393). A solution (2 L) containing the major soluble components in Tank 48 (sodium salts of hydroxide, nitrate, nitrite, sulfate, aluminate, and carbonate) was prepared from reagent grade chemicals. An excess of Pu-239 (0.45 mg of Pu in acidic nitrate solution) and depleted uranium (30 mg of U in acidic nitrate solution) were added to the salt solution and stirred for one week to saturate the solution. Excess solids were removed using a filter with nominal 0.45 micron pore size. MST (2 g) was added to the filtered salt solution and stirred for one week to load the actinides onto the MST solids. The actinide-loaded MST was filtered, rinsed lightly with water, and dried at room temperature. The dried solids contained 0.26 wt % uranium.

IV. Results and Discussion

Tank 48H Data and Information

Tank 48H Operation

Starting on September 2 and continuing through September 29, 1995, 37,300 gallons of sodium tetraphenylborate were pumped to Tank 48H in eleven separate additions. These solutions contained a total of 14.6 kg of benzene. Appendix A outlines the timing of these additions and other events described herein. In addition, much of the data and information contained in this section and the remainder of the document were obtained from data reports issued by J. D. Menna, M. R. Williams, J. L. Kelly, and D. A. Zupon. These reports are too large to list or include in an appendix. A bibliography is available from the authors of this document.

During this time period, a number of other tank variables were recorded. Of particular interest for this report are the temperature of the liquid phase in the tank and the oxygen concentration in the vapor space in the tank. Tank temperatures were recorded by two thermocouple poles (small diameter tubes inserted in the D2 and D4 risers that contained thermocouples at different heights). Figure 3 represents the average of the lower two thermocouples from the D2 riser. These temperatures were recorded approximately every 4 hours. Figure 4 contains oxygen concentrations for the vapor space in Tank 48H over the same time period from one of two gas chromatographs mounted on Tank 48H. These data were collected at intervals ranging from 3 to 15 minutes. Outlying data points were culled from the data set. Data points were removed when the following criteria were met: the retention time for the GC varied by more than 1 second for the average retention time; the data point varied by more than 50% from its immediate neighbor data points and when the data point was taken from the port at the top of the tank. Next, data was extracted from the data set at 6 hour intervals and prepared for Figure 4.

Inspection of Figure 3 and Figure 4 indicate that during the addition of NaTPB, the temperature and oxygen concentration remained relatively constant at values of 33 °C and between 5 and 6 vol %, respectively. Following addition, the slurry pumps were operated for an extended period to provide mixing for the precipitation. This pump operation produced a measurable increase in the temperature in Tank 48H as indicated by Figure 3 since cooling coils were unavailable at that time.

On October 9, the first of three pump tests was performed. This test involved the operation of all 4 pumps for an extended period of time followed by operation of one pump for a brief period of time. This test was characterized by a nearly constant benzene release from the liquid phase to the vapor space that maintained the tank vapor space at nearly 60 ppm of benzene for a period of greater than 36 hours. Inspection of Figure 3 indicates that a temperature increase was associated with this operation. The oxygen concentration in the vapor space in Tank 48H remained relatively constant.

Following completion of the pump test on October 12, the tank remained quiescent until October 20. At that time, filtration of decontaminated salt solution commenced and continued until October 25. During filtration, approximately 140,000 gallons of filtrate were removed and the temperature of the liquid in Tank 48H remained relatively constant at approximately 39 °C.

The first filtration stage was followed by the second pump test starting on October 26 and continuing until October 29. During this operation, the temperature in the tank again increased measurably while the oxygen concentration in the vapor space remained relatively constant. Benzene concentrations were again found to be higher than anticipated; however, a measurable decrease in the benzene release rates was observed during this process after 24 hours of pump operation. A water addition was made during this test, but no change in the release rate for benzene was observed. The second pump test was followed by the second filtration stage from November 2 through November 7 that brought the liquid volume in Tank 48H to approximately 160,000 gallons. This filtration stage was marked by the same trends as observed during the previous concentration: namely, periods of relatively constant temperature and oxygen concentrations.

On November 9, the third pump test started. Due to the lower liquid level in the tank, the pumps caused a marked increase in the liquid phase temperature to a maximum value of 52 °C. However, the oxygen concentration again remained relatively constant during this time period. For a third time, the peak benzene release rate was higher than anticipated. The rate declined after approximately 24 hours of pump operation. Three water additions were made to Tank 48H during this time and none resulted in measurable increases in the benzene release rate.

The third pump test was followed by an extended quiescent time period. During this time, the ventilation to Tank 48H was shut down on three separate occasions. The first of these (from November 15 through November 20) was followed by a short period during which Tank 48H was ventilated with air. The period of time during which air ventilation was employed is marked by the large spike in the oxygen concentration in Figure 4. The second ventilation test ran from November 24 through November 26 while the third test ran from November 26 through November 30. Each of these three tests was marked by an increase in the oxygen concentration in the vapor space of Tank 48H. Upon restoration of nitrogen based ventilation, the oxygen concentration returned to values obtained during previous tests. Because no pumps operated in Tank 48H during this time period, the tank contents cooled. When pump operations commenced on December 1, the liquid phase in Tank 48H had cooled to approximately 30 °C.

On December 1, all four slurry pumps were operated for approximately 3.5 hours. Pump operation was then halted due to high (2000 ppm) benzene readings in the tank vapor space. This event was followed by periodic pump operation to deplete benzene from the tank between December 8 to January 3. During this time period, the contents of

the tank cooled further to 25 °C. From January 3 through March 5 the tank was quiescent. On March 5, one slurry pump was restarted at low speed (600 rpm). A large quantity of benzene was seen immediately in the head space, and portions of the tank vapor space reached benzene concentrations in excess of 4000 ppm within 14 minutes. The benzene concentration varied across the tank vapor space. Pump operation was terminated after 14 minutes.

Starting on March 8, periodic pump operations were resumed in an effort to deplete benzene from the tank. This effort is still in progress. Initial operations employed only one slurry pump. As

Figure 3. Tank 48H Temperature Profile for August 1995 through April 1996.

Figure 4. Tank 48H Oxygen Profile for August 1995 through April 1996.

benzene release rates decreased, additional pumps were started sequentially. By April 25, all four pumps were operating at maximum speed of 1180 rpm. From November 5 to April 22, 8500 kg of benzene were removed from Tank 48H.

Excess NaTPB in Tank 48H

During September 1995, 37,300 gallons of 0.55 molar NaTPB solution were added to Tank 48H. This quantity exceeded that required to precipitate the cesium and potassium in Tank 48H. A small fraction of the excess NaTPB dissolved. The remainder, the quantity present above the solubility limit, precipitated as insoluble NaTPB solids. In addition to the NaTPB added in September, there was a residual amount of potassium tetraphenylborate (KTPB) remaining in Tank 48H from the 1983 demonstration. The amount of this residual KTPB is calculated to be approximately 8400 kg. Since the slurry in Tank 48H was washed during the 1983 demonstration, no insoluble NaTPB was left from that test, and the amount of soluble tetraphenylborate ion, was not significant.

Analysis of Tank 48H samples from September 1995 through January 1996 indicate that the majority of the excess sodium tetraphenylborate was still present in the tank at the beginning of December. Samples obtained on December 18 and again in January indicated that more than 95% of the excess NaTPB had decomposed. Subsequent samples have shown an increase in both soluble cesium and potassium ion concentrations, indicating all excess NaTPB in Tank 48H eventually decomposed. [Ref. 7]

Given the fate of the excess NaTPB in Tank 48H, the exact quantity of this excess NaTPB becomes important for analyzing the incident. Calculation of the amount of excess NaTPB is based upon a number of variables. [Ref. 8] These include the total amount of fresh NaTPB added, the amount of residual NaTPB present, the soluble potassium and cesium ion concentrations, and any minor variations due to other precipitating species such as mercury. The largest source of error in this calculation is the analysis of soluble potassium. Prior to ITP startup, samples were obtained from Tank 48H in July 1995. [Ref. 9] The reported potassium ion concentrations in these samples ranged from 0.023 molar to 0.033 molar. The 37,300 gallons of NaTPB solution added to Tank 48H was based upon a soluble potassium ion concentration of 0.033 molar. This corresponds to a 31% (6600 kg) excess of NaTPB. Mass balances performed during removal of the benzene inventory from Tank 48H have shown that 12,200 kg of NaTPB decomposed. This quantity of excess NaTPB would imply that the soluble potassium ion concentration was in fact nearly 0.023 molar and not 0.033 molar.

Decomposition of NaTPB and Benzene Generation in Tank 48H

From October 1 through November 5, approximately 50 kg of benzene were removed from Tank 48H. Based on the benzene vaporization rate at the end of the third pump test, the tank contained less than 20 kg of benzene on November 14.

Approximately 8500 kg of benzene were removed from Tank 48H between December 1 and April 25. Thus, if one assumes a length of time during which the decomposition occurred, it is possible to estimate the benzene generation rate in Tank 48H. In Figure 5, two values are reported for the benzene generation rate after November 14. These two rates are based on the assumptions that the reaction reached completion on either December 8 (25,000 $\mu\text{g/L/hr}$), when pump operation was resumed, or December 28 (12,500 $\mu\text{g/L/hr}$), when analysis of the tank sample confirmed the absence of excess NaTPB, respectively. Figure 5 also presents estimates for the benzene generation rate based on previous studies of copper catalyzed decomposition. The rate after December 28 assumes a soluble TPB⁻ concentration calculated from a literature solubility correlation.[Ref. 22] Note that the scale for the vertical axis in Figure 5 is logarithmic.

Tank 48H Sample Results

Tank 48H was initially sampled per a defined sampling plan.[Ref. 10] At the onset of elevated benzene concentrations in the vapor space, samples were obtained more frequently. Surface samples were normally obtained by a dip bottle. Less frequently, samples were obtained using the variable depth sampler (VDS). When sampling, the contents of the tank were agitated prior to obtaining the sample. However, January and February samples were obtained without mixing the tank. Samples were analyzed by inductively coupled plasma emission spectroscopy (ICP-ES), inductively coupled plasma mass spectroscopy (ICP-MS), ion chromatography, high pressure liquid chromatography (HPLC), gas chromatography (GC), and titration. The results of the analyses are shown in Table 2. Other components included nitrate, nitrite, fluoride, chloride, phosphate, sulfate, oxalate, and

Figure 5. Estimates of Benzene Generation Rates for Tank 48H

Table 2. Tank 48H filtrate analyses.

Sample Date	Cs-137 (nCi/g)	K ⁺ (mg/L)	Benzene (g/L) ^a	Phenol (mg/L)	PBA (mg/L)	Soluble Boron (mg/L)	Copper (mg/L)	OH ⁻ (molar)
10/12	3	ND ^b	ND	189	<10	104	1.2	2.5
11/5	<0.5	ND	ND	220	<10	108	1.2	ND
12/1 (12/8) ^c	<0.5	ND	ND	550	850	392	<0.2	2.1
12/18 (12/28)	27	ND	ND	860	1800	610	1.4	2.6
1/5 (1/7)	50	ND	ND	740	1500	614	ND	2.7
1/12 (1/16)	71	ND	ND	729	1580	616	ND	2.6
1/21 (1/22)	78±15	1.8±.7	6.3	740±180	1730±190	561±10	ND	2.39±.06
1/26 (1/29)	62±14	1.6±.4	3.1	820±10	1860±20	588±2	ND	2.50±.02
2/10 (2/12)	78±15	2.4±1.0	6.9±4.0	980±20	1940±80	544±70	ND	2.47±.05
2/23 (2/26)	114±30	2.3±.6	ND	1030±10	1770±10	504±33	ND	2.14±.09
3/22 (3/24)	164	4.7	3.6±1.1	880	1710	566	ND	2.15
4/13 (4/15)	344±36	6.0±.8	0.41	1190±47	1565±38	533±26	ND	2.08±.08

^aBenzene data is obtained directly from slurry rather than filtrate alone.

^bND indicates analysis was not performed.

^cDates within parentheses indicate that date the sample was filtered.

formate, showed no significant changes and are not included. Examination of the data with respect to time provides clues to the extent of the decomposition reaction.

With respect to cesium-137, values less than 10 nCi/g are considered "decontaminated" and within normal process expectations. Examination of the data indicates that prior to December 1, the cesium-137

concentration was low and within normal process expectations. This indicates that sodium tetrphenylborate was in excess. After December 1, the concentration begins to increase, coincident with the loss of excess NaTPB. The increase from December 1 through March 22 is linear at a rate of 1.36 nCi/g·day. This rate is substantially lower than expected during storage in Tank 49H, 8 nCi/g·day, and observed after the 1983 demonstration, 16 nCi/g·day. [Ref. 11] The differences in composition (washed vs. unwashed precipitate) and dose rate are the most likely reasons for the different decomposition rate.

Potassium ion concentration was monitored starting January 21. The presence of very low levels of potassium ion confirm that degradation of KTPB has been minimal. These data, coupled with the cesium-137 data, support the conclusion that insoluble CsTPB and KTPB are not decomposed catalytically as found for the soluble NaTPB. The small increases in concentration of both species can be attributed to the expected small rates of radiolytic and thermal decomposition.

Benzene analysis of the KTPB slurry in Tank 48H was not attempted until mid-January. Samples obtained while the tank was static between mid-January and into February indicated that as much as 5500 kg of "free" benzene existed in Tank 48H. Roughly 8500 kg of benzene have been removed from the tank since the mixing pumps were restarted in early March. The poor agreement obtained from analysis is probably due to sampling variations (i.e., low values resulting from loss of benzene during sampling and transport) and bias in the analysis.

High Pressure Liquid Chromatography (HPLC) analyses were used to measure phenol and phenylboric acid (PBA) in Tank 48H filtrate samples. The initial phenol concentration (189 mg/L on October 12) is due to phenol in the 37,300 gallons of NaTPB solution (which accounts for 120 mg/L), and the remainder is presumed to be due to the decomposition of KTPB precipitate from 1983. A significant jump in concentration was noticed between November 5 and December 18. A steady or slight increase in concentration has been observed since mid-December. This may be due to the relatively slow decomposition of PBA, other unidentified decomposition products (e.g., diphenylboric acid, triphenylboron, CsTPB, and KTPB).

Similar behavior to phenol was observed for PBA. One distinct difference between PBA and phenol is that phenol is a stable end product from the decomposition of NaTPB while PBA is an unstable intermediate that undergoes further decomposition. As with phenol, a significant jump in concentration was observed between November 5 and December 18. Since December 18, PBA has remained within the range of 1500 - 2000 mg/L. The variations shown in Table 2 are believed to be due to random variations in the sampling and analysis.

The soluble boron concentration was measured by ICP-ES. This method provides a measure of total boron. All soluble boron species (e.g., sodium borate, PBA, diphenylboric acid and TPB) contribute to this value. Since this analysis is performed upon filtrate, insoluble boron-containing species do not contribute to the total boron value.

Therefore, the soluble boron concentration is a direct measure of the extent of decomposition of all tetraphenylborate species. As observed with phenol, the initial boron concentration is probably due to a combination of residual boron species in the 37,300 gallons of NaTPB solution and decomposition of precipitate remaining from the 1983 demonstration. As noted with previous analyses, a jump in concentration was observed between November and mid-December. Since mid-December, the concentration of soluble boron has been relatively constant. This evidence supports the theory that only NaTPB was catalytically decomposed and that the catalytic reaction has drastically reduced.

Tank 48H filtrate was analyzed for copper since it had previously been identified as a NaTPB decomposition catalyst. Analysis by both ICP-ES and ICP-MS confirmed the presence of 1.2 to 1.4 mg/L copper in samples from September through mid-December. The December 1 sample did not contain copper and this result is not currently understood.

The free hydroxide concentration in Tank 48H varied between 2.1 and 2.7 molar. This wide variance is due largely to analytical/sampling error. Hydroxide concentration is important to tank corrosion control and the concentration must be maintained above 1 molar when the nitrate concentration is less than 1 molar. Nitrate and nitrite concentrations in Tank 48H have been steady at $0.53 \pm .05$ and $0.64 \pm .05$ molar, respectively.

In addition to benzene, phenol, PBA, and sodium borate, biphenyl is a decomposition product of NaTPB. Samples from January 12 and January 21 were extracted with hexane and analyzed for biphenyl. This method of isolating the compound was necessary since biphenyl is a solid that is almost completely insoluble in the salt solution. The biphenyl concentration ranged from 1390 to 1690 mg/L. It should be noted that sampling a heterogeneous solution such as this can produce unreliable data.

Tank 48H Material Balance and Reaction Stoichiometry

A mass balance based on Tank 48H benzene releases through April 22, 1996 is given in Table 3. The mass balance indicates that after April 22, there was as much as 906 kg of benzene remaining in Tank 48H; the actual value would be lower if the initial potassium concentration was somewhat higher than assumed. The following assumptions were made in generating this mass balance.

- Initial Tank 48H K^+ concentration was 0.027 M. This is the lowest concentration obtained from sample analyses of the tank. [Ref. 9] Though these analyses indicated a range of K^+ concentration values in Tank 48H initially, this mass balance assumes the lowest K^+ result because benzene releases have already exceeded the available NaTPB for higher concentrations.
- Initial Tank 48H volume was 1.78×10^6 L (470,000 gal).

Table 3. Tank 48H Organics Mass Balance.

Species	Amount		Equivalent Benzene	
	Moles	kg	Moles	kg
NaTPB Destroyed	35,500	12,200	142,000	11,100
KTPB Destroyed	92.7	33.2	371	29.0
CsTPB Destroyed	0.06	0.03	0.24	0.02
Benzene Released (Oct. 1 - Nov. 5)	641 ^a	50.0	641	50.0
Benzene Released (Nov. 5 - Apr. 22)	109,000 ^a	8,500	109,000	8,500
PBA	8,100	1,000	8,100	633
Phenol (Oct. 12 - Nov. 5)	633	59.6	633	49.4
Phenol (since Nov. 5)	6,680	623	6680	518
Biphenyl	2,730	421	5,460	427
Terphenyl	141	32.5	423	33.0
Diphenyl Mercury	81.0	38.7	162	12.7
Remaining			11,300	906

^aThese benzene masses used measured GC benzene concentrations, and Tank 48H ventilation purge rate data in scfm (assumed to be at 0 °C and 1 atm). There was no correction applied for humidity. As this report neared completion, personnel discovered that the purge rate assumed a reference temperature of 70 °F. Additionally, the GC benzene analyses are made on dry air while ventilation flow rate is measured for humid air. The total effect of these combined corrections should reduce the benzene release numbers by 10 to 15%.

- 80,800 moles of NaTPB (27,600 kg) in 1.41×10^5 (37,300 gal) were added to Tank 48H.
- 40,900 moles (14,000 kg) of NaTPB precipitated as KTPB and CsTPB.
- 4,320 moles (1,480 kg) of soluble NaTPB in 1.31×10^6 L (346,000 gal) were transferred to Tank 50H.

- Tank 48H volume for most of the period between November 9, 1995 and March 31, 1996 averaged 6.11×10^5 L (161,000 gal). This increased to $\sim 6.40 \times 10^5$ (169,000 gal) on April 12.
- Phenylboric Acid (PBA) sample analyses indicated no significant change in PBA concentration since December 18. The PBA created is therefore based on the sample analyzed on April 15, 1996.
- Phenol concentrations seem to be trending up slightly; therefore, the phenol created is based on the results of the most recent Tank 48H sample. The concentration on November 5, 1995, prior to NaTPB destruction is subtracted from this. Additionally, since the sample results indicate that some phenol was created prior to November 5 (~ 633 moles), this has been added into this number.
- Biphenyl is based on the average of samples taken on January 12, 1996 and January 21, 1996. The contents of Tank 48H were assumed to be separated into a slurry phase containing solids, and a supernate phase with no solids, it was assumed that the results of the biphenyl analyses were good for the solids containing phase only and that the phase containing no solids also contained no biphenyl. The biphenyl concentration was corrected to an overall concentration for the whole tank. The biphenyl contained in Tank 48H on November 5, 1995 (based on the amount of biphenyl continued in the NaTPB added to Tank 48H) was subtracted.

Table 4. Production of Organic Species from Destruction of Tetraphenylborate.

Species	Moles Produced per mole TPB Destroyed
Benzene	3.08
PBA	0.23
Phenol	0.21
Biphenyl	0.08
Terphenyl	0.004
Diphenyl Mercury	0.002
Total	3.68

Note: Two phenyl groups are needed to produce biphenyl and diphenyl mercury; three are needed to produce terphenyl. One each is needed to produce each of the other species. This missing 0.34 moles of material is the result of the unaccounted for material. It is assumed to be ~ 906 kg of entrained benzene in Tank 48H.

Appendix B shows how the organics mass balance calculations were made. Table 4 gives the stoichiometric yield of the major decomposition products per molecule of NaTPB destroyed. It is based on the mass balance in Table 3.

As stated above, previous Tank 48H mass balances used different assumptions for the amount of NaTPB destroyed. These assumptions depended primarily on the initial K^+ concentration assumed in Tank 48H and the amount of NaTPB added in September. The K^+ analyses ranged from 0.023 M (implying the destruction of 35,500 moles of TPB or 11,100 kg of equivalent benzene) to 0.033 M (implying the destruction of 17,700 moles of TPB or 5,530 kg of equivalent benzene). [Ref. 9]

An alternative method to calculate the mass balance is to assume that the change in soluble boron concentration is an accurate measure of the amount of NaTPB destroyed. Prior to the rapid catalytic reaction, the boron concentration was 104 mg/L of which 33 mg/L was due to soluble NaTPB. The average boron concentration since December 18 is 565 ± 41 . The change attributable to TPB⁻ decomposition is approximately 500 mg/L. This corresponds to a total of 28,200 moles of NaTPB or 8800 kg of benzene.

The current generation rate of benzene from destruction of CsTPB and KTPB is estimated to be 13 $\mu\text{g/L/hr}$ or a total of 0.2 kg/day. This generation rate was obtained by linear regression of soluble K^+ and Cs-137 data obtained between December 8, 1995 and April 15, 1996 (Figure 6). The data are reasonably linear during that period although the most recent Cs sample shows a larger jump than expected. The fits of the data indicate that soluble K^+ and Cs^+ began appearing in Tank 48H about mid to late December.

Figure 6 also shows the soluble boron concentration. Soluble boron is almost constant since late December, especially when one considers that the volume in the tank has increased from approximately 154,000 gallons to 189,000 gallons since the ITP concentration phase. Since the boron concentration has been virtually constant since late December, it was decided to compare the soluble K^+ and Cs^+ concentrations to the B concentration. Figure 7 shows that the Cs^+ and K^+ concentrations nearly parallel each other.

Figure 8 gives the boron, hydroxide and organics (PBA and phenol) data for November 5, 1995 through April 15, 1996. The lines through the data represent linear regression fits of the data. The fits of the boron and organics data are each broken into two parts with a break in mid to late December. This corresponds to the time that all of the NaTPB in Tank 48H was completely destroyed. After this time, the concentrations of boron and the organics are expected to be reasonably constant with a slight decrease due to the addition of water to the tank. The boron and hydroxide concentrations show this decrease, while the organics concentrations still indicate a slightly increasing concentration.

Figure 6. Tank 48H soluble boron, potassium, and cesium concentrations.

Figure 7. Molar ratio of potassium and cesium to boron in Tank 48H filtrate.

As with the soluble K^+ and Cs^+ , a plot of the ratio of the hydroxide and organics concentrations was produced (Figure 9). The hydroxide decreases slightly with respect to boron. The organics, however, still seem to be increasing slightly with respect to boron concentration.

NaTPB Cold Feeds

Eleven batches of NaTPB solution were added to Tank 48H during September. The cumulative volume of the batches was 37,300 gallons. Each batch was within specification. [Ref. 12] Benzene analysis was performed by gas chromatography. Phenol, PBA and biphenyl were analyzed by HPLC. Table 5 provides data from the analyses. Addition of the NaTPB solution to the 506,000 gallons of waste present in Tank 48H in September would have produced a composite waste solution with a PBA concentration of 45 mg/L, a phenol concentration of 111 mg/L, and a biphenyl concentration of 8 mg/L.

Of the eleven batches added to Tank 48H, seven were prepared by Aquafine, Inc. (i.e., batches designated with an AC prefix). The other four were prepared by Holley Oak Chemical Company. All eleven were prepared from the original NaTPB material supplied by AFF Inc.. This material contains significant quantities of NaTPB decomposition products as evidenced by the organics analysis and the brown color of the solution.

Figure 8. Tank 48H soluble boron, hydroxide, and organics concentrations.

Figure 9. Molar ratio (soluble) of hydroxide and organics to boron in Tank 48H.

Boulder Scientific Company (BSC) serves as an alternate supplier of NaTPB to SRS and supplied the largest portion of material used in the 1983 demonstration. For comparative study, six batches of BSC NaTPB powder were sampled and analyzed for organic content by gas chromatograph and HPLC. Table 6 lists data from the analyses. Analysis indicates that all six met specifications. Furthermore, each is significantly more pure than AFF NaTPB, with respect to NaTPB decomposition product impurities. The difference in organic impurities is probably due to their production methods. AFF obtained the material by extraction while BSC obtained the material by crystallization. Crystallization is a purification technique and, by doing so, BSC purified the material. Toluene was found in small quantities in each BSC sample. It was, most likely the crystallization solvent used. For additional comparison, reagent grade NaTPB powder from Aldrich Chemical Company was analyzed by HPLC and found to contain <10 mg/L each of PBA, phenol, and biphenyl.

Kinetics of Copper-Catalyzed NaTPB Decomposition

Stability data from previous studies of copper-catalyzed NaTPB decomposition were examined in an effort to derive a rate expression for this reaction. [Ref. 2,3] Previously identified variables demonstrated to affect the rate of reaction included the soluble TPB⁻ concentration, copper concentration, and hydroxide concentration.

Table 5. Sodium tetraphenylborate solution analyses for those batches of material added to Tank 48H.

Batch	Volume (gal)	NaTPB (molar)	Benzene (mg/L)	PBA (mg/L)	Phenol (mg/L)	Biphenyl (mg/L)
AC-15	2735	0.53	143	515	1146	40
AC-16	3650	0.57	179	948	1410	20
AC-16	2342	0.56	80	758	1096	39
AC-17	3200	0.55	48	315	2400	59
AC-17	3907	0.59	169	315	2400	59
AC-18	2006	0.59	161	274	1500	224
AC-18	3301	0.63	190	274	1500	224
D0528	5097	0.53	<20	809	1249	32
D0528	5103	0.54	12	809	1249	32
D0528	1965	0.54	24	809	1249	32
D0559	4033	0.54	33	632	1229	56
Average	3390	0.56	103	609	1500	105

Table 6. Organic analyses from prepared solutions of Boulder Scientific Company NaTPB powder.

Batch	NaTPB (molar)	Benzene (mg/L)	PBA (mg/L)	Phenol (mg/L)	Biphenyl (mg/L)	Toluene (mg/L)
BSC-142-186A	0.539	13.6	<10	<10	15	29.5
BSC-142-250A	0.540	3.3	<10	<10	17	22.2
BSC-237-165A	0.533	15.1	207	<10	24	8.9
BSC-237-217A	0.534	10.9	<10	<10	17	0.9
BSC-237-280A	0.529	4.5	<10	<10	16	<1
BSC-237-324A	0.530	3.2	<10	<10	15	<1
Average	0.534	8.4	<43	<10	17	<11

A kinetics analysis of the data indicated that tetraphenylborate decomposition most closely fit a first order effect. The rate expression shown in Equation 1 was obtained from the analysis where all concentrations are in molarity and $[\text{TPB}^-]$

$$\text{Rate} = k[\text{Cu}][\text{TPB}^-]/[\text{OH}^-] \quad (1)$$

$$\begin{aligned} \text{and } k &= 0.078 \text{ hr}^{-1} \text{ at } 23^\circ\text{C}, \\ k &= 3.7 \text{ hr}^{-1} \text{ at } 40^\circ\text{C}, \\ k &= 90 \text{ hr}^{-1} \text{ at } 65^\circ\text{C}, \end{aligned}$$

represents the concentration of soluble tetraphenylborate ion. A graph of $\ln k$ vs $1/T$ (where T is in K) is shown in Figure 10. From the graph, an activation energy, E_a , of 140 KJ/mole was obtained.

NaTPB Decomposition Catalysts

Copper

Copper was initially investigated as the cause of catalytic NaTPB decomposition in Tank 48H. As mentioned in the introduction, copper concentrations as low as 0.10 mg/L are capable of initiating the reaction. Tank 48H was analyzed and found to contain approximately

Figure 10. A kinetics plot of $\ln k$ vs $1/T$ for the copper-catalyzed decomposition of NaTPB.

1.4 mg/L soluble copper. All sources of material in Tank 48H were examined for copper content to determine the possible contaminant. Table 7 lists the copper concentration and contributing volumes for these potential sources. Based upon the data, the source of copper contamination was the waste itself. A precipitate slurry sample obtained from Tank 48H in the late 1980's was found to contain 7.5 mg/L of insoluble copper. This supports the observation that the salt solution waste itself is contaminated with copper prior to treatment. Data is not available to assess the copper contribution from Tank 38H.

Speculation focused upon the solubility of copper in caustic waste solution. D. T. Hobbs investigated this question and found that the copper solubility profile passes through a minimum at a hydroxide concentration of 0.01 molar.[Ref. 13] At the high hydroxide concentrations found in Tank 48H, the soluble copper concentration is above 1.8 mg/L and may be an order of magnitude higher. Copper solubility as a function of hydroxide concentration and waste type is shown graphically in Figure 11. Copper was observed to increase significantly in concentration at higher hydroxide concentrations. At pH 10 and pH 12, the concentration of copper in high activity waste (HAW) and low activity waste (LAW) simulants was less than 0.2 mg/L. In the HAW simulant, the copper concentrations were 32.6 and 342 mg/L, at 1.2 molar and 5.0 molar hydroxide concentrations, respectively. In the LAW simulant, the copper concentrations were 1.78 and 190 mg/L, at 1.2 molar and 5.0 molar hydroxide concentrations, respectively. The lower copper concentrations in the LAW simulant compared to the HAW simulant are attributed to coprecipitation with ferric hydroxide that was also in the simulant. These results in this study are higher than, but consistent with, the trends reported for cupric oxide in aqueous solutions of sodium hydroxide.[Ref. 14]

Table 7. Potential Tank 48H copper contaminant sources.

Source	Volume (kgal)	Copper Concentration (mg/L)
Bearing water and other miscellaneous additions	10	0.003 (soluble)
monosodium titanate	2	<0.0001 (total)
NaTPB solution	37.3	<1 (soluble)
Tank 48H (July 1995)	420	<4 (soluble)
Tank 38H	130	undetermined

Figure 11. Copper solubility as a function of hydroxide concentration and waste type. [Ref. 13]

Potential Catalysts

A literature review was performed on tetraphenylborate chemistry and discussions were held with both internal and external experts in the areas of tetraphenylborate chemistry, catalysis, and radiolysis. [Ref. 15] The purpose of these investigations was to identify potential TPB⁻ decomposition catalysts. From these reviews, more than twenty-five metals were postulated as potential catalysts.

For comparative purposes, Tank 48H filtrate was analyzed by ICP-ES and ICP-MS. Table 8 lists the metals observed and their respective concentrations. Less than values are provided for those species which were analyzed for but found to be less than their detection limit. In addition, Tank 48H sludge (pre-ITP Batch 1) was analyzed. For informational purposes, the availability of solubility data for these metals in alkaline waste simulants is shown. An additional column notes if the postulated catalysts were previously tested for the ability to catalytically decompose sodium tetraphenylborate.

In addition to the listed metals, aluminum (0.6 - 2.9 wt %), phosphorous (0.01 - 0.04 wt %), calcium (0.09 - 0.21 wt %), barium (0.02 - 0.03 wt %), and magnesium (0.05 - 0.08 wt %) were detected in the Tank 48H sludge. Silicon (18 ppm) and phosphorous (340 ppm) were identified in the Tank 48H filtrate by ICP-ES. Gallium (1.39 ppm),

Table 8. Summary Table of Postulated Catalysts.

Postulated Catalysts	Concentration in Tank 48H Filtrate by ICP-ES (ppm) (a)	Concentration in Tank 48H Filtrate by ICP-MS (ppm) (a)	Concentration in Tank 48H Solids (wt % of total insolubles) (b)	Available Solubility Data (c)	Catalytic Activity
copper	1.4 (d)	ND	0.009 - 0.05	yes	active(f, g)
manganese	< 0.27	ND (e)	0.07 - 0.7	yes	inactive(f)
chromium	68	73	0.08 - 0.15	no	inactive(h)
ruthenium	ND	0.8	ND	no	not tested
palladium	ND	0.4	ND	no	not tested
rhodium	ND	0.2	ND	no	not tested
uranium	ND	1.0	0.02 - 0.03	yes	not tested
iron	< 1.4	ND	0.4 - 0.9	yes	inactive(j)
mercury	ND	< 0.05	ND	no	inactive(g)
zinc	7.7	4.2	0.01 - 0.04	yes	inactive(g)
molybdenum	10.8	12	ND	yes	not tested
silver	ND	< 0.01	ND	yes	not tested
nickel	< 2.3	ND	0.01 - 0.04	yes	inactive(f)
platinum	ND	< 0.01	ND	no	not tested
antimony	ND	< 0.05	ND	yes	not tested
bismuth	ND	ND	ND	no	not tested
cadmium	< 0.46	< 0.05	ND	yes	not tested
cerium	ND	< 0.01	ND	yes	not tested
cobalt	< 1.8	ND	ND	yes	not tested
lanthanum	< 0.27	ND	ND	yes	not tested
technetium	ND	2	ND	no	not tested
thallium	ND	< 0.01	ND	no	not tested
tin	2.3	0.9	ND	yes	not tested
titanium	< 0.09	ND	3.8 - 6.2	yes	not tested
zirconium	< 0.46	< 0.05	ND	yes	not tested

(a) Sample taken on December 1, 1995.

(b) Reference 16 - Sample from July 1995 and represents pre-reaction material. The total insoluble solids concentration in the sample was 0.55 wt %.

(c) Unpublished data from D. T. Hobbs.

(d) Result is from a sample taken from Tank 48H on December 18, 1995.

(e) ND indicates data for the specific metal was not obtained.

(f) Reference 17.

(g) Reference 2.

(h) Reference 2 showed chromium to be inactive while that reported in Reference 17 indicated chromium was an active catalyst.

(i) References 2, 17, and 18 showed iron to be inactive while that reported in Reference 19 indicated iron was an active catalyst.

selenium (0.8 ppm), lead (1.5 ppm), and arsenic (0.1 ppm) were observed in Tank 48H filtrate by ICP-MS. As noted in the table, some species were previously tested for catalytic activity in sodium tetraphenylborate solution. Other species tested, in addition to those in the table, included lead, magnesium, phenol, PBA, borax, and hydrogen peroxide. Each was determined to be inactive.

Isopropanol and methanol were present in large quantities in the 1983 Demonstration but were present in much smaller quantities in Batch 1. The concentrations of methanol and isopropanol in the 1800 gallons of monosodium titanate added to Batch 1 were 50 mg/L and 139 mg/L, respectively. It has been speculated that the presence of large quantities of alcohol may have prevented a radical decomposition NaTPB in the 1983 demonstration. Another theory speculates that the presence of organic decomposition products (e.g., triphenylboron, phenol, phenylboric acid, or a radical species) may initiate or be involved in the catalytic decomposition. Previous experiments performed to test this theory did not show that any of these have catalytic activity.[Ref. 2]

Non-Radioactive Simulant Slurry Recipe

Based upon the list of potential catalysts, a recipe for a representative, non-radioactive precipitate slurry simulant was developed.[Ref. 15] This is shown in Table 9. The recipe represents a hypothetical simulant that contains the primary components of Tank 48H precipitate slurry. The composition of non-radioactive simulants tested were varied depending upon the objective of the test being performed.

Table 9. Non-radioactive precipitate slurry simulant.

Component	Concentration
Na ⁺	4.7 M
OH ⁻	2.7 M
NO ₂ ⁻	0.70 M
NO ₃ ⁻	0.69 M
AlO ₂ ⁻	0.17 M
SO ₄ ²⁻	0.010 M
CO ₃ ²⁻	0.19 M
Cl ⁻	0.014 M
F ⁻	0.008 M
PO ₄ ³⁻	0.006 M
TPB ⁻	0.0033 M
copper (aq)	1.4 mg/L
chromium (aq)	73 mg/L
ruthenium (aq)	0.8 mg/L
palladium (aq)	0.4 mg/L
rhodium (aq)	0.2 mg/L
iron (aq)	1.4 mg/L
zinc (aq)	7.7 mg/L
molybdenum (aq)	12 mg/L
tin (aq)	2.3 mg/L
KTPB (s)	4.0 wt %
NaTPB (s)	0.6 wt %
MST (s)	0.20 wt %
Sludge (s)	0.20 wt %

Characterization of Tank 48H Insoluble Solids

Different types of insoluble solids exist in Tank 48H. These include KTPB, NaTPB, MST, sludge, CsTPB, biphenyl, terphenyl, and diphenylmercury. The distribution of the primary insoluble species as a percentage of the total amount of insoluble solids as a function of time (pre-startup through post-TPB degradation) is shown in Table 10. Table 11 provides the percentage of these four insoluble species in Tank 48H salt solution over the same time period.

Table 10. Composition of insoluble solids in Tank 48H from July 1995 through March 1996.

(July 1995 represents the tank condition prior to startup. October 1995 represents the tank condition after startup but prior to concentration. November 1995 represents the tank condition after concentration but prior to NaTPB degradation. March 1996 represents the tank condition after NaTPB degradation.)

Component	July 1995	October 1995	November 1995	March 1996
KTPB (g/100 g solids)	76	78.4	78.4	89.3
NaTPB (g/100 g solids)	0	12.2	12.2	0
MST (g/100 g solids)	11	5.4	5.4	6.2
Sludge (g/100 g solids)	13	4	4	4.5
Total Solids (g/100 g soln)	0.55	1.7	5.6	4.9

Table 11. Insoluble solids composition in Tank 48H from July 1995 through March 1996.

(July 1995 represents the tank condition prior to startup. October 1995 represents the tank condition after startup but prior to concentration. November 1995 represents the tank condition after concentration but prior to NaTPB degradation. March 1996 represents the tank condition after NaTPB degradation.)

Component	July 1995	October 1995	November 1995	March 1996
KTPB (g/100 g soln)	0.418	1.33	4.39	4.38
NaTPB (g/100 g soln)	0	0.207	0.683	0
MST (g/100 g soln)	0.060	0.092	0.302	0.304
Sludge (g/100 g soln)	0.072	0.068	0.224	0.220
Supernate (g/100 g soln)	99.45	98.3	94.4	95.1

Investigations into potential catalysts included attention on sludge as a potential heterogeneous catalyst to promote the decomposition of NaTPB. Many of the individual species identified earlier as potential catalysts are present in sludge. For this reason, the sludge composition of Tank 48H was examined.[Ref. 16] In addition to Tank 48H, the composition of Tank 51H sludge was examined.[Ref. 20] Tank 51H sludge has been used in tests as a surrogate for Tank 48H to decouple the influence of monosodium titanate from the sludge proper. The compositions of Tank 48H and Tank 51H sludge are shown in Table 12. In addition to sludge, researchers speculated that MST -- with adsorbed plutonium, uranium and other metal species -- may act as an active heterogeneous catalyst.

Table 12. Characterization of Tank 48H and Tank 51H sludge compositions.

Component	Tank 48H [Ref. 16] (g/100 g sludge)	Tank 51H [Ref. 20] (g/100 g sludge)
iron	4.17	24.60
sodium	38.14	8.74
aluminum	11.60	6.39
uranium	0.20	3.42
manganese	0.76	2.53
calcium	1.09	2.38
magnesium	0.48	1.16
silicon	NA ^a	0.63
phosphorous	0.18	0.53
nickel	0.16	0.26
chromium	0.91	0.17
mercury	NA	0.15
potassium	NA	0.05
copper	0.16	0.03
titanium	NA	0.02
plutonium	0.007	0.01
silver	NA	0.01
ruthenium	NA	0.003
rhodium	NA	0.001
palladium	NA	0.001
zinc	0.16	NA
barium	0.18	NA
oxygen & water	41.80	48.91

^aNA signifies that the species either wasn't detected or its concentration wasn't able to be accurately determined due to chemical interference.

Experimental Tests

Ventilated Radioactive Tests

Researchers performed radioactive tests to duplicate the NaTPB reaction in Tank 48H and to investigate the effect of different variables on NaTPB decomposition. Initial tests focused on the effect of potential soluble catalytic species. Figure 12 shows the rate of benzene generation obtained from Tank 48H filtrate (Nov. 5 sample). The filtrate was continuously ventilated with 10 mL/min air, stirred, and heated at 40 °C. The as-received filtrate generated benzene at a rate of 2 µg/L/hr. Sufficient AFF NaTPB solution (prepared from a composite of the archived samples remaining from the batches added to Tank 48H in September) was added to the filtrate to produce 1.8 wt % insoluble NaTPB. At that time, the benzene generation rate increased to 74 µg/L/hr. The rate peaked and eventually yielded a rate that varied from 20 to 50 µg/L/hr. Addition of excess potassium ion did not affect the rate. This lack of effect is believed largely due to the continued degradation of NaTPB intermediate decomposition products not precipitated by potassium. The cause of the jump in benzene production upon addition of NaTPB solution indicates that there was probably very little TPB⁻ remaining in the filtrate. Presumably, most, if not all, of the benzene generation activity is due to the 1.5 mg/L copper present in the filtrate. Appendix C contains data from this test.

Figure 12. Benzene generation rate as a function of time for Tank 48H filtrate.

Another radioactive test assessed the impact of sludge on NaTPB decomposition. At the time of the test, Tank 48H sludge and MST solids were not available. Also, the researchers wanted to determine the influence of the sludge without the presence of MST. Hence, 0.2 wt % Tank 51H sludge was used. Tank 48H filtrate (Nov. 5 sample) was used as the solution medium. A 3 wt % excess of oven-dried AFF NaTPB powder was added to the filtrate. The oven-dried AFF NaTPB powder was prepared for use by overnight low-temperature (40 °C) evaporation of AFF NaTPB solution (prepared from a composite of the archived samples remaining from the batches added to Tank 48H in September). This method of preparation was necessary to prevent dilution of the Tank 48H filtrate. The solution was continuously ventilated with 10 mL/min air, stirred, and heated at 40 °C. Data from the test are shown in Figure 13 and contained in Appendix D.

The solution almost instantaneously began to generate benzene. The rate increased linearly until it reached a maximum of 672 $\mu\text{g/L/hr}$. The rate of benzene generation then decreased linearly. To study the effect of temperature, the reaction temperature was raised from 40 to 50 °C to simulate the maximum temperature observed in Tank 48H (~52 °C). An immediate increase from 362 to 795 $\mu\text{g/L/hr}$ in the benzene generation rate was observed. The benzene generation rate peaked at

Figure 13. Benzene generation rate for Tank 48H filtrate containing 0.2 wt % Tank 51H sludge and oven-dried AFF NaTPB.

916 $\mu\text{g/L/hr}$. After this occurred, the rate of benzene generation began to decrease linearly. Eventually, the benzene generation rate reached steady state at approximately 40 $\mu\text{g/L/hr}$. Later in the test, the ventilation gas was changed from air to argon. In doing so, the benzene generation rate increased from 40 to 92 $\mu\text{g/L/hr}$.

Several observations result from this test. First, the method of preparation (i.e., low-temperature evaporation) may affect the stability of NaTPB. Second, the presence of Tank 51H sludge may promote the decomposition of NaTPB. Third, a 10 °C increase in temperature results in an increase in the benzene generation rate. Fourth, use of an inert gas for ventilation results in an increase in the benzene generation rate. The latter two observations will be discussed in further detail later in this section.

Tank 48H sludge and MST solids were isolated from a December sample of Tank 48H precipitate slurry. These solids were added to Tank 48H filtrate (Nov. 5 sample) to produce a combined sludge and MST solids content of 0.51 wt %. In comparison, Tank 48H contained 0.52 wt % sludge and MST solids after concentration (i.e., after November 7). Again, a 3 wt % excess of oven-dried AFF NaTPB powder was added to the filtrate. The oven-dried AFF NaTPB powder was prepared as described for the previous test. The test solution was continuously ventilated with 10 mL/min air, stirred, and heated at 40 °C. Data from the test is shown in Figure 14 and listed in Appendix E.

The initial benzene generation rate was approximately 2035 $\mu\text{g/L/hr}$ and increased rapidly to a maximum of almost 8600 $\mu\text{g/L/hr}$. Afterwards, the rate of benzene generation decreased almost equally as fast. Following 450 hr of testing, the reaction temperature was raised to 50 °C and the ventilation gas switched from air to nitrogen. An immediate increase in the benzene generation rate from 751 to 6021 $\mu\text{g/L/hr}$ was observed. After this increase, the rate of benzene generation again decreased. Eventually, the benzene generation rate reached steady state at approximately 900 $\mu\text{g/L/hr}$ at 50 °C. At that time, the reaction temperature was lowered to 40 °C. As a result, the benzene generation rate decreased from 941 to 362 $\mu\text{g/L/hr}$. A few days later, the temperature was again increased to 50 °C; the benzene generation rate increased from 326 to 812 $\mu\text{g/L/hr}$. Soon thereafter, potassium nitrate was added to the test. As observed previously in Figure 12, no significant effect on the benzene generation rate was observed.

Several observations can be drawn from this test. As evidenced in the previous test, the method of preparation (i.e., low-temperature evaporation) may affect the stability of NaTPB. Second, the presence of Tank 48H sludge and MST solids results in increased benzene generation rates, as compared to Tank 51H sludge. Once again, the

Figure 14. Benzene generation rate for Tank 48H filtrate in the presence of 0.51 wt % Tank 48H sludge and MST solids and containing oven-dried AFF NaTPB.

benzene generation rate is affected by both a 10 °C change in temperature and the use of an inert gas for ventilation. The latter observations will be discussed in further detail later in this section.

The stability of oven-dried NaTPB was investigated to permit differentiation between the effects of sludge, MST, and the method of preparing the NaTPB. In this test, Tank 48H filtrate (Nov. 5 sample) at a temperature of 40 °C and with a ventilation of 10 mL/min air was stirred and monitored for two days. During this time, the benzene generation rate was observed to be 1 µg/L/hr. At that time, oven-dried AFF NaTPB powder (prepared as described in the previous two tests) was added to the filtrate. In less than 100 hours after the addition, the benzene generation rate increased to 1732 µg/L/hr. After the benzene generation rate had decreased and reached a steady state, simulated Tank 48H MST was added to the test mixture. No increase in the benzene generation rate was observed. This data is shown in Figure 15, and listed in Appendix F at the end of this document.

One observation that can be made from this test is that oven-drying does affect the stability of AFF NaTPB. Recall from Figure 12 that when AFF NaTPB solution is added to Tank 48H filtrate, a much smaller

benzene generation rate was achieved. Also, the addition of simulated Tank 48H MST did not result in an increase in the benzene generation rate. This indicates catalysis by uranium-bearing MST is minimal or non-existent. However, this result may not hold true for Tank 48H MST since no plutonium was found when the simulated MST was analyzed (even though it was present in the solution used to prepare the simulated MST). It has been speculated that uranium or plutonium on MST may be a NaTPB decomposition catalyst. Uranium analysis data for the simulated MST was not available at the time this document was prepared.

Further study on oven-dried NaTPB was conducted in an attempt to discern if the instability observed with oven-dried AFF NaTPB would be observed with reagent grade NaTPB (from Aldrich Chemical Company) treated in the same manner. Tank 50H filtrate (sample was obtained in mid-March and diluted with water to simulate Tank 48H filtrate) was heated to a temperature of 40 °C, stirred, and ventilated with an air flow of 10 mL/min. The benzene generation rate produced from the filtrate alone was measured and found less than 10 µg/L/hr. After 24 hr, oven-dried reagent grade (Aldrich) NaTPB powder (prepared as described in the previous tests) was added to the filtrate. The benzene generation rate increased over the next 350 hr until it reached a maximum at 651 µg/L/hr. No sludge or MST solids were ever added to this test. The data clearly show that even the best available NaTPB is susceptible to decomposition. However, the extent of decomposition, based upon the benzene generated, is less than that

Figure 15. Benzene generation rate for Tank 48H filtrate containing oven-dried AFF NaTPB and simulated MST solids.

observed with oven-dried AFF NaTPB. This suggests that the AFF NaTPB contains more unstable NaTPB intermediates than does the reagent grade material. This data is shown in Figure 16 and listed in Appendix G.

A test similar to the test depicted by Figure 13 was conducted. The only difference between the tests was that the amount of Tank 51H sludge added to this test was half of that added in the previous one. A sufficient quantity of Tank 51H sludge was added to Tank 48H filtrate (Nov. 5 sample) to result in a concentration of 0.1 wt %. A 3 wt % excess of oven-dried AFF NaTPB powder was added to the filtrate. The oven-dried AFF NaTPB powder was prepared in the same manner as in all other tests. The solution was continuously ventilated with 10 mL/min air, stirred, and heated at 40 °C. Benzene generation rate data from the test are shown in Figure 17 and listed in Appendix H.

The solution initially generated benzene at a rate of 45 µg/L/hr. The rate of increase from this test was substantially lower and appeared to level off at approximately 200 µg/L/hr. Subsequently, the ventilation gas was switched from air (10 mL/min) to nitrogen (10 mL/min). Once again, the benzene generation rate immediately increased from 192 to 415 µg/L/hr. Unlike the temperature increase,

Figure 16. Benzene generation rate for Tank 50H filtrate (diluted to simulate Tank 48H filtrate) containing oven-dried AFF NaTPB.

Figure 17. Benzene generation rate for Tank 48H filtrate containing 0.1 wt % Tank 51H sludge and oven-dried AFF NaTPB.

this increase was temporary. At the end of the test, a candidate reaction inhibitor, sodium sulfide, was added to the solution. The benzene generation rate decreased rapidly. The data suggest that the candidate inhibitor was effective. However, due to the scatter within the data, further tests are needed to verify the results.

One observation from this test is that the benzene generation rate is less than half that observed in the first Tank 51H sludge test. This could result from the decrease in activity due to a decrease in the quantity of catalyst. Another observation is the use of an inert gas for ventilation results in a temporary increase in the benzene generation rate.

Two additional radioactive tests were performed with Tank 48H filtrate (Nov. 5 sample). The first test was similar to the test represented by Figure 13. The only difference in this test from the original was that 3 wt % of untreated reagent grade NaTPB powder (from Aldrich) was used. In addition to the untreated reagent grade NaTPB, the Tank 48H filtrate also contained 0.2 wt % Tank 51H sludge. It was heated at 40 °C, stirred, and ventilated with air at 10 mL/min. Benzene generation from the mixture was monitored for over 700 hours. Data from the test is shown graphically in Figure 18 and

Figure 18. Benzene generation rate for Tank 48H filtrate containing 0.2 wt % Tank 51H sludge and untreated reagent grade NaTPB.

listed in Appendix I. The rate of benzene generation was much lower than observed in the earlier test (see Figure 13) and it appeared to reach a steady state of approximately 100 $\mu\text{g/L/hr}$. Later in the test, the ventilation gas was switched with the same results as seen in previous tests. A temporary increase in benzene generation was observed. The rate eventually stabilized near 40 $\mu\text{g/L/hr}$.

The second benzene generation rate test was similar to the test represented by Figure 14. This test, like the difference described in the previous test, used 3 wt % of untreated reagent grade NaTPB powder (from Aldrich) in place of oven-dried AFF NaTPB. Also, a smaller amount (0.25 wt % instead of 0.51 wt %) of Tank 48H sludge and MST was added to the test mixture. The Tank 48H filtrate was heated at 40 °C, stirred, and ventilated with air at a flow rate of 10 mL/min. Again, benzene generation was monitored over the next 1000 hours. Benzene generation rate data for this test are shown in Figure 19 and listed in Appendix J.

Like the data from the previous test shown in Figure 18, benzene generation was much lower than observed in Figure 14. A nearly steady state rate of approximately 100 $\mu\text{g/L/hr}$ was observed. Subsequently, the reaction temperature was raised to 50 °C and the ventilation gas switched from air to argon. An immediate increase in

Figure 19. Benzene generation rate for Tank 48H filtrate containing untreated reagent grade NaTPB and 0.25 wt % Tank 48H sludge and MST.

the benzene generation rate from 135 to 593 µg/L/hr was observed. The benzene generation rate reached steady state at approximately 400 µg/L/hr at 50 °C. After approximately 300 hr at this condition, the ventilation gas was switched back to air. No significant change in the benzene generation rate was observed over the next 400 hours.

The data shown in Figure 18 and Figure 19 indicate that untreated reagent grade NaTPB is much less reactive than oven-dried NaTPB. In addition, both tests indicate that switching to an inert gas results in a temporary increase in benzene generation. The data from the first 250 hours of reaction suggest that Tank 51H sludge and Tank 48H sludge and MST behave similarly (i.e., they appear equally active as a catalyst) under similar conditions.

The final radioactive test investigated the reactivity of NaTPB from another vendor, Boulder Scientific Company (BSC). The test was similar to the first test of reagent grade NaTPB from Aldrich Chemical Company. A December 18 sample of Tank 48H filtrate was heated at 40 °C, stirred, and ventilated with air at a flow rate of 10 mL/min. The benzene generation rate from the filtrate alone was observed quite high at the start of the test (294 µg/L/hr) and decreasing with time. Data from this test is shown in Figure 20 and listed in Appendix K.

More than a month earlier, a sample of Tank 48H filtrate from December 18 was monitored by D. D. Walker and found to exhibit the same phenomena. Interestingly, both filtrate samples exhibited similar rates of decrease and both samples produced nearly 300 $\mu\text{g/L/hr}$ benzene at the start of each test. The December 18 filtrate samples were unlike the previously used November Tank 48H filtrate samples in that the NaTPB present in November was all decomposed by December 18. As a result, December 18 filtrate contains significantly higher quantities of PBA, phenol, and other decomposition products. Therefore, the benzene being generated from the December 18 filtrate samples resulted from the continuing decomposition of NaTPB intermediate products such as PBA and diphenylboric acid. The fact that both samples, which yielded the same result, were tested more than a month apart suggests that the intermediates were stabilized between tests. The most probable explanation of this stabilization was that the storage temperature was sufficiently low to retard the decomposition.

After the high rate of benzene generation from the filtrate had been baselined, the BSC NaTPB was added to the filtrate. An immediate spike in the benzene generation rate was observed. This is not atypical and, in fact, is seen any time that crystallized NaTPB

Figure 20. Benzene generation rate for Tank 48H filtrate containing untreated Boulder Scientific Company NaTPB powder and 0.2 wt % Tank 51H sludge.

powder is added to a solution (see Figure 18 and Figure 19 for these same spikes at the start of the reactions). The benzene generation rate returned almost immediately to the expected baseline without further increase. Eventually, 0.2 wt % Tank 51H sludge was added to the test mixture. A small increase in the benzene generation rate was observed. However, the benzene generation rate then paralleled the expected Tank 48H filtrate baseline suggesting that a slow reaction was occurring. The data contained in this test suggest that BSC NaTPB powder is stable (like the reagent grade NaTPB from Aldrich). The data also provides insight into the probable cause of elevated benzene observed in Tank 50H in December 1995. This will be discussed in a later section.

Summary of Radioactive Tests

The ventilated and stirred radioactive tests provided several observations and insights into possible variables in the decomposition of NaTPB. However, none of the tests provided the "smoking gun" evidence of the exact cause of the NaTPB decomposition reaction observed in Tank 48H. Results of the nine tests described in the above section are summarized in Table 13. The highest average benzene generation rate observed in the tests was 2214 $\mu\text{g/L/hr}$ over a period of nearly two months. However, even this rate is not comparable to the Tank 48H reaction. The benzene produced in the test represents the decomposition of only 8.3 wt % of the NaTPB in the test. None of the additives (i.e., Tank 51 H sludge, Tank 48H sludge and MST, soluble catalysts in Tank 48 filtrate, or NaTPB source) tested in these continuously stirred and ventilated systems produced a reaction similar to that in Tank 48H. Recall that one criterion in the search for the cause of the reaction was complete decomposition of the NaTPB. The extent of reaction observed in the tests indicates that the bulk of the NaTPB tested was stable and

Table 13. Summary of Benzene Generation Rates for Radioactive Tests.

	Type of NaTPB	Sludge/Solids	Reaction Time (hr)	Average Benzene Generation Rate ($\mu\text{g/L/hr}$)	Benzene Generated (wt % of NaTPB)
Figure 12	AFF Soln.	None	1430	30	0.203
Figure 13	AFF Powder ^a	0.2 wt % Tk 51H	979	341	0.910
Figure 14	AFF Powder ^a	0.5 wt % Tk 48H	1384	2214	8.344
Figure 15	AFF Powder ^a	Simulated MST	569	773	1.196
Figure 16	Aldrich ^a	None	502	308	0.443
	AFF Powder ^a	0.1 wt % Tk 51H	572	204	0.318
Figure 17					
Figure 18	Aldrich	0.2 wt % Tk 51H	787	76	0.164
Figure 19	Aldrich	0.2 wt % Tk 48H	984	342	0.918
Figure 20	BSC	0.2 wt % Tk 51H	647	38	0.068

^arepresents oven-dried NaTPB powder.

unreactive in the conditions employed and that the small amount of decomposition observed was more likely due to impurities and a small fraction of unstable material.

Two main influences on the NaTPB decomposition reaction that were identified in the radioactive tests were the influence of temperature and ventilation gas. These were briefly mentioned when describing each test. The effect of both temperature changes and ventilation gas switches in each test are summarized in Table 14. In those tests with a 10 °C temperature change, there was an average change (absolute value) in the benzene generation rate of 254%. In those tests where there was a switch in ventilation gas from air to, an average change (absolute value) in the benzene generation rate of 193% was observed. In the two events where there was both a 10 °C temperature rise and a switch in ventilation gas, an average change (absolute value) in the benzene generation rate of 624% was observed. Based upon the individual event changes of 254% and 193%, a dual change would be expected to produce an average change of 490%. While there is much scatter in the data, it is clear that both a 10 °C increase in temperature and a switch in ventilation gas from air to an inert gas produce drastic increases in the benzene generation rate.

Ventilated Non-Radioactive Tests

Two ventilated, non-radioactive tests that simulated Tank 48H were conducted. The tests were similar to each other in that both contained 4.5 wt % tetraphenylborate solids (prepared from AFF NaTPB solution) in a Tank 48H salt solution simulant. Each was spiked with 1.4 mg/L copper as copper nitrate. One contained more NaTPB

Table 14. Percent change in the benzene generation rate as a result of changes in temperature and ventilation gas.

Figure #	Initial		Final		Change in Benzene Generation Rate (% absolute value)
	Condition	Benzene Generation Rate (µg/L/hr)	Condition	Benzene Generation Rate (µg/L/hr)	
12	40 °C	362	50 °C	916	253
12	50 °C	104	40 °C	53	196
12	air	52	N ₂	100	192
13	40 °C, air	751	50 °C, N ₂	6021	802
13	N ₂	2331	air	941	248
13	50 °C	941	40 °C	326	289
13	40 °C	326	50 °C	901	276
16	air	192	N ₂	415	216
17	air	74	N ₂	147	199
18	40 °C, air	135	50 °C, N ₂	593	439
18	N ₂	376	air	348	108

(relative to potassium) while the other did not have any NaTPB (only KTPB was present). The tests were conducted similarly to all other ventilated tests. The precipitate slurry was heated at 40 °C while 10 mL/min of air was flowed over the surface of the stirred mixture.

The benzene generation rate of the solution containing the excess of NaTPB ranged from 38 µg/L/hr at the start of the test to 12 µg/L/hr near the end of the test. The test was run for over 500 hours. The benzene generation rate of the solution containing only KTPB ranged from 39 µg/L/hr to 14 µg/L/hr at the end of the test. Again the test duration was more than 500 hours. The data suggest that these non-radioactive simulants reacted similarly to each other but did not simulate the rapid decomposition reaction observed in Tank 48H. Data from these tests are contained in Appendix L (excess NaTPB test) and Appendix M (KTPB only test).

Given the low rates (relative to Tank 48H) observed in the above mentioned two ventilated non-radioactive slurry tests, two additional ventilated, non-radioactive tests were performed using NaTPB solutions. These tests mimic tests performed in 1990 where rapid decomposition was observed. Each test was identical to the other except for the ventilation gas. The tests were conducted in much the same manner as the ventilated radioactive tests. In these tests, reagent grade NaTPB solution (0.5 molar NaTPB and 0.1 molar NaOH) was spiked with 10 mg/L copper nitrate. The solutions were heated at 70 °C and ventilated at a flow rate of 10 mg/L. The first test was ventilated with air while the second test was ventilated with nitrogen. The benzene generation rate was measured daily. Benzene generation rate data for the air ventilated test is shown in Figure 21 and listed in Appendix N. Benzene generation rate data for the nitrogen ventilated test is shown in Figure 22 and listed in Appendix O. Unlike in the radioactive tests, the solution was sampled periodically and analyzed for PBA, phenol, biphenyl, TPB⁻, and hydroxide. This data along with the cumulative amount of benzene generated are listed in Table 15 for the air ventilated test and Table 16 for the nitrogen ventilated test.

The data show that two distinct reaction mechanisms were responsible for the decomposition process. In air, an induction period of nearly 100 hr was observed during which time hydroxide appears to be slowly consumed. After the reaction initiated, a benzene generation rate in excess of 2,000,000 µg/L/hr was obtained. The rate of benzene generation decreased linearly as a result of the decreasing TPB⁻ concentration. Small quantities of the decomposition product phenol was produced as was the intermediate decomposition product PBA. Biphenyl, which is highly insoluble in aqueous salt solutions, was observed in trace amounts. The benzene to phenol mole ratio was 9.42 to 1 after 90.8 % decomposition of the NaTPB had been achieved. In addition, the color of the solution became dark brown-black during the reaction with the largest degree of color change occurring after the induction period was over.

In the nitrogen ventilated test, no induction period was observed. Reaction was almost instantaneous and the benzene generation rate was at least 1,800,000 µg/L/hr. One subtle difference between the two

Figure 21. Benzene generation rate for the air ventilated non-radioactive test with reagent grade NaTPB solution.

Table 15. Analytical data from the air ventilated decomposition of NaTPB solution in the presence on 10 mg/L copper.

Reaction Time (hr)	NaTPB Remaining (moles)	Cumulative Benzene Generated (moles)	PBA (moles)	Phenol (moles)	Biphenyl (moles)	Free Hydroxide (molarity)
0	0.0500	0.0000	0.0000	0.0000	0.0000	0.0963
18.1		0.0000				
42.9	0.0494	0.0001	0.00039	0.00048	<0.00004	0.0938
72.0		0.0003				
92.7	0.0465	0.0006	0.00010	0.0022	<0.00004	0.0819
115.8		0.0076				
139.4		0.0459				
165.0	0.0114	0.1017	0.0133	0.0107	0.000045	0.4144
190.2		0.1311				
212.4	0.0046	0.1433	0.0007	0.0152	<0.00007	0.5125
236.2		0.1466				

Table 16. Analytical data from the nitrogen ventilated decomposition of NaTPB solution in the presence of 10 mg/L copper.

Reaction Time (hr)	NaTPB Remaining (moles)	Cumulative Benzene Generated (moles)	PBA (moles)	Phenol (moles)	Biphenyl (moles)	Free Hydroxide (molarity)
0	0.0500	0.0000	0.0000	0.0000	0.0000	0.0963
19.5		0.0527				
43.1	0.0181	0.0975	0.0257	0.0005	<0.00004	0.3625
68.6		0.1261				
93.4	0.0079	0.1435	0.0220	0.0021	<0.00004	0.5106
116.3		0.1542				
139.5		0.1651				
164.8	0.0033	0.1748	0.0155	0.00071	<0.00004	0.4388
190.0		0.1808				
212.7	0.0047	0.1882	0.0089	0.00042	<0.00007	0.4419
237.0		0.1925				

Figure 22. Benzene generation rate for nitrogen ventilated non-radioactive test with reagent grade NaTPB solution.

tests was that the rate of benzene generation in nitrogen did not decrease linearly but rather appeared to decrease exponentially with decreasing TPB⁻ concentration. Another difference observed in this

test was the reaction stoichiometry. Only trace amounts of phenol were formed. Biphenyl was not observed in the HPLC chromatograms. Biphenyl is highly insoluble in aqueous salt solutions and would not be expected to be seen in HPLC chromatograms of filtrate samples. However, an insoluble organic, presumably biphenyl, was observed floating in small beads on the surface of the solution. This contrasts the air ventilated test in which no insoluble biphenyl beads were observed in the test solution. The benzene to phenol mole ratio was 448 to 1 after 90.6 % decomposition of the NaTPB had been achieved. In this test, the color of the solution remained clear throughout the entire test.

Non-Ventilated, Non-Radioactive (Bottle) Tests

Series A Test

These tests represent an initial attempt to determine the effect of various chemical species on the rate of decomposition of simulated Tank 48 slurries. Portions of simulated Tank 48H slurry (100 mL) were prepared and placed in polyethylene bottles with screw caps. A different combination of minor components was added to each bottle. The bottles were incubated in ovens at either 40 or 70 °C. Samples were taken each week and analyzed for soluble boron, phenol, and phenylboric acid. No effort was made to exclude air. The slurries were calculated to contain 0.7 wt % excess NaTPB solids. The pre-test expectations of large increases in the decomposition products were never observed during the seven weeks of testing. Post-test evaluation of several slurries showed no excess NaTPB present. It is probable that a combination of potassium impurities in the sludge and low tetraphenylborate in the AFF/Aquafine solutions combined to significantly reduce the actual excess NaTPB relative to the calculated amount. Despite the low total amount of decomposition measured, the results do suggest potential effects due to minor components. The test matrix is shown in Table 17. The test variables are listed below.

<u>Variable</u>	<u>Components</u>
NaTPB source	reagent grade (Aldrich) or AFF/Aquafine
Temperature	70 °C or 40 °C
Soluble Cu	1.5 mg/L, added as Cu(II) salt
Soluble minor salt components	Mo(VI) 12 mg/L Cr(VI) 73 mg/L Si(IV) 18 mg/L Se(VI) 0.8 mg/L As(IV) 0.1 mg/L Zn(II) 7.7 mg/L

(Continued on the next page)

Soluble minor	Pb(II)	1.5 mg/L
salt components	Fe(III)	1.4 mg/L
(continued)	Sn(II)	2.3 mg/L
	Ru(III)	0.8 mg/L

Sludge 2.4 g/L

The sludge was predried and contained the following components:

Al	4.8	wt % of dry sludge
Fe	28.8	wt % of dry sludge
Mn	5.9	wt % of dry sludge
Ru	0.23	wt % of dry sludge
Pd	0.11	wt % of dry sludge
Rh	0.06	wt % of dry sludge
Cr	0.2	wt % of dry sludge
Cu	0.1	wt % of dry sludge
Mg	0.1	wt % of dry sludge
Ni	2.5	wt % of dry sludge
Pb	0.3	wt % of dry sludge
Zn	0.2	wt % of dry sludge
Zr	2.5	wt % of dry sludge

MST	2.4 g/L. (MST was not pre-loaded with U and Pu)
MnO ₂	2.4 g/L

Alcohols	isopropanol	80 mg/L
	methanol	8 mg/L

Benzene 2.5 g/L

Pre-irradiation A portion of the AFF slurry was irradiated to a dose of 1.1 Mrad prior to the addition of other minor components.

The results are shown in Figure 23 through Figure 25. The results near the latter half of the test (27-49 days) have been corrected for bias in the analysis based on a standard submitted with each batch of samples. The standard was not included during the first half of the test. Soluble boron (Figure 23) appears to have increased significantly in several bottles at fourteen days. The only bottles that did not show this jump were the ones at 40 °C. The subsequent decrease in soluble boron in many of these bottles is unexplained since none of the major soluble decomposition products containing boron (sodium borate, phenylboric acid, or diphenylboric acid) approached their saturation limits. These results suggest that the available NaTPB excess decomposed between 7 and 14 days following the start of the test. The phenylboric acid results (Figure 24) also suggest that decomposition occurred at about the same time as indicated by the soluble boron results. The subsequent disappearance of this compound is expected since it is known to hydrolyze to benzene and sodium borate at a slow rate without catalyst present. The

Figure 23. Boron results for Series A tests.

phenol results (Figure 25) showed three patterns in different samples: (1) no change, (2) gradual increase during the entire test, and (3) rapid initial increase followed by a leveling off.

Considering the results for all three products and emphasizing the later data points, the results suggest the following generalizations:

- Temperature increases significantly promote decomposition,
- Neither reagent grade (test A) nor AFF/Aquafine NaTPB (test C) decompose if none of the minor components are present,
- AFF/Aquafine NaTPB (test D) appears more susceptible to degradation in the presence of (only) soluble Cu than reagent grade NaTPB (test B),
- MnO_2 has no effect alone (test E),
- Preirradiation increases decomposition (test J versus test G),
- Sludge and soluble copper promote decomposition,
- Other components (minor soluble compounds, MST, alcohols, or benzene) do not increase decomposition over the effect of the sludge or soluble copper.

These generalizations are not conclusively proven by these Series A tests and further work is suggested.

Figure 24. Phenylboric acid results for Series A tests.

Figure 25. Phenol results for Series A tests.

Table 17. Series A Test Matrix.

Test ID	Temp. (°C)	NATPB Source	Additives							
			Copper	Soluble Minor	Sludge	MST	MnO ₂	Alcohol	Benzene	Pre-Irrad.
A	70	Aldrich								
B	70	Aldrich	+ ^a							
C	70	AFF								
D	70	AFF	+							
E	70	AFF					+			
F	70	AFF			+					
G	70	AFF	+	+	+	+				
H	70	AFF	+	+	+	+		+		
I	70	AFF	+	+	+	+			+	
J	70	AFF	+	+	+	+				+
K	40	AFF	+	+	+	+				
L	40	AFF	+	+	+	+			+	
M	40	AFF	+	+	+	+				+

^a+ indicates the additive was present in the test sample.

Table 18. Results of NaTPB Solution Bottle Test.

Elapsed Time (days)	Benzene (g/L)		
	Bottle A (air, 0.1 M OH ⁻)	Bottle B (air, 0.4 M OH ⁻)	Bottle C (N ₂ , 0.1 M OH ⁻)
0	0.010	0.0009	0.019
2	45	34	57
4	64	48	61
7	64	48	61

NaTPB Solution Test

The purpose of these experiments was to determine the effect of benzene and sodium hydroxide on the decomposition rate. It had been postulated that a layer of benzene might provide a non-aqueous phase which would promote the decomposition reaction. Hydroxide had been postulated as a potential inhibitor of the reaction. Portions of the same solution described above for the non-radioactive ventilated tests (See Figure 21 and Figure 22) were placed in 125-mL glass bottles and closed with septa-lined caps. In this test, the solutions were not stirred. The first bottle was sealed under air. The second bottle was sealed under air after additional sodium hydroxide was added to increase the concentration to 0.40 molar. The third bottle was sealed and then purged with nitrogen. The bottles were placed in an oven at

70 °C for 15 minutes, then removed and sampled. After 24 hours, a visible layer of benzene was observed in all three bottles. After 48 hours, the benzene layer was removed by syringe and the volume measured. In addition, a portion of the aqueous phase was removed and analyzed for phenol and phenylboric acid by HPLC. The removal of benzene and sampling for analysis was repeated after 4 and 7 days, at which time the experiment terminated. Table 18 shows the results of the analyses for benzene. Large amounts of phenol, phenylboric acid, and unidentified products (possibly triphenylboron and diphenylboric acid) were found in the aqueous phase while biphenyl was found in the benzene phase. The potential yield of benzene is 156 g/L. It is uncertain why the reaction appears to have stopped without going to completion.

Series 1 Sealed Stainless-Steel Bottle Tests.

Researchers studied the decomposition of tetraphenylborate slurries using sealed ~150 mL stainless steel vessels stored unstirred at a temperature of 70 °C. A black polymeric material, possibly either neoprene or viton, was used as the sealing gasket material. Three vessels were prepared with 120 mL slurries with various additives present. All of the slurry came from the same ~0.5 L batch. The composition of the slurry and the various additives are shown in Table 19. The slurry was prepared to be ~4.7 M Na⁺ and to have a Tank 48H simulated salt solution content with theoretically 4 wt % KTPB and 0.6 wt % NaTPB. Slurry was prepared using solid powder-like Aquafine NaTPB. These tests investigated the combined effects of radiation and temperature compared to temperature effects only. Another purpose for conducting these tests was to investigate the effects of nine additional soluble metal ion additives and some trace levels of various organic species. Previous initial Series A tests in sealed polyethylene bottles at 70 °C did not contain these nine soluble metal components nor the trace organics. The organic components were added to approximately the known levels of organics present in Tank 48H slurries prior to the excessive benzene production. One vessel was exposed to 70 °C and received no irradiation. The other two vessels were intermittently irradiated to approximate a 24,000 rad/day dose rate (~ 15 minutes every other day at a dose rate of ~2x10⁵ rad/hr) and exposed to 70 °C when not being irradiated. The dose of ~24,000 rad/day approximates the daily dose received by the radioactive slurry in Tank 48H. This dose was based on a measured Cs-137 specific activity of ~ 400,000 Ci / 160,000 gallons of radioactive slurry in Tank 48H. This amount of radioactive C-137, which is the predominant radionuclide contributing to the radioactivity of the slurry, was determined from an acid digestion of an actual slurry sample followed by gamma spectroscopy.

Figure 26 and Figure 27 show the amounts of decomposition products produced as a function of time over ~ 1,000 hours of testing. Figure 26 shows the results for the 70 °C exposed slurry with additives and no radiation exposure. Figure 27 shows one of the duplicate irradiated and 70 °C exposed slurries with additives. Benzene yields were measured by sealing 0.25-0.5 mL of the slurry in sealed 1.0 L glass bulbs. After evaporation, benzene in the vapor space of the bulbs was measured by gas chromatography. All other products were

Table 19. Tank 48H batch #1 Aquafine tetraphenylborate simulant slurry.^a

Salt Content	Soluble Additives ^b (mg/L)		Solid Additives
4.7 M Na ⁺	1.7 Cu(II)	0.3 Ru(III)	0.17 wt % Sludge
2.7 M OH ⁻	12 Mo(VI)	0.6 Ag(I)	0.17 wt % MST
0.7 M NO ₂ ⁻	60 Cr(VI)	2.2 Hg(II)	0.11 wt % SiO ₂
0.69 M NO ₃ ⁻	16 Si(IV)	12.2 Ca(II)	
0.01 M SO ₄ ²⁻	1 Se(VI)	0.1 Sr(II)	
0.19 M CO ₃ ²⁻	0.04 As(IV)	0.05 La(III)	
0.014 M Cl ⁻	8.8 Zn(II)	0.3 Ce(IV)	
0.008 M F ⁻	1.2 Pb(II)	0.4 Cd(II)	
0.006 M PO ₄ ³⁻	2.6 Fe(III)	0.04 Co(II)	
0.003 M TPB ⁻	2.1 Sn(II)		

^a Tetraphenylborate slurry prepared to be 4.6 wt % total solids with 4.0 wt % KTPB and 0.6 wt % NaTPB.

^b Trace levels (0.1 to 0.2 g/L) of organics (benzene, diphenylmercury, triphenylborane, diphenylboric acid, PBA, phenol and biphenyl) were also added.

Figure 26. Concentrations of products from thermal stainless steel bottle tests.

Figure 27. Concentrations of products from thermal and irradiated stainless steel bottle tests.

measured as soluble species in the aqueous filtrate of the slurry after filtering with a 0.45 µm filter. Each time the slurry was sampled the vessels were removed from the oven, allowed to cool, and the tops removed. After brief stirring to thoroughly mix the slurries, a total of ~10 mL of the slurry was removed by pipette for the benzene and filtrate analyses. The slurries were then resealed and put back in the oven at 70 °C.

There appears to be no difference in the irradiated and unirradiated systems. Both of the duplicate irradiated slurries showed nearly identical results. Initially, for ~3 weeks, no decomposition was observed. Liquid-chromatographic measurements on the filtrate from the slurries indicated no soluble TPB was present for this 3 week period. It was later realized (after the slurries had been prepared and the tests started) that the original solid Aquafine NaTPB was only ~87 % pure. Therefore, at the ~480 hour test time period, researchers added solid reagent grade Aldrich NaTPB material to the slurries. Three grams of the solid NaTPB was added to each vessel which at 480 hour contained ~90 mL of slurry. This ~33 g/L addition of reagent grade NaTPB was calculated to equal the amount that was deficient in the starting slurries due to the use of only ~87 % pure solid Aquafine NaTPB. As shown in Figure 26 and Figure 27, four days after adding the NaTPB, rapid increases in decomposition products occurred for an additional ~8 days, then leveled off. The low amounts of benzene in the final analyses are suspected to be due to evaporative losses. At the time of this final sampling, only 20-30 mL of the

original 120 mL of slurry remained in the vessels. Follow-up bottle tests in steel vessels with Teflon™ gasket seals, described below, will investigate these effects further.

Product yields can be summarized as follows. Approximately 35 g/L of benzene formed. A maximum rate of production is calculated in the range of 150,000 to 200,000 ug/L/hr, i.e. ~30 g/L benzene formed in 150 to 200 hours. Phenol reached about 4 g/L and phenylboric acid reached about 3 g/L. The phenylboric acid then rapidly decreased to near zero again. Soluble boron reached 1 g/L, roughly equal to the theoretical yield from decomposition of the 33 g/L of reagent grade NaTPB added at the 480 hour time. Two other decomposition products detected in the aqueous filtrates showed transient behavior over a 150-200 hour time period consisting of rapid increases followed by rapid decreases to near zero. These two species are most likely triphenylboron and diphenylboric acid. This identification is based on comparison to standard solutions prepared and submitted during the several weeks of testing. The triphenylboron and diphenylboric acid standards were prepared from reagent-grade compounds described below (see Reaction of Phenylboron Compounds Section). It is assumed that these two aqueous species were destroyed by alkaline hydrolysis processes.

These experiments appear to approximate the behavior in Tank 48H better than previous tests involving stirred and gas purged slurries. Several factors may contribute to the decomposition such as sealed non-stirred containers, a long induction period with no excess NaTPB present, and the presence of nine additional minor sludge ingredients and organics (relative to similar previous Series A tests in sealed polyethylene bottles) added as soluble components (see Table 19).

Follow-up Bottle Test

Following the results described above for the Series 1 Sealed Stainless Steel Bottle Test, similar experiments were repeated in glass vessels. The same slurry composition and all of the same minor components except the organic decomposition products (other than benzene) were used. These vessels were sealed using ground glass stopcocks to provide better isolation from air than obtained with polyethylene bottles. The ground glass stopcocks became frozen in place after extended heating in the presence of the alkaline salt solution, and the reaction could only be sampled once after the start of the experiment. However, the results (Table 20) show that significant decomposition of the excess NaTPB occurred within 9 days at 70 °C. This result indicates that the materials of construction used for the container were not important, and that one or more of the minor components is instrumental in promoting the decomposition. The results are consistent with the postulate that limiting the amount of air available may be important in promoting the reaction. Other features of the decomposition are similar to Tank 48H: the reaction occurred rapidly over a short period of time, consumed the bulk of the excess NaTPB, and the major product was benzene. The average benzene generation rate over the 9 day period was 270,000 µg/L/hr.

Table 20. Results of Follow-up Bottle Test.

Component	Time (days)	Minor Component Concentrations	
		None (g/L)	All (g/L)
Benzene	0	.0036	0.39 ^a
	9	.0036	6.7
Phenol	0	<.1	<.1
	9	<.1	0.66
PBA	0	<.1	<.1
	9	.1	2.2
TPB ⁻	0	15	16
	9	14	1.6

^aThe initial benzene concentration is due to liquid benzene added as a minor component to the slurry.

Series 2 Sealed Stainless-Steel Bottle Tests

The dual purposes of these tests were to investigate the differences between Aquafine slurry decomposition with and without additives at 70 °C, and to compare the decomposition behavior of the Aquafine tetraphenylborate slurry versus the BSC tetraphenylborate slurry, both with candidate catalyst additives at 70 °C. None of the slurries in these tests were irradiated. Tests were initiated in the 150 mL steel vessels stored at 70 °C. The vessel lids had been modified to allow vapor-space sampling and slurry sampling through a 3/8 inch gas chromatographic septum. Sampling the vessels in this manner allowed vapor space gas analyses and slurry analyses without opening and exposing the systems to air during sampling. Teflon™ gaskets were used as sealing material in place of the previous black polymeric materials.

A stirring bar was added to each sealed vessel to allow for brief stirring immediately before each slurry sampling. One vessel was prepared with 125 mL of Aquafine NaTPB slurry with various potential catalyst additives present. Another vessel contained only the Aquafine NaTPB slurry with no soluble or solid potential catalysts present. A vessel contained Boulder Scientific Company NaTPB slurry with various potential catalyst additives present. Both of the vessels containing Aquafine tetraphenylborate slurries were prepared from the same ~0.5 L batch of tetraphenylborate slurry. The composition of the tetraphenylborate slurries and the various additives, which were identical to the additives used in the Series 1 Sealed Stainless-Steel Bottle Tests, are shown in Table 21. Both tetraphenylborate slurries were prepared to have a sodium ion concentration of ~4.7 molar and to have a Tank 48H simulated salt solution content with theoretically 4 wt % KTPB and 1.5 wt% NaTPB. The amount of solid NaTPB was purposely increased for these slurries

(NaTPB = 1.5 wt %) relative to the Series 1 Sealed Stainless Steel Bottle Tests (NaTPB = 0.6 wt %). This was done to assure an adequate excess of NaTPB initially present in the slurries. Based on results of the previous Series 1 Sealed Stainless Steel Bottle Tests, it was expected that perhaps all of this 1.5 wt % NaTPB would decompose to benzene, PBA and phenol. Both the Aquafine and Boulder tetraphenylborate slurries were prepared using ~0.55 M TPB⁻ aqueous solutions as the Aquafine and Boulder NaTPB source, respectively. Each test was sampled periodically over 300 hours and analyzed for benzene (in both the vapor and liquid), phenol, PBA, and TPB⁻.

Figure 28 through Figure 31 show the amounts of decomposition products produced as a function of time over ~300 hours of testing. At the time of this writing, these tests are ongoing and are planned to continue for ~ 700 hours. Examination of the benzene data (Figure 28) from the BSC and AFF tests that contained the potential catalysts indicate little difference in reactivity between the two sources of NaTPB. The amounts of benzene measured to date in these two slurries, ~ 1.6×10^7 to 1.8×10^7 ug/L, is in the range expected from complete decomposition of the original 1.5 wt % of solid NaTPB present and the ~ 0.001 molar soluble tetraphenylborate present in the initial slurries. Further comparison of the two AFF NaTPB tests indicate that in the absence of the potential catalysts, AFF NaTPB is relatively stable at 70 °C over the ten day test period.

Table 21. Composition of AFF and Boulder Scientific Tank 48H simulant slurries.^a

Salt Content	Soluble Additives ^{b,c} (mg/L)		Solid Additives ^c
4.7 M Na ⁺	1.7 Cu(II)	0.3 Ru(III)	0.17 wt % Sludge
2.7 M OH ⁻	12 Mo(VI)	0.6 Ag(I)	0.17 wt % MST
0.7 M NO ₂ ⁻	60 Cr(VI)	2.2 Hg(II)	0.11 wt % SiO ₂
0.69 M NO ₃ ⁻	16 Si(IV)	12.2 Ca(II)	
0.01 M SO ₄ ²⁻	1 Se(VI)	0.1 Sr(II)	
0.19 M CO ₃ ²⁻	0.04 As(IV)	0.05 La(III)	
0.014 M Cl ⁻	8.8 Zn(II)	0.3 Ce(IV)	
0.008 M F ⁻	1.2 Pb(II)	0.4 Cd(II)	
0.006 M PO ₄ ³⁻	2.6 Fe(III)	0.04 Co(II)	
0.003 M TPB ⁻	2.1 Sn(II)		

^aBoth Aquafine and Boulder TPB slurry prepared to be 5.5 wt % total solids with 4.0 wt % KTPB and 1.5 wt % NaTPB.

^bTrace levels (0.1 to 0.2 g/L) of organics (benzene, diphenylmercury, triphenylborane, diphenylboric acid, PBA, phenol and biphenyl) were also added.

^cOne of the Aquafine TPB slurry systems contained no soluble nor solid additives.

Figure 28. Benzene generation from sealed stainless-steel bottle tests using different vendor supplies of NaTPB.

Figure 29. Phenol generation from sealed stainless-steel bottle tests using different vendor supplies of NaTPB.

Similar conclusions can be made from the phenol (Figure 29) and PBA (Figure 30) data. We note that the benzene concentrations shown are an order of magnitude greater than either phenol or PBA. Figure 31 shows the soluble tetraphenylborate data. The soluble tetraphenylborate (see Table 20) appears to be decreasing as the reaction proceeds in both the AFF and BSC slurries with additives, relative to its apparent stability in the AFF NaTPB slurry with no additives present.

NaTPB Decomposition Reaction Intermediates and Products

The behavior of NaTPB decomposition products and intermediates in Tank 48H is only partially understood. Much information concerning potential intermediates, their solubility, and their reactivities remain unknown. For example, current HPLC methodologies cannot quantify triphenylboron or diphenylboric acid (DPBA). Hence, the behavior of these intermediates in the decomposition reaction scheme are only speculative. Work is in progress to address these inadequacies.

Solubility of Boron-Containing Intermediates

One previously unknown parameter was the solubility of boron in these alkaline solutions. Boron concentration in Tank 48H filtrate has provided a means of determining the extent of reaction. To this end, the solubilities of several boron compounds in 4.7 molar sodium salt

Figure 30. Phenylboric acid generation from sealed stainless-steel bottle tests using different vendor supplies of NaTPB.

solution (~ 2 molar OH^-) were measured. The solubility of boric acid, $\text{B}(\text{OH})_3$, was greater than 120 g/L. This equates to a boron solubility greater than 21 g/L. The solubility of borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, was greater than 80.4 g/L realizing a boron solubility greater than 9 g/L. The solubility of PBA was determined as greater than 15 g/L but less than 30 g/L. The solubility of tetraphenylborate has been well studied. Its solubility is approximately 0.003 molar for these solutions, resulting in a boron solubility of 32 mg/L. The conclusion that can be drawn from this is that Tank 48H and the small scale experiments have not approached the solubility limit for boron or PBA.

Reaction of Phenylboron Compounds

Also unknown were the rates and product distribution from the continued reaction of NaTPB decomposition product intermediates. Simple tests were conducted with an air atmosphere at 70 °C in which weighed portions of NaTPB, triphenylboron hydroxy complex, DPBA ethanolamine complex, anhydrous DPBA, and PBA were placed in a 2.0 molar sodium salt solution (0.6 M OH^-) for seven days. Aliquots of each test were taken at the start of test and again after 3 days and 7 days. These were analyzed by HPLC. Table 22 provides results from the tests.

Figure 31. Tetraphenylborate consumption in sealed stainless-steel bottle tests using different vendor supplies of NaTPB.

The results show that NaTPB is relatively stable under these conditions. The triphenylboron hydroxy complex is undetectable by HPLC, however, phenol is formed from the material. The data suggest the triphenylboron hydroxy complex was entirely decomposed in the first 3 days. The DPBA ethanolamine complex is observed by HPLC but it is not quantifiable. Area counts from the HPLC were used to measure its relative concentration. The data suggest that it is more stable than the triphenylboron hydroxy adduct and comparable to PBA in terms of stability. Note that the DPBA ethanolamine complex contained an insignificant amount of PBA impurity at the start of the test. Anhydrous DPBA appears to be slightly less stable than the ethanolamine complex. Note that the anhydrous DPBA contained little or no PBA impurity at the start of the test. The data indicate that PBA and phenol are the only decomposition products. Phenylboric acid is more stable than any of the other compounds except NaTPB itself. The decomposition of PBA in air produces approximately 50% phenol and 50% unknown (most likely benzene).

Benzene Generation in Tank 50H

During the time in which rapid decomposition of NaTPB and large benzene generation rates were observed in Tank 48H, elevated levels of benzene (9.0 mg/L, Ref. 5) were observed in Tank 50H salt solution. This level was both a flammability and regulatory concern to the downstream Saltstone facility. Initially, personnel thought soluble tetraphenylborate, in the decontaminated filtrate transferred from Tank 48H to 50H during concentration, was decomposing and producing the elevated benzene. However, given the more moderate Tank 50H temperatures (25 - 30 °C), it seems more probable that an intermediate product (e.g., diphenylboric acid or triphenylboron hydroxy complex) from the early stages of NaTPB decomposition in Tank 48H was transferred into Tank 50H during the final concentration phase in Tank 48H. Examination of the Tank 48H filtrate analyses in Table 2 indicates that the NaTPB decomposition reaction was beginning at that time. The potassium concentration in Tank 50H also supports the theory that something other than NaTPB was decomposing to produce benzene. A Tank 50H sample from late December was found to contain 265 mg/L of soluble potassium. This suggests that an excess of potassium (relative to NaTPB) existed in Tank 50H during November and that any soluble TPB⁻ would have precipitated as KTPB.

No benzene concentration data exists between the first week of November and the first week of December. It is during this time that the highest benzene generation rate most likely occurred. Therefore, it is difficult to determine the highest rate directly from Tank 50H data. Instead, the initial benzene generation rates, described earlier and shown in Figure 20, observed from the December 18 Tank 48H filtrate sample is the best data available to predict the highest rate observed in Tank 50H. In two different samples measured more than a month apart, an initial benzene generation rate of 300 µg/L/hr was observed from the continued decomposition of NaTPB intermediates. The concentration of these intermediates were unknown. As such, it is impossible to determine if 300 µg/L/hr is conservative.

Table 22. Decomposition of Phenylboron compounds in salt solution at 70 °C.

A. NaTPB			
Time (days)	PBA (mg/L)	Phenol (mg/L)	NaTPB (mg/L)
0	<20	<20	140
3	<20	<20	135
7	<20	<20	121
B. Triphenylboron hydroxy complex			
Time (days)	PBA (mg/L)	Phenol (mg/L)	Triphenylboron hydroxy complex
0	<20	33	not observed
3	27	100	not observed
7	20	100	not observed
C. DPBA (ethanolamine complex)			
Time (days)	PBA (mg/L)	Phenol (mg/L)	DPBA (HPLC area units)
0	30	<20	11.2
3	380	210	9.55
7	720	420	7.92
D. DPBA (anhydrous)			
Time (days)	PBA (mg/L)	Phenol (mg/L)	DPBA (HPLC area units)
0	320	<20	13.5
3	720	260	11.3
7	1380	770	9.83
E. PBA			
Time (days)	PBA (mg/L)	Phenol (mg/L)	
0	5080	≤20	
3	4370	460	
7	3580	820	

phenyl radical and biphenylboron radical products of reactions 3 and 4 could undergo further reactions involving dimerization, oxidation, and alkaline-adduct hydrolysis. The products of which would be various dimers, phenol, phenylboric acid, benzene, and biphenyl (see Appendix P).

A separate postulated scheme involves phenyl transfer to a copper ion, forming a metal-phenyl adduct and triphenylboron. Reactions 7 - 12 show this scheme with copper, a metal known to exhibit the proposed chemistry.

The above scheme would involve a catalytic cycle (reactions 8-12) without redox reactions of the Cu(II) species after reduction as in reaction 7. The copper-phenyl adduct shown in reaction 9 could alternatively undergo hydrolysis by water, or:

This reaction pathway might also lead to a catalytic cycle, involving reaction 8 and reactions 13-14.

Both of the two generalized schemes postulated above, reactions 1-6 or reactions 7-14, could be facilitated or accelerated by the presence of a separate benzene layer within the slurry or by a separate solid phase acting as a heterogeneous catalysis site. The formation of a benzene layer or localized regions of benzene liquid within the aqueous tetraphenylborate slurry could effect the solubility of an otherwise insoluble catalyst, (e.g., a metal species present as their solid metal hydroxide or metal oxide forms, in a caustic aqueous media). The existence of solid particles within a tetraphenylborate slurry, such as sludge comprised of iron, manganese, nickel and aluminum oxides and hydroxides, or titanate existing as monosodium titanate solids could serve to provide an active site for heterogeneous catalysis. In the case of a heterogeneous catalysis site, the solid could serve to provide an appropriate site for adsorption of a catalytically active soluble metal cation and the soluble tetraphenylborate anion, which would otherwise not react in solids-free solutions (i.e., in tetraphenylborate slurries not containing such heterogeneous solid catalysts).

In radioactive tetraphenylborate slurries, radiation effects could also play a role in the catalytic processes. Various strong reducing agents such as the hydrated electron and hydrogen atom, as well as

V. Mechanistic Implications

Portions of the following section are derived from information and suggestions provided by the ITP Process and Mechanisms Panel. A more detailed discussion of the mechanistic implications, with emphasis on possible oxygen effects, and references pertaining thereto are contained in Appendix P.

Mechanistic Reaction Schemes Involving Alkaline

Decomposition of Tetraphenylborate Anion (TPB⁻) in Presence of Soluble and/or Solid Catalysis Species

The proposed mechanism for tetraphenylborate decomposition involves dephenylation of tetraphenylborate. The first scheme shown below represents a homogeneous catalytic homolysis of the C-B bond of tetraphenylborate. Removal of the first phenyl group involves a free radical process. Reaction 1 shows an oxidizing agent (M), acting as a catalytic species, undergoing reduction in an electron transfer step involving the original tetraphenylborate anion. Reaction 2 involves oxidizing the catalyst to complete the redox couple. Examples of the catalytic oxidant in reaction 1 include soluble copper or other soluble multivalent cations. The oxidant in reaction 2 could be molecular oxygen or possibly an oxygen-containing organic species. For ITP slurries, this oxidant shown in reaction 2 could also be a separate dissolved cation species different from the original M^{+x} shown in reaction 1. In the case of a completely anoxic system a catalytic decomposition of tetraphenylborate can also be postulated involving only Cu(I) cation (see reactions 7-12 presented and discussed below).

- 1) $(C_6H_5)_3B(C_6H_5)^- + M^{+x} \rightarrow (C_6H_5)_3B(C_6H_5)\cdot + M^{+(x-1)}$
- 2) $M^{+(x-1)} + \text{Oxidant} \rightarrow M^{+x} + \text{Reduced Oxidant}$
- 3) $(C_6H_5)_3B(C_6H_5)\cdot \rightarrow (C_6H_5)_3B + (C_6H_5)\cdot$
- 4) $(C_6H_5)_3B(C_6H_5)\cdot \rightarrow (C_6H_5)_2B\cdot + (C_6H_5)_2$
- 5) $(C_6H_5)_3B + OH^- (+3H_2O) \rightarrow B(OH)_4^- + 3C_6H_6$
- 6) $(C_6H_5)_3B(C_6H_5)^- + B(OH)_4^- + 3H_2O \rightarrow B(OH)_4^- + (C_6H_5)B(OH)_3^- + 3C_6H_6$

Subsequent reactions of the tetraphenylboron radical, $(C_6H_5)_3B(C_6H_5)\cdot$, are shown in reactions 3 and 4. Reactions of the resulting triphenylboron, $(C_6H_5)_3B$, are shown in reaction 5. This reaction would presumably occur in several successive steps involving initial hydroxide adduct formation and subsequent hydrolysis (see Appendix P). Reaction 6 gives an example of a phenyl transfer to boron (the $B(OH)_4^-$ species resulting from reaction 5) by the parent tetraphenylborate, followed by hydrolysis. The product species $B(OH)_4^-$ in reaction 6 could then undergo continuous cyclic reactions with the parent tetraphenylborate. We note that the product species of reactions 5 and 6 involve predominately benzene formation. The

strong oxidizing agents such as the hydroxyl radical (or O^- in strongly alkaline solutions), and H_2O_2 are all well-established primary products of radiolytic water decomposition. Additionally the reactions of these primary radiolytic products with both nitrate and nitrite in the tetraphenylborate slurry would form the potentially redox-active NO_2 and NO radicals. These two radical species could participate in redox chemistry associated with an active catalyst. Preliminary high temperature experiments designed to test the effects of radiolysis on slurries with various potential catalysts added (see Series 1 Sealed Stainless Steel Bottle Tests) indicated no significant differences in tetraphenylborate decomposition at 70 °C with and without radiation exposure. However, similar planned tests at lower temperatures (i.e., in the more applicable temperature range of 25-50 °C) might indicate that radiolysis effects do significantly contribute to the overall tetraphenylborate decomposition in the presence of catalysts at these lower temperatures.

Further decomposition schemes, as they apply to relatively simple two-component alkaline TPB/copper(II) solutions, are discussed in Appendix P.

VI. Potential High Level Waste System Effects

Tank 50H and Saltstone

As discussed in an earlier section, elevated levels of benzene (9.0 mg/L, Ref. 5) were observed in Tank 50H salt solution at the same time as the rapid decomposition of NaTPB was occurring in Tank 48H. This level was both a flammability and regulatory concern to the downstream Saltstone facility. The formation of benzene in Tank 50H was likely due to the continued decomposition of an intermediate product (e.g., diphenylboric acid or triphenylboron hydroxy complex) produced in the early stages of the rapid NaTPB decomposition in Tank 48H. This intermediate was likely transferred into Tank 50H during the final concentration phase in Tank 48H. In separate laboratory tests, benzene generation rates of 300 $\mu\text{g/L}$ were observed from the continued decomposition of NaTPB intermediates in Tank 48H filtrate. This value represents the best information available in regards to determining the benzene generation rate that occurred in Tank 50H. Since the concentration of the intermediates in Tank 50H at the time of the reaction were unknown, it is impossible to determine if 300 $\mu\text{g/L/hr}$ is conservative.

SRTC prepared Saltstone with a sample of Tank 50H salt solution collected in January 1996. Benzene evolution rates measured over 48 days were between 0.02 and 0.2 $\mu\text{g/L/hr}$ [Ref. 21-23] which are below the rates measured in comparable 1985 tests [Ref. 24]. TCLP and Constituent Concentration in Waste ("Totals") tests were performed for benzene in Saltstone samples cured for 7, 14, and 28 days at ambient temperature and 60 °C. [Ref. 23, 25] In these tests, the measured benzene concentrations remained below the regulatory limits.

Late Wash

The Late Wash Technical Bases requires the slurry feed to Late Wash from ITP to contain less than 700 ppm of benzene. [Ref. 26] Analysis of the data from Tank 48H indicates that the current benzene concentration in Tank 48H is approximately 550 ppm. Thus, it would appear that ITP will be able to supply material that meets this criteria. Additional data indicates that the benzene generation rate in Tank 48H as of April 25 is 13.2 $\mu\text{g/L/hr}$. At this reaction rate, in excess of 600 days without pump operation would be required to return the benzene concentration in Tank 48H to 700 ppm. This reaction appears governed by the solubility of potassium tetraphenylborate and temperature. During most of the time over which the low (13.2 $\mu\text{g/L/hr}$) benzene generation rate was observed, the temperature in Tank 48H was less than 30 °C.

The sodium ion concentration in Tank 48H for the first batch is approximately 4.7 molar. Decreasing the sodium ion concentration in Tank 48H to less than 1 molar by washing would produce an order of magnitude increase in the KTPB solubility (see Figure 32). [Ref. 27] Since the reaction to produce benzene appears first order in TPB⁻ ion, washing would produce an order of magnitude increase in reaction rate. Thus, a significant quantity of benzene could build into a

washed slurry at a faster rate than for an unwashed slurry. However, this analysis does not reflect any benefit be obtained by removing soluble catalyst from the slurry.

While the limit for feed to the Late Wash Facility has been specified as 700 ppm, it may prove impractical to maintain this material at a concentration below 700 ppm. A less restrictive limit has been proposed that the material in the Late Wash Facility should not exceed 1200 ppm in benzene. This limit maintains the benzene concentration in the slurry below the solubility limit for the associated salt solution (~1260 ppm). Researchers now realize that crediting mass transfer considerations in analyses will allow a larger benzene inventory while maintaining the same effective safety margin. However, future studies are needed to establish the acceptance of the proposed limit although preliminary data indicate this approximate value.

If all of the NaTPB is consumed prior to transfer to Late Wash such that the reaction rate depends on KTPB solubility, one may estimate allowable storage times in the Late Wash Facility based on a 13.2 $\mu\text{g/L/hr}$ generation rate. Such a prediction is provided in Figure 33. Inspection of this figure indicates that storage times in excess of 100 days would be required to increase the benzene concentration in the facility from 700 to 1200 ppm. However, this calculation assumes the temperature in the facility is maintained at 25 °C, no insoluble NaTPB is transferred to Late Wash, the KTPB solubility employed in this calculation is correct, and no additional NaTPB is added in the Late Wash Facility.

An increase in the storage temperature would produce an increase in the reaction rate and thus a proportional decrease in the allowable storage time. If insoluble NaTPB is transferred to the Late Wash Facility, the reaction rate can be expected to be quite large and allowable storage times would decrease to less than 4 days. Addition of NaTPB in the Late Wash Facility would increase the free TPB ion concentration, but not necessarily produce insoluble NaTPB. A fraction of this TPB⁻ ion would be consumed through precipitation of potassium and cesium. It is possible to estimate the allowable storage time based on the quantity of excess NaTPB. Such estimates are shown in Figure 34. Inspection of this figure indicates that even small (25 gallons) additions of excess NaTPB to the Late Wash Precipitate Tank will require significantly shorter storage times.

The above analysis is limited by a number of constraints. Use of this analysis should be made with these limitations in mind. Primarily, the temperature is assumed as 25 °C. Increases in temperature will increase reaction rates. No credit has been taken for the removal of soluble catalysts. The removal of soluble catalysts would likely produce measurable decreases in generation rates. The existing solubility data for KTPB was assumed accurate for both high and low sodium ion concentrations. The benzene generation rate was assumed to be 13.2 $\mu\text{g/L/hr}$ for a 4.7 molar slurry with no insoluble NaTPB present. This analysis has ignored the operational case wherein insoluble NaTPB is present in the feed to

Late Wash. The presence of such material would result in significantly higher reaction rates and lower allowable storage times.

Figure 32. KTPB solubility as a function of sodium concentration.[Ref. 27]

Figure 33. Late Wash allowable storage times (without NaTPB additions).

Figure 34. Late Wash allowable storage times (as a function of NaTPB additions).

The above analysis suggests the possible need for additional restraints on the Late Wash operating envelope. Such restraints might include limiting the feed to the Late Wash Facility to below 700 ppm, limiting the allowable addition of NaTPB to less than 25 gallons of 0.5 M NaTPB, or requiring the ability to provide mixing to the Late Wash Precipitate Tank in less than 4 days. Additional calculations will determine which, if any, of these restraints provide the needed safety margin. The calculations will require information including specification of the feed composition for Late Wash and, in particular, the degree of washing achieved in Tank 48H. A second requirement for specification of restraints involves identification of the required excess for the NaTPB addition in Late Wash. To determine the quantity required for this addition requires information regarding the concentration of soluble K^+ and Cs^+ present in the feed to Late Wash.

Tank 22H

Tank 22H is the receipt tank for ITP washwater and Late Wash filtrate. This tank contains a small quantity of sludge. This sludge has not been adequately characterized to assess the ability of the solids to catalyze the decomposition of NaTPB. Because of this concern, the use of Tank 22H as a receipt tank has been suspended until such time that concerns surrounding this issue can be resolved. [Ref. 28]

VII. Recommendations for Further Testing

Future tests are required to integrate the ventilated, non-radioactive NaTPB solution tests with the conditions of Tank 48H during the rapid decomposition of NaTPB. Specific variables that need to be studied in greater detail are TPB⁻ concentration, hydroxide concentration, oxygen concentration, copper concentration, and other additives used in the non-radioactive bottle tests. In addition, the use of inhibitors to prevent future NaTPB decomposition should be pursued. Other tasks being pursued include the use of boron NMR to study the NaTPB decomposition reactions and initiating Tank 48H and Batch #2 simulations in the SRTC Shielded Cells. The ultimate goal of this program is to develop a well characterized kinetic expression of NaTPB decomposition.

VIII. Quality Assurance

All work was conducted in accordance with the DWP&HT Quality Assurance Procedures Manual, 1Q43. This experimental program was conducted at the request of High Level Waste Engineering. Data collected during this project are contained in the authors' notebooks and files.

IX. Acknowledgments

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Appendix A. Tank 48H Event Log for September, 1995, through April, 1996.

<u>Date</u>	<u>Time</u>	<u>Event</u>
9/2	1418	Addition of 3200 gallons of STPB containing 48 mg/L of benzene. Slurry pumps operated for period of 2 hours 47 minutes.
9/7	415	Addition of 3900 gallons of STPB containing 169 mg/L of benzene. Slurry pumps operated for period of 15 hours 34 minutes.
9/8	541	Addition of 2006 gallons of STPB containing 169 mg/L of benzene. Slurry pumps operated for period of 8 hours 44 minutes.
9/10	440	Addition of 3300 gallons of STPB containing 190 mg/L of benzene. Slurry pumps operated for period of 11 hours 16 minutes.
9/11	1320	Addition of 3650 gallons of STPB containing 179 mg/L of benzene. Slurry pumps operated for period of 14 hours 12 minutes.
9/19	1320	Addition of 2342 gallons of STPB containing 80 mg/L of benzene. Slurry pumps operated for period of 12 hours 53 minutes.
9/26	1125	Addition of 2735 gallons of STPB containing 143.7 mg/L of benzene. Slurry pumps operated for period of 13 hours 40 minutes.
9/27	2357	Addition of 5097 gallons of STPB containing <20 mg/L of benzene and 5103 gallons of STPB containing 112 mg/L of benzene. Slurry pumps operated for period of 16 hours 36 minutes.
9/29	141	Slurry pumps operated for period of 10 hours and 39 minutes.
9/29	1541	Addition of 4033 gallons of STPB containing 33 mg/L of benzene and 1965 gallons of STPB containing 24 mg/L of benzene. Slurry pumps operated for period of 27 hours 47 minutes.
9/30	1306	2100 gallons of sodium titanate added.
9/30	1947	Slurry pumps operated, at 885 rpm for period of 21 hours and 37 minutes. Rate increase to 1180 rpm for 20 hours and 26 minutes.

10/9	1100	Started 4 slurry pumps at 1180 rpm with ventilation rate of ~ 600 scfm. Pumps allowed to run for 48 hours and 14 minutes.
10/12	128	Started 1 slurry pump at 1180 rpm for 2 hours and 3 minutes.
10/20		Filtration commenced to tank volume of 361,000 gallons.
10/25		Filtration completed.
10/26	1420	Started one slurry pump at 1180 rpm for 12 hours and 50 minutes. All four slurry pumps operated for 42 hours and 50 minutes at 1180 rpm. During this time, 1300 gallons of water was added to Tank 48H. Pump speed reduced to 885 rpm for 10 hours.
11/2		Filtration commenced to tank volume of ~ 160,000 gallons.
11/7		Filtration completed.
11/9	1715	B1 slurry pump started.
11/10	930	Remaining slurry pumps started.
11/11	1147	Exhaust alarm trip.
	1202	Slurry pumps trip.
	1247	Exhaust restarted.
	1330	Slurry pumps restarted.
	1514	Slurry pumps shut down.
	2240	Slurry pumps restarted.
11/12	1630	Water addition.
	2101	Water addition.
11/13	018	Water addition.
	142	GCs lost.
	851	B4 and V1 slurry pumps shut down.
	1329	Exhaust trip.
	1420	Slurry pumps shutdown.
	1519	B1 and V2 slurry pumps restarted.
	1954	Slurry pumps shut down.
11/15	055	Ventilation shut down.
11/20	048	Air based ventilation started.
11/24	1041	Ventilation shut down.
11/26	433	Ventilation started.
11/26	1617	Ventilation shut down.

11/30	1650	Ventilation started.
12/1	1220	Started slurry pumps for VDS sample.
	1553	Slurry pump operation halted due to high benzene concentrations in the vapor space.
12/8	2238	Benzene Depletion Pump Runs initiated. Intermittent slurry pump operation continued until 1/3/96.
1/3/96	734	Slurry pump operation halted. Tank remained quiescent until 3/5/96.
3/5	1336	Operated slurry pump V-1 at 600 rpm for 14 minutes.
3/8	1311	Operated slurry pump B-4 for 20 hours and 19 minutes. During subsequent pump operation, pump speed was incrementally increased. Following this slurry pump B-1 and V-2 operated individually.
3/24	725	Operated slurry pumps V-1 and V-2 for 25 hours 1 minute. Periodic operations with two pumps continued until 4/9.
4/3	1430	Reduced purge exhaust flow to 490 scfm (variable ventilation test).
	1845	Increased purge exhaust flow to 550 scfm.
4/4	255	Restored purge exhaust flow to 850 scfm.
4/9	1554	Started third pump. Continued periodic three pump operation until 4/16.
4/16	1050	Started fourth pump.

Appendix B. Benzene Mass Balance Calculations.**Excess NaTPB Calculations**

Results of samples taken prior to the addition of NaTPB to Tank 48H indicated that the soluble potassium concentration in Tank 48H at that time was between 0.023 M and 0.033 M. [Ref. A] Additionally, some cesium (both radioactive and non-radioactive) was contained in Tank 48H. For the purposes of this calculation, cesium was ignored because the concentration was much less than that of soluble potassium (K^+). The volume of the contents of Tank 48H was approximately 1.78×10^6 L. Multiplying this volume by a concentration of 0.23 M gives a total of 40,940 moles of soluble K^+ . A total of 80800 moles (1.41×10^5 L) of NaTPB was added to Tank 48H. Of this, 40,940 moles precipitated as insoluble KTPB and CsTPB, leaving 39,860 moles of NaTPB in Tank 48H. Some of this was in the form of dissolved NaTPB and some was in the form of solid NaTPB. During the concentration phase of the ITP process, some of the soluble NaTPB was transferred to Tank 50H. The amount was calculated by first calculating the solubility of NaTPB in Tank 48H using the following equation. [Ref. B]

$$[NaTPB] = \left\{ \frac{0.684 + 0.00324(T)}{1 - 0.00324(T)} \right\} \{ 1.08e^{-1.22(X)} \}$$

where $[NaTPB]$ = the solubility of NaTPB in the salt solution in molarity,
 T = the solution temperature in °C and
 X = the total sodium ion (Na^+) concentration in molarity

Using the Tank 48H Na^+ concentration in November of 4.7 M and a tank temperature of 40 °C, gives a NaTPB solubility of 0.0033 M. With 1.31×10^6 L of salt solution pumped to Tank 50H (in October and early November), this gives 4,320 M of soluble NaTPB transferred from Tank 48H. This left 35,540 M of NaTPB in Tank 48H after concentration. If this NaTPB degrades completely to benzene, four moles of benzene may be formed by each mole of NaTPB, giving 142,160 M of potential benzene.

Benzene Release Calculations

Benzene releases have been calculated using the data collected from Tank 48H. These data have been stored on the WG020 fileserver. Tank 48H vent rate data were obtained directly from files in the dcs_data directory. The gas chromatography data and tank temperatures were obtained from files in the gc_data directory. The GC #1 and tank ceiling temperature data were used. Tank 48H data were given in scfm and were corrected for temperature. The GC data were given in volume

percent benzene. The ideal gas equation was used to calculate the amount of benzene. Data were supplied every half hour. The following equation was used to calculate the benzene released during every half hour.

$$R_{Bz} = \frac{\left(\left(\frac{(C_{Bz1} + C_{Bz2})}{2} \right) / 100 \right) \left(\frac{(F_1 + F_2)}{2} \right) \left(\frac{\left(\left(\frac{(T_1 + T_2)}{2} \right) + 273 \right)}{273} \right) ((D_2 - D_1)(24)(60))}{\left(\left(\frac{(T_1 + T_2)}{2} \right) + 273 \right) (1.314)} \quad (78)$$

where R_{bz} = benzene release in lb during the time period in question,
 C_{Bz} = benzene concentration in vol % from GC #1,
 F = Tank 48H vent flow in scfm,
 T = Tank 48H ceiling temperature in °C,
 D = time at which data is taken (one day = 1),
 78 = molecular weight of benzene in lb/lb-mole and
 1.314 = ideal gas constant (R) in (ft³) (atm) / (lb-mole) (K).

For the purposes of this calculation the pressure is assumed to be constant as 1 atmosphere and is therefore left out of the equation. The subscripts 1 and 2 refer to data at the start and end of the half hour. To calculate the total release over a period of time, the data are summed over that period of time.

Calculation of Tank 48H PBA, Phenol and Biphenyl Content

Results of Tank 48H samples analyzed between December 28, 1995 and April 15, 1996 indicate that the PBA concentration has remained constant over that period. Since sample analyses indicated no PBA in Tank 48H after the slurry concentration phase in early November, there was no need to subtract out the initial Tank 48H content. PBA is completely soluble at the concentrations in question. Therefore, there is no need to account for settling of the solids in the tank. Therefore, the sample results obtained between December 28, 1995 and

April 15, 1996 were averaged to give the concentration used in the mass balance. For PBA, the average of nine sample results between December 28, 1995 and April 15, 1996 was 1717 mg/L. This gives a total of 1050 kg.

The phenol in Tank 48H was calculated in much the same way, using the April 15, 1996 sample result (8100 moles). Additionally, because there was initially some phenol in the tank prior to degradation of the NaTPB, the initial amount (November 5 sample, 162,000 gal., result - 1420 moles) was subtracted out. Sample results also indicated that some phenol appeared between October 12 and November 5. This amount (633 moles) was also shown in the mass balance.

Limited data is available for the calculation biphenyl, terphenyl and diphenyl mercury contents of Tank 48H. Data are only available for samples taken on January 12 and 21, 1996. Additionally, there is data on the biphenyl contained in the NaTPB added to Tank 48H during precipitation. To obtain the contents used in the mass balance, the January 12 and 21 data were averaged; it is assumed that by that time, biphenyl, terphenyl and diphenyl mercury concentrations were essentially constant. The average results were 1541 mg/L for biphenyl, 102 mg/L for diphenyl mercury and 114 mg/L for terphenyl.³ These three materials are all insoluble. At the time the samples were taken in January, the slurry phase had begun to separate from the clear supernate phase. The samples taken were representative of the slurry phase only and not the whole tank. The sample results had to be corrected to a tank average concentration. The average solids content of Tank 48H dip samples taken between January 21 and February 10, 1996 is 8.2 wt %. If the tank had been well mixed the solids content was calculated to have been 3.8 wt %.⁴ Concentrations representative of the entire tank contents may be obtained by multiplying the actual sample results by the ratio between the well-mixed solids content and the unmixed solids content. This gives concentrations of 714 mg/L, 53 mg/L and 47 mg/L of biphenyl, terphenyl and diphenyl mercury, respectively. These concentrations were converted to total amounts of the respective materials. Because there was an initial amount of biphenyl present (96 moles) that number was subtracted from the total to give the amount of biphenyl created in Table 1.

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Appendix C. Benzene generation rate data obtained from
Tank 48H filtrate and AFF NaTPB solution.

Reaction Time (hrs)	Benzene Generation Rate ($\mu\text{g/L/hr}$)
8.8	2.6
58.5	3.6
106.6	2.8
131.3	2.3
154.4	3.2
178.6	2.9
201.2	1.8
225.4	1.4
271.2	1.8
307.4	1.7
321.0	16.2
344.7	15.0
371.7	22.0
400.2	26.9
472.0	38.7
491.2	41.0
513.8	39.5
562.6	64.9
586.8	64.8
631.8	58.1
655.2	74.2
681.8	39.9
704.4	52.1
729.2	32.8
774.9	33.0
826.2	30.8
850.4	40.8
873.0	28.8
904.1	32.7
921.0	28.6
970.5	25.9
993.0	23.6
1021.6	20.6
1039.5	26.2
1063.9	23.8
1136.2	39.2
1160.2	35.6
1184.2	37.1
1206.9	29.2
1239.1	46.1
1309.6	50.8

Reaction Time (hrs)	Benzene Generation Rate ($\mu\text{g/L/hr}$)
1337.0	44.9
1361.5	33.5
1381.4	44.7
1407.7	26.0
1430.5	46.6

**Appendix D. Benzene generation rate data obtained from
Tank 48H filtrate, oven-dried AFF NaTPB powder,
and 0.2 wt % Tank 51H sludge.**

Reaction Time (hrs)	Benzene Generation Rate ($\mu\text{g/L/hr}$)
2.8	50.6
19.2	60.0
24.3	70.2
40.6	121.7
49.0	170.1
64.0	205.0
87.8	405.6
111.9	477.9
138.0	540.0
144.6	618.0
162.4	652.4
168.0	672.1
184.8	647.4
208.8	630.8
234.2	575.7
256.2	509.2
281.2	487.1
305.5	443.3
328.5	437.7
336.0	461.4
337.5	447.6
359.0	411.4
378.5	362.4
381.8	751.6
383.8	795.0
386.0	785.0
400.6	810.0
407.0	827.6
426.5	916.0
449.3	802.1
475.0	636.2
496.8	558.6
527.8	510.0
547.8	402.1
571.0	385.1
577.7	347.1
592.5	296.8
616.0	205.1
648.2	201.8
666.0	142.2
697.2	132.9

Reaction Time (hrs)	Benzene Generation Rate ($\mu\text{g/L/hr}$)
711.8	124.0
737.8	103.7
760.5	52.8
787.8	47.0
816.0	43.9
835.1	52.5
857.8	26.8
860.1	66.4
867.8	70.7
887.3	92.0
907.1	87.3
910.4	73.6
929.4	98.6
931.7	100.3
956.4	65.9
958.2	86.6
959.1	87.3
979.4	78.0

**Appendix E. Benzene generation rate data obtained from
Tank 48H filtrate, oven-dried AFF NaTPB powder,
and 0.51 wt % Tank 48H sludge and MST.**

Reaction Time (hrs)	Benzene Generation Rate ($\mu\text{g/L/hr}$)
3.0	2035
22.7	2224
25.0	2093
42.5	6984
45.6	4209
47.8	4958
48.9	5302
66.5	8596
91.7	7397
115.2	6142
138.1	4388
161.7	3661
187.1	2668
213.2	2639
234.2	2236
259.4	1566
281.5	1356
305.5	1254
329.4	1010
356.8	992
381.7	867
426.8	794
449.5	751
457.1	6021
472.1	4218
479.2	3883
498.2	3556
522.3	3130
546.2	2555
570.0	2742
593.9	2460
618.3	2637
642.2	2922
667.2	2484
692.5	2244
714.0	2228
789.6	2331
808.9	2482
833.2	2342
857.7	1818
884.5	1691

Reaction Time (hrs)	Benzene Generation Rate ($\mu\text{g/L/hr}$)
904.8	1526
953.9	1383
979.2	1231
1003.2	1188
1025.8	1158
1050.1	1061
1073.7	1096
1095.8	978
1121.9	952
1147.1	886
1169.5	941
1193.8	941
1198.1	362
1220.0	354
1266.4	326
1268.5	812
1288.0	901
1291.8	806
1293.9	813
1296.2	770
1320.2	934
1344.2	887
1359.4	856
1384.5	819

Appendix F. Benzene generation rate data obtained from
Tank 48H filtrate, oven-dried AFF NaTPB powder,
and simulated Tank 48H MST.

Reaction Time (hrs)	Benzene Generation Rate ($\mu\text{g/L/hr}$)
10.1	1.0
31.8	0.9
57.3	117.2
82.8	572.2
106.1	1329.0
133.1	1731.5
203.0	1350.1
228.2	1082.5
251.0	924.0
272.8	778.1
296.7	711.8
320.9	734.8
345.8	714.1
371.6	649.5
416.7	756.1
442.0	640.0
471.0	547.0
489.8	484.2
539.5	451.2
568.7	406.5

Appendix G. Benzene generation rate data obtained from Tank 48H filtrate and oven-dried reagent grade NaTPB powder from Aldrich Chemical Company.

Reaction Time (hrs)	Benzene Generation Rate ($\mu\text{g/L/hr}$)
3.2	9.1
20.2	4.3
45.7	13.9
96.0	51.8
121.2	119.3
140.9	148.5
165.2	192.7
189.8	276.9
216.2	345.4
236.8	409.6
286.1	485.5
311.4	516.2
335.4	488.1
357.9	525.0
382.1	651.0
405.9	431.6
427.8	417.0
454.0	307.1
479.1	327.8
501.7	325.4

Appendix H. Benzene generation rate data obtained from
Tank 48H filtrate, oven-dried AFF NaTPB powder,
and 0.1 wt % Tank 51H sludge.

Reaction Time (hrs)	Benzene Generation Rate ($\mu\text{g/L/hr}$)
3.0	45.1
17.5	62.9
48.5	93.2
68.5	105.3
90.5	173.3
113.5	211.3
137.0	205.7
161.1	206.2
186.7	204.8
212.8	186.6
233.0	191.7
259.0	191.6
260.5	298.4
263.5	414.9
281.7	394.8
309.6	304.2
337.5	277.2
357.0	298.7
381.7	290.1
408.0	216.9
428.7	244.0
450.9	234.7
477.5	186.7
500.8	155.0
523.4	223.4
528.6	203.8
530.5	139.9
531.4	108.4
546.1	56.9
551.1	50.6
572.5	38.2

Appendix I. Benzene generation rate data obtained from Tank 48H filtrate, untreated reagent grade NaTPB powder (from Aldrich), and 0.2 wt % Tank 51H sludge.

Reaction Time (hrs)	Benzene Generation Rate ($\mu\text{g/L/hr}$)
2.4	198.2
16.9	47.9
21.6	54.1
25.6	52.4
42.1	64.6
65.1	72.7
93.3	81.2
121.5	100.3
140.5	103.0
165.2	121.6
191.8	101.0
212.3	106.8
234.8	106.2
261.0	103.0
284.2	83.2
306.9	79.1
331.1	87.6
356.2	74.1
364.4	110.8
366.6	139.8
386.7	147.0
404.2	112.6
426.5	110.0
450.3	71.2
458.7	89.2
473.4	74.3
497.9	63.4
526.2	57.4
551.1	47.0
596.2	44.7
618.2	41.0
643.8	41.8
667.1	37.6
693.5	39.2
715.3	38.4
738.3	37.3
764.7	38.8
787.3	39.0

Appendix J. Benzene generation rate data obtained from Tank 48H filtrate, untreated reagent grade NaTPB powder (from Aldrich), and 0.25 wt % Tank 48H sludge and MST.

Reaction Time (hrs)	Benzene Generation Rate ($\mu\text{g/L/hr}$)
2.7	264.2
4.7	197.4
21.5	72.4
42.2	78.7
64.4	93.3
89.4	77.5
113.2	78.7
137.2	87.4
164.7	117.0
189.6	117.8
234.7	133.1
257.1	134.6
264.7	593.2
279.9	531.4
287.1	435.6
305.7	428.6
329.8	475.5
354.0	412.1
377.4	463.8
404.7	464.6
426.1	498.1
449.8	544.6
475.0	414.8
500.2	452.6
521.6	376.0
597.4	360.9
616.7	380.3
641.1	347.6
665.5	356.7
692.4	384.0
712.4	331.6
761.8	339.6
786.8	422.0
810.7	387.3
833.2	449.2
857.4	477.4
880.9	474.9
904.1	466.1
929.7	438.0
954.8	480.4
977.2	254.6
984.3	376.1

Appendix K. Benzene generation rate data obtained from Tank 48H filtrate, untreated Boulder Scientific Company NaTPB powder, and 0.2 wt % Tank 51H sludge.

Reaction Time (hrs)	Benzene Generation Rate ($\mu\text{g/L/hr}$)
5.6	294.4
24.1	278.2
47.1	236.2
73.5	231.2
96.2	217.4
101.7	336.6
119.5	240.6
142.9	236.1
170.1	210.9
191.8	191.2
241.9	267.0
267.2	341.0
286.8	263.7
311.2	240.0
335.7	232.6
361.8	205.6
382.4	202.3
431.7	169.2
480.8	158.6
503.3	141.2
527.5	142.1
551.1	145.1
573.2	141.5
599.6	100.6
624.7	100.9
647.2	100.8

Appendix L. Benzene generation rate data from ventilated, non-radioactive tests with Tank 48H simulant containing 4.5 wt % NaTPB and KTPB solids and spiked with 1.4 mg/L copper.

Reaction Time (hrs)	Benzene Generation Rate ($\mu\text{g/L/hr}$)
55.1	37.7
105.9	35.2
130.8	30.5
158.3	29.6
177.8	26.7
201.2	22.6
227.3	22.1
250.3	24.7
273.2	18.3
301.8	18.5
319.8	16.3
344.1	16.0
370.7	16.0
416.8	13.3
441.0	12.4
464.6	15.1
486.6	12.1
518.5	14.9

Appendix M. Benzene generation rate data from air ventilated, non-radioactive tests with Tank 48H simulant containing 4.5 wt % KTPB solids (no excess NaTPB) and spiked with 1.4 mg/L copper.

Reaction Time (hrs)	Benzene Generation Rate ($\mu\text{g/L/hr}$)
55.1	38.9
130.8	37.8
158.3	31.7
177.8	28.6
201.2	27.6
227.3	25.3
250.3	24.3
273.2	22.1
301.8	21.6
319.8	19.2
344.1	15.0
370.7	17.2
441.0	15.4
464.6	14.1
486.6	14.4
518.5	21.7

Appendix N. Benzene generation rate data for the air ventilated non-radioactive test with reagent grade NaTPB solution.

Reaction Time (hrs)	Benzene Generation Rate ($\mu\text{g/L/hr}$)
18.1	1.688e+3
42.9	2.861e+3
72.0	7.888e+3
92.7	1.366e+4
115.8	4.222e+5
139.4	2.030e+6
165.0	1.315e+6
190.2	5.880e+5
212.4	2.247e+5
236.2	1.073e+5

Appendix O. Benzene generation rate data for the nitrogen ventilated non-radioactive test with reagent grade NaTPB solution.

Reaction Time (hrs)	Benzene Generation Rate ($\mu\text{g/L/hr}$)
19.5	1.810e+6
43.1	1.118e+6
68.6	6.276e+5
93.4	4.356e+5
116.3	3.491e+5
139.5	3.337e+5
164.8	2.312e+5
190.0	2.083e+5
212.7	2.210e+5
237.0	1.561e+5

Appendix P. Reactions Involving Alkaline Solution

Decomposition of Tetraphenylborate Anion (TPB⁻) in Presence of Trace Copper.

Catalytic Reaction Mechanisms Involving Metal-Redox Couple

The decomposition of aqueous tetraphenylborate in the presence of copper has been previously investigated in alkaline solutions. [Ref. A] The tests were prompted by concerns about aqueous TPB⁻ decomposition during interim storage, prior to batch additions as cold feed material in the ITP process. These previous experiments have recently received much attention as relatively simple, prototypical experiments for investigating the reactivity of soluble TPB⁻ in the presence of copper. Current tests involving TPB⁻/Cu(II) solutions are indicating that trace levels of copper(II) ion can possibly completely decompose the TPB⁻ (see Ventilated Non-Radioactive Solution Tests in text). The solutions in the present tests are 0.1 M OH⁻ and 0.5 M TPB⁻ and contain 10 ppm Cu(II) (~1.6x10⁻⁴ M). Present tests were suggested and designed specifically to investigate the effects of aerated and inert atmospheres on TPB⁻ decomposition. The original tests were carried out in sealed plastic bottles whereas the current tests involve flowing a gas (air or nitrogen) over constantly-stirred 100-mL solutions. Pertinent questions to be addressed by the current investigations are:

- 1) Is copper catalytically involved to the same extent with and without air present, i.e. does one system indicate catalytic reactions while another only reacts stoichiometrically?
- 2) Are the TPB⁻ decomposition product yields significantly different with and without air present, i.e. is either benzene or phenol formed at the exclusion of the other?

Catalytic properties of copper are suspected to be dependent on the redox reactions of the Cu(II)/Cu(I) couple. One possibility is that copper could be catalytic in aerated systems but inactive in similar anoxic systems with both gaseous and dissolved O₂ removed. Several industrial copper catalyzed chemical processes are reported to be sustained in the presence of air. [Ref. B/C] In a continuously aerated solution the dissolved oxygen in solutions could be replenished to provide an unlimited source of oxidant.

Table P-1 shows the molar amounts of dissolved species present in a 100-mL solution of 0.1 M OH⁻, 0.5 M TPB⁻, and 10 ppm Cu(II), with dissolved air from the atmosphere initially present. Comparing the relative amounts of copper and TPB⁻ in Table 1 suggests that a catalytic reaction scheme would be necessary for the complete destruction of the original TPB⁻. A stoichiometric reaction between copper and TPB⁻ would only decompose ~0.06% of the original 0.5 molar TPB⁻ present. Also note from the data in Table P-1 that only 0.2% of

Table P-1. Amounts of dissolved species present in the 100-mL aerated $\text{OH}^-/\text{TPB}^-/\text{Cu(II)}$ system.

Species	Concentration (molar)	Quantity (moles)	Maximum Percent TPB^- Decomposed (%)
TPB^-	0.5	0.050	not applicable
Cu(II)	0.00016	0.000016 ^a	0.06 ^b
O_2	0.00025 ^c	0.000025	0.2 ^d

^a Actual dissolved Cu(II) could be lower due to its solubility equilibrium with solid hydrated copper hydroxide $\text{Cu(H}_2\text{O)}_4(\text{OH})_2$ in alkaline solution (see text).

^b Assume stoichiometric reaction between original Cu(II) present and TPB^- , i.e. $2 \text{TPB}^- + \text{Cu(II)} \rightarrow 2 \text{TPB}^\cdot + \text{Cu}^0$.

^c Aqueous concentration of O_2 from dissolved air in equilibrium with the atmosphere at standard conditions.

^d Assume stoichiometric reaction between Cu(II) and TPB^- with subsequent oxidation of 4 Cu(I) by O_2 (see reaction 2 in text) until original amount of dissolved O_2 in solution is depleted. This would likely apply for a solution that was prepared in an open vessel, sealed and continuously purged with a nitrogen-flow over the gas-space in the vessel.

the Cu(I) generated in reaction 1 (see below) could be re-oxidized from reaction with the initial amount of dissolved O_2 present in the 100-mL of solution.

Generalized equations describing TPB^- decomposition involving copper catalysis can be written as:

- 1) $\text{TPB}^- + \text{Cu(II)} \rightarrow (\text{TPB}^- \text{ decomposition products}) + \text{Cu(I)}$
- 2) $\text{Cu(I)} + \text{O}_2 \rightarrow \text{Cu(II)} + \text{O}_2^-$

where TPB^- decomposition products are any of the various observed end-products such as benzene, phenol, biphenyl, and phenylboric acid.

Aerated Alkaline Solutions with $\text{Cu(II)}/\text{Cu(I)}$ -Redox Couple

Suggested reactions describing TPB^- decomposition in the aerated $\text{TPB}^-/\text{Cu(II)}$ alkaline solutions can be generalized as follows:

Primary Reactions

- 1) $(\text{C}_6\text{H}_5)_3\text{B}(\text{C}_6\text{H}_5)^- + \text{Cu}^{2+} \rightarrow (\text{C}_6\text{H}_5)_3\text{B}(\text{C}_6\text{H}_5)^\cdot + \text{Cu}^+$
- 2) $4\text{Cu}^+ + \text{O}_2 \rightarrow 4\text{Cu}^{2+} + 2\text{O}_2^-$ ($2\text{O}_2^- + 2\text{H}_2\text{O} \rightarrow 4\text{OH}^-$)
- 3) $(\text{C}_6\text{H}_5)_3\text{B}(\text{C}_6\text{H}_5)^- + \text{Cu}^+ \rightarrow (\text{C}_6\text{H}_5)_3\text{B}(\text{C}_6\text{H}_5)^\cdot + \text{Cu(s)}$
- 4) $(\text{C}_6\text{H}_5)_3\text{B}(\text{C}_6\text{H}_5)^\cdot + \text{Cu}^{2+} + \text{OH}^- \rightarrow (\text{C}_6\text{H}_5)_3\text{B} + (\text{C}_6\text{H}_5)\text{OH} + \text{Cu}^+$
- 5) $(\text{C}_6\text{H}_5)_3\text{B}(\text{C}_6\text{H}_5)^\cdot + \text{Cu}^+ + \text{OH}^- \rightarrow (\text{C}_6\text{H}_5)_3\text{B} + (\text{C}_6\text{H}_5)\text{OH} + \text{Cu(s)}$

For simplicity copper ion is shown in the above equations as Cu(II) or Cu(I) ion. In alkaline solution the Cu(II) ion would exist as the cuprate ion $\text{Cu}(\text{H}_2\text{O})_2(\text{OH})_4^{2-}$ and Cu(I) as $\text{Cu}(\text{OH})_2^-$. Cuprate concentrations would be limited by its equilibrium with hydrated copper hydroxide solid via:

Reactions 1 and 3 as shown above could possibly be fast electron transfer, perhaps diffusion-limited reactions with rate constants possibly on the order of 1×10^8 to $1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$. Another possibility for reactions 1 and 3, instead of electron transfer, would be formation of a copper-coordinated boron complex. Such a reaction sequence will be discussed later in this report discussion.

Radiation chemistry studies have shown that both Cu(II) and Cu(I) rapidly react with the hydrated electron, e_{aq}^- , in aqueous, neutral pH 4-7, solution with $k(\text{Cu(II)} + \text{e}_{\text{aq}}^- \rightarrow \text{Cu(I)}) = 3.5 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ and $k(\text{Cu(I)} + \text{e}_{\text{aq}}^- \rightarrow \text{Cu(0)}) = 2.7 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$, respectively. [Ref. D] Reaction 2 shows oxygen, an obvious oxidant available in the aerated system, reacting to oxidize the Cu(I) to Cu(II). This reaction as written shows that one oxygen molecule could potentially oxidize four Cu(I) to Cu(II). The oxidation of Cu(I) by O_2 could be in competition with the other reactions involving TPB^- and $\text{TPB} \cdot$ reductions of Cu(I) to metallic copper, reactions 3 and 5 respectively. If a solution were continuously supplied with O_2 , it would seem that the necessary conditions for the copper-catalyzed decomposition of TPB^- via reactions 1-7 shown above could exist.

Reactions 6 and 7 describe the decomposition of the tetraphenylboron radical species formed in reactions 1 and 3. Reaction 6 is speculative while reaction 7 has been postulated in connection with experimental studies involving pulse radiolysis of aqueous tetraphenylborate. [Ref. E]

Further possible secondary reactions involving the products of reactions 6 and 7 above are listed in the schemes below. Several of the reaction sequences shown below have been previously proposed in experimental studies pertaining to the radiolysis of tetraphenylborate [Ref. F-H], the acid protolysis of tetraphenylborate [Ref. I], the radiolysis of benzene [Ref. J-M], and the radiolysis of phenol. [Ref. N] The initial sequence below indicates triphenylboron in equilibrium with hydroxytriphenylborate. While the hydroxide adduct is reported to be fairly stable in organic solvents, a published account indicates that it will hydrolyze moderately rapidly in cold water and rapidly in dilute sodium hydroxide solutions. [Ref. O] Other published studies have discussed the possible role of oxygen in the hydrolysis of triphenylboron. [Ref. H and Ref. I] Studies on the aqueous stability of

triphenylboron conducted in the present study (see Reaction of Phenylboron Compounds in the text) indicate that triphenylboron (obtained as the ~ 9 wt % NaOH adduct solution in water, $(C_6H_5)_3B \cdot NaOH$, from Aldrich Chemical Co.) is likely to be completely decomposed in aerated 2.0 molar salt solutions at 70°C within ~ 3 days.

Secondary Reactions

Reactions of Triphenylboron $(C_6H_5)_3B$:

•Alkaline-adduct/Hydrolysis

Note: It can be postulated that a phenyl radical transfer could occur between the original parent TPB $^-$ and the $B(OH)_4^-$ end-product formed in reaction 11 above. Indirect evidence exists in the literature to support such a phenyl radical transfer. [Ref. P] This reaction would suggest a chain-propagation sequence as follows:

•Oxidation/Hydrolysis

•Alkaline-adduct/Oxidation/Hydrolysis - Scheme A

•Alkaline-adduct/Oxidation/Hydrolysis - Scheme B

In the reaction sequences 13-15, 16-19, and 20-23 shown above, involving oxidation reactions of molecular oxygen, the initiating reactions 13, 16, and 20 as written would involve a two step process. Using $\text{(C}_6\text{H}_5\text{)}_3\text{B}$ as an example, these steps would involve the following two reactions:

These reaction sequences 13-15, 16-19, and 20-23 are thus postulated to occur via molecular oxygen attack as opposed to a less likely oxygen atom oxidation of the B-C species. Alternative molecular oxidation of the B-C species could involve insertion of O_2 itself (essentially a di-radical species) into the boron-phenyl bond, followed by subsequent homolytic or heterolytic O-O bond rupture as shown below:

Reactions of Phenyl Radical (C_6H_5): Reactions of Diphenylboron Radical (C_6H_5)₂B:

In addition to reactions 24 and 29 above, the phenyl radical and the diphenylboron radicals could also react with each other:

This reaction as shown would produce triphenylboron which could undergo any of the postulated decomposition steps shown in reactions 8-12 above. The overall scheme presented above for copper-catalyzed tetraphenylborate decomposition in aerated solutions assumes that the presence of dissolved molecular oxygen is critical in oxidizing Cu(I) (see reaction 2), thus providing a channel for the catalysis mechanism involving the redox couple of Cu(II)/Cu(I).

Deaerated (Anoxic) Alkaline Solutions

If molecular oxygen is excluded from the overall scheme presented for the aerated solutions above, the following set of reactions could describe in general terms the copper catalyzed decomposition of TPB⁻ in deaerated solutions:

Primary Reactions in Absence of Oxygen

- 1) $(\text{C}_6\text{H}_5)_3\text{B}(\text{C}_6\text{H}_5)^- + \text{Cu}^{2+} \rightarrow (\text{C}_6\text{H}_5)_3\text{B}(\text{C}_6\text{H}_5)^\cdot + \text{Cu}^+$
- 3) $(\text{C}_6\text{H}_5)_3\text{B}(\text{C}_6\text{H}_5)^- + \text{Cu}^+ \rightarrow (\text{C}_6\text{H}_5)_3\text{B}(\text{C}_6\text{H}_5)^\cdot + \text{Cu(s)}$
- 4) $(\text{C}_6\text{H}_5)_3\text{B}(\text{C}_6\text{H}_5)^\cdot + \text{Cu}^{2+} + \text{OH}^- \rightarrow (\text{C}_6\text{H}_5)_3\text{B} + (\text{C}_6\text{H}_5)\text{OH} + \text{Cu}^+$
- 5) $(\text{C}_6\text{H}_5)_3\text{B}(\text{C}_6\text{H}_5)^\cdot + \text{Cu}^+ + \text{OH}^- \rightarrow (\text{C}_6\text{H}_5)_3\text{B} + (\text{C}_6\text{H}_5)\text{OH} + \text{Cu(s)}$
- 6) $(\text{C}_6\text{H}_5)_3\text{B}(\text{C}_6\text{H}_5)^\cdot \rightarrow (\text{C}_6\text{H}_5)_3\text{B} + (\text{C}_6\text{H}_5)^\cdot$
- 7) $(\text{C}_6\text{H}_5)_3\text{B}(\text{C}_6\text{H}_5)^\cdot \rightarrow (\text{C}_6\text{H}_5)_2\text{B}^\cdot + (\text{C}_6\text{H}_5)_2$

Secondary Reactions in Absence of Oxygen

Reactions of Triphenylboron $(\text{C}_6\text{H}_5)_3\text{B}$:

•Alkaline-adduct/Hydrolysis

- 8) $(\text{C}_6\text{H}_5)_3\text{B} + \text{OH}^- \rightarrow (\text{C}_6\text{H}_5)_3\text{BOH}^-$
- 9) $(\text{C}_6\text{H}_5)_3\text{BOH}^- + \text{H}_2\text{O} \rightarrow (\text{C}_6\text{H}_5)_2\text{B}(\text{OH})_2^- + \text{C}_6\text{H}_6$
- 10) $(\text{C}_6\text{H}_5)_2\text{B}(\text{OH})_2^- + \text{H}_2\text{O} \rightarrow (\text{C}_6\text{H}_5)\text{B}(\text{OH})_3^- + \text{C}_6\text{H}_6$
- 11) $(\text{C}_6\text{H}_5)\text{B}(\text{OH})_3^- + \text{H}_2\text{O} \rightarrow \text{B}(\text{OH})_4^- + \text{C}_6\text{H}_6$

Note: It can be postulated that a phenyl transfer could occur between the original parent TPB⁻ and the $\text{B}(\text{OH})_4^-$ end-product formed in reaction 11 above. This reaction would suggest a chain-propagation sequence as follows:

- 12) $(\text{C}_6\text{H}_5)_3\text{B}(\text{C}_6\text{H}_5)^- + \text{B}(\text{OH})_4^- \rightarrow (\text{C}_6\text{H}_5)_3\text{B}(\text{OH})^- + (\text{C}_6\text{H}_5)\text{B}(\text{OH})_3^-$
- 9) $(\text{C}_6\text{H}_5)_3\text{BOH}^- + \text{H}_2\text{O} \rightarrow (\text{C}_6\text{H}_5)_2\text{B}(\text{OH})_2^- + \text{C}_6\text{H}_6$
- 10) $(\text{C}_6\text{H}_5)_2\text{B}(\text{OH})_2^- + \text{H}_2\text{O} \rightarrow (\text{C}_6\text{H}_5)\text{B}(\text{OH})_3^- + \text{C}_6\text{H}_6$
- 11) $(\text{C}_6\text{H}_5)\text{B}(\text{OH})_3^- + \text{H}_2\text{O} \rightarrow \text{B}(\text{OH})_4^- + \text{C}_6\text{H}_6$

Anoxic Reactions of Phenyl Radical (C_6H_5): Anoxic Reactions of Diphenylboron Radical (C_6H_5)₂B: Reaction of Phenyl Radical (C_6H_5) with Diphenylboron Radical (C_6H_5)₂B:

In the above section describing tetraphenylborate decomposition under anoxic conditions, the proposed mechanistic schemes, namely reactions 1, and reactions 3-7, offer no suggested mechanism for reoxidation of the Cu(I) ion to complete the redox couple of Cu(I)/Cu(II). We note that it is unlikely that perhaps the oxygen-containing species phenol or phenylboric acid could act as Cu(I) oxidants based on a literature account in which it is shown that phenylboric acid acts as a reductant towards Cu(II) to form Cu(I). [Ref. Q] However a reaction sequence is presented below in which the Cu(I) ion could catalytically decompose tetraphenylborate without involving Cu(II) after Cu(II) is initially reduced to Cu(I) (see reactions 36-40 presented below). This proposed catalysis could be initiated in the anoxic scheme by a coupling of the Cu(I) with the tetraphenylboron radical, i.e. an alternate reaction to that of reaction 5 above, in which it is postulated that Cu(I) is reduced to metallic copper by the tetraphenylboron radical.

A broad comparison of the two different generalized schemes involving aerated catalytic decomposition of tetraphenylborate and anoxic catalytic decomposition of tetraphenylborate also suggest that benzene is possibly the most predominant end-product in the anoxic scheme (see anoxic scheme, reactions 8-12 and reaction 34 (the product of which, $(C_6H_5)_3B$, could proceed to decompose via reactions 8-12), and reactions 36-40 below). Further studies involving the decomposition of aqueous triphenylboron, i.e. dissolved air effects, pH effects, the effects of high levels of soluble salts, temperature effects (and perhaps even the effects of dissolved metal species that could potentially catalyze the triphenylboron decomposition), are needed to better understand the postulated reaction scheme in reactions 8-12.

Catalytic Reaction Mechanism not Involving Metal-Redox Couple

It was previously mentioned that the initial Cu(II) plus TPB⁻ reaction could be postulated to react via a simple electron transfer-type process (see reaction 1 in the catalysis mechanism sections above) or alternatively via a Cu-B complex. The possibility of tetraphenylborate hydrolysis in a series of reactions that does not involve any copper redox chemistry (after the Cu(I)B(C₆H₅)₄ intermediate is formed) is shown below.

Literature accounts suggest that the initial reactions 35 and 36 are probable.[Ref. R,S] The Cu(I)B(C₆H₅)₄ complex is reported to hydrolyze readily to benzene in contrast to a relatively more stable uncomplexed tetraphenylborate anion. The tetraphenylboron radical and triphenylboron produced in the above reactions 35 and 36, respectively, could subsequently decompose by the previously mentioned schemes involving reactions 6 and 7 for (C₆H₅)₄B[·] and reactions 8-12 for triphenylboron ((C₆H₅)₃B).

References

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Appendix Q. D. D. Walker "Excess NaTPB in Tank 48
Batch #1 (U)", March 28, 1996.

INTER-OFFICE MEMORANDUM
Savannah River Site

28-Mar-1996 02:05pm EST

To: See Below

From: Darrel Douglas Walker (WALKER-DD-T5550)
Dept: SRL/IWT
Tel : 5-2612

Excess NaTPB in Tank 48 Batch #1

There has been some discussion lately about the amount of excess sodium tetraphenylborate in Tank 48H. I have maintained that the excess in the tank was about 16%, whereas Paul Rutland has maintained that about 31% excess was added to the tank last September. Many others believe that we have used a 50% excess. After discussions with Paul yesterday, I agree that his value of 31% is the correct value. However, please note that the following two statements are both correct:

In September, a 31% excess of NaTPB was added over the theoretical amount required.

In November/December, all of the excess NaTPB decomposed. This excess was 16 wt % of the tetraphenylborate in the tank.

The difference is due to definitions of excess and is not due to any misunderstanding of how much NaTPB was added or how much potassium was in the tank. If you are interested in the details, please read on. Also, I have contacted Rob Swingle to discuss the values that he is using in the benzene material balance. He will make some minor changes to align his calculations with the values used by Rutland and Rick Fowler. However, one significant difference will remain. Swingle will continue to use a more accurate measure of the soluble tetraphenylborate that was sent to Tank 50 in the filtrate. The final tank volume and sodium concentration were slightly different than the pre-batch predictions, which resulted in a large difference in the soluble amount (note that the soluble amount is a minor part of the total).

The correct definition of excess for the NaTPB addition made in September is based on two amounts: (1) the theoretical amount of NaTPB needed to precipitate the Cs and K, and react with mercury, and (2) how much more than this amount was actually added. Rutland's calculation using amounts measured in gram-moles is:

$$\% \text{ Excess} = 100 \times (\text{Total} - \text{Theoretical}) / (\text{Theoretical})$$

The theoretical amount of NaTPB is obtained from the measured value for K+ with 8% additional for precipitation of Cs and reaction with mercury. In September, the K+ concentration was 0.033 molar and the tank contained 456,000 gallons of waste. Thus, the theoretical amount of NaTPB was 61,600 gram-moles. Beyond the theoretical amount, additional NaTPB is added to (1) saturate the salt solution and (2) create solid NaTPB solids. To saturate the solution required 3600 g-moles of NaTPB. The requirement for NaTPB solids is to add an additional 0.0075 molar NaTPB for the final tank volume. Note that this last component is independent of the amount of K+ to be precipitated and, when expressed as a percentage, will vary from

Appendix R. D. D. Walker "Rate of Decomposition in Tank 48H (U)", April 3, 1996.

DON'T SAY IT - WRITE IT

TO: Todd Wright LOCATION 704-H DATE 4/3/96

FROM: D. D. Walker PHONE NO. 5-2612 LOCATION 773-A

Rate of Decomposition in Tank 48H

Attached is the graph you requested. The following are some comments about the "Expected" rate of increase of Cs-137 in the liquid phase.

Current Tank 49

The current rate of increase of Cs-137 in Tank 48 is 1.36 nCi/g per day. This is based on data since December 1. It would appear from the graph that all the excess NaTPB was decomposed at approximately that time, initiating the increase in soluble Cs-137.

Tank 49 Storage expectations

The rate of degradation of precipitate due to radiolysis was studied in small-scale tests following the 1983 demonstration. Based on these experiments the ITP, Late Wash, and Acid Hydrolysis processes expected about 7.5% decomposition per year (for slurry containing 36 Ci Cs-137 per gallon). When this result is adjusted to the current tank composition (2.5 Ci/gal), the expected rate for Cs-137 is 8 nCi/g per day. This is line shown for the "Expected" on the attached graph.

1983 Demonstration

Following the 1983 demonstration, the Cs-137 concentration in the solution was measured over a period of three years. It increased linearly at a rate of about 22 nCi/g per day. If the results of the small scale tests are extrapolated to the composition following the 1983 demonstration, the expected rate of increase was 16 nCi/g per day.

Summary

The current mix of precipitates from 1983 and 1995 are decomposing at a rate that is slower than expected. The slow rate could be due to reprecipitation of Cs-137 by some residual (but low) level of excess NaTPB in the tank. Although analyses of tank samples do not show any excess, the sensitivity of the analysis cannot rule out a residual NaTPB

content of up to 200 lbs. A second possibility is that the rate may accelerate with time. The experimental rates and post-1983 demo rate are based on time periods that are long compared to the 100 days since the Cs-137 began to increase in early December 1995.

CC: W. L. Tamosaitis
S. D. Fink
M. J. Barnes
R. A. Jacobs
B. G. Croley
J. D. Menna
P. L. Rutland
E. W. Holtzscheiter

Cs-137 Activity in Tank 48H Filtrate

Appendix S. M. R. Poirier, "Preliminary Benzene Evolution Rates During Saltstone Curing " (U),
SRT-WHM-96-0014, February 28, 1996.

Westinghouse Savannah River Company
Inter-Office Memorandum

SRT-WHM-96-0014

February 28, 1996

To: W. B. Van Pelt, 676-1T

From: M. R. Poirier, 676-T *MRP*

Preliminary Benzene Evolution Rates During Saltstone Curing

Summary

High Level Waste Engineering requested SRTC to determine the rate of benzene release during saltstone curing as part of the TCLP tests. SRTC prepared saltstone with the January 1996 Tank 50H sample and issued report SRT-WHM-96-0013 summarizing preliminary (7 day TCLP and benzene evolution and 14 day TCLP) results.

Benzene evolution rates as reported earlier for 4 and 7 day samples, and new data for 11, and 14 day samples ranged from 0.012 to 0.172 $\mu\text{g/L/hr}$, which is below the rate measured in the 1985 tests.¹ Additional samples are being collected to measure benzene evolution rates over 28 days, and longer, and another report will be issued when that work is completed.

Background

Analyses of the liquid and vapor in Tank 50H have shown liquid benzene concentrations of 2 - 8 mg/l and vapor benzene concentrations of 10 - 50 mg/l.² High Level Waste Engineering requested SRTC to determine the rate of benzene release during saltstone curing, especially as related to tetraphenylborate decomposition.

The amount of free benzene going to grout is much less than the amount measured in Tank 50H due to inherent process losses.¹ Prior tests¹ sought to measure benzene evolution only from sodium tetraphenylborate. The current tests are measuring benzene evolution from potassium tetraphenylborate and free benzene. Since potassium tetraphenylborate solubility is less than sodium tetraphenylborate solubility, the benzene evolution rates in the current tests will be lower than the rates in previous tests¹.

Results

A sample of Tank 50H salt solution was collected in January 1996 and used for these tests. Saltstone samples were prepared containing 46 wt.% salt solution, 5.4 wt.% cement, 24.3 wt.% flyash, and 24.3 wt.% slag. The saltstone was placed in a reaction kettle and the kettle sealed. Air was circulated through the reaction kettle at approximately 20 ml/min and passed through a charcoal filter as it exited to remove and collect any benzene which evolved. An additional sample was prepared using salt simulant rather than Tank 50H salt solution.

W. B. Van Pelt

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SRT-WHM-96-0014

The charcoal filters were changed after 4, 7, 11, and 14 days, and submitted to ADS to determine the accumulation of benzene on the filter. Table 1 shows the results. The benzene evolution rates ranged from 0.012 to 0.172 $\mu\text{g/L hr}$. Some scatter exists in the benzene evolution data. The reasons for the scatter are the difficulty in extracting the benzene from the charcoal filter and the small amount of benzene evolved during the test.

Table 1. Benzene Evolution Rates^{3,4,5}

<u>Time (days)</u>	<u>Salt Source*</u>	<u>Benzene Collected</u>	<u>Benzene Evolution Rate</u>
0 - 4	Simulant	< 0.1 μg	< 0.026 $\mu\text{g/Lhr}$
0 - 4	Tank 50H	0.185 μg	0.048 $\mu\text{g/Lhr}$
0 - 4	Tank 50H	0.130 μg	0.034 $\mu\text{g/Lhr}$
0 - 4	Tank 50H	0.164 μg	0.041 $\mu\text{g/Lhr}$
4 - 7	Simulant	0.035 μg	0.012 $\mu\text{g/Lhr}$
4 - 7	Tank 50H	0.061 μg	0.021 $\mu\text{g/Lhr}$
4 - 7	Tank 50H	0.323 μg	0.110 $\mu\text{g/Lhr}$
4 - 7	Tank 50H	0.487 μg	0.172 $\mu\text{g/Lhr}$
7 - 11	Simulant	0.053 μg	0.013 $\mu\text{g/Lhr}$
7 - 11	Tank 50H	0.256 μg	0.064 $\mu\text{g/Lhr}$
11 - 14	Simulant	0.106 μg	0.037 $\mu\text{g/Lhr}$
11 - 14	Tank 50H	0.139 μg	0.049 $\mu\text{g/Lhr}$

* Benzene levels measured in Tank 50H were 2 - 8 mg/L. The initial benzene in the grout was approximately 0.2 mg/L due to sample handling losses, which would be typical of losses in the Saltstone process.¹

Figure 1 compares the benzene evolution rates in this test with the results from previous SRTC tests.¹ The benzene evolution rates during the first 14 days of curing in the 1996 test are at or below the evolution rates measured in the previous test. In the previous test, the maximum benzene evolution rate occurred between 7 and 12 days after the curing started.¹ Additional samples will be collected at 21, and 28 days. These results will be reported when received.

References

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2. D. D. Walker, M. J. Barnes, R. F. Swingle, and R. A. Peterson, "Recent Tetraphenylborate Decomposition Results", SRT-LWP-96-008, January 22, 1996
3. J. E. Young, "Analysis Results; ADS.3-67987, -8, and -9", Inter-Office Memorandum, February 16, 1996. (Attachment 1)
4. J. E. Young, "MRP Charcoal Tube Analysis", Inter-Office Memorandum, February 13, 1996. (Attachment 2)
5. J. E. Young, "Orbo Tube Data", Inter-Office Memorandum, February 26, 1996. (Attachment 3)

W. B. Van Pelt

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SRT-WHM-96-0014

Figure 1. Benzene Evolution Rate During Saltstone Curing

cc: W. L. Tamosaitis, 773-A
H. D. Harmon, 719-4A
B. T. Butcher, 773-43A
J. R. Fowler, 704-Z
T. E. Britt, 730-2B
D. D. Walker, 773-A
R. A. Peterson, 676-T
R. M. Satterfield, 719-4A

S. D. Fink, 773-A
B. G. Croley, 241-120H
C. A. Langton, 773-43A
T. D. Lookabill, 704-Z
M. K. Gupta, 730-2B
M. J. Barnes, 773-A
R. F. Swingle, 773-A
IWT File, 676-1T

W. B. Van Pelt

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SRT-WHM-96-0014

Attachment 1

INTER-OFFICE MEMORANDUM
Savannah River Site

16-Feb-1996 09:21am EST

To: Michael R Poirier (POIRIER-MR-Y5714 @A1@SASRS5)
CC: Pamela R. Waller (WALLER-PR-W2490 AT A1 AT SLSRP1)
CC: Jeffrey C. Griffin (GRIFFIN-JC-T8054 AT A1 AT SLSRP1)
From: John E. Young, ADS (YOUNG-JE-T6035 AT A1 AT SLSRP1)
Dept: Analytical Development S
Tel: (803) 725-3565

Analysis results; ADS 3-67987, -8, and -9 [u]

We have completed the analysis of your charcoal tube samples submitted on 2/15.

The results are tabulated;

ADS#	Cust#	FileID	ug benzene on tube
3-67987	MRP4	15e\09	0.0345
3-67988	MRP5	15d\07	0.0613
3-67989	MRP6	15d\08	0.3230

statistical method detection
limit, prepared under ideal conditions 0.15 (1)

(1) concentration at which 99% of analyses performed will generate a detectable signal.

As you will note, the values are very close to the method detection limit. For best accuracy, and least influence from environmental contamination, at least 1 ug of benzene should be loaded onto the tube prior to analysis. It would be advised, if possible, to scale your experiments up accordingly.

W. B. Van Pelt

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SRT-WHM-96-0014

Attachment 2

INTER-OFFICE MEMORANDUM
Savannah River Site

13-Feb-1996 11:40am EST

To: Michael R Poirier (POIRIER-MR-Y5714 @A1@SASRS5)
CC: Pamela R. Waller (WALLER-PR-W2490 AT A1 AT SLSRP1)
From: John E. Young, ADS (YOUNG-JE-T6035 AT A1 AT SLSRP1)
Dept: Analytical Development S
Tel: (803) 725-3565

MRP charcoal tube analysis

Data is documented in WSRC-NB-94-62, p.159

ADS#	Cust ID	Benzene, ug on tube	TCE, ug on tube
3-67535	MRP2	0.185	0.95
3-67536	MRP3	0.130	9.5
3-67537	MRP1	<0.1	9.9

During the analysis of your samples, it was noted that a variety of compounds (other than benzene) were increasing throughout the ADS sequence number series. The compounds were mainly light freons and trichloroethene. Since trichloroethene is present in SRTC air from process water offgas, this data was computed and presented for your information.

Sample results were corrected for chemical recovery inefficiencies as measured from the chemical recovery of benzene and TCE on this same batch of charcoal tubes.

W. B. Van Pelt

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SRT-WHM-96-0014

Attachment 3

INTER-OFFICE MEMORANDUM
Savannah River Site

26-Feb-1996 10:59am EST

To: Michaël R Poirier (POIRIER-MR-Y5714 @A1@SASRS5)

From: John E. Young, ADS (YOUNG-JE-T6035 AT A1 AT SLSP1)
Dept: Analytical Development S
Tel: (803) 725-3565

ORBO tube data

ADS#	CustID	Benzene, ug on tube
3-68240	MRP7	0.053
3-68241	MRP8	0.256
3-68242	MRP9	0.164
3-68258	MRP11	0.139
3-68259	MRP12	0.487
3-68260	MRP10	0.106

detection limit 0.150

Please note the ordering difference between ADS# sequence and MRP# sequence
in the last batch.

Appendix T. M. R. Poirier, "Benzene Evolution Rates During Curing of Saltstone Prepared with Tank 50 Salt Solution", SRT-WHM-96-0029.

Westinghouse Savannah River Company
Inter-Office Memorandum

SRT-WHM-96-0029

April 26, 1996

To: W. B. Van Pelt, 676-1T

From: M. R. Poirier, 676-T MRP

Benzene Evolution Rates During Curing of Saltstone Prepared with Tank 50 Salt Solution

Summary

High Level Waste Engineering requested SRTC to determine the rate of benzene release during saltstone curing. SRTC prepared saltstone with the January 1996 Tank 50H sample, placed the saltstone in a sealed reaction kettle, circulated air through the kettle, and passed the air through a charcoal filter to collect benzene. The charcoal filters were analyzed to measure the benzene evolution rate.

Benzene evolution rates measured over 55 days ranged from 0.02 to 0.2 $\mu\text{g/L hr}$, which is below the rate measured in the 1985 tests.¹ The maximum evolution rate occurred between four and seven days after the curing began.

Background

Analyses of the liquid and vapor in Tank 50H have shown liquid benzene concentrations of 2 - 8 mg/l and vapor benzene concentrations of 10 - 50 mg/l.² High Level Waste Engineering requested SRTC to determine the rate of benzene release during saltstone curing, especially as related to tetraphenylborate decomposition.

The amount of free benzene going to grout is much less than the amount measured in Tank 50H due to inherent process losses.¹ Prior tests¹ sought to measure benzene evolution only from sodium tetraphenylborate. The current tests are measuring benzene evolution from potassium tetraphenylborate and free benzene. Since potassium tetraphenylborate solubility is less than sodium tetraphenylborate solubility, the benzene evolution rates in the current tests will be lower than the rates in previous tests¹.

Results

A sample of Tank 50H salt solution was collected in January 1996 and used for these tests. Saltstone samples were prepared containing 46 wt.% salt solution, 5.4 wt.% cement, 24.3 wt.% flyash, and 24.3 wt.% slag. The saltstone was placed in a reaction kettle and the kettle sealed. Air was circulated through the reaction kettle at approximately 20 ml/min and passed through a

W. B. Van Pelt

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SRT-WHM-96-0029

charcoal filter as it exited to remove and collect any benzene which evolved. An additional sample was prepared using salt simulant rather than Tank 50H salt solution.

The charcoal filters were changed after 4, 7, 11, 14, 21, 28, 35, and 55 days, and submitted to ADS to measure the accumulation of benzene on the filter. Table 1 shows the results. The benzene evolution rates ranged from 0.02 to 0.2 $\mu\text{g/L hr}$. Some scatter exists in the benzene evolution data. The reasons for the scatter are the difficulty in extracting the benzene from the charcoal filter and the small amount of benzene evolved during the test.

Table 1. Benzene Evolution Rates^{3,4,5,6,7,8,9}

Time (days)	Salt Source*	Benzene Collected	Benzene Evolution Rate	ADS #
0 - 4	Simulant	< 0.1 μg	< 0.026 $\mu\text{g/Lhr}$	3-67537
0 - 4	Tank 50H	0.185 μg	0.048 $\mu\text{g/Lhr}$	3-67535
0 - 4	Tank 50H	0.130 μg	0.034 $\mu\text{g/Lhr}$	3-67536
0 - 4	Tank 50H	0.164 μg	0.041 $\mu\text{g/Lhr}$	3-68242
4 - 7	Simulant	0.035 μg	0.012 $\mu\text{g/Lhr}$	3-67987
4 - 7	Tank 50H	0.061 μg	0.021 $\mu\text{g/Lhr}$	3-67988
4 - 7	Tank 50H	0.323 μg	0.110 $\mu\text{g/Lhr}$	3-67989
4 - 7	Tank 50H	0.487 μg	0.172 $\mu\text{g/Lhr}$	3-68259
7 - 11	Simulant	0.053 μg	0.013 $\mu\text{g/Lhr}$	3-68240
7 - 11	Tank 50H	0.256 μg	0.064 $\mu\text{g/Lhr}$	3-68241
7 - 14	Tank 50H	0.513 μg	0.079 $\mu\text{g/Lhr}$	3-68595
11 - 14	Simulant	0.106 μg	0.037 $\mu\text{g/Lhr}$	3-68260
11 - 14	Tank 50H	0.139 μg	0.049 $\mu\text{g/Lhr}$	3-68258
14 - 21	Simulant	0.127 μg	0.020 $\mu\text{g/Lhr}$	3-68590
14 - 21	Tank 50H	0.347 μg	0.054 $\mu\text{g/Lhr}$	3-68594
14 - 21	Tank 50H	0.580 μg	0.084 $\mu\text{g/Lhr}$	3-69025
21 - 28	Simulant	0.122 μg	0.018 $\mu\text{g/Lhr}$	3-69026
21 - 28	Tank 50H	0.322 μg	0.047 $\mu\text{g/Lhr}$	3-69013
21 - 35	Tank 50H	1.20 μg	0.089 $\mu\text{g/Lhr}$	3-69886
35 - 55	Tank 50H	1.91 μg	0.100 $\mu\text{g/Lhr}$	3-71101

* Benzene levels measured in Tank 50H were 2 - 8 mg/L. The initial benzene in the grout was approximately 0.2 mg/L due to sample handling losses, which would be typical of losses in the Saltstone process.¹

Figure 1 compares the benzene evolution rates in this test with the results from previous SRTC tests.¹ The benzene evolution rates during 55 days of curing in the 1996 test are at or below the evolution rates measured in the previous test. In the previous test, the maximum benzene evolution rate occurred between 7 and 12 days after the curing started.¹ In this test, the maximum evolution rate occurred between 4 and 7 days after the curing started.

References

1. S. B. Oblath, "Benzene Evolution During the Curing of Saltstone", DPST-86-645, September 2, 1986.
2. D. D. Walker, M. J. Barnes, R. F. Swingle, and R. A. Peterson, "Recent Tetraphenylborate Decomposition Results", SRT-LWP-96-008, January 22, 1996
3. J. E. Young, "Analysis Results; ADS 3-67987, -8, and -9", Inter-Office Memorandum, February 16, 1996. (Attachment 1)

W. B. Van Pelt

3

SRT-WHM-96-0029

4. J. E. Young, "MRP Charcoal Tube Analysis", Inter-Office Memorandum, February 13, 1996. (Attachment 2)
5. J. E. Young, "Orbo Tube Data", Inter-Office Memorandum, February 26, 1996. (Attachment 3)
6. J. E. Young, "Orbo Tube Data", Inter-Office Memorandum, March 1, 1996. (Attachment 4).
7. J. E. Young, "Orbo Tube Analysis Results", Inter-Office Memorandum, March 11, 1996. (Attachment 6)
8. LIMS Report, Sample ID 300069886, March 27, 1996.
9. LIMS Report, Sample ID 300071101, April 24, 1996.

Figure 1. Benzene Evolution from Saltstone Prepared with Tank 50 Solution

cc: W. L. Tamosaitis, 773-A
H. D. Harmon, 719-4A
B. T. Butcher, 773-43A
J. R. Fowler, 704-Z
T. E. Britt, 730-2B
D. D. Walker, 773-A
R. A. Peterson, 676-T
R. M. Satterfield, 719-4A
S. R. Wilson, 704-28S

S. D. Fink, 773-A
B. G. Croley, 241-120H
C. A. Langton, 773-43A
T. D. Lookabill, 704-Z
M. K. Gupta, 730-2B
M. J. Barnes, 773-A
R. F. Swingle, 773-A
E. J. Freed, 704-Z
IWT File, 676-1T

W.B. Van Pelt

4

SRT-WHM-96-0029

Attachment 1

INTER-OFFICE MEMORANDUM
Savannah River Site

16-Feb-1996 09:21am EST

To: Michael R Poirier (POIRIER-MR-Y5714 @A1@SASRS5)

CC: Pamela R. Waller (WALLER-PR-W2490 AT A1 AT SLSRP1)

CC: Jeffrey C. Griffin
(GRIFFIN-JC-T8054 AT A1 AT SLSRP1)

From: John E. Young, ADS (YOUNG-JE-T6035 AT A1 AT SLSRP1)

Dept: Analytical Development S

Tel: (803) 725-3565

Analysis results; ADS 3-67987,-8, and -9 [u]

We have completed the analysis of your charcoal tube samples submitted on 2/15.

The results are tabulated;

ADS#	Cust#	FileID	ug benzene on tube
3-67987	MRP4	15e\09.	0.0345
3-67988	MRP5	15d\07	0.0613
3-67989	MRP6	15d\08	0.3230

statistical method detection
limit, prepared under ideal conditions 0.15 (1)

(1) concentration at which 99% of analyses performed will generate a detectable signal.

As you will note, the values are very close to the method detection limit. For best accuracy, and least influence from environmental contamination, at least 1 ug of benzene should be loaded onto the tube prior to analysis. It would be advised, if possible, to scale your experiments up accordingly.

W. B. Van Pelt

5

SRT-WHM-96-0029

Attachment 2

INTER-OFFICE MEMORANDUM
Savannah River Site

13-Feb-1996 11:40am EST

To: Michael R Poirier (POIRIER-MR-Y5714 @A1@SASRS5)
CC: Pamela R. Waller (WALLER-PR-W2490 AT A1 AT SLSRP1)
From: John E. Young, ADS (YOUNG-JE-T6035 AT A1 AT SLSRP1)
Dept: Analytical Development S
Tel: (803) 725-3565

MRP charcoal tube analysis

Data is documented in WSRC-NB-94-62, p.159

ADS#	Cust ID	Benzene, ug on tube	TCE, ug on tube
3-67535	MRP2	0.185	0.95
3-67536	MRP3	0.130	9.5
3-67537	MRP1	<0.1	9.9

During the analysis of your samples, it was noted that a variety of compounds (other than benzene) were increasing throughout the ADS sequence number series. The compounds were mainly light freons and trichloroethene. Since trichloroethene is present in SRTC air from process water offgas, this data was computed and presented for your information.

Sample results were corrected for chemical recovery inefficiencies as measured from the chemical recovery of benzene and TCE on this same batch of charcoal tubes.

W. B. Van Pelt

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SRT-WHM-96-0029

Attachment 3

INTER-OFFICE MEMORANDUM
Savannah River Site

26-Feb-1996 10:59am EST

To: Michael R Poirier (POIRIER-MR-Y5714 @A1@SASRS5)

From: John E. Young, ADS (YOUNG-JE-T6035 AT A1 AT SLSRP1)
Dept: Analytical Development S
Tel: (803) 725-3565

ORBO tube data

ADS#	CustID	Benzene, ug on tube
3-68240	MRP7	0.053
3-68241	MRP8	0.256
3-68242	MRP9	0.164
3-68258	MRP11	0.139
3-68259	MRP12	0.487
3-68260	MRP10	0.106

detection limit 0.150

Please note the ordering difference between ADS# sequence and MRP# sequence
in the last batch.

W. B. Van Pelt

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SRT-WHM-96-0029

Attachment 4

INTER-OFFICE MEMORANDUM
Savannah River Site

01-Mar-1996 11:12am EST

To: Michael R Poirier

(POIRIER-MR-Y5714 @A1@SASRS5)

From: John E. Young, ADS
Dept: Analytical Development S
Tel: (803) 725-3565

(YOUNG-JE-T6035 AT A1 AT SLSRP1)

orbo tube data

ADS# CustID# Benzene, ug on tube

3-68590	MRP13	0.127 (<PQL)
3-68594	MRP14	0.347
3-68595	MRP15	0.513

Practical quant limit 0.29

W. B. Van Pelt

8

SRT-WHM-96-0029

Attachment 5

INTER-OFFICE MEMORANDUM
Savannah River Site

11-Mar-1996 08:50am EST

To: Michael R Poirier

(POIRIER-MR-Y5714 @A1@SASRS5)

From: John E. Young, ADS
Dept: Analytical Development S
Tel: (803) 725-3565

(YOUNG-JE-T6035 AT A1 AT SLSRP1)

ORBO tube analysis results

WSRC-NB-95-162 p.130

ADS#3-69013; MRP17; benzene=0.322 ug on tube
ADS#3-69025; MRP18; benzene=0.580 ug on tube
ADS#3-69026; MRP16; benzene=0.122 ug on tube (<0.160)

Statistically significant (1)
analyzed concentration benzene=0.160 ug on tube
level for this workup

(1) as determined by detection limit evaluation performed
on 3/6/96.

Appendix U. M. R. Poirier, "TCLP Benzene Results and Preliminary Benzene Generation Rates from Saltstone Prepared with the January 1996 Tank 50H Sample", SRT-WHM-96-0013, February 22, 1996.

Westinghouse Savannah River Company
Inter-Office Memorandum

SRT-WHM-96-0013

February 22, 1996

To: B. T. Butcher, 773-43A

cc: W. L. Tamosaitis, 773-A
W. B. Van Pelt, 676-1T
J. R. Fowler, 704-Z
T. D. Lookabill, 704-Z
T. E. Britt, 730-2B
M. K. Gupta, 730-2B

From: M. R. Poirier, 676-T *MRP*

TCLP Benzene Results and Preliminary Benzene Generation Rates from Saltstone Prepared with the January 1996 Tank 50H Sample

Summary

High Level Waste Engineering requested SRTC to determine the rate of benzene release during saltstone curing and to determine whether the saltstone will pass the Toxic Characteristic Leaching Procedure (TCLP) test.

SRTC prepared saltstone with the January 1996 Tank 50H sample. The saltstone passed 7 and 14 day TCLP tests for benzene. A sample which was cured at 60° C for 14 days also passed the TCLP test for benzene, although the measured benzene concentration was 2 - 5 times higher than in the samples cured at room temperature. A 28 day TCLP test will be performed by a certified laboratory, and the results will be reported when received.

Benzene generation rates measured after 4 days and 7 days ranged from 0.02 to 0.11 µg/L hr. Additional samples are being collected to measure benzene generation rates over 28 days, and another report will be issued when that work is completed.

Introduction

Analyses of the liquid and vapor in Tank 50H have shown liquid benzene concentrations of 2 - 8 mg/l and vapor benzene concentrations of 10 - 50 mg/l.[†] High Level Waste Engineering requested SRTC to determine the rate of benzene release during saltstone curing and to determine whether the saltstone prepared from the current contents of Tank 50H will pass the TCLP test.

B. T. Butcher

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SRT-WHM-96-0013

Results

A sample of Tank 50H salt solution was collected and used for these tests. Saltstone samples were prepared containing 46 wt.% salt solution, 5.4 wt.% cement, 24.3 wt.% flyash, and 24.3 wt.% slag. The saltstone was placed in a reaction kettle and the kettle sealed. Air was circulated through the reaction kettle at approximately 20 ml/min and passed through a charcoal filter as it exited to remove and collect any benzene which evolved.

Two other Saltstone samples were prepared (by C. A. Langton) with Tank 50H salt solution using the same saltstone mixture. One sample cured for 14 days, at ambient temperature in an open vessel, and the other cured for 14 days in an oven at 60° C.

After curing, the saltstone samples were collected, frozen in liquid nitrogen for six hours, and crushed. The samples (2 - 2.5g) were placed in a zero-headspace extractor and extracted with acetic acid (TCLP results) or methanol ("Totals" results) for 18 hours.

Table 1 shows the results.² The benzene is well below the regulatory limits for Constituent Concentration in Waste Extract (TCLP) and Constituent Concentration in Waste ("Totals"). The benzene concentration in the TCLP extract ranged from 0.9 - 2.7 µg/L, well below the regulatory limit of 500 µg/L. The benzene in the "Totals" test ranged from 54 - 240 µg/kg, well below the regulatory limit of 10,000 µg/kg.

Table 1. Benzene TCLP Results

Sample #	TCLP Result	"Totals" Result	TCLP limit	"Totals" limit
7 day ambient	1.1 ± 0.1 µg/L	54 ± 13 µg/kg	< 500 µg/L	< 10,000 µg/kg
14 day ambient	0.9 ± 0.1 µg/L	120 ± 26 µg/kg	< 500 µg/L	< 10,000 µg/kg
14 day 60° C	2.7 ± 0.1 µg/L	240 ± 5 µg/kg	< 500 µg/L	< 10,000 µg/kg

No significant difference in the TCLP benzene concentration was observed between the 7 day sample and the 14 day, ambient temperature sample. When the curing temperature was increased to 60° C, the TCLP benzene concentration increased by 2.5 - 3X.

The "totals" benzene concentration measured in the 14 day, ambient sample was 2 - 2.5X higher than in the 7 day sample. The "totals" benzene concentration in the 14 day, 60° C sample was 2X higher than in the 14 day ambient sample.

A Saltstone sample will be collected after 28 days, and submitted to a certified laboratory for a 28 day TCLP test. Those results will be reported when they are received.

The charcoal filters were changed after four days and seven days, and submitted to ADS to determine the accumulation of benzene on the filter. Table 2 shows the results.^{3,4} The benzene evolution rates ranged from 0.02 to 0.11 µg/L hr.

Table 2. Benzene Evolution Rates

Time (days)	Benzene Collected	Benzene Evolution Rate
0 - 4	.185 µg	0.048 µg/L hr
0 - 4	.130 µg	0.034 µg/L hr
4 - 7	.061 µg	0.021 µg/L hr
4 - 7	.323 µg	0.11 µg/L hr

Some scatter exists in the benzene evolution data. The reasons for the scatter are the difficulty in extracting the benzene from the charcoal filter and the small amount of benzene evolved during the

B. T. Butcher

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SRT-WHM-96-0013

test. According to previous SRTC test data, the maximum benzene evolution rate would be expected between 7 and 12 days after the curing started.⁵ Additional samples will be collected at 11, 14, 21, and 28 days. These results will be reported when received.

References

1. D. D. Walker, M. J. Barnes, R. F. Swingle, and R. A. Peterson, "Recent Tetraphenylborate Decomposition Results", SRT-LWP-96-008, January 22, 1996
2. J. E. Young, "Total and TCLP Extractable VOA Analysis Results", SRT-ADS-96-0060, February 21, 1996. (Attachment 1)
3. J. E. Young, "Analysis Results; ADS 3-67987, -8, and -9", Inter-Office Memorandum, February 16, 1996. (Attachment 2)
4. J. E. Young, "MRP Charcoal Tube Analysis", Inter-Office Memorandum, February 13, 1996. (Attachment 3)
5. S. B. Oblath, "Benzene Evolution During the Curing of Saltstone", DPST-86-645, September 2, 1986.

B. T. Butcher

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SRT-WHM-96-0013

Attachment 1

INTER-OFFICE MEMORANDUM

Savannah River Site

21-Feb-1996 01:52pm EST

To: See Below

From: John B. Young, ADS (YOUNG-JE-T6035 AT A1 AT SLSRP1)
Dept: Analytical Development S
Tel: (803) 725-3565

Total and TCLP extractable VOA analysis results [u]

SRT-ADS-96-0060

Summary:

ADS has completed analyses in support of your program. The following data are presented in raw, unrounded values as measured from the sample preparation and analysis replicates. Statistical summary data is provided with each sample type, with the proper number of significant figures.

Regulatory classification:

Data is reported as Constituent Concentration in Waste (CCW) as "Total" and Constituent Concentration in Waste Extract (CCWE) as "TCLP", to provide nomenclature correlation with the EPA's Land Disposal Restriction regulations (LDR).

In general, TCLP values for benzene are used only to show that a solid waste is/is not a SCDHEC/EPA regulated hazardous waste. For this purpose, a sample of the TCLP extract is tested for benzene at a regulatory limit of 0.5 mg/L. This procedure (TCLP) was formerly referred to in the LDR as the Constituent Concentration in the Waste Extract (CCWE).

The EPA's Land Disposal Regulations are applicable to determine if a regulated hazardous waste had been adequately treated for subsequent direct land disposal. The LDR regulatory concentration for benzene is based on a "total" benzene measurement. The logic behind this regulatory classification is based on the fact that the reference technology, incineration, will destroy (rather than immobilize) the organic constituents. The LDR limit for total benzene is expressed as the Constituent Concentration in the Waste (CCW), and is 10 mg/kg.

The inorganic (metallic) constituents are regulated under the LDR as CCWE's because they are treated by immobilization, rather than destruction. Therefore, in the case of toxic metals, LDR compliance is based on the TCLP extract measurements.

Please note that these analyses were performed by a laboratory that is not certified by the state of South Carolina for analyses required for specific permit analysis requirements. Generally, data that is required to be submitted to DHEC requires laboratory certification for the specific media.

B. T. Butcher

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SRT-WHM-96-0013

All reported data should be accompanied with this flag.

Experimental:

CCW - Totals: Total VOA's were determined by ultrasonication-assisted methanol extraction, as specified in ADS 2656, "Gas Chromatography/Mass Spectrometry for Volatile Organics - Contract Laboratory Program Method". Quantitation was performed using a custom developed selected ion monitoring mass spectrometric method. In this method, only the m/e of the ions of interest are monitored, which greatly increases sensitivity and signal to noise ratio.

The practical quantitation levels of the three compounds of interest were 25, 600, and 1500 ug/kg for benzene, 2-propanol, and n-butanol, respectively (for this sample series preparative workup).

CCW - Total concentrations are listed in Table 1.

Table 1

analysis results, CCW, constituent concentration in waste
all results are in the units ug/kg (1)

ADS# \ Cust ID	benzene	2-propanol	n-butanol
3-68044	46.7	1636	<1500
\ Poirier-MRP3-A-total	48.5	1585	<1500
3-68045	48.0	1536	<1500
\ Poirier-MRP3-B-total	72.8	835	<1500

MRP-3 summary; total benzene = (54 +/- 13) ug/kg
total 2-propanol = (1400 +/- 380) ug/kg

3-68046 Langton	135.3	1219	<1500
\ Langton-14D-STP-A-total			
3-68047	105.9	707	<1500
\ Langton-14D-STP-B-total			

Langton 14 day room temp cure summary;
total benzene = (120 +/- 26) ug/kg
total 2-propanol = (960 +/- 450) ug/kg

3-68048	240.5	1569	<1500
\ Langton-14D-60D-A-total			
3-68049	234.4	746	<1500
\ Langton-14D-60D-B-total			

Langton 14 day 60 degree cure summary;
total benzene = (240 +/- 5) ug/kg
total 2-propanol = (1200 +/- 730) ug/kg

B. T. Butcher

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SRT-WHM-96-0013

Notes:

(1) Land disposal restriction (LDR) regulatory concentrations are listed in the units of mg/kg, and should not be confused with the results listed here

CCWE - TCLP: Toxicity Characteristic Leaching Procedure (TCLP) preparative extractions were performed using a reduced scale zero headspace extractor (ZHE). 2-2.5 gram samples of reduced particle size concrete were extracted for 18 hours in 0.1N acetic acid. TCLP-extractable VOA's were measured using the same analysis method listed above for the total VOA's.

The practical quantitation levels of the three compounds of interest are 0.6, 4, and 38 ug/L for benzene, 2-propanol, and n-butanol, respectively (for this sample series preparative workup).

Table 2

analysis results, CCWE, constituent concentration in waste extract, all results are in the units ug/L (1)

ADS# Cust ID	benzene	2-propanol(2)	n-butanol
3-68056	1.3	180.1	<38
\Poirier-MRP3-A-TCLP/VOA	1.1	170.4	<38
3-68057	1.1	175.8	<38
\Poirier-MRP3-B-TCLP/VOA	1.0	167.9	<38

MRP-3 summary; TCLP benzene = (1.1+/-0.1) ug/L
TCLP 2-propanol = (170 +/- 5) ug/L

3-68058 Langton	0.8	166.0	<38
\Langton-14D-STP-A-TCLP/VOA			
3-68059	0.9	204.2	<38
\Langton-14D-STP-B-TCLP/VOA			

Langton 14 day room temp cure summary;
TCLP benzene = (0.9+/-0.1) ug/L
TCLP 2-propanol = (190+/-34) ug/L

3-68060	2.6	150.1	<38
\Langton-14D-60D-A-TCLP/VOA			
3-68061	2.7	175.7	<38
\Langton-14D-60D-B-TCLP/VOA			

Langton 14 day 60 degree cure summary;
TCLP benzene = (2.7+/-0.1) ug/L
TCLP 2-propanol = (160+/-23) ug/L

B. T. Butcher

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SRT-WHM-96-0013

Notes:

(1) Land disposal restriction (LDR) regulatory concentrations are listed in the units of mg/L, and should not be confused with the results listed here.

(2) Follow-up preparative laboratory extraction blanks showed the extract to contain 2-propanol at 38 ug/L, and will positively bias analyses results. The observation is attributed to the popularity of isopropanol as a current solvent in commercial chemical products.

B. T. Butcher

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SRT-WHM-96-0013

Attachment 2

INTER-OFFICE MEMORANDUM
Savannah River Site

16-Feb-1996 09:21am EST

To: Michael R Poirier (POIRIER-MR-Y5714 @A1@SASRS5)
CC: Pamela R. Waller (WALLER-PR-W2490 AT A1 AT SLSRP1)
CC: Jeffrey C. Griffin (GRIFFIN-JC-T8054 AT A1 AT SLSRP1)
From: John E. Young, ADS (YOUNG-JE-T6035 AT A1 AT SLSRP1)
Dept: Analytical Development S
Tel: (803) 725-3565

Analysis results; ADS 3-67987,-8, and -9 [u]

We have completed the analysis of your charcoal tube samples submitted on 2/15.

The results are tabulated;

ADS#	Cust#	FileID	ug benzene on tube
3-67987	MRP4	15e\09	0.0345
3-67988	MRP5	15d\07	0.0613
3-67989	MRP6	15d\08	0.3230

statistical method detection
limit, prepared under ideal conditions 0.15 (1)

(1) concentration at which 99% of analyses performed will generate a detectable signal.

As you will note, the values are very close to the method detection limit. For best accuracy, and least influence from environmental contamination, at least 1 ug of benzene should be loaded onto the tube prior to analysis. It would be advised, if possible, to scale your experiments up accordingly.

B. T. Butcher

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SRT-WHM-96-0013

Attachment 3

INTER-OFFICE MEMORANDUM
Savannah River Site

13-Feb-1996 11:40am EST

To: Michael R Poirier (POIRIER-MR-Y5714 @A1@SASRS5)
CC: Pamela R. Waller (WALLER-PR-W2490 AT A1 AT SLSRP1)
From: John E. Young, ADS (YOUNG-JE-T6035 AT A1 AT SLSRP1)
Dept: Analytical Development S
Tel: (803) 725-3565

MRP charcoal tube analysis

Data is documented in WSRC-NB-94-62, p.159

ADS#	Cust ID	Benzene, ug on tube	TCE, ug on tube
3-67535	MRP2	0.185	0.95
3-67536	MRP3	0.130	9.5
3-67537	MRP1	<0.1	9.9

During the analysis of your samples, it was noted that a variety of compounds (other than benzene) were increasing throughout the ADS sequence number series. The compounds were mainly light freons and trichloroethene. Since trichloroethene is present in SRTC air from process water offgas, this data was computed and presented for your information.

Sample results were corrected for chemical recovery inefficiencies as measured from the chemical recovery of benzene and TCE on this same batch of charcoal tubes.

Appendix V. C. A. Langton "Saltstone TCLP Results Versus Curing Time and Initial Benzene Concentration (U)", SRTC-WED-96-0163, February 27, 1996.

WESTINGHOUSE SAVANNAH RIVER COMPANY
SAVANNAH RIVER TECHNOLOGY CENTER

SRTC-WED-96-0163

February 27, 1996

To: B. T. Butcher, 773-43A

From: C. A. Langton, 773-43A

Saltstone TCLP Results Versus Curing Time and Initial Benzene Concentration (U)

Summary

Saltstone samples which were prepared with salt solution collected from Tank 50 in mid January, 1996 and cured for 14 and 28 days passed the TCLP test for benzene. The saltstone production runs from December, 1995 were also non hazardous. Saltstone made with early 1996 Tank 50 solution is expected to be non hazardous. Based on these results Saltstone production can be resumed. Results are summarized in Table 1.

Results

Saltstone samples collected from the Z-Area production runs on December 5, 12, and 18 were cured for 44, 50, and 57 days, respectively, before being subjected to the TCLP extraction test for benzene. These samples were made with salt solution containing relatively high concentrations of benzene, 6 to 8.5 mg/L, and tetraphenyl borate concentrations of 295 +/- 135 mg/L. The TCLP results for benzene extracted from the December samples ranged from 12.4 to 15.4 µg/L. (SRTC-LWP-96-019) The TCLP limit for benzene is 500 µg/L.

In order to determine whether the salt solution currently in Tank 50 will result in non hazardous saltstone, i.e., pass the TCLP test for benzene, laboratory samples were prepared at SRTC with solution collected in mid January, 1996.

Results indicate that the solution contained 2.3 ± 0.8 mg/L benzene and 295 ± 135 mg/L tetraphenyl borate. (The January sample had about 4x less benzene than did the December sample.) TCLP results for benzene extracted from these saltstone samples after 14 and 28 days curing at ambient temperature were 1 ± 0.1 μ g/L. This is well below the TCLP limit. TCLP results for Saltstone cured for 14 and 28 days at 60° C were 2.7 ± 0.1 and 4.7 ± 0.2 μ g/L, respectively, which is also well below the limit for benzene.

The January Saltstone samples resulted in TCLP values about 5x less than the December samples. This corresponds to less benzene in the Tank 50 Solution in January 1996 versus December 1995.

In addition the total benzene concentrations in the saltstone samples after 7, 14 and 28 days curing were 54 ± 13 , 120 ± 26 , 90 ± 8 μ g/kg, respectively. After 14 and 28 days curing at 60° C the total concentration of benzene in the saltstone was 240 ± 5 , 360 ± 24 μ g/kg, respectively. Since the total concentration of benzene in the samples is below the TCLP limit there is no question that these samples pass the regulatory requirements. Finally a comparison of the amount of benzene extracted versus the total benzene present in the samples indicates that saltstone retains 64 to 86% of the total benzene (14-36% is extracted in the TCLP test.) The worst case for this comparison is the sample cured for 7 days at ambient temperature; 64% of the benzene was retained in the saltstone. (SRT-ADS-96-0060)

Discussion

Analytical results for benzene in liquid and especially solid samples is very sensitive to sample handling. Saltstone samples prepared for TCLP extractions in SRTC were frozen in liquid nitrogen to minimize benzene loss during crushing. The crushed material was transferred into the zero-head extractor in less than three minutes, again to minimize benzene losses i.e., maximize the amount available for extraction.

SRTC-ADS personnel follow protocols for analyses and documentation in accordance with the RCRA/CERCLA requirements. SRTC/IWT and Saltstone personnel use the ADS laboratory to complement results obtained from a SC DHEC certified laboratory. ADS has the capability of providing very quick response and special attention for samples which are not routine. To date SRTC-ADS results and certified vendor results have been consistent for all types of TCLP analyses requested. The ADS detection limit and quantitation limit for benzene are better than the RCRA/CERCLA requirement. An example of using these two analytical services in parallel is illustrated in the TCLP-Hg results in WSRC-RP-95-835.

Recommendations

- Resume Saltstone production based on 14 day TCLP results.
- Follow up on proposed changes in the LDR regulations and their impact on Saltstone.

Table 1: Summary of TCLP Data for Saltstone Cured for 7 to 57 days.

Tank 50 Sample Date Collected	Tank 50 Analyses*		Saltstone Preparation	Curing Conditions		TCLP Benzene	
	Benzene mg/L	TPB mg/L		Time (days)	Temp (°C)	Results µg/L	Limit µg/L
December, 1995	5-8.5	<160-431	Z-Area Production Runs	44-57	23+/-1	12.1-15.4 SRT-ADS-96-0060	500
January 15-31, 1996	1.50-2.3	<160-431	SRTC/IWT Laboratory Samples	14	23+/-1	0.9+/- 0.1 SRT-ADS-96-0034	500
January 15-31, 1996	1.50-2.3	<160-431	SRTC/IWT Laboratory Samples	14	60+/-2	2.7+/-0.1	500
January 15-31, 1996	1.50-2.3	<160-431	SRTC/IWT Laboratory Samples	28	23+/-1	1.0+/_0.01	500
January 15-31, 1996	1.50-2.3	<160-431	SRTC/IWT Laboratory Samples	28	60+/-	4.7+/-0.2	500

* ITP Laboratory Results

Appendix W. J. E. Young, "ITP Tank H50 Saltstone Feed - Benzene Analysis Data (U)", SRT-ADS-95-0294, December 21, 1995.

INTER-OFFICE MEMORANDUM
Savannah River Site

12-21-1995 03:29 EST

To: See Below

From: John E. Young, ADS
Dept: Analytical Development S
Tel : (803) 725-3565

(YOUNG-JE-T6035)

ITP Tank H50 Saltstone Feed - Benzene Analysis Data [u]

SRT-ADS-95-0294

ADS has completed analysis of your sample submission batch received on 11/20 at approximately 10 PM.

Prior to sample analysis, instrument calibration verification was performed by the analysis of four replicate determination of benzene calibration standards obtained from two separate sources. All of the standard values were within QC startup specifications. QC data are listed below.

Blank verification was performed using boiled distilled water. No benzene (<10ppb) was detected in the blank water.

ADS laboratory tracking ID numbers have not yet been assigned, so the results are listed by ITP ID#.

Customer ID	Benzene, mg/l (ppm)	Report value
ITP-219	9.28 mg/l 8.63 mg/l	(9.0 +/- 0.6) mg/l
ITP-220	8.76 mg/l 9.06 mg/l	(8.9 +/- 0.3) mg/l
Z-saltstone	3.22 mg/l 3.21 mg/l	(3.2 +/- 0.01) mg/l

Uncertainty is calculated by the range between duplicates / 1.128, per Standard Methods, 17th ed., 1-15.

Startup Calibration Verification QC Data

Standard ID	Benzene, ug/l (ppb)	% of actual	within CLP limits(1)
Cal. Chk 100	95.1	95.1%	yes
Cal Chk 50	51.2	102.4%	yes

Cal Chk 50	48.4	96.8%	yes
Cal Chk 100	92.0	92.0%	yes
Blank	< 10 (0.2)	NA	yes

(1) CLP - Contract Laboratory Program, QC requirements for CERCLA site evaluation protocol.

Distribution:

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Appendix X. M. A. Schmitz, "NaTPB Analysis" (U), Inter-Office memorandum, January 14, 1996.

INTER-OFFICE MEMORANDUM
Savannah River Site

01-14-1996 14:39 EST

To: See Below

From: Mark A. Schmitz

(SCHMITZ-MA-O6036 AT A1 AT SASRS0)

Dept: NMPD

Tel : 208-2666; Fax 8-1462

NaTPB Analysis

My laboratory notebook contains data on grab samples taken from all containers of NaTPB received between August 1982 and January 1983. There were a total of 272 containers and I believe everything used in the Demo was taken from those drums. (My memory tells me most of the containers were 40 gallon fiber drums or 55 gallon metal drums and containing 100 to 200lbs of material.) The majority of the material was provided by Boulder Scientific Company, but Raylo and AFF were large contributors. My records have the following for each container:

My Number: 1-272

Supplier Name: Boulder Scientific, Raylo, AFF, or Noah (Preiser Scientific)

Purity Requested: 95 or 99%

Vendor Lot No.

Receipt Date at SRP

Lab Date Acceptance (Date TNX Lab pulled grab sample)

ADD Submittal Date

ADD Lab Submittal No.

Drum Weight

Weight Loss %

Analytical Purity-%NaTPB (as measured by SRL)

Composite Group (explained below)

High Level Cave DF (explained below)

Manufacturer Analysis-%NaTPB

The grab samples were assembled into composites identified as A through M. Vendors were not mixed. Each composite was used in a precipitation and filtered with Lien-Mow Lee's High Level Cave cross flow filter. I do not have the DF results, only the date that the composites were submitted.

Keep in mind, the bulk of the material used in the Demo came from Boulder and Raylo, then AFF, then Naoh. All of the material was shipped in solid form to AFF, who put the NaTPB into solution. The 0.5 Molar solution was then transported by tanker truck to SRP for use in the Demo.

If you have questions, please contact me at 8-2666.

Distribution:

To: Lester L Kilpatrick

(KILPATRICK-LL-T4896 @A1@SASRS5)

CC: Barbara A. Hamm

(HAMM-BA-O6216 @A1@SASRS2)